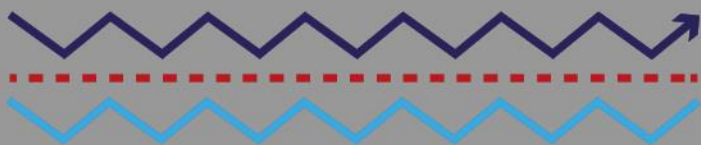




ABSTRACT BOOK

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EUROMEMBRANE

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KEYNOTE LECTURES

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With the transition to a sustainable, circular economy and a strong emphasis on the recovery and reuse of materials, minerals and nutrients, membrane technology will become increasingly important. Associated to this, the complexity of separations will increase requiring membranes with molecular selectivity suitable for the specific recovery of target valuable components. This comes with demanding membrane characteristics in terms of properties and separation performance. Obviously with this in mind, dedicated membrane design and tunable membrane development and production methods are essential.

In this presentation several methods to tailor membrane morphology and separation properties in the framework of recovery and reuse are discussed. Polymer membranes are currently often prepared using methods like phase separation and interfacial polymerization. Although phase separation was already extensively explored about a decade ago, still this method offers multiple directions to tune membrane morphology. This allows to a certain extent control over pore size and membrane polymer-component interactions, but real molecular separations are out of reach still as phase separation results in broad pore size distributions and interactions are limited due to the use of only few membrane polymer chemistries. To move beyond these limitations, several new concepts only recently explored for the preparation of membranes are evaluated. Starting from methods to tailor retention and permeability at a component level, methods to produce highly porous membrane structures or bi-continuous polymer films are presented. Finally, the role of self-organizing materials as a route to true molecular selectivity is discussed. Parallel to this, multiple examples of the characteristics and performance of membranes developed with these advancing methods are given.

Biomimetic Membranes: Quo Vadis?

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The properties of biological structures including membrane proteins capable of efficient selective transport are providing inspiration for developing new separation technologies. In creating selective materials proteins can be incorporated directly in a suitable matrix or their function can be mimicked by de novo designed structures. Here I point to basic design features of nanostructures facilitating selective water transport and relate them to progress and challenges in biomimetic membrane research and innovation.

Membrane technology and the WEF nexus - thoughts on current status and potential future

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The Water-Energy-Food (WEF) nexus is a framework and concept which is increasingly being used to express the interactions and the dependencies or interdependencies between three key sectors of our global society; water, energy and food. Although not fully defined, or at times suggesting different views as a function of which sector is referencing the WEF nexus, it has become an increasingly important framework for guiding research and policies. The basis for this framework is not novel, however, establishing the WEF nexus has been attributed to the World Water Day (March 2011) and subsequent Bonn2011 Conference: Water Energy and Food Security Nexus–Solutions for the Green Economy. The initial driving force was related to water security and has since evolved around the interdependencies and integration to achieve a sustainable management of our key natural resources.

In the last two to three decades membrane technology has become an increasingly important tool in the water industry, enabling new approaches and alternative strategies for sustainable management of a natural resources necessary for the existence and development of any society. One only needs to look at RO technology and it's impact on providing fresh water from non-conventional saline sources. Further the commercialization and implementation of MBR technologies for advanced treatment of wastewater's, opening the potential for water reclamation and reuse in many parts of the world. As various membrane technologies have been taken into use, a clear paradigm shift in how we view and manage our scarce water resources is apparent. Within the context of the WEF nexus, academia / industry / governance have expanded this to take into account key challenges with regard to energy and food. The water-energy nexus has had more attention in recent years, with a growing focus to also include the food sector. After all, the food sector does not only have the largest demand on our fresh water sources but also requires a significant amount of energy.

The WEF nexus is often closely linked the the UN Sustainable Development Goals (SDGs), addressing several key issues such as irradiating poverty, securing water and food for all and increasing the quality of life for the global population. Issues that increasingly challenge achieving these goals are population growth, urbanization, climate change, poverty, health, to mention a few. Within this context "urban agriculture" has emerged as a growing discipline, providing an alternative (or additional) strategy to meet the SDGs and future challenges. This presentation aims to highlight both current and potential membrane based technologies that can enable addressing some of these challenges and taking into account the WEF nexus framework.

Membranes towards 2050 ~ Fuel cells, Water electrolysis, Disease diagnosis and Water purification

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Carbon Neutrality should be realized before 2050, and we should imagine the world in 2050. For example, the OECD Environmental Outlook to 2050 predicts the world in 2050 as follows 1). 1) World population is more than 9 billion, 2) Economic scale will be 400% compared to 2012, 3) Energy consumption will be 180%, 4) 70% of the world population live in city area. In addition, 5) In OECD countries, 25% will be aged over 65 years old, 6) 40% of the world's population is stressed by water shortages due to increased water demand, and 7) 240 million people cannot access to water supply. Energy consumption will be 1.8 times, and less people will live in country side. Medical expenses become more prominent, and the competition to secure water will arise due to the increase in water demand. Not only energy and CO₂ emission issues, but also medical care and water shortages need to be considered at the same time. Membrane technologies are one of the key technologies for solving these problems.

Renewable energy will to be introduced as much as possible. The renewable energy should be converted into hydrogen or hydrogen carriers by water electrolysis, and stored and transported, and used as electricity by fuel cells or hydrogen turbines at the required time and place. For polymer electrolyte fuel cells, high temperature and low humidity operation is required, and the electrolyte membrane development is important. Pore-filling thin electrolyte membranes enable us to develop high performance polymer electrolyte fuel cells 2). Water electrolysis using anion exchange membranes can efficiently produce hydrogen without using precious metals, and development of highly durable anion exchange membranes are key to achieve the technology 3). Those new membranes and design strategies based on the degradation mechanisms 4) will be explained.

For the aging society, we are developing membranes that can diagnose diseases at home. If we can easily diagnose our illness at home within a short period, the medical expenses will be reduced. Diagnosis membranes will be explained 5). Finally, we will introduce the anti-fouling membrane and design strategy of membrane surfaces. Anti-fouling technology that suppresses clogging of membrane surface and pores are important in aiming for maintenance-free water treatment plant. Introducing a technology that precisely control the membrane surface by grafting of twitter ion polymers 6).

Membrane technologies are important technologies in various fields, and contribute to the world in 2050.

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Keywords: Electrolyte membranes, fuel cells, water electrolysis, bio sensors, anti-fouling

**ORAL/POSTER
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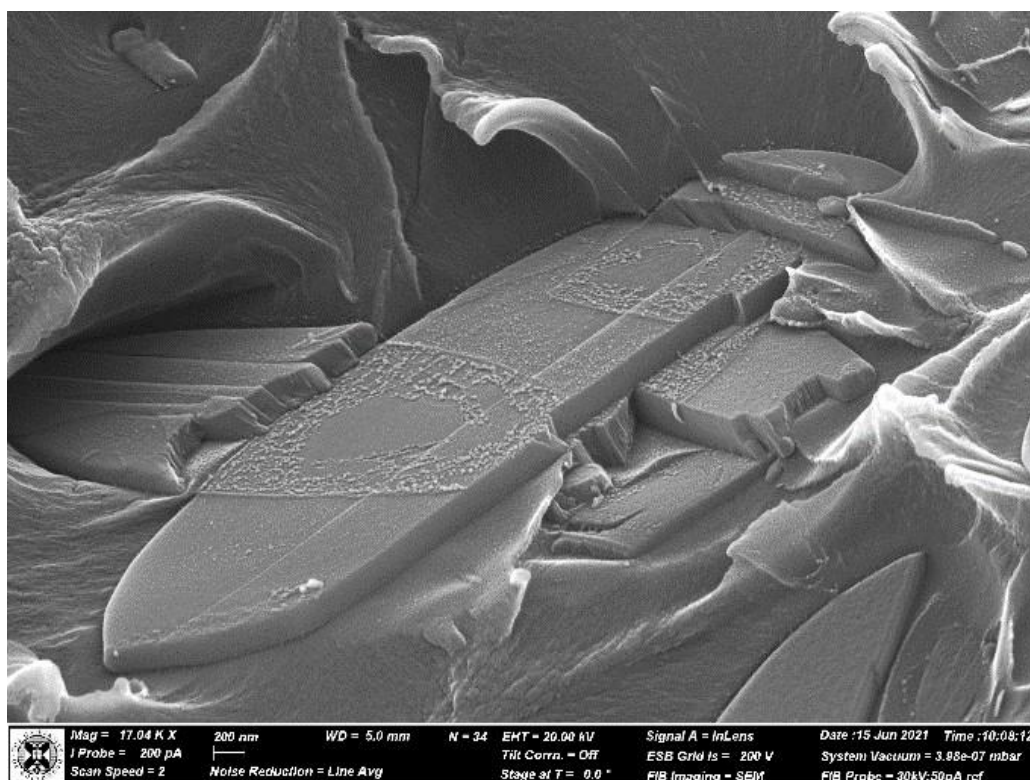
2-Dimensional imidazole framework into polymer matrix for gas separation

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Main topic: Gas separation

Mixed Matrixes Membranes (MMMs) are composite membranes made by combining a filler (dispersed phase) and a polymer matrix (the continuous phase). By using two materials with different transport properties, these membranes have the potential to synergistically combine the easy processability of polymers and the superior gas-separation performance of filler materials, and therefore provide separation properties surpassing the Robeson upper bound. We report here the fabrication of high performance MMMs composed of two-dimensional imidazole framework (ZIF-L) as fillers at different loadings with 2 polymers (PEBAX/Matrimid) with different permeability-selectivities properties. The ZIF-L nanosheets were synthesized in zinc salt and 2-methylimidazole (Hmim) aqueous solution at room temperature; they presented a leaf-like shape with high aspect ratio. The separation performance of the MMMs was evaluated by pure gas tests (N₂, CO₂, H₂ and CH₄) at ambient temperature and pressure. The dispersion and orientation of nanosheets fillers was studied by SEM-FIB analysis. The ZIF-L nanosheets were uniformly dispersed with preferential orientation parallel to the membrane, enhancing the tortuous path and thus increasing the diffusion rate difference between large molecules and small molecules and improving the selectivity of the MMMs.

Figure: ZIF-L into Matrimid.



A chemical-mechanical ex-situ aging of perfluorosulfonic-acid membranes for fuel cells: impact on the structure and the functional properties

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Main topic: Ageing of polymeric membranes

Background, Materials and Methods, Results, Conclusions

Nowadays, proton-exchange membrane fuel cells (PEMFCs) offer an attractive and efficient alternative to replace fossil fuels but are still facing durability and performance issues restraining their widespread commercialization. In recent years, countless studies have been carried out to provide a better understanding of the aging phenomena and identified the degradation of the polyelectrolyte membrane as one of the main factor limiting the PEMFC lifetime. In these studies, it was clearly demonstrated that the membrane is exposed to harsh conditions entailing important chemical and mechanical stresses that may lead to severe degradations of membranes chemical structure and functional properties and, in worst cases, to the fuel cell shutdown [1]. Although it is commonly admitted that chemical and mechanical stresses interact with each other to accelerate the membrane degradation [2], this assertion may not be clearly evidenced so far and, in any case, a clear understanding of these interactions and their impact on the structure and the properties of PFSA membranes is required.

We recently developed a custom-made device able to expose the membrane simultaneously to a mechanical fatigue and an aggressive chemical environment in conditions close to that observed during fuel cell operation. In the present study, we investigated the contribution of the mechanical fatigue to the chemical degradation of PFSA membranes and the impact of the conjoint stress on the structure and the functional properties of membranes. The mechanical fatigue consisted in applying a sinusoidal compressive stress oscillating between 0 and 5 or 10 MPa at 0.1 Hz while the chemical stress was induced by circulating a 3 vol.% H₂O₂ solution for mild conditions or a Fenton solution containing 1 ppm of Fe²⁺ and 3 vol.% of H₂O₂ solution for aggressive conditions.

The results demonstrated that, in spite of significant polymer decomposition and morphological evolutions, neither the water sorption and self-diffusion properties nor the chemical structure of the polymer repeat unit were altered by conjoint mechanical and chemical stress. Moreover, aged membranes were assembled with gas diffusion electrodes (GDEs) and tested in single cell: the impact on cell performances was negligible since aged membranes remained functional despite the severe solicitations exerted.

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A comparative study of vacuum and direct contact membrane distillation for ammonia and phosphorus recovery from wastewater

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Main topic: Membrane contactors and membrane distillation

Recovery of ammonia (NH₃) and phosphorous (P) from municipal wastewater is important to minimize the environmental impact of their discharge and to comply with the concept of circular economy. Technologies have been established to recover P in form of struvite (MgNH₄PO₄·6H₂O) for its use as a fertilizer. NH₃ is usually converted to molecular nitrogen and released to the atmosphere; however, NH₃ recovery in form of NH₃/H₂O mixture is relevant for numerous applications such as manufacturing of cleaning agent, sanitizers and liquid fertilizer. Membrane distillation (MD), a process driven by the partial vapor pressure across a hydrophobic membrane, has demonstrated the potential of concentrating the non-volatiles while, at the same time, removing volatiles from a solution. Among various configurations of MD, vacuum and direct contact MD have been extensively studied. The current study compares the performance of direct contact and vacuum MD (VMD) for simultaneous recovery of NH₃ and P from wastewater in form of NH₃/H₂O mixture and struvite, respectively. The study finds that while both the configuration are equally effective to concentrate P, the control over removal efficiency of NH₃ in the two configurations becomes the bottleneck under different pH conditions. For wastewater with high pH, VMD almost completely removes NH₃ before reaching substantial P concentration, thereby eliminates the possibility of struvite formation. DCMD on other hand, only partly removes NH₃ while concentrating P, therefore, for struvite recovery from a high pH wastewater, DCMD is better option. For low pH wastewater, VMD is preferred choice as it removes NH₃ more effectively than DCMD but still leaves ample NH₃ in the wastewater for struvite formation. The characteristics of obtained struvite crystals do not show any dependence upon the type of the configuration (DCMD or VMD) applied.

A comprehensive theoretical framework for the sub- and supercritical sorption and transport of CO₂ in polymers

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Main topic: Transport models

Background

The description of CO₂ solubility and transport in polymers in both **sub- and supercritical conditions** with a unified approach is rather challenging, due to the complexity of the trends and phenomena involved. The problem, however, is of paramount importance in several applications like supercritical CO₂ processing and handling, packaging, membrane separation.

Modelling must take into account: i) the state of equilibrium (rubbery) or non-equilibrium (glassy) of the polymer, ii) phase changes of the penetrant with temperature and pressure, iii) the sorption-induced rubbery transition if the polymer is initially glassy, iv) the dependence of the penetrant diffusion coefficient on the sorbent concentration.

Materials and Methods

A unified strategy was used to model the solubility and permeability of CO₂ in a rubbery (**PDMS**) and glassy (**Matrimid**) polymer in a wide range of temperatures and pressure (recently reported data: Houben et al. J. Membr. Sci. 620 (2021) 118922), which extended from the sub- to the supercritical state of the gas.

Solubility was modelled using the Sanchez-Lacombe Lattice Fluid (LF) equation of state (EoS) and its nonequilibrium version, the Non-Equilibrium Lattice Fluid (NELF) model [1]. The Standard Transport (ST) model [2], developed combining EoS or Non-Equilibrium Thermodynamics frameworks with a simple description of penetrant transport, based on the chemical potential gradient as driving force, was used to calculate CO₂**permeability**.

Results

The LF EoS correctly represents the inflection in the **sorption isotherms** occurring at the transition from gas-like to liquid-like densities of CO₂ around the critical pressure. In the case of PDMS, the LF EoS was applied in the whole pressure range, while in the case of Matrimid, the NELF model was applied in the low pressure range, where the polymer is glassy, and the LF EoS was applied at high pressure. The gas concentrations that induce the glass transition in Matrimid were estimated and compared favorably with Chow's model results. The predicted **CO₂-induced dilation** compared favorably with experimental data.

CO₂**permeability isotherms** for PDMS and Matrimid were calculated at the same conditions. The two materials display qualitatively very different trends, that, remarkably, can be reproduced with the same modelling framework, using only two concentration-independent adjustable parameters.

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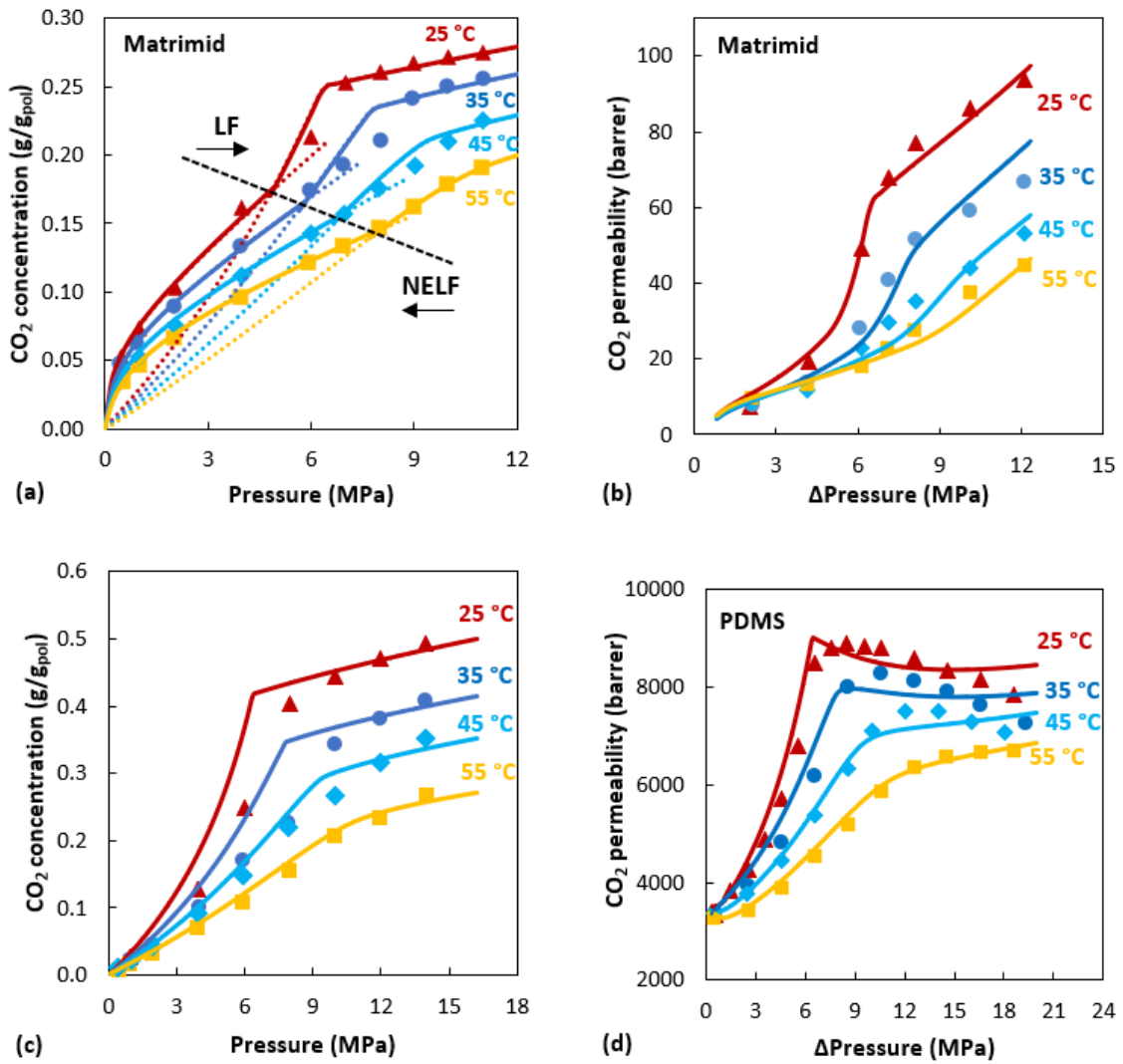


Figure 1. CO₂ sorption in (a) Matrimid and (c) PDMS at different temperatures. Solid lines: SL EoS/NELF model calculations. Dotted lines represent the concentration that would be obtained using the SL EoS in the glassy region and the NELF model in the rubbery region respectively. Permeability of CO₂ in (b) Matrimid and (d) PDMS at different temperatures. Lines: ST model calculations. **Symbols:** Experimental data from Houben et al. *J. Membr. Sci.* 620 (2021) 118922. Triangles: 25 °C. Circles: 35 °C. Diamonds: 45 °C. Squares: 55 °C.

A DNA-membrane reactor

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Main topic: Membrane reactors

One way to approximate the ingenuity of biological membranes while maintaining the robustness of artificial membranes is the use of hybrid materials. We have studied modular systems comprising functional-DNA and mesoporous anodized aluminum oxide (AAO). Functional nucleic acids are highly versatile molecular building blocks: thanks to their specific hybridization they enable systematically creating nanoscale structures; they may specifically recognize a wide variety of molecules; and they may even serve as biocatalysts [1]. Recently, DNA was shown to be capable of catalyzing a 1,3-dipolar reaction which does otherwise not exist in living systems [2]. However, commonly the applications of functional nucleic acids are limited to aqueous environments, because molecular organic solvents widely annihilate their function or their thermal or conformational stability.

In this study we made use of the intrinsic property of DNA-modified membranes of creating a reactive interface between compartments of different chemical composition, similarly to what biological membranes do in a far more ingenious manner under physiological conditions. For this purpose, AAO membranes were functionalized with DNA whose chirality can be transferred directly to a metal-catalyzed reaction, and in particular a copper(II)-catalyzed Diels–Alder reaction. In this way, we created a prototype of what might be denominated a DNA-membrane reactor.

We studied the immobilization efficiency and functional stability of DNA under prolonged operation of the reactor and compared the results with homogenous DNA-catalysis. In particular, we focused on how non-aqueous solvents may enhance product recovery but maintain the function and stability of the membrane-based DNA.

The results suggest that we can use versatile functional molecules such as nucleic acids beyond physiological conditions and in a DNA-membrane reactor which offers mechanical robustness and the specific enzymatic activity of DNA.

Reference 1:

[1] G. Roelfes and B.L. Feringa, *Angewandte Chemie*, 2005, 3230-3232

Reference 2:

[2] I. Rivilla et al., *Chem Sci.*, 2017,7038-7046

A Further Development of the Liquid-Liquid Porometry for Characterization of Hydrophobic Membranes and Hollow Fibers

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Main topic: New characterisation methods

Background

As membrane research and applications move towards smaller pore sizes, there is an increasing demand for accurate methods to measure pore sizes in the submicron range. Among different characterization techniques, the Liquid-Liquid Porometry (LLP) seems to be of particular interest because it allows measuring through pores down to 2 nm and is suited for characterization of very fragile membranes, which normally get damaged when analyzed by gas-liquid porometry (GLP). This work examines different liquid combinations, in particular for the characterization of hydrophobic membranes, and explores the suitability of LLP for hollow fiber characterization.

Materials and Methods

Selected polycarbonate flat sheet track-etched membranes and PTFE membranes were characterized with liquid-liquid porometer POROLIQTM1000 AQ/ML using different wetting and displacement liquid combinations. Next to the isobutanol/water combination, the isobutanol/Porefil pair was tested as an alternative for hydrophobic materials. The interfacial tension of all combinations was measured using a DCAT9 equipment and the Du Noüy ring. The samples were also characterized by gas-liquid porometer (POROLUXTM500 and POROLUXTM1000) and when possible with SEM to validate the results obtained by LLP. The selected hollow fiber membranes were characterized by using the isobutanol/water or isobutanol/Porefil combination.

Results

The results of the polycarbonate flat sheet track-etched membranes obtained by LLP and GLP showed a good agreement between each other and with the pore size quoted by the manufacturer. The flat sheet PTFE membrane was measured with the POROLIQTM1000ML using the isobutanol/water and also the isobutanol/Porefil combination. Comparable results were obtained despite using different liquid pairs and the data agreed with the values expected by the manufacturer. As the interfacial tension between two liquids is much lower than the surface tension at the interface gas-liquid, the LLP uses typically lower pressures. This led to the successful measurements of hollow fiber membranes, which normally burst or collapse when measuring by GLP.

Conclusions

Liquid-liquid porometry has proven to be a powerful tool to measure pore sizes of flat sheet and hollow fiber membranes. A studied water free liquid combination has been explored and successfully applied for characterization of hydrophobic membranes. The presented work is also a practical guide on how to prepare and measure fragile hollow fibers by liquid-liquid porometry.

Reference 1:

Calvo J.I., Bottino A., Capannelli G. and Hernandez A. Pore size distribution of ceramic UF membranes by liquid-liquid displacement porosimetry, *Journal of Membrane Science* 310 (2008) 531–538.

A graphene oxide-based nanofiltration membrane for the catalytic abatement of organic pollutants in wastewater under dark conditions

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Main topic: Novel membrane materials

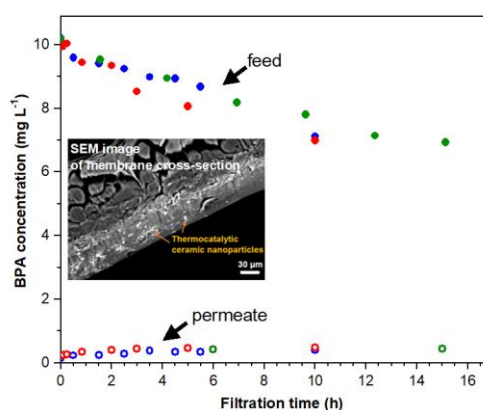
Ce-doped strontium ferrate is a perovskite material able to generate reactive oxygen species for the abatement of water organic contaminants, with no need for an external light source [1]. Therefore, this perovskite has been used to degrade different water pollutants at mild temperatures, and we have recently coupled this technology with membrane distillation for the simultaneous production of clean water and degradation of organic pollutants [2]. In this work, we combined this perovskite with graphene oxide to obtain new thermocatalytic nanocomposites. We tested the new materials in the degradation of a model water pollutant, namely bisphenol A. Material composition was optimized to obtain a nanocomposite with enhanced degradation rates compared to the pure perovskite. Following this development, nanofiltration membranes were fabricated by depositing thin films of this nanocomposite material over a commercial polyethersulfone ultrafiltration sheet. The membrane was tested in a cross-flow apparatus with model solutions and with a real wastewater effluent, showing rejection > 98% towards bisphenol A and water permeance comparable to commercial nanofiltration membranes. When tested at 50 °C, the membrane showed the ability to degrade bisphenol A during filtration under dark conditions. The figure presents the bisphenol A concentration in feed and permeate for three replicas of a degradation experiment, making evident the good reproducibility of performances for different membrane samples, also when prepared from separated batches. The degradation process can function with no need for external light sources or addition of chemicals. The data obtained in this work suggest that the new graphene oxide-perovskite membrane can be conveniently used for water decoloration, especially for industrial effluents, which often have already a temperature suitable for the thermocatalytic process or that can be heated on-site either by recovering low-grade waste heat or by solar thermal energy. The results presented at this conference were obtained in the frame of two European projects: H2020-MSCA-ITN-2017 (AQUALity, Grant Agreement n. 765860) and NanoPerWater (EUREKA, Eurostars Cut-off 12, Project number: 113625).

Reference 1:

M. L. Tummino, E. Laurenti, F. Deganello, A. Bianco Prevot, G. Magnacca, Revisiting the catalytic activity of a doped SrFeO₃ for water pollutants removal: Effect of light and temperature. *Appl. Catal. B Environ.* 207 (2017) 174–181.

Reference 2:

K. Janowska, V. Boffa, M. K. Jørgensen, C. A. Quist-Jensen, F. Hubac, F. Deganello, F. E. B. Coelho, and G. Magnacca, "Thermocatalytic membrane distillation for clean water production," *npj Clean Water*, 3 (2020) 1–7.



A greener route to prepare membranes for gas separation processes

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Main topic: Novel membrane materials

Membrane technology has gathered interest as an environmentally friendly alternative to traditional separation processes, as the energy consumption and the use of chemicals are significantly reduced. However, nowadays, membrane preparation mostly involves the use of harmful and toxic solvents for their preparation which goes against the increasing concern over the environmental impact of chemical products (Figoli *et al.*, 2014). More specifically, in the nonsolvent-induced phase separation (NIPS) process, the selection of solvent/non-solvent plays a crucial factor in the final membrane structural properties and future separation performance.

In this work, an alternative preparation method of polyether block amide PEBAX 1074(ARKEMA) membranes using the green solvent Rhodiasolv®Polarclean(Solvay)/water as pair in NIPS is reported. In addition, membranes prepared using Rhodiasolv®Polarclean (PC) were compared with the ones prepared with N-methyl-pyrrolidone (NMP), considering dope solutions with different polymer concentrations (between 11-25wt.%).

An extensive characterization was performed to the membranes prepared, involving Fourier-transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC), scanning electron microscope (SEM), swelling analysis, mechanical properties, and gas permeation studies for helium, nitrogen, oxygen, hydrogen, methane, and carbon dioxide.

PEBAX 1074 was dissolved in both solvents with a strong dependence of its viscosity with temperature. The casted membranes presented a dense cross-section (Figure 1a-b) regardless of the preparation conditions with no apparent chemical differences in their composition. Regarding the gas separation properties, a CO₂ selective behavior over the other tested gases was observed. Regardless of the dope solution concentration, PC-based membranes surpassed NMP-based membranes in what concerns CO₂ permeability. Optimal preparation conditions were determined for improved CO₂ selectivity over other gases (Figure 1c for pair CO₂/N₂).

Dense membranes based on elastomer PEBAX 1074 were successfully prepared using green solvent Rhodiasolv®Polarclean. The proposed NIPS preparation method using Rhodiasolv®Polarclean showed potential to substitute highly toxic solvents as NMP in the preparation of membranes for CO₂ separation.

Reference 1:

Figoli, A., Marino, T., Simone, S., Nicolò, E. Di, Li, X.-M., He, T., Tornaghi, S., & Drioli, E. (2014). Towards non-toxic solvents for membrane preparation: a review. *Green Chemistry*, 16(9), 4034–4059. <https://doi.org/10.1039/C4GC00613E>

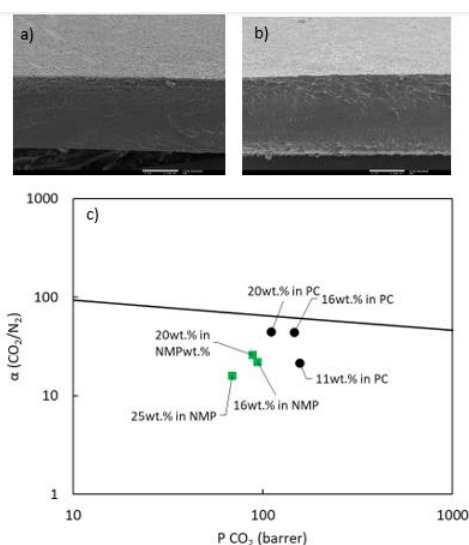


Figure 1. SEM cross-section images for: a) 20wt.% PX 1074 in PC; and b) 20wt.% PX 1074 in NMP; and c) CO₂/N₂ Robeson upper-bound and pure gas permeation data for PEBAX 1074 membranes prepared with different polymer concentrations in PC and NMP.

A lab-scale ultrafiltration module with built-in spacers

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Main topic: Module design

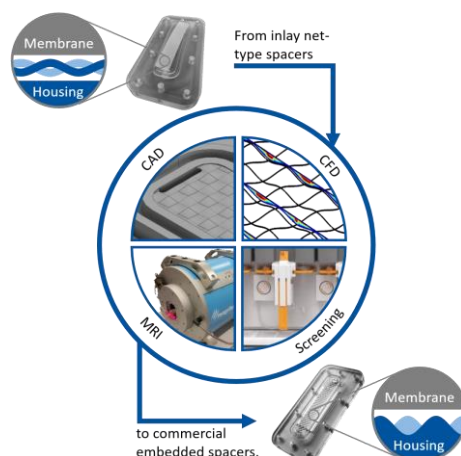
Ultrafiltration membrane modules are a common application in, for example, fermentation-broth purification or pharmaceutical production. However, with time they lose their filtration accuracy due to concentration polarization and fouling. Turbulence promoters, so-called spacers, reduce these effects. Conventional mesh-type spacers are manually placed on top of the membrane, which makes it unsuitable for single-step module production. Regarding manufacturing costs of single-use membrane modules in particular, an effective membrane module design at low production costs is desired. This issue can be tackled by built-in spacers. They are implemented as part of the feed channel inside the module housing enabling manufacturing by injection moulding. In this study¹, we present a novel approach towards a shorter fabrication time using built-in spacers while showing better performance than mesh-type spacers at the same time.

An extensive preliminary study using three-dimensional computational fluid dynamics (3D-CFD) succeeded in the selection of a promising structure: A sinusoidal corrugation. To prove an increase in permeate flux, 3D-CFD simulations coupled with mass transfer investigated the impact of flow and shear rate distribution on concentration polarization. The results proved a close correlation between areas of high shear rates and regions of low concentrations at the membrane surface. A model for a concentration- and pressure-related permeate flux proved the desired permeate flux increase. Rapid prototyping enabled a fast implementation of the built-in structure in a module prototype. Experimental verification succeeded with the sinusoidal corrugation outperforming mesh-type spacers in filtration experiments with bovine serum albumin. To better understand this effect, the module prototype was further investigated online and in-situ by low-field and high-field magnetic resonance imaging velocimetry. The observed flow characteristics imply mass transfer orthogonal to the flow direction and mixing effects downstream the module despite a laminar flow regime.

This study provides a simple methodology to compare complex spacer geometries. Simulations accord very well with experiments and show clear advantage over commercial net-type spacers. The model represents the beginning for further optimization of ultrafiltration membrane modules. The final built-in spacer structure shows 10% to 30% higher permeate fluxes compared to conventional mesh-type spacers and is suitable for single-step production.

Reference 1:

[1] K. Baitalow, D. Wypysek, M. Leuthold, S. Weisshaar, J. Lölsberg, M. Wessling. A mini-module with built-in spacers for high-throughput ultrafiltration, *J. Membr. Sci.* (2021) 119602.



A mechanistic predictive model of selective drug permeation through immortalized human colorectal adenocarcinoma cell line: mapping permeation trajectory and prediction of permeability

Tanmoy K, DEB

Main topic: Transport models

A mechanistic predictive model of selective drug permeation through immortalized human colorectal adenocarcinoma cell line: mapping permeation trajectory and prediction of permeability

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¹ Tremplin A., Lyon, France

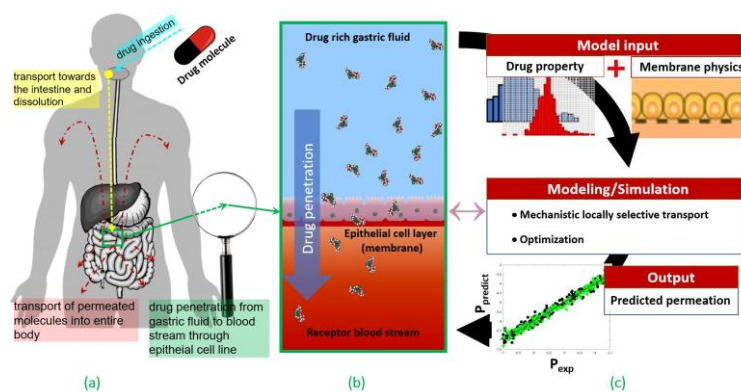
² Last position hold: Marie Skłodowska-Curie ESR, Erasmus Mundus Fellow (Joint European Masters in EM3E-4SW, 2013-2015). Email: deb.tanmoy.kanti@gmail.com

The permeability through the epithelial cell line (ECL) membrane of the human intestine is a vital marker of ensured bioavailability of oral drugs. To this context, the CaCO-2 cell model (an immortalized human colorectal cancer cell) is broadly adopted as a mammalian ECL surrogate to study (*in vivo*) drug permeation.

For the definition of drug transport from gastric fluid to the blood vesicle by permeation (penetration of drug following "selectively chosen local penetration route" within cellular matrix of CaCO-2 setup), a relatively complete mechanistic model is developed in this paper, which counts active, passive cell membrane, precellular transport, and neutral mode of transcellular pathway. This model calculates apparent drug permeability (P_{app}) as the inverse of the sum of all local barrier functions on the molecular penetration trajectory. The modeling scheme was completed by a use and optimization of the support vector machine (SVM) framework (with Gaussian kernel). All computations were carried out in Python's computational environment.

The model validation and parameter quantification were done using CaCO-2 permeation data from 1600 drug compounds (literature-based). The paracellular pathway was discovered to be the most common within the analyzing dataset. Active membrane transport ranked second, followed by passive cytoplasmic, and then passive membrane (lateral) transport. Permeation routes with $R^2 > 0.80$ and $MSE > 0.4$ may be regarded reasonable based on the large size and wide molecular space captured within the data set. Moving on, the deployment of optimized SVM enhanced P_{app} prediction with $R^2 = 0.91$ and $MSE = 0.30$.

The study demonstrates a clear correlation between the molecular (drug) property and transport trajectories inside ECL matrix, and had plausibly tuned it to a usable mathematical scheme (a tool for drug product developer) of P_{app} prediction. The analysis also emphasized the exceptional functionality of mechanistic - predictive (machine learning) based model coupling for comprehensive exploration of the P_{app} .



(a) a simplified schematic representation of drug transport from bulk oral ingestion to uptake by body stream; (b) drug permeation through ECL (translation to *in vivo* experimentation) where selectivity is imposed by the epithelial layer; and (c) model heart: bridging molecular property in the gastro - intestinal fluid phase, membrane physics, and P_{app} .

N.B. : Anatomical broadcasting is not employed for anything other than scaling up the notion from bulk drug ingestion to molecular absorption by the human body.

A micro-dimensional yttria-stabilised zirconia (YSZ) hollow fibre with open micro-channel structures for fluid separation and chemical reaction

Banjerdteerakul, Kornkamol

Main topic: Inorganic membranes

Ceramic hollow fibre membranes have shown superior stabilities under high temperatures and corrosive environments. However, due to limitations in the spinneret design, the spun fibres normally exhibit larger than 2 mm in diameter, resulting in low packing density compared to the polymeric counterparts. Here, we prepare yttria-stabilised zirconia (YSZ) hollow fibres with outer diameter down to 600 μm by stretching the nascent hollow fibre using gravitational force. Also, using a delayed phase inversion phenomenon, a plurality of radial micro-channels opening from interior surface of hollow fibres can be realised. The resultant hollow fibre shows promising permeation characteristics and high fracture strength owing to the robustness of YSZ. It also possesses an extremely high surface area/volume ratio compared to the conventional tubular or planar designs, which means that the prepared hollow fibre can be used to further develop a more compact device. Moreover, the open micro-channels in fibre cross section generates further features, which allow such fibres to be used as a good substrate for coating advanced membranes such as zeolites, metal organic framework (MOFs) or graphene as well as for developing compact devices such as catalytic contactors, micro-reactors, continuous membrane emulsification, etc. for fluid separation and chemical reaction.

A microfluidic cell for thin-film characterization: an isotope selectivity study

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¹Technion-IIT

Main topic: new characterisation methods

Thin-film composite membranes are constantly evolving, yet there is much room for improvement. The removal of certain non-charged species, such as boron, complicates existing processes and still awaits a breakthrough, transport of non-charged molecules remains mostly in the shadows and there is a need to better understand the fundamental mechanisms governing their permeation.

To address this challenge we have built a microfluidic cell that allows studying water and solute transport through ultrathin films in the osmotic flow regime, whereby diffusion is the major transport mechanism. The cell consists of two half cells, acting as parallel flow compartments separated with a membrane supported on an open isoporous alumina support, also acting as an electrode for *in-situ* impedance spectroscopy. Here, we employed the cell for observing counter-current permeation of two isotopic species of water, H₂O and D₂O, fed to separate compartments, with or without added kosmotropic and chaotropic salts, KCl and MgSO₄, rejected to a significantly different degree by the membrane. The concentration of water and heavy water in each compartment were quantified and permeation rates were calculated for each isotope using FTIR-ATR spectroscopy.

We observed a pronounced isotopic selectivity, resulting in an asymmetry between the flows of H₂O and D₂O. We also observed that added salt drastically reduces H₂O and D₂O permeation rates, which we presume is mainly related to concentration polarization, but may also be partly related to kosmotropicity/chaotropicity of the salts. We propose a simple model to describe the results and deduce permeability of each species. The results shed light on the mechanism of water permeation and largely unexplored isotope selectivity of polyamide membranes.

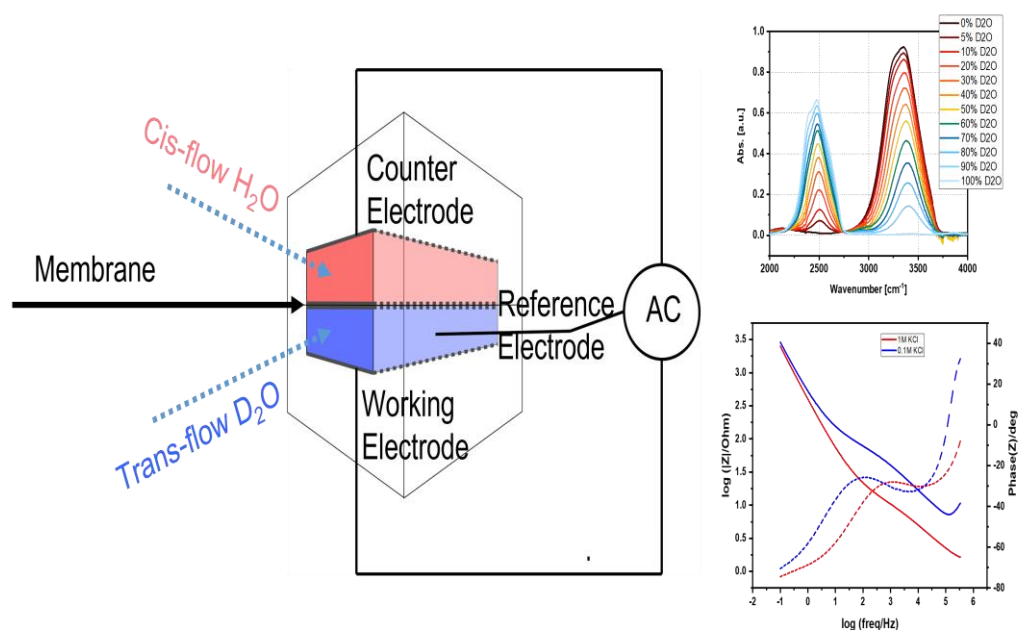


Figure 1: Cross-sectional scheme of our custom-made microfluidic flow cell (Left). IR spectra of H₂O/D₂O mixtures (Top right) and impedance spectra indicative of salt-rejecting properties of the polyamide films in different salt solutions (Bottom-right).

A model-based analysis of pulsed-electric fields to reduce electro dialysis fouling.

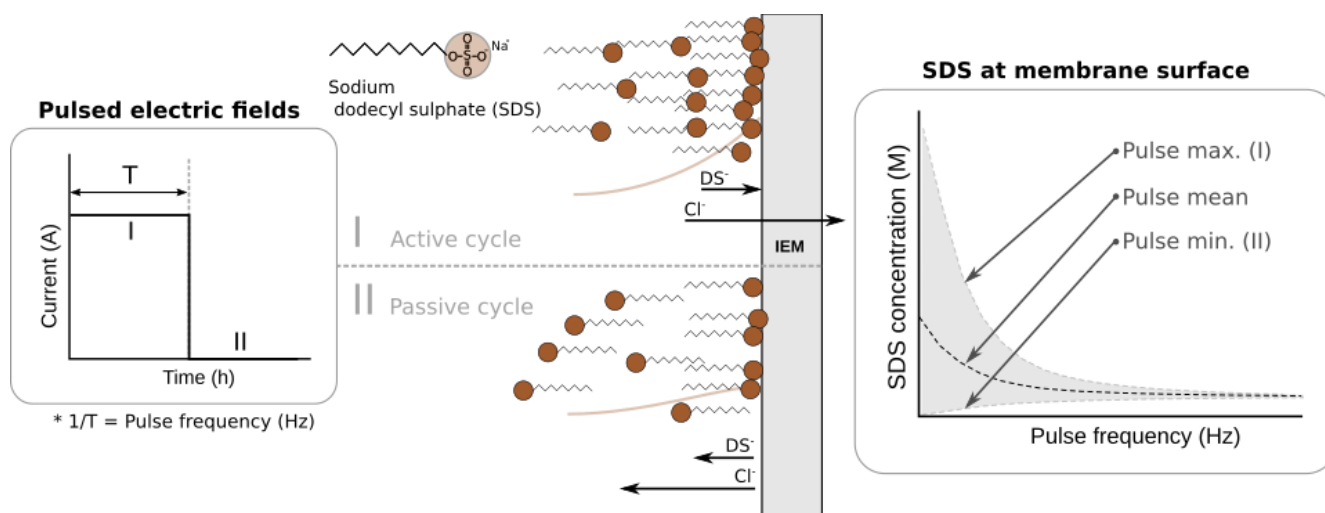
De Jaegher, Bram - Co-Author^{1,2}; De Schepper, Wim - Co-Author³; Verliefde, Arne - Co-Author⁴; Nopens, Ingmar - Co-Author⁴

¹Ghent University (UGent), ²Flemish institute for scientific research (VITO), ³Flemish Institute for Technological Research (VITO), ⁴Ghent University

Main topic: Electro-membrane processes

Membrane fouling remains a limiting factor in a lot of membrane separation processes and electro dialysis is not an exception. Especially when processing the complex mixture of inorganic and organic compounds and colloids that make up bio-based process streams, the occurrence of scaling, organic fouling and colloidal fouling severely hampers the application potential of electro dialysis. It has been shown that the severity of fouling can be reduced by applying a fluctuating electric field. This procedure is known as pulsed electric fields (PEF). However, the application of PEF can lead to higher energy consumption and only some frequencies seem to lead to beneficial results. This research aims to gain insight into (1) the mechanisms of PEF fouling reduction and (2) how to optimise the pulse frequency and duty cycle to reduce fouling while limiting the energy consumption.

In literature, the suppression of fouling is accounted to a combination of three effects; the reduction of concentration polarisation, the promotion of electroconvection and the suppression of water splitting. However, these effects have yet to be substantiated quantitatively from a fouling perspective. This research focuses on the effect of PEF on concentration polarisation by developing a Nernst-Planck model to simulate the evolution of a ternary solution of sodium, chloride and sodium dodecyl sulphate (SDS) during PEF. The effect of the pulse parameters on the boundary layer concentration of SDS is studied along with an evaluation of the current efficiency and energy consumption. The simulations illustrate the counter-productivity of low-frequency pulses which lead to an increase in fouling severity while high frequencies pulses reduce the fouling rate. However, at high frequencies, there is a trade-off with energy consumption as capacitive effects lead to the reduction of the current efficiency during a galvanostatic operation of the system. Our research shows that the optimal pulse frequency depends on the characteristics of the fouling molecule and the characteristics of the electro dialysis stack and explains why different optimal frequencies have been proposed in the literature.



A modular millifluidic filtration system for in depth fouling investigation

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Main topic: Membrane fouling and cleaning

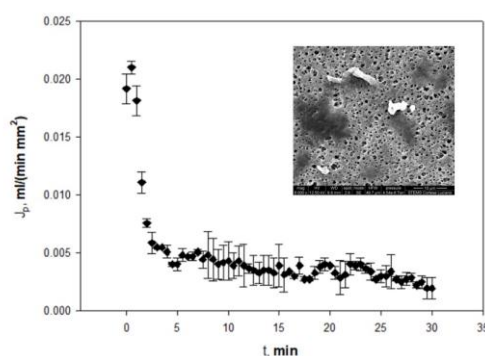
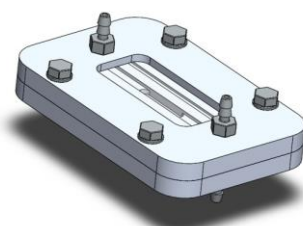
Fouling – that is the accumulation of feed stream components on a membrane surface – is an almost unavoidable phenomenon, which results in rapid permeate flux decline and process throughput loss. An interesting approach to fouling investigation concerns the use of milli- and microfluidic systems in which low amounts of fluid are processed in channels whose diameter can reach few micrometers. As a matter of fact, the effects governing flux usually occur at small time and spatial scales, the latter corresponding to pore dimensions. Studying fouling in micro-sized geometries would therefore allow achieving key insights regarding the interactions between foulants and membrane surface and how these affect species deposition [1]. In this study, fouling dynamics of a Bovine Serum Albumin (BSA) solution were investigated by means of an originally designed millifluidic filtration module, whose principal feature consists of its modularity. Indeed, thanks to the presence of multiple inlets/outlets, the module can be operated equally in dead end and crossflow filtration modes and an auxiliary current on the permeate side, e.g. a dialysate stream, may be added if needed. Specifically, a quantitative systematic analysis was carried out testing module's performances and BSA fouling behavior at constant pressure with three different pumping systems, i.e. a peristaltic pump, a syringe pump and a pressure pump. Both the peristaltic pump and the syringe one were used for crossflow filtration experiments, whereas dead end filtration was performed using the pressure pump. An additional peristaltic pump was employed for crossflow filtration tests in the presence of a secondary stream on the permeate side. Fouling evolution was monitored by measuring permeate flux over time; blocking filtration laws were then used to interpretate experimental data and individuate the underlying blocking mechanism [1,2]. Ultimately, the structure of the fouling deposits were studied with the help of SEM micrographs of the processed membranes, allowing a more complete interpretation of the experimental flux data. Results show how, despite the similar process conditions, the pumping system plays a key role in terms of fouling evolution.

Reference 1:

Cirillo, A.I.; Tomaiuolo, G.; Guido, S. Membrane Fouling Phenomena in Microfluidic Systems: From Technical Challenges to Scientific Opportunities. *Micromachines* 2021, 12, 820.

Reference 2:

Iritani, E. A Review on Modeling of Pore-Blocking Behaviors of Membranes During Pressurized Membrane Filtration. *Drying Technology* 2013, 31, 146--162, doi:10.1080/07373937.2012.683123.



A more sustainable approach in membranes preparation: γ -Valerolactone as a green solvent for PVDF membranes

Figoli, Alberto - Co-Author¹; Russo, Francesca - Co-Author¹; De Caro, Maria Francesca - Co-Author¹; Galiano, Francesco - Co-Author¹

¹Institute on Membrane Technology (ITM-CNR)

Main topic: Advanced fabrication methods

Polymeric membranes are generally prepared by phase inversion techniques requiring the use of toxic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone and tetrahydrofuran. Despite these dipolar aprotic solvents are very effective in dissolving a large variety of polymers, they can pose serious risks for human health and rise several environmental concerns. Therefore, also in view of the stricter environmental regulations, it is imperative to find new benign candidates able to replace the traditional harmful solvents [1]. A new generation of green or more sustainable solvents applied for membrane preparation saw the light in the last decade [2]. In this work, γ -Valerolactone (GVL) was chosen as an innovative renewable green solvent for the preparation of polyvinylidene fluoride (PVDF) membranes. GVL is a biodegradable, non-toxic chemical obtained from the acid hydrolysis of cellulose based biomass. Membranes were prepared by coupling vapor induced phase separation (VIPS) and non-solvent induced phase separation (NIPS) techniques using polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) as pore forming agents. The structure of the membranes was tailored by acting on the exposure time to humidity during VIPS process (from 0 to 5 min) and by varying the water coagulation bath composition during NIPS process (water and water/isopropanol). Prepared membranes were, then, fully characterised. From the results, it was clear that the different exposure times of the cast film to relative humidity played a pivotal role in the determining the final architecture of the membranes. It was possible, indeed, to produce membranes with a finger-like structure (NIPS) and a spherulitic structure (VIPS-NIPS) or characterised by macrovoids when water/isopropanol was used as a coagulation bath. The membranes presented a pore size in the range of ultrafiltration and microfiltration (from 0.04 to 0.84 μm) and good water permeability making them ideal to be applied in water filtration processes. The exposure time to humidity was beneficial in favouring the formation of membranes with a larger pore size. The overall results showed that traditional toxic solvents can be effectively replaced by safer alternatives (such as GVL) leading to the production of membranes with comparable properties and performance of the ones prepared with classic approaches.

Reference 1:

A. Figoli, T. Marino, S. Simone, E. Di Nicolò, X.M. Li, T. He, S. Tornaghi, E. Drioli, Towards non-toxic solvents for membrane preparation: A review, *Green Chem.* 16 (2014) 4034

Reference 2:

F. Russo, F. Galiano, F. Pedace, F. Aricò, A. Figoli, Dimethyl isosorbide as a green solvent for sustainable ultrafiltration and microfiltration membrane preparation, *ACS Sustainable Chem., Eng.*, 8, 2020, 659-668

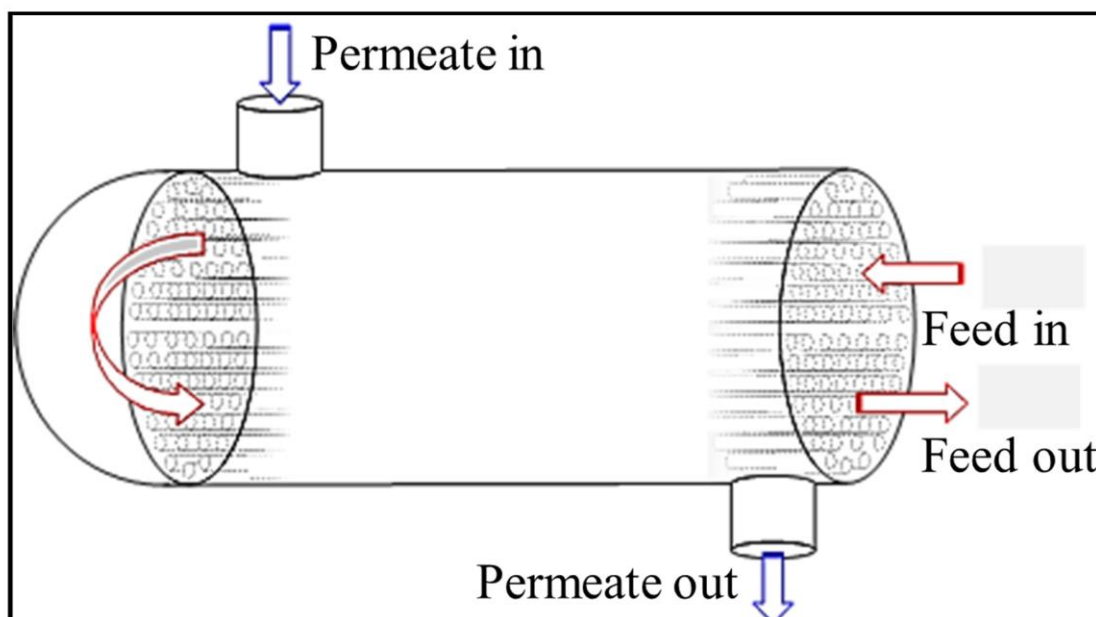
A novel double pass membrane module for internal heat recovery in membrane distillation

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Main topic: Membrane contactors and membrane distillation

Membrane distillation (MD) is a promising thermal-energy-driven process to treat high concentrated solutions. Direct contact MD (DCMD) is the simplest operating configuration of the process however; high specific thermal energy consumption remains the main obstacle in commercial adoption of this configuration. The current study presents a novel membrane module for DCMD with the potential to recover heat within the module. The feed flows in two passes within the module whereas the permeate flows only once before exiting the module as shown in the figure below. As expected, hot feed stream loses heat due to the conduction and convection across the membrane during first pass that results into decrease in its temperature along the module. Temperature of the permeate stream, on the other hand, increases during its flow from inlet to the outlet permeate port. Under appropriate conditions, determined by the pass length, operative conditions (feed velocity and temperature) and heat/mass transfer area in each pass, the outlet temperature of feed in the first pass becomes less than the outlet temperature of the permeate stream. Under these conditions, first and second feed passes serve the purpose of mass transport across the membrane (i.e. generation of mass flux) and heat recovery from the permeate stream, respectively. The performance of the module was validated initially experimentally and subsequently through a mathematical model to study the effect of pass-length, area in each pass and operative conditions including feed velocity and temperature. The results demonstrate that, when operated under the appropriate conditions, the new module has potential to decrease STEC more than 30%. Thus, the novel multipass membrane modules presented in this work offers a new solution to make compact modules for DCMD with a heat recovery arrangement integrate within the module.



A novel iso-porous membrane based on the green polymer with ultra-high porosity

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Main topic: Bio-medical applications

Conventional porous polymeric membranes usually consist of a random network of pores with a wide distribution of pore sizes. The tortuous porous channels and the wide distribution of pore sizes cause a high flow resistance and reduced filtration performance. These problems can be avoided by using iso-porous membranes that contain pores of uniform size and shape. However, producing membranes with narrow pore size distribution (PSD) and high porosity is still challenging to this day. In this work, a novel iso-porous membrane with inverse opal structures was developed. A low-cost green polymer was chosen for this membrane, which made this membrane an economical and ecologically friendly option. Thanks to the self-assembly of the nano-particle templates, this iso-porous membrane obtained an ultra-high porosity (up to $\sim 3 \times 10^{13}$ pore/m² by SEM measurement, and surface porosity > 80%). By tuning the parameters, the porosity, pore size, and thickness of this iso-porous membrane could be well-adjusted. By applying the different crosslinking agents, the hydrophilicity of this membrane could be switched as well. Combined with a porous substrate and an ultra-thin, hydrophilic iso-porous top-layer, high water permeances were achieved ($> 4200 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$). This ultra-high porosity and narrow pore size distribution membrane could be beneficial for various biomedical applications (such as the removal of viruses and bacterias, controlled long-term drug delivery), as well as in many other fields.

Reference 1:

Klaus-Viktor Peinemann, Volker Abetz, Peter F. W. Simon. Asymmetric superstructure formed in a block copolymer via phase separation. *Nat. Mater.* 6, 992–996 (2007).

Reference 2:

Seon Ju Yeo, Gwan H. Choia, Pil J. Yoo. Multiscale-architected functional membranes utilizing inverse opal structures. *J. Mater. Chem. A*, 5, 17111-17134 (2017).

A Novel Non-woven Fabric-based ECTFE Membranes for Direct Contact Membrane Distillation Applications

Ursino, Claudia - Co-Author¹; Ounifi, Ibtissem - Co-Author²; Di Nicolò, Emanuele - Co-Author³; Drioli, Enrico - Co-Author¹; Criscuoli, Alessandra - Co-Author¹; Figoli, Alberto - Co-Author¹

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Main topic: Membrane contactors and membrane distillation

The development of new composite membranes and new membranes materials is gaining popularity. In fact, the necessity to produce highly performing membranes, adapting or using novel polymers or again employing surface functionalization techniques, opens to new research area. In this scenario, an interesting fluoropolymer, used for membrane preparation, is a lower melting point grade of Halar[®] Ethylene-Chlorotrifluoroethylene (ECTFE) named LMP ECTFE. It presents comparable properties with standard Halar[®] in terms of hydrophobicity, mechanical properties and solvent resistance, but lower crystallinity. In fact, standard Halar[®] was solubilized in organic toxic solvents, at high temperature, and the membranes are usually prepared via thermally induced phase separation (TIPS) technique [1]. Instead, LMP ECTFE possesses the unique and advanced properties of the fluoropolymers, thanks to the presence of F-C bond, but it is more workable. Moreover, often fluoropolymers are used as surface modifier/coating material for preparing membranes suitable for membrane distillation (MD). In fact, the commonly membranes used for MD are not designed specifically for this process but are adapted and generally, costly, and not easy to be fabricated. In this context, a new direction is the preparation of porous fluoropolymer composite membranes, as in this work, using non-woven fabric to be dip-coated with LMP ECTFE porous membranes. Specifically, only the 7 wt.% of LMP ECTFE was dissolved at low temperature, in a non-toxic binary diluent system, consisting of di-ethyl Adipate (DEA) and di-ethylene Glycol (DEG), selected as primary and secondary diluent, respectively. Experimental parameters, as the effect of DEG concentration (0-5-7 wt.%) and the influence of the immersion time (3-5-7 s) during the dip-coating, were studied and evaluated. The produced membranes were characterized in terms of morphologies (SEM and AFM), contact angle, porosity and pore size and water permeability. Direct contact membrane distillation (DCMD) experiments using water and salty solution 0.6 M (NaCl) as feed, were performed for selected supported membranes, obtaining a stable water flux (22 L/m²h at 60°C) and a rejection (R%) value comprised from 94.95 to 99.82%. The results show how it is possible to produce supported hydrophobic LMP ECTFE membranes in the MF/UF range for MD applications [2].

Reference 1:

C. Ursino, S. Simone, L. Donato, S. Santoro, M. P. De Santo, E. Drioli, E. Di Nicolò, A. Figoli, ECTFE membranes produced by non-toxic diluents for organic solvent filtration separation, *RSC Adv.*, 6 (2016), 81001

Reference 2:

C. Ursino, I. Ounifi, E. Di Nicolò, X.Q. Cheng, L. Shao, Y. Zhang, E. Drioli, A. Criscuoli, A. Figoli, Development of non-woven fabric-based ECTFE membranes for direct contact membrane distillation application, *Desalination* 500 (2021) 114879

A polymer inclusion membrane with an ionic liquid as a carrier for the recovery of bismuth

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Main topic: Facilitated transport membranes

The considerable and increasing uses of bismuth in most industrial sectors, especially in advanced technologies, have given rise to a great interest in developing selective and non-polluting processes for its recovery and separation. This metal is present in metal ores and in used equipments at extremely low concentrations and require very difficult mining and refining procedures.

In the present study, we report the development of a polymer inclusion membrane (PIM) incorporating two ionic liquids (ILs) for the transport of Bi(III) from hydrochloric acid solutions. PIMs consist of a polymer, which provides mechanical strength, the carrier, which is the responsible of the extraction process, and sometimes also a plasticizer can be used to provide elasticity. Hence, PIMs can be tailor-made depending on the characteristics of the analyte, incorporating either commercial extractants or specifically synthesized ligands. The stability, versatility and easy manufacturing show PIMs as a useful separation technique to be taken into account.

The ILs evaluated in this study are Aliquat 336 (R'R₃N+Cl⁻) and trihexyl(tetradecyl)phosphonium chloride, THTDPCI (R₃R'₃P+Cl⁻), both commercial and acting as anion-exchangers. Parameters affecting the membrane composition, the stripping agent and metal content have been investigated for PIMs made of cellulose triacetate (CTA) and 2-Nitrophenyl octyl ether as the plasticizer, and the ILs as carriers. It has been found that both ion-exchangers are very efficient for the transport of Bi(III) from hydrochloric acid solutions. Moreover, among the different stripping agents, the use of either HNO₃ or H₂SO₄ has allowed the recovery of Bi(III) at efficiencies > 90%. The separation abilities of the PIMs incorporating both ILs have been evaluated using mixtures of Bi(III) and Pb(II), Sb(III) and Mn(II).

Finally, the stability of the new PIMs has been investigated using a membrane composition of 30%CTA, 25% carrier (Aliquat336 or THTDPCI) and 45% NPOE during seven time cycles of transport, repeated every 24h. It was found that it was possible to reuse PIMs with satisfactory recovery factors of Bi(III).

Acknowledgement: This work was supported by the Ministerio de Ciencia, Innovación y Universidades (MCIU) through project PID2019-107033GB-C22/AEI /10.13039/501100011033.

A safe drinking water supply and arsenic removal by recycled reverse osmosis membrane

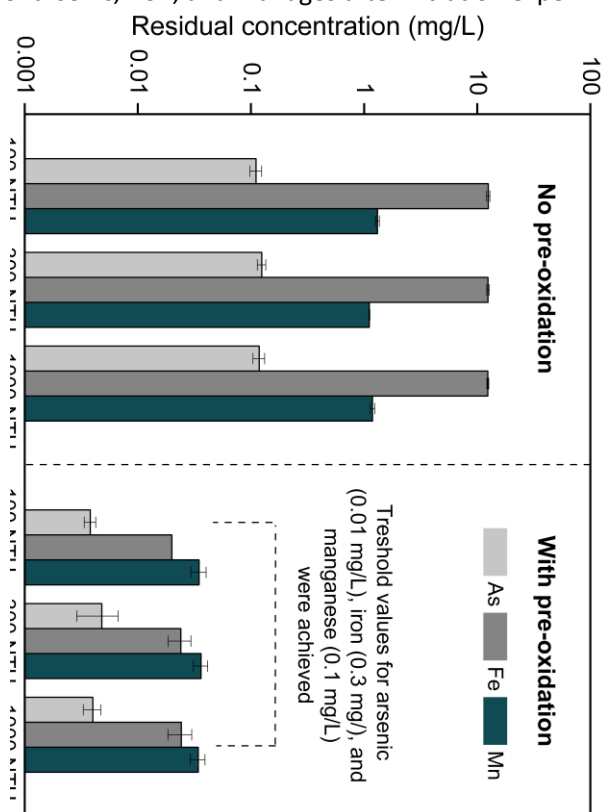
Ramos, Ramatisa - Main Author¹; Moreira, Victor - Co-Author¹; Lebron, Yuri - Co-Author¹; de Paula, Eduardo - Co-Author; Santos, Lucilaine - Co-Author^{1,2}; Amaral, Míriam - Co-Author¹

¹Universidade Federal de Minas Gerais (Brazil), ²Pontifícia Universidade Católica de Minas Gerais (Brazil)

Main topic: Drinking water

Although considered as a naturally occurring compound, arsenic (As) has its occurrence in environmental matrices intensified by anthropogenic activities. The deleterious effects on human health due to As-contaminated water consumption are well established in the literature. However, the costs related to advanced water treatments hamper their implementation in short-income countries. Therefore, a low-cost treatment process is proposed to overcome the As occurrence in drinking water. The process relies on an integrated pre-oxidation process followed by recycled reverse osmosis (r-RO) membranes, a low-cost membrane obtained via chemical oxidation of end-of-life reverse osmosis membranes. The recycling procedure consisted of the immersion of a RO membrane module (FilmTec BW30, average permeability 3.0 L/h·m²·bar, 39 m²) in a commercial sodium hypochlorite bath (~300,000 ppm·h) at room temperature (25°C), for 4h. Water samples of different turbidities (100 -1000 NTU) and concentrations of As (0.015 or 0.2 mg/L), Fe (0.13 – 25 mg/L), and Mn (0.48 – 1.5 mg/L) underwent a pre-oxidation procedure using NaOCl (0.96 mg/mg_{As}) for 1h in a Jar-test. Pre-oxidation was followed by filtration tests by r-RO at 1 bar and 2,4 L/min of recirculation flow rate. The average permeate flux decreased from 71.8 ± 5.2 – 65.2 ± 8.7 L/m²·h when the turbidity increased from 100 to 1000 NTU. With an increase in turbidity, the predominant fouling mechanism went from standard blockage to cake layer formation. This change may be closely associated with an increase in the particle's concentration present in the medium that is likely to accumulate over the membrane surface. The contribution of a pre-oxidation process is evident for As, Fe, and Mn removal at levels recommended by the World Health Organization (Figure 1). The experimental circumstances, which were representative of real conditions, favored the formation of insoluble complexes of iron-arsenic and iron-manganese that could have co-precipitated. In this case, steric hindrance and size exclusion was the main mechanism responsible for their removal. Besides its efficiency in water treatment, the advantages of r-RO could be extended to environmental aspects by extending the use of end-of-life membranes that would be simply discarded.

Figure 1. Residual concentration of arsenic, iron, and manganese after filtration experiments.



A supported liquid membrane for the monitoring of selected antibiotics in water samples

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Main topic (mandatory) Facilitated transport membranes

Tetracyclines (TCs) are a broad spectrum of antibiotics which are widely used for both prevention and treatment of bacterial infections in both humans and animals. The widespread use of TCs could lead to find their residues in surface waters and animal based foods, and due to their potential adverse effects on environment and humans, it is critical to develop reliable analytical methods for routine monitoring of TCs. Among the TCs commercially available, four are the most commonly applied to food-producing animals: tetracycline (TC), oxytetracycline (OTC), chlortetracycline (CITC) and doxycycline (DC). These compounds are highly polar and may exist with different charges depending on the pH of the sample.

In this study, we present the development of a supported liquid membrane (SLM) system as a sample pretreatment method to isolate TCs and, therefore, facilitating their analysis by conventional HPLC-UV instrumentation. Taking into account that TCs are pH-dependent, we have investigated the possibility of using the commercial anion-exchange extractant tricaprylmethylammonium chloride (Aliquat 336) as carrier for the four compounds. The influence of the different chemical parameters affecting the transport of TCs through the SLM has been studied, being the effect of pH in the feed phase primordial. The best extraction conditions were achieved by adjusting the pH of the aqueous feed phase to 12 and using as receiving phase a 10^{-2} M HCl solution. Moreover, the composition of the liquid membrane has also been optimized in terms of carrier concentration and organic solvent. Better results were obtained when working with a 0.5 M Aliquat 336 in decaline solution.

The developed SLM system allowed the determination of TCs from spiked tap water, river water, synthetic swine wastewater and wastewater samples.

Acknowledgement: This work was supported by the Ministerio de Ciencia, Innovación y Universidades (MCIU) through project PID2019-107033GB-C22/AEI /10.13039/501100011033.

Reference 1 (Max 50 words):

Garcia-Rodriguez, Aida; Matamoros, Victor; Kolev, Spas D.; Fontas, Claudia. Development of a polymer inclusion membrane (PIM) for the preconcentration of antibiotics in environmental water samples. *Journal Of Membrane Science* 2015, 492, 32 - 39.

Reference 2 (Max 50 words):

S. Shariati, Y. Yamini, A. Esrafil, Carrier mediated hollow fiber liquid phase microextraction combined with HPLC-UV for preconcentration and determination of some tetracyclines antibiotics, *J. Chromatogr. B*, 2008, 877, 393-400.

farinelli, giulio - Co-Author¹

¹Politecnico di Torino

Main topic: Membrane contactors and membrane distillation

The treatment of hypersaline wastewaters is a challenging task, especially if these streams contain high concentrations of organics and hydrocarbons, such as in typical produced and flowback waters. Conventional reverse osmosis is limited to values of total dissolved solids in the feed solution of < 50 g/L. On the other hand, phase –change based desalination processes, such as membrane distillation (MD), may efficiently be applied to desalinate brines using low-grade heat as the driving force.

As highly hydrophobic membranes are used in MD, organics and biological foulants generally present in produced water tend to deposit onto the membrane, causing a dramatic impairment of the performance of the process. Since the membrane materials in MD are highly hydrophobic the high organic content of a shale gas water can reasonably wet the membrane and eventually freely pass through the membrane leaving in the permeate highly toxic and harmful organic compounds. Advanced oxidation processes, such as Fenton or modified Fenton reaction, are promising low-energy and low-cost pre-treatment for MD, since they effectively mineralize organics and hydrocarbons, thus helping the production of a cleaner and safer permeate. The Fenton process employs iron ions and hydrogen peroxide in order to generate the highly reactive hydroxyl radical as active species to oxidize the substrates. However, the Fenton process is highly inhibited in a high-salinity effluent, because chloride ions can scavenge the hydroxyl radicals. On the other hand, a modified-Fenton process, where iron ligands are used, is less sensitive to chloride scavenging, thus is the most promising treatment for organic compounds in a hypersaline wastewater. In this work, Fenton and modified Fenton reaction are evaluated as pre-treatment processes for the desalination of a synthetic produced water using MD. The results of this coupling show great potential in a high performance TOC removal in a hypersaline solution signing a milestone in the route toward the zero-liquid discharge.

Ag-MOFs as biocidal reservoirs for sustainable (bio)fouling mitigation and biofilm inhibition in membrane processes.

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¹PhD student

Main topic: Novel membrane materials

Membrane technologies are vastly used for water purification and wastewater treatment. These membranes are, however, severely susceptible to fouling through pollutant adhesion, pore clogging, and biofilm formation as a result of rapid microbial proliferation.

Metal-organic-frameworks (MOFs) are 2D and 3D networks formed through the liaison of a spectrum of metal nodes and organic linkers. Utilization of these highly tunable compounds as surface modifiers can impart target properties to the membranes, such as improved hydrophilicity and antimicrobial potency, with higher compatibility with the membrane as well as a more prolonged stability compared to purely inorganic modifiers. There are multiple pathways towards modifying membranes with MOFs, including direct deposition, in-situ growth, and UV-grafting. Using these compounds in conjunction with highly hydrophilic coatings such as zwitterions and acrylic acid can lead to a combination of a “defensive” antifouling strategy with an “offensive” antibiofouling approach, thus preventing both foulant/microbial attachment and biofilm formation.

In our study, a streamlined pathway of in-situ functionalization of forward osmosis membranes with both Ag-MOFs and zwitterions resulted in a 50% decline in water contact angle, indicating a heightened wettability. The zwitterionic layer also played a key role in the MOFs deposition and growth, thus significantly boosting silver loading of the membranes. Membranes showed a new-found resilience toward (bio)fouling; they retained at least 75% and 80% of their initial fluxes in fouling tests against sodium alginate and biofouling tests against *E. coli*, respectively, after 24 hr of filtration. Bacterial inactivation rates amounted to 76%, making the membrane surfaces inhospitable for microbial proliferation. Also, 30-day silver leaching from these membranes remained under 1 µg/L, which is well below the WHO safety limit for drinking water (0.1 mg/L). These results indicate that Ag-MOFs can act as safe and efficient biocidal reservoirs that provide sustainable antibiofouling activity for the membranes in prolonged operation and their deployment on membranes could be accomplished via facile surface-modification methods.

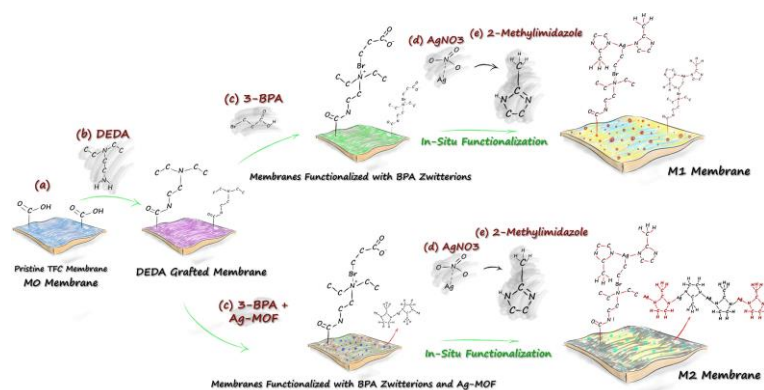


Figure 1. Illustrative scheme of the steps involved in surface-modification of membranes

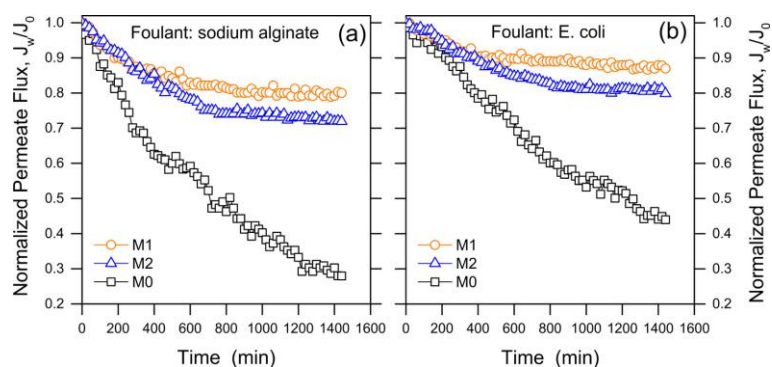


Figure 2. Anti(bio)fouling performance of the pristine (M0) and of the surface-modified membranes (M1, M2) during FO filtration tests.

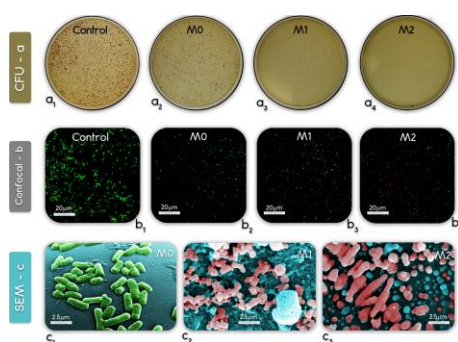


Figure 3. Results of antibacterial activity of the pristine (M0) and surface-modified membranes (M1, M2) against *E. coli*: (a1–4) heterotrophic plate count of cells, (b1–4) live/dead microscopy images of cells, and (c1–3) SEM images of bacteria upon contact with the membranes

Reference 1:

In Situ Ag-MOF Growth on Pre-Grafted Zwitterions Imparts Outstanding Antifouling Properties to Forward Osmosis Membranes ACS Appl. Mater. Interfaces 2020, 12, 32, 36287–36300

Ageing study and self-cleaning properties assessment of a PVDF-PVP-TiO₂ hollow fiber membrane

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Main topic: Ageing of polymeric membranes

In the past few years, PVDF-TiO₂ membranes have been investigated as a way to associate self-cleaning and super hydrophilicity properties through photocatalysis, with *a priori* great chemical and mechanical resistance of the backbone material [1]. Nevertheless, PVDF stability has only been the subject of a few studies.

In this framework, we conducted an ageing study on a hollow fiber (HF) PVDF-PVP-TiO₂ membrane to assess the impact of UV irradiation on the physical and chemical structure of the membrane under various conditions. HFs were irradiated at 1 mW/cm² while soaking in a static aqueous medium.

When irradiated in ultra-pure (UP) water for 16 days, HFs lost 50% of tensile strength and 75% of elongation at break. The average HF wall thickness measured by SEM and the dry mass of HFs decreased by 45% and 50% respectively. FTIR spectra performed on HFs showed that every functional group of PVDF and PVP was attacked by highly oxidative OH° radicals produced through UV irradiation of TiO₂. Polymer degradation and TiO₂ nanoparticles release were confirmed through soaking medium analysis.

When irradiated in a methylene blue (MB, chosen at first as model pollutant) solution for 16 days, HFs showed no signs of significant morphological or chemical modifications and no quantifiable amounts of fluorine or titanium were found in the soaking solution. MB concentration decreased by 90% during the first 7 days of irradiation, as MB is degraded by consuming OH° radicals which effectively divert them from oxidizing HF components. After the first MB oxidation step, MB degradation products keep on consuming OH° until mineralization [2], explaining why no modifications were observed on HFs even after a significant drop in MB concentration.

Work is now in progress to assess the self-cleaning properties of the membrane. HF were pre-clogged by BSA adsorption/filtration, and are now being UV irradiated in UP water. Degradation of the BSA layer is quantified through FTIR analysis of the membrane surface.

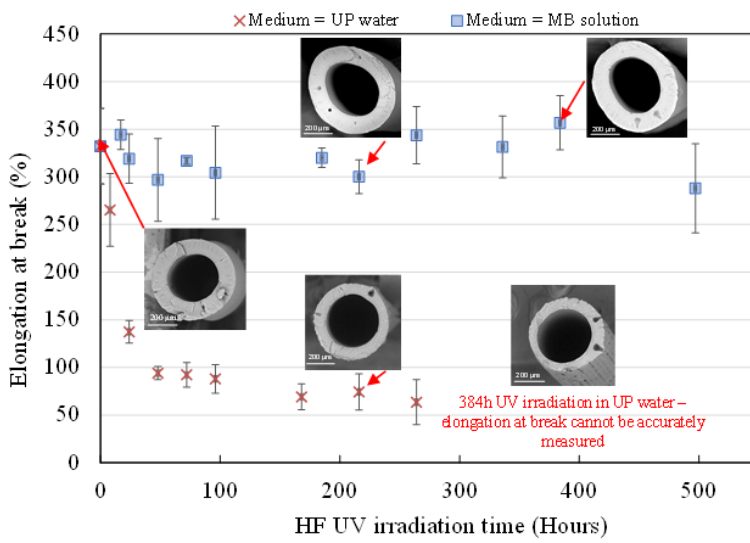
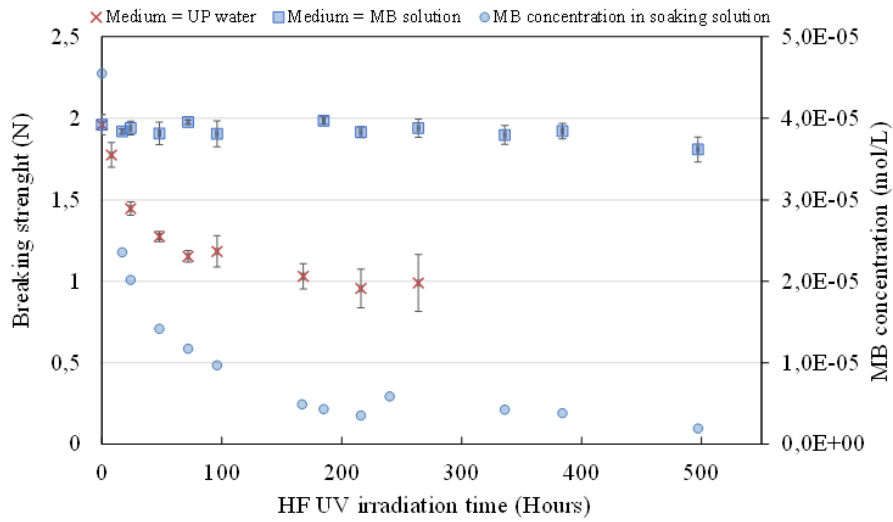
Ageing conditions selected in this first work seems to be too harsh for sustainable operation. Future work plans to determine an operating irradiation power that would not degrade the material but still provide self-cleaning properties to the membrane.

Reference 1:

M. Romay, N. Diban, M.J. Rivero, A. Urriaga, I. Ortiz, Critical issues and guidelines to improve the performance of photocatalytic polymeric membranes, 2020. <https://doi.org/10.3390/catal10050570>.

Reference 2:

A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Herrmann, Photocatalytic degradation pathway of methylene blue in water, Appl. Catal. B Environ. 31 (2001) 145–157. [https://doi.org/10.1016/S0926-3373\(00\)00276-9](https://doi.org/10.1016/S0926-3373(00)00276-9).



Alkaline and enzymatic cleaning of polymer membranes: an original protocol to evidence strengths and weaknesses of formulated detergents and go ahead in formulation of efficient prototypes

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Main topic: Membrane fouling and cleaning

The cleaning efficiency of a detergent is generally checked by the mean of a set of long-term filtrations with the detergent under evaluation.

Recently, we proposed an original methodology designed to rapidly evaluate if a prototype formulation can be promising or not, allowing to evidence cleaning efficiency for a given application (membrane, fouling fluid) together with an estimation of short & long-term possible degradation of the membrane. Part of this approach was first successfully applied to the development of a non-oxidizing biocide useful for RO membrane that was proved to be harmless toward a (spiral) polyamide membrane (DEPTACID WCM, Hypred-Kersia) [1].

In this study we have gone ahead and applied the overall methodology to develop new alkaline detergents to clean PES/PVP membranes used in skim milk ultrafiltration. The irreversible fouling at cleaning start being made of proteins, in the selected pH range (11.0 – 12.4), the heart of the detergent efficiency is the surfactant system. However, its selection remains difficult even for specialists. Up to 10 detergent prototypes can be tested in one day permitting the selection of the more promising prototypes. Long term filtration (here 50 h in the detergent at target concentration of use) was only conducted on pre-validated detergent minimising the development cost. A single ATR-FTIR analysis, able to (i) evaluate the cleaning efficiency, (ii) identify the (irreversible) adsorption of detergent components on the membrane and (iii) evidence the membrane short/long term degradation is reliable for decision making on formulation whereas microwave activation is relevant for long term ageing evaluation [1,2].

Surprisingly, some very efficient surfactants with respect to the membrane cleaning were able to induce unexpected membrane degradation and had to be rejected. Nevertheless, the development of an alkaline detergent efficient for PES/PVP membrane cleaning was successful and a new detergent is now commercially available (DEPTAL UF L1, Hypred-Kersia). The primary methodology was also extended to risk evaluation associated to surfactant leakage and to storage evaluation of spiral membrane at diluted concentration (12-18 months). Finally, the evaluation of a set of enzymatic detergents useful for the cleaning of skim milk UF PES based membrane began.

Reference 1:

[1] L. Le Petit, M. Rabiller-Baudry, R. Touin, R. Chataignier, P. Thomas, O. Connan, R. Péron, Efficient and rapid multiscale approach of polymer membrane degradation and stability: Application to formulation of harmless non-oxidative biocide for polyamide and PES/PVP membranes, *Separation and Purification Technology*. 259 (2021) 118054. <https://doi.org/10.1016/j.seppur.2020.118054>.

Reference 2:

[2] M. Rabiller-Baudry, L. Paquin, C. Lepéroux, H. Diallo, H. Al Jawad, C. Sepré, How microwaves can help to study membrane ageing, *Environmental Technology*. 41 (2020) 2314–2336. <https://doi.org/10.1080/09593330.2018.1564072>.

ALTERNATIVE FOR APPLICATION OF VINASSE IN FERTIRRIGATION

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Main topic (mandatory) Wastewater treatment

Vinasse, the residue generated in the production of ethanol, presents itself as one of the main burden of the sugar-alcohol sector, precisely because of its high generation, since for each liter of ethanol produced, 10 to 13 liters of vinasse are generated (Silva *et al.*, 2019). An ecofriendly way of disposing this waste is its raw application in agricultural soil via fertigation. However, when carried out in an uncontrolled manner, it presents disadvantages such as soil salinization, loss of its productive capacity and loss of groundwater quality, in addition to often becoming economically unfeasible, since the long distances traveled to the application areas linked to the high volumes of raw vinasse to be disposed of, makes the economic radius prevail over the benefits presented by fertigation. Thus, an alternative for the resource recovery of this effluent in agricultural areas is its treatment through the association of membrane treatment techniques such as ultrafiltration (UF) and nanofiltration (NF). To this end, the characteristics of their applications to the soil by fertigation were analyzed for the raw vinasse (VB) and the conjunction of the concentrate of UF and NF (UF+NF). The raw vinasse, in a dose of 369.1 m³ ha⁻¹ year⁻¹, with 2.540 kg of potassium per m³, has the capacity to fertigate an area of 9,832 hectares, a value which is similar to 13,770 football fields, while the UF+NF conjunction, with a dose of 407.8 m³ ha⁻¹ yr⁻¹, with 2.299 kg k m⁻³, would need 6,051 hectares to apply the dose, in the first year. Both effluents presented similar organic load applied to the soil and in compliance with what is recommended in the literature (VB = 12.149-ton COD ha⁻¹ and UF+NF = 11.780-ton COD ha⁻¹). Thus, the application of the UF and NF conjugate proved to be an excellent alternative for crop fertigation and requiring a smaller application area.

Reference 1 (Max 50 words):

SILVA, M. M.; MAZEIRO, R.; OLIVEIRA, L. S.; RUBIO, J. C. C. Aproveitamento da vinhaça residual da produção do etanol para geração de biogás: uma revisão. RETEC, v.12, n.2, p. 17-25, 2019.

Amine-Modified Ultrafiltration Membranes as Anion Adsorbing Materials

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Main topic: Microfiltration/Ultrafiltration

Water pollution and water scarcity are urgent global challenges, nowadays. Besides microbiological contaminations, (geogenic) chemicals like arsenate (AsO_4^{3-}) and chromate (CrO_4^{2-}) are harmful pollutants in water. Both contaminants are highly genotoxic and causes serious illnesses like cancer and fetal malformation. Therefore, it is important to eliminate these contaminants from drinking water completely.

Anion adsorbing membranes provide an interesting possibility to remove negatively charged metal oxyanions in a one-step procedure without adding chemicals to the water. A promising way to prepare anion-adsorber materials is to introduce (positively charged) amine groups on polymeric membranes. The application of anion adsorbing ultrafiltration membranes is very interesting, in particular because the membranes can operate at low pressures and therefore, with low energy consumption.

In this study, polyacrylonitrile (PAN) ultrafiltration membranes were post-modified to create amine functionalities on the surface of the membranes. [1] Different modification strategies were used to generate primary, secondary, tertiary and quaternary amine groups on the membranes. The membranes were characterized regarding their chemical (e.g. zeta potential, amine content, IR spectra) and material properties (e.g. membrane surface area, pore size, water permeance). The analysis showed a change of the surface charge due to introduction of amine groups while the membrane performance was not affected by the modification.

Additionally, the chromate and arsenate adsorption behavior of the modified membranes was analyzed. The modified membranes showed significantly increased adsorption capacities of both anions. These results were very promising for drinking water applications. Therefore, further optimization of the modification and implementation in application-oriented filtration experiments are part of the ongoing study.

Reference 1:

Glass, S., Mantel, T., Appold, M., Sen, S., Usman, M., Ernst, M. and Filiz, V. (2021), Amine-Terminated PAN Membranes as Anion-Adsorber Materials. *Chemie Ingenieur Technik*. <https://doi.org/10.1002/cite.202100037>

Amphiphilic copolymer thin-film composite membranes

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Main topic: Organic solvent nanofiltration

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In chemical and pharmaceutical industry, the recovery or exchange of organic solvents is increasingly important to create more sustainable processes. Special properties, in particular stability under process conditions, are necessary for the use in organic solvent nanofiltration or pervaporation. One established material is polydimethylsiloxane (PDMS). Amphiphilic thin-film composite membranes show promising, potentially tunable separation performance due to a barrier structure with microphase-segregated morphologies,^[1] but are only rarely studied until now. Our approach is to explore interpenetrating network (IPN) membranes based on PDMS and poly-(2-dimethylaminoethyl)-methacrylate (PDMAEMA) (cf.^[2]) in order to obtain thin-film composite membranes with a tunable barrier structure. Therefore, a thin PDMS layer is dip-coated on top of a porous polyacrylonitrile (PAN) support. In a second step, the PDMS membrane is placed in a solution of DMAEMA monomer, a cross-linker monomer and a photo-initiator, followed by cross-linking copolymerization activated via UV irradiation. To further promote microphase separation in the IPN, the PDMAEMA can be functionalized to a polyzwitterion via sulfobetainization using propane-1,3-sultone in a third step.^[2]

One important factor is the PDMS itself, which can be influenced by the crosslinker fraction and the curing temperature during preparation (**Figure 1**).

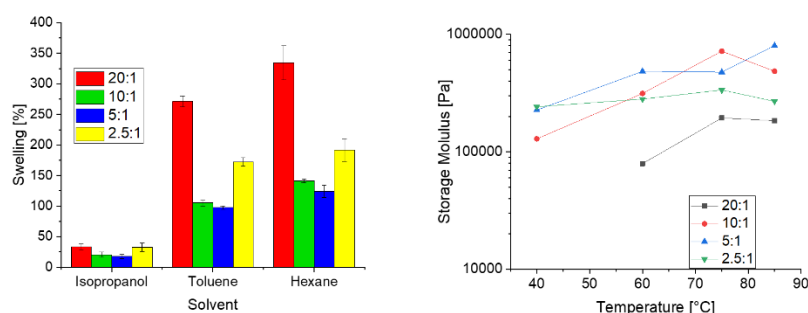


Figure 1: Degree of swelling of PDMS films in different solvents depending on the PDMS/crosslinker ratio (left) and storage modulus of films with different PDMS/crosslinker ratio cured at different temperatures (right).

The second important aspect is the formation and separation performance of the IPN. The feasibility has been demonstrated using a commercial PDMS thin-film composite membrane (Pervap 4060, DeltaMem AG) which had been converted into a PDMS-PDMAEMA-IPN composite membrane. Nanofiltration data for different organic solvents indicate that the formation of the amphiphilic IPN leads to changed barrier properties because the permeability of non-polar hexane is largely reduced while that of polar isopropanol is increased (**Figure 2**).

Ongoing work is devoted to elucidating the influences of the cross-linking density and the procedure for fabricating the IPN and to evaluating the novel membranes with respect to permeance and selectivity in separation of mixtures by nanofiltration.

Reference 1:

[1] T. Miyata, J. I. Higuchi, H. Okuno, T. Uragami, *Journal of Applied Polymer Science* 1996, 61, 1315-1324.

Reference 2:

[2] A. Dundua, S. Franzka, M. Ulbricht, *Macromolecular Rapid Communications* 2016, 37, 2030-2036.

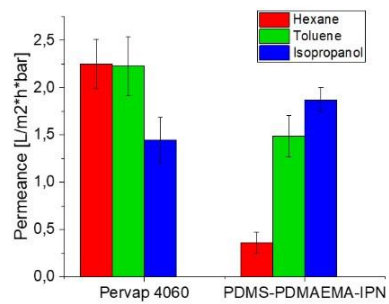


Figure 2: Nanofiltration permeances for different organic solvents of a novel PDMS-PDMAEMA-IPN membrane and the precursor PDMS membrane.

An analysis of the effect of Zeolitic Imidazolate Framework (ZIF-8) addition on the separation properties of Polysulfone at various temperatures

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Main topic: Gas separation

The permeability of H₂, He, CO₂, O₂, CH₄, and N₂ at temperatures up to 65°C was measured in dense, thick composite films formed by amorphous Polysulfone (PSf) and particles of the size-selective Zeolitic Imidazolate Framework 8 (ZIF-8) at loadings up to 16 wt%. The morphological and structural properties of the membranes were analysed via SEM and density measurement showing a good compatibility between the phases. Pressure decay analysis for direct solubility and diffusivity measurements was performed for He, CH₄, N₂, and CO₂ for pure PSf and PSf/16% ZIF-8 membranes at temperatures up to 65°C.

The addition of ZIF-8 to PSf enhances the H₂ and He permeabilities up to 480% with respect to the pure polymer, while the ideal H₂/CO₂ and He/CO₂ selectivities of MMMs reach values up to 30-40% higher than those of pure PSf. The relative permeability and diffusivity enhancements are higher than those obtained in other polymers such as PPO with the same amount of filler, possibly due to the smaller PSf free volume, and they are an increasing function of the gas kinetic diameter. The diffusivity trends indicate that the ZIF-8 diameter is large enough to allow diffusion of CH₄ and N₂. Indeed, the addition of filler lowers significantly the activation energy of diffusion and permeation, especially for the larger gases and more markedly than what observed in other similar mixed matrix membranes. This trend is confirmed by direct solubility and diffusivity measurements. The Maxwell-Wagner-Sillars model is able to represent the MMM H₂/CO₂ separation performance below filler fractions of about 10wt%.

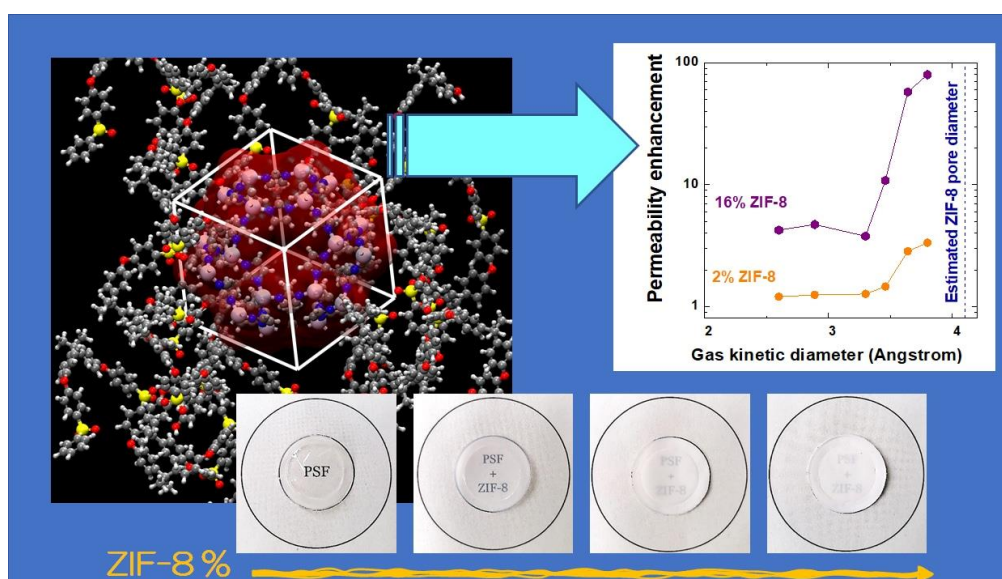
The results of the present and previous works indicate that ZIF-8 is a valid possible permeability-enhancing additive to be used on those materials for which this parameter is critical, and for those gas couples, such as H₂/CO₂ and He/CO₂, where its addition is not detrimental to the selectivity.

Reference 1:

Papchenko, K.; Risaliti, G.; Ferroni, M.; Christian, M.; De Angelis, M.G. An Analysis of the Effect of ZIF-8 Addition on the Separation Properties of Polysulfone at Various Temperatures. *Membranes* 2021, 11, 427.

Reference 2:

Benedetti, F.M.; De Angelis, M.G.; Degli Esposti, M.; Fabbri, P.; Masili, A.; Orsini, A.; Pettinau, A. Enhancing the Separation Performance of Glassy PPO with the Addition of a Molecular Sieve (ZIF-8): Gas Transport at Various Temperatures. *Membranes* 2020, 10, 56.



An efficient low-cost, no-chemicals, water-recycling method for the production of pure phycocyanin from *Arthrospira maxima*

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Main topic: Bio-separations and bio-refinery

Spirulina (*Arthrospira platensis*), a blue-green coil shaped cyanobacterium, is known in the food and nutraceutical sectors as an important source of water soluble proteins, antioxidants, vitamins and minerals [1]. It is an important source of C-phycocyanin (CPC), a water soluble protein belonging to the phycobiliprotein family having a great potential for industrial and commercial exploitation due to its therapeutic properties including antioxidant, anti-inflammatory and anti-cancer activities.

The purification of CPC from Spirulina generally involves a combination of different techniques including sonication, extraction, centrifugation, chromatography, ion exchange and dialysis [2]. Here we report the results on CPC yields compared among extraction methodologies from a strain of *Arthrospira maxima*, cultivated in a farm devoted to produce food additives for human consumption.

The simplest, the environmental and energetic sustainable methodology gave the best yield and quality of phycocyanin tested by means the SDS-PAGE patterns and mass spectrometry analysis. Samples produced at different extraction times were purified by ultrafiltration (UF) using a stirred dead-end filtration system equipped with a polyethersulphone membrane having a molecular weight cut-off of 20 kDa. Filtration experiments were performed at an operating pressure of 2.0 ± 0.1 bar and a temperature of 25 ± 2 °C up to a volume reduction factor (VRF) of 5. After UF, the remaining retentate was diafiltrated with distilled water in order to increase the recovery of phycocyanins in the retentate. Ultrafiltrated samples were processed by electrophoretic analyses in order to assess proteins quality and purity and to check contamination by nucleic acids.

In the selected operating conditions, the rejection of the UF membrane towards phycocyanin resulted higher than 97.8% independently by the extraction yields and times. The concentration of CPC in the final retentate resulted of about 0.9-1.1 g L⁻¹, about 5-fold when compared to the concentration of CPC in the crude extract (0.19 g L⁻¹).

The integrated extraction-UF process provides an efficient low-cost and no-chemicals method for the production of pure phycocyanin suitable for commercialization as additive in protein food, antioxidant in pharmacological and therapeutics and natural dye in cosmetics and pastry.

Reference 1:

[1] Grosshagauer S., Kraemer K., Somoza V. The true value of Spirulina. *Journal of Agricultural and Food Chemistry*, 68 (2020) 4109-4115

Reference 2:

[2] Cruz de Jesús V., Gutiérrez-Rebolledo G.A., Hernández-Ortega M., Valadez-Carmona L., Mojica-Villegas A., Gutiérrez-Salmeán G., Chamorro-Cevallos G. Methods for extraction, isolation and purification of C-phycocyanin: 50 years of research in review. *International Journal of Food and Nutritional Science*, 3 (2016) 1- 10

An Efficient Method to Determine Membrane Molecular Weight Cut-Off Using Nanoparticles

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Main topic: New characterisation methods

Membrane processes are more and more used because they are more energy and environmentally friendly than other separation techniques. The initial selection of the membrane for any application is usually based on its Molecular Weight Cut-Off (MWCO). However, there is a lack of a quantitative, liable, and rapid method to determine the MWCO of the membrane. In this study, a methodology to determine the MWCO, based on the retention of fluorescent silica nanoparticles (NPs), is presented [1]. Two Membranes, M1 and M2 of different pore sizes, have been investigated. A particle tracking analysis with a nanosight allows to determine the variation of NP number vs. Np Size and to calculate the retention curves at all times. The reproducibility of the experiments was validated. The retention rates of NPs with sizes larger, closer to, and smaller than the membrane pore size given by the manufacturer at optimized experimental conditions were studied. It was shown that the retention of NPs changed over the filtration process due to the membrane fouling: as expected, a shift of the MWCO value is observed whatever the experiment as a function of the filtration process duration. So, the selectivity of the membrane should be detected at the first few minutes of the filtration process. The membranes used presented good retention rates curves with different sizes of NPs, increasing gradually until they formed a plateau at 100% of retention. This allows determining the MWCO at a 90% retention rate according to the French Standard NF X 45-103 [1] although another could be selected. The reliability of this methodology, which presents a rapid quantitative way to determine the MWCO, is in good agreement with the value given by the manufacturer. A MWCO of 181.5 nm has been determined for Membrane M2 with NPs of 300 nm, and 110 nm for the Membrane M1 with the NPs of 200 nm, close to the values given by the supplier (200 and 100 nm, respectively) [2].

Reference 1:

AFNOR, norme française NFX45-103, diffusée by the French Association of Normalization, 1997, Paris La Défense, France.

Reference 2:

Fadel, M., Y. Wyart and P. Moulin, An efficient method to determine membrane molecular weight cut-off using fluorescent silica nanoparticles, *Membranes* 10 (2020), 271, 1-14.

An Innovative Mining System: The Sea

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Main topic: Membrane contactors and membrane distillation

Membrane crystallization (MCr) is an innovative membrane process that allows both the extraction of freshwater and the recovery of valuable minerals from supersaturated feed solutions. The most interesting aspect of MCr is brine mining, due to its high economic potential. That is the reason why a great deal of research effort is addressed to salt crystallization from brines. With the objective to simulate the complexity of salty solutions present in the Sea, the biggest potential source of metals and minerals, new studies are aimed at crystallizing specific salts from multi-salt systems.

Here, we highlight why MCr configuration is a key factor that determines the occurrence or non-occurrence of crystallization of certain salts, especially NaCl and LiCl, by comparing results obtained from direct contact membrane distillation (DCMD) and vacuum membrane distillation (VMD). The impact of temperature polarization and fluid dynamics on salt crystallization is explored. The possibility of tuning the formation of specific polymorphs for the different salts will be discussed.

We also present experimental results related to the crystallization of Na₂SO₄ in a Na₂SO₄/NaCl mixture, at three different relative concentrations of the two salts. Experimental observations showing how impactful the feed temperature can be in inducing different Na₂SO₄ morphologies are included too.

An integrated membrane-assisted biorefinery process for the recovery of biophenols from *Castanea sativa* shell

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Main topic: Bio-separations and bio-refinery

Chestnut shell (*Castanea sativa* Mill.), an abundant agro-industrial by-product generated during chestnut peeling process, is usually discarded or used as fuel. However, this by-product has been recognized as a remarkable source of biophenols, such as gallic and ellagic acids, well recognized for their protective activities as antioxidants and the prevention of several types of human diseases [1].

The growing interest of both consumers and producers towards these substances has intensified research efforts to develop novel and sustainable procedures for their extraction, separation, and purification in an efficient and environmentally friendly manner without affecting their stability [2].

In this contest, this work was aimed at investigating, for the first time, an integrated biorefinery strategy for the extraction, separation and concentration of bioactive compounds (mainly gallic and ellagic acids) from dried chestnut shell. The process is based on a preliminary extraction of dried chestnut shell followed by clarification, fractionation and concentration of the extract with ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes in a sequential design. The extraction process has been optimized for obtaining the maximum yield of polyphenols by following an eco-friendly route. At this purpose, different parameters such as extraction temperature and type of solvent (water and alcohol/water mixture) have been optimized. The obtained results showed a maximum polyphenol yield of about 6.6 g/L at an operating temperature of 50 °C and a water-to-solid ratio of 9 mL/g.

The aqueous extract was previously clarified with hollow fiber UF membranes of 500 kDa in order to remove macromolecules and suspended solids. Then, the UF permeate has been treated by a spiral-wound NF membrane (MWCO, 300-500 Da): an average permeate flux of about 50 L/m²h was measured in selected operating conditions. Ellagic acid was totally recovered in the retentate stream, while most of gallic acid was recovered in the permeate and concentrated through a final RO step with the production of clean water (RO permeate).

The proposed process, based on circular economy approach, allows (i) the recovery of valuable compounds for the formulation of functional ingredients and (ii) minimise the highly expensive and environmentally risky disposal of chestnut shell.

Reference 1:

Pinto D., de la Luz Cádiz-Gurrea M., Vallverdú-Queralt A., Delerue-Matos C., Francisca Rodrigues F. *Castanea sativa* shells: A review on phytochemical composition, bioactivity and waste management approaches for industrial valorization, *Food Research International* 144 (2021) 110364

Reference 2:

Conidi C., Drioli E., Cassano A. Membrane-based agro-food production processes for polyphenol separation, purification and concentration, *Current Opinion in Food Science* 23 (2018) 149-164

Analyzing the effect of viscous flow, diffusive transport and mixture non-idealities in organic solvent nanofiltration with ceramic membranes using Maxwell-Stefan theory

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Main topic: Organic solvent nanofiltration

With pore sizes between 1 and 10 nm, the transport mechanism of solutes and solvents in ceramic nanofiltration membranes lies in the transition region between those of ultrafiltration membranes (viscous transport) and 'tight', reverse osmosis membranes (diffusive transport). Furthermore, the relative contributions of both transport mechanisms, as well as solute partitioning, can be expected to be solvent dependent. The Maxwell-Stefan equations can be used to describe membrane transport when both diffusive and viscous transport is occurring.^{1,2} Moreover, the effect of the solvent on solute partitioning and flux can be taken into account by employing activity coefficient models. In this contribution, the effect of these different interconnected phenomena on flux and rejection is studied theoretically using Maxwell-Stefan theory. A global sensitivity analysis is performed to investigate the effect of membrane, solute and solvent specific parameters on modelled flux and rejection. For model solutes, the effect of non-idealities in the external solvent phase is taken into account, investigating the effect on rejection. Furthermore, the relative contribution of pressure driven diffusion, viscous flow and concentration driven diffusion is quantified and critically evaluated. Such an analysis allows to gain a more fundamental understanding of the governing dominant transport mechanism for a given membrane/solvent/solute combination, as well as allowing for a reduction in model complexity.

Reference 1:

Mason, E. A.; Lonsdale, H. K. Statistical-Mechanical Theory of Membrane Transport. *J. Memb. Sci.* 1990, 51 (1–2), 1–81. [https://doi.org/10.1016/S0376-7388\(00\)80894-7](https://doi.org/10.1016/S0376-7388(00)80894-7).

Reference 2:

Noordman, T. R.; Wesselingh, J. A. Transport of Large Molecules through Membranes with Narrow Pores - The Maxwell-Stefan Description Combined with Hydrodynamic Theory. *J. Memb. Sci.* 2002, 210 (2), 227–243. [https://doi.org/10.1016/S0376-7388\(02\)00351-4](https://doi.org/10.1016/S0376-7388(02)00351-4).

Anti-biofouling membranes via hydrogel electron beam modification – a fundamental and applied study

Fischer, Kristina - Co-Author; Lohmann, Jessica - Co-Author; Schmidt, Eva - Co-Author; Blaich, Theresa Helene - Co-Author; Belz, Carsten - Co-Author; Thomas, Isabell - Co-Author; Schulze, Agnes - Co-Author

Main topic: Membrane fouling and cleaning

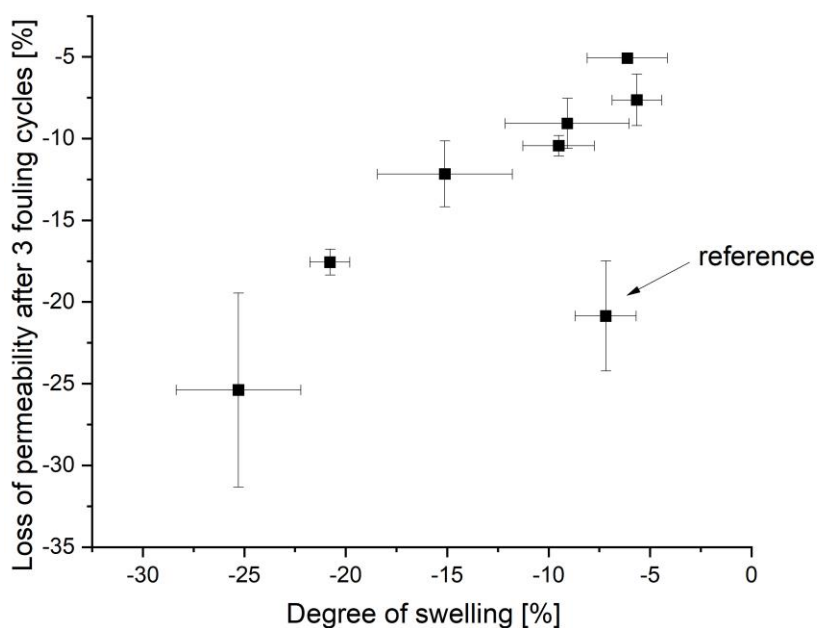
Membranes are increasingly applied in wastewater treatment. Membrane polymers like polyethersulfone (PES) are hydrophobic and tend to foul due to hydrophobic interactions. This leads initially to adsorption, clogging of the pores, whereby the throughput capacity decreases significantly. The pressure has to be increased and the energy consumption is rising accordingly. Biofouling makes up 45% of the total fouling and is irreversible.

In this work, different membranes (polyethylene terephthalate (PET) track etched and PES ultrafiltration) have been modified with a thin layer of a hydrogel via electron-beam modification, which avoids the usage of toxic photoinitiators. Anti-biofouling properties of hydrogels have been proven due to their smooth, non-sticking, and hydrophilic surface in different research papers and were studied here on the basis of fundamental research (laboratory algae fouling tests) and applied long time studies in wastewater treatment membrane modules (filtration area 1.5 m²).

For the fundamental study, different monomers and cross linking agents have been applied on PET track etch membranes to study the effect of hydrophilicity, roughness, surface charge, and degree of swelling on algae fouling. The PES ultrafiltration membrane was treated in a similar way with poly(ethylene glycol) diacrylate (PEGDA) as a monomer.

The hydrophilicity, roughness, and surface charge have an insignificant effect on algae fouling. Only the degree of swelling had an impact on the biofouling. The hydrogels with the lowest degree of swelling, thus with the highest cross linking degree, showed the lowest loss of permeability after fouling (see figure). The modification of the PES membrane with PEGDA resulted in a higher permeability after backwashing (algae fouling tests) of 35%, which proves that the biofouling agents can be more easily removed. During the cleaning of wastewater over several month, the overall permeability is higher (ca. 10%) with a module equipped with PEGDA modified membranes compared to a module with reference membranes.

Modification of membranes with hydrogels decreases biofouling, thus enhances the overall permeability. Decreasing the degree of swelling results in lower biofouling.



Application of Bipolar Electrodialysis to the generation of alkaline and acidic solutions from concentrated seawater brines from saltworks

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Main topic: Electro-membrane processes

The scarcity of raw materials in the European Union has made necessary to obtain them from secondary resources. Within this context, sea mining has been postulated as one of the most promising alternatives. One example is sea saltworks, which produce a concentrated waste known as brine (~200 g/L NaCl) commonly discharged to the sea. The wide availability of brines along the Mediterranean coastline with high salinity (20-40 times higher than seawater) makes possible the design of an efficient process for raw material recovery within a circular economy context. In order to provide a sustainable solution, the EU-H2020 SEArcularMINE project intends to recover critical materials from saltwork brines. To avoid the need for external reagents to carry out the recovery processes, the concentrated brines will be used to generate the required alkaline and acidic reactants using electrodialysis with bipolar membranes (EDBM), promoting a fully circular process.

The aim of this work is to study the generation of NaOH and HCl from NaCl-rich brines by EDBM. The feasibility of the process was tested using a laboratory cell in a batch configuration. One of the requirements of the SEArcularMINE process was to achieve concentrations of 1 M HCl and NaOH. In order to achieve it, different parameters were evaluated, such as membrane stack configuration, ion-exchange membrane types, current applied (50-100 A/m²), flow cell velocity (3.5-7 m/s) using an initial 2M NaCl concentration. In addition, the time-evolution profiles of ion concentration in each stream were monitored using ion-chromatography and titration. Initial results showed a production of HCl and NaOH up to 1M, depending on the current applied. Preliminary tests found negligible the flow cell velocity effect, whereas the membrane type changed dramatically the process performance.

Application of hydrophobic hollow fibers polypropylene membranes as aerator devices in wastewater treatment

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Main topic: Wastewater treatment

The aeration process is the transfer of oxygen from a gaseous phase to a liquid one (e.g. water or wastewater). This is an essential operation for the proper functioning of many wastewater treatments that require oxygen, such as biological processes and chemical oxidations aimed at the reduction of BOD (biological oxygen demand), COD (chemical oxygen demand), ammonia and non-biodegradable organic compounds [1]. The main drawback affecting the process is the low solubility of oxygen in water which limits the mass transfer at the gas/liquid interface. Thus, the surface available for the mass transfer into a certain liquid volume is one key parameter of the process that needs to be improved. Since porous membranes, depending on their configuration, can exhibit a high packing density (surface area/volume), they could be a promising alternative to improve the contact between air and the aqueous liquid phase. In bubble-free aeration the total surface available for the mass-transfer is the surface of the membrane acting as interface between the liquid and gas phases. The bubble-free membrane contactor can be desirable for some applications in wastewater treatment since it could be a nice option when: (1) oxygen requirements are too high for conventional aeration systems, (2) volatile organic compounds are present and consequentially bubbling of air would cause their stripping, (3) the composition of the wastewater causes foaming, (4) biofilm is the working mode desired for a biological process [2]. Membrane technology makes even possible working with bubbles, with a raising of interfacial area owing to the additional bubble surface. The aim of this work is to study the application of hydrophobic polypropylene hollow fiber membranes in the aeration of both clean water and a wastewater during the biological oxidation process. The water aeration experiments consisted in an initial chemical consumption of the dissolved oxygen by sodium sulphite, and subsequently oxygen was replenished by feeding the membrane with air by using the hollow fiber membranes. During the tests the dissolved oxygen concentration was collected as function of time (Figure 1) and the specific overall mass transfer coefficient ($K_L a$) was estimated.

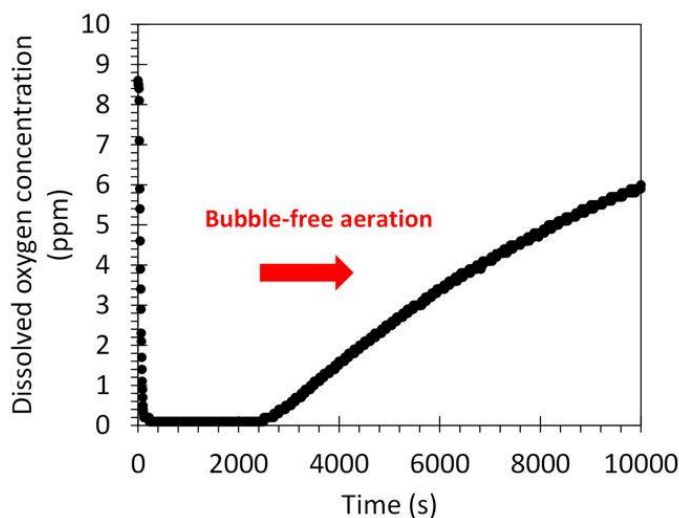
We acknowledge SIMAM S.p.A. for the financial support.

Reference 1:

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Reference 2:

P. Côté, J.L. Bersillon, A. Huyard, Bubble-free aeration using membranes: mass transfer analysis, J. Memb. Sci. 47 (1989) 91–106.



Application of Nanofiltration Membrane in the Separation of Drug Residues from Aqueous Solutions

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Main topic: Nanofiltration/Reverse Osmosis

Background, Materials and Methods, Results, Conclusions

The work is focused on the use of nanofiltration in the removal of drugs (diclofenac, ibuprofen, and acetaminophen) from wastewater. First, the commercially available nanofiltration membranes (AFC 80, AFC 40, AFC 30) were characterized by demineralized water and the ability of the membrane to reject these drugs was then tested. The effect of operating conditions on the rejection and permeate flux was evaluated. Operating conditions studied were mainly the effect of the transmembrane pressure (5–30 bar), ionic strength (0–10 g L⁻¹ NaCl) and volumetric flow rate (5–15 l min⁻¹).

It has been shown that increasing the transmembrane pressure increases the permeate flux and drug rejection (see Fig. 1). Drug rejection also increases with increasing bulk feed flow rate but decreases with increasing ionic strength (NaCl concentration in feed). Experimental data indicated that concentration polarization existed in this membrane separation process. The stable permeation flux and high rejection of drugs indicated the potential of NF for the recovery of drugs from pharmaceutical wastewater.

Fig. 1 Dependence of rejection on transmembrane pressure for AFC 40 membrane.

From the obtained results (higher rejection and relatively high fluxes), both „loose” membranes can be recommended for the separation of DIC and IBU from water, but membrane AFC 40 is a better choice due to higher flux and rejection. A dense membrane, AFC 80, can be recommended for the separation of acetaminophen.

Acknowledgements

The Ministry of Education, Youth and Sports of the Czech Republic, Project “Long-term conceptual development of a research organization”, and Project CZ.02.2.69/0.0/0.0/18_053/0016969 “International mobility of employees of the University of Pardubice II”, financially supported this work.

Aqueous Phase Separation Membranes: A step towards sustainable membrane development

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¹University of Twente

Main topic: Advanced fabrication methods

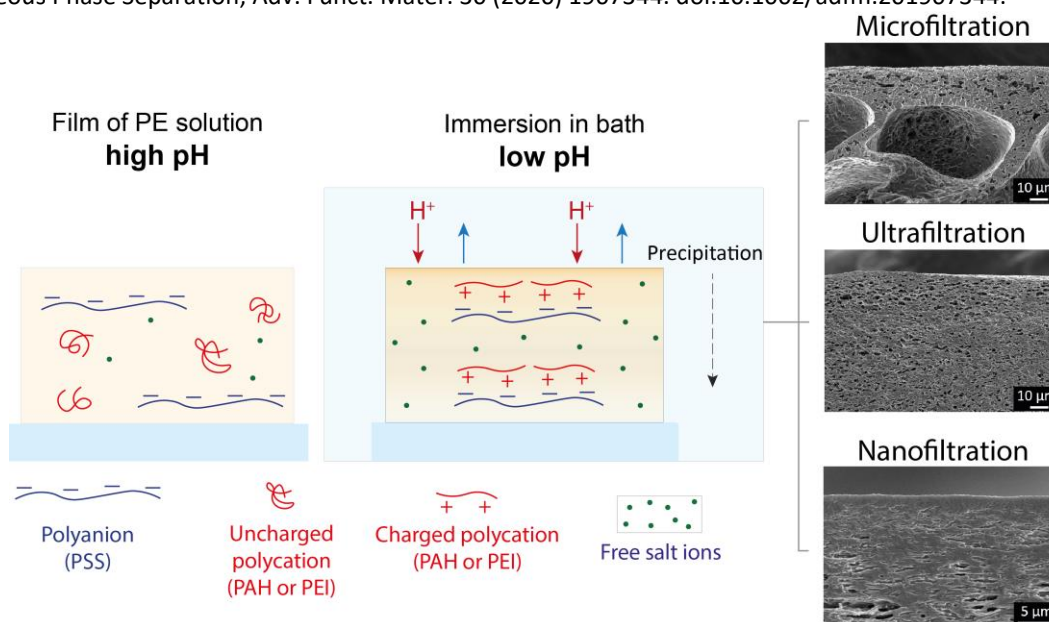
Traditionally polymeric membranes are prepared using the Non-solvent induced phase separation (NIPS) technique. It is a versatile technique that has been used for decades to obtain polymeric membranes for all different sorts of applications. The major downside, however, is that NIPS profoundly relies on organic solvents such as *N*-Methyl Pyrrolidone (NMP) to dissolve the polymers. NMP is a reprotoxic solvent and consequently is restricted within the European Union [1]. Herein, we present a special technique for polymeric membrane fabrication where water is used as a solvent. The new Aqueous Phase Separation (APS) technique employs polyelectrolyte complexation to achieve phase separation. A mixture of a strong polyanion PSS, Poly(sodium 4-styrene sulfonate), and weak polycation such as PAH, Poly(allylamine hydrochloride), or Polyethyleneimine (PEI) is prepared at high pH where the weak polycation is uncharged. Immersing this polyelectrolyte solution in a relatively low pH bath (pH~1 or pH~4) charges the weak polycation which instantly forms a polyelectrolyte complex (PEC) with PSS. The PEC is insoluble in water and precipitates as a white solid film, a membrane (Schematic 1). The thermodynamics of the polyelectrolyte solution can be manipulated by changing the pH. On the other hand, the kinetics of phase inversion can be controlled via numerous parameters such as the pH, salinity and concentration of buffer in the coagulation bath, concentration of the polyelectrolyte solution, and the molecular weights of the polyelectrolytes. The pore size of the PSS-PAH membranes obtained using the APS approach could be tuned from ~200 nm to ~2 nm, making them useful for micro-, ultra-, and nanofiltration applications [2]. Similarly, the PSS-PEI membranes prepared in pH ~4 buffers resulted in microfiltration (pore size ~80 nm) and also dense nanofiltration type membranes having a molecular weight cut-off of ~200 Da. In addition, the APS approach is adapted for hollow fiber geometry using PSS-PEI, thereby enhancing the scalability of the process. The numerous tuning parameters available in APS allows for the production of the sustainable flat sheet as well as hollow fiber membranes with excellent separation performance and stability. The APS technique opens a new chapter in the field of sustainable membrane production.

Reference 1:

J. Sherwood, T.J. Farmer, J.H. Clark, Catalyst: Possible Consequences of the N-Methyl Pyrrolidone REACH Restriction, Chem. 4 (2018) 2010–2012. doi:10.1016/j.chempr.2018.08.035.

Reference 2:

M.I. Baig, E.N. Durmaz, J.D. Willott, W.M. de Vos, Sustainable Membrane Production through Polyelectrolyte Complexation Induced Aqueous Phase Separation, Adv. Funct. Mater. 30 (2020) 1907344. doi:10.1002/adfm.201907344.



Aqueous phase separation of responsive polymers for sustainable membrane preparation.

Nielen, Wouter - Main Author¹; de Vos, Wiebe - Co-Author; Willott, Joshua - Co-Author
¹EMI Twente

Main topic: Advanced fabrication methods

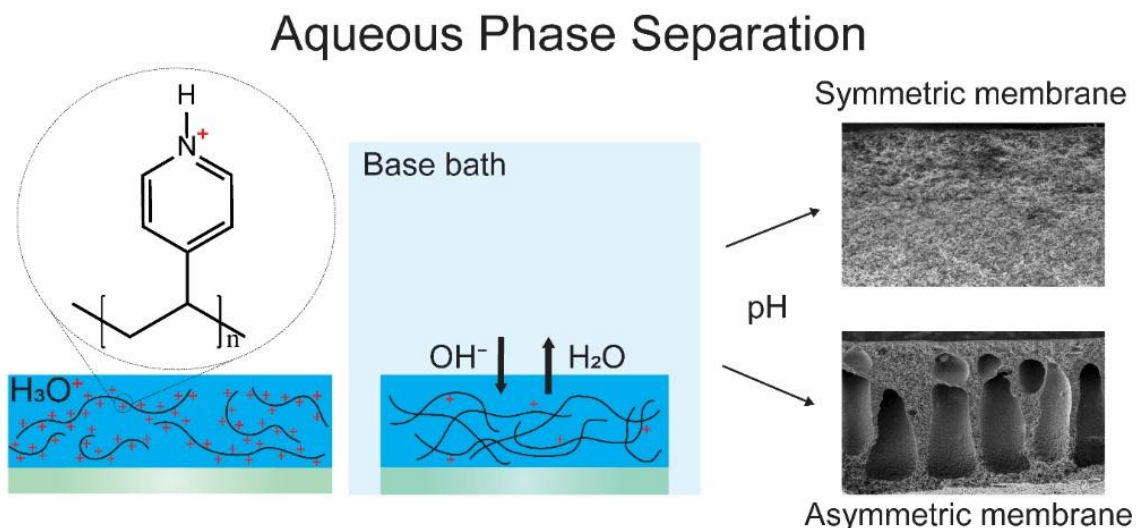
Membranes are often used in environmentally friendly applications and as a sustainable alternative to conventional processes. Unfortunately, the vast majority of polymeric membranes are produced via an unsustainable and environmentally unfriendly process that requires large amounts of harsh reprotoxic chemicals like N-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF). In this work, we investigate an aqueous phase separation (APS) system that uses weak polyelectrolytes, whose charge is dependent on the pH (weak polyelectrolytes) to produce membranes. Specifically, poly(4-vinyl pyridine) (P4VP) and the copolymer polystyrene-alt-maleic acid (PSaMA) are used. P4VP is a polybase which can be dissolved a low pH and precipitated at a high pH to prepare a membrane. For PSaMA the pH switch is the opposite as it is a polyacid which can be precipitated at a low pH. Additionally, PSaMA contains both responsive monomers required for the aqueous phase separation and unresponsive hydrophobic monomers that provide additional mechanical stability to the resultant membranes. This work demonstrates that by controlling the precipitation of P4VP and PSaMA, it is possible to prepare a wide range of membranes, from open microfiltration membranes capable of treating oily waste water, to dense nanofiltration-type membrane with excellent micropollutant retentions and high mechanical stability. The only solvents used in this APS system are water, acid and base, thus avoiding reprotoxic solvents which makes the APS process more sustainable and environmentally friendly compared to conventional membrane fabrication methods.

Reference 1:

Aqueous Phase Separation of Responsive Copolymers for Sustainable and Mechanically Stable Membranes. Nielen, W. M.; Willott, J. D.; de Vos, W. M. ACS Applied Polymer Materials, 2020, 2 (4), 1702-1710.

Reference 2:

Stimuli-Responsive Membranes through Sustainable Aqueous Phase Separation. Willott, J. D.; Nielen, W. M.; de Vos, W. M. ACS Applied Polymer Materials, 2020, 2 (2), 659-667.



Arsenic Removal in Water Treatment via Tailored Anionic Nanofiltration Membrane

Ulbricht, Mathias - Co-Author¹; Jurnal, Aisha Sean - Main Author¹

¹Universität Duisburg-Essen

Main topic: Nanofiltration/Reverse Osmosis

Membrane processes are used for a wide range of purposes and are also a preferable technology for arsenic (As) removal treatment. The recommended limit of arsenic in drinking water from WHO guidelines (2001) is 10 µg/L. Prominent results were shown by a negatively charged “loose” nanofiltration (NF) membrane, where the rejection of As(V) was ~90% for feed concentrations from 10 to 316 mg/L. However, the rejection of As(III) decreased from 28 to 5% in the same concentration range^[1]. To remove As(III) is more complicated and challenging due to its non-ionic state. Thus, the aim for this work is to obtain NF membranes that have a high rejection independent of As speciation with adequate permeance.

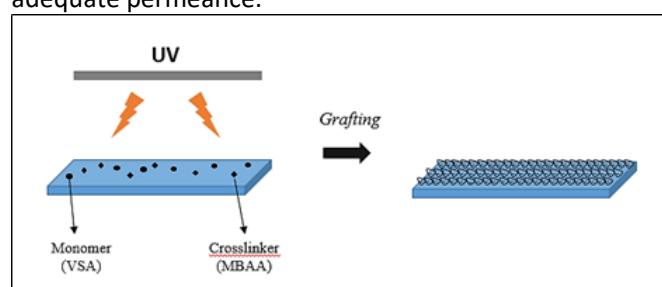


Figure 1. Schematic of surface functionalization using UV-grafting.

The modification of UF membrane towards NF application could be achieved by using polyelectrolytes as the active layer through post-functionalization on the membrane surface, e.g. via photo-grafting (Figure 1). Surface functionalization with ionic hydrogels had been previously shown by using vinyl sulfonic acid (VSA) monomer with N,N'-methylenebisacrylamide (MBAA) as the cross-linker monomer on polyethersulfone (PES) UF membrane^[2]. VSA as a functional monomer was chosen because it yields a high charge density polyelectrolyte hydrogel that is ionic throughout the entire pH range. PES membrane was also chosen due to its reactivity upon excitation with the UV light, which activates the graft copolymerization on the membrane surface.

The separation mechanism of NF membrane regarding the charge and size effects is more apparent in the tailored anionic NF membranes with 1.5% mole MBAA due to its higher rejection of anionic compound (As(V)) and non-ionic compound (As(III)) than with the lower concentration of crosslinker (0.75%; Figure 2). In comparison to NF90, the rejection of As(III) by the “30-1.5%” membrane is even higher with adequate water permeance. Its salts rejection is ~89% for sodium sulphate and ~64% for sodium chloride, which is also a suitable performance for NF membrane application. Essentially, the tailored anionic NF membranes “30-1.5%” is favorable for removing the different As species for production of safe drinking water.

Reference 1:

[1] Akbari, H., A. Rashidi Mehrabadi, and A. Torabian. "Determination of nanofiltration efficiency in arsenic removal from drinking water." *Journal of Environmental Health Science & Engineering* 7.3, 273-278, 2010.

Reference 2:

[2] Bernstein, R., E. Antón, and M. Ulbricht, "UV-Photo Graft Functionalization of Polyethersulfone Membrane with Strong Polyelectrolyte Hydrogel and Its Application for Nanofiltration," *ACS Appl. Mater. Interfaces*, vol. 4, no. 7, pp. 3438–3446, 2012.

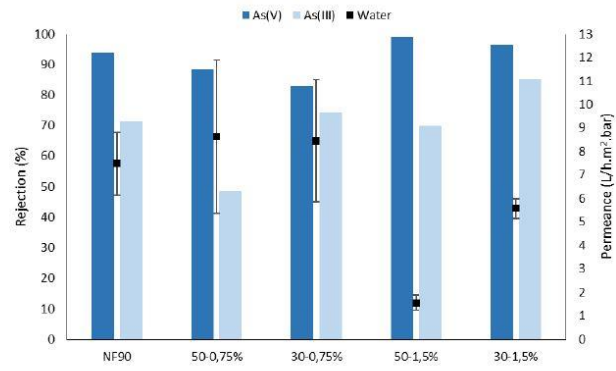


Figure 2. Separation performance as function of As speciation for tailored anionic NF membranes prepared with 25 wt% VSA on two different UF base membranes (50 and 30 kDa) and using two different crosslinker concentrations (0.75 and 1.5%mol MBAA) at 18 minutes UV irradiation in comparison with commercial NF90 membrane.

Artificial Water Channels- toward Biomimetic Membranes for Desalination

BARBOIU, Mihail - Main Author

Main topic: Biomimetic and bioinspired membranes

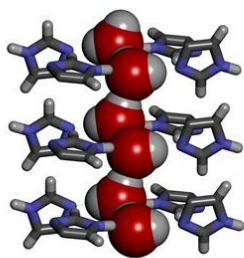
This lecture discusses the incipient development of the first artificial water channels systems. We include only systems that integrate synthetic elements in their water selective translocation unit. Therefore, we exclude peptide channels because their sequences derive from the proteins in natural channels. We review many of the natural systems involved in water and related proton transport processes. We describe how these systems can fit within our primary goal of maintaining natural function within bio-assisted artificial systems. In the last part, we present several inspiring breakthroughs from the last decade in the field of biomimetic artificial water channels. All these examples demonstrate how the novel interactive water-channels can parallel biomolecular systems. At the same time these simpler artificial water channels offer a means of understanding water structures useful to understanding many biological scenarios. Moreover they can be used for the preparation of highly selective membranes for desalination.

Reference 1:

M. Di Vincenzo, A. Tiraferri, V.-E. Musteata, S.Chisca, R.Sougrat, L.-B. Huang, S. P. Nunes, M. Barboiu, Nat. Nanotechnol. 2021, 16, 190-196.

Reference 2:

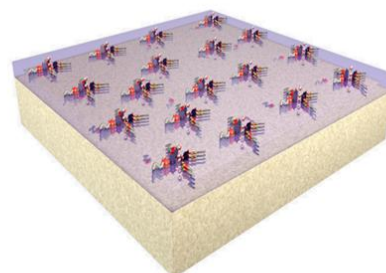
M. Di Vincenzo, et al. Proc. Natl. Acad. Sci. USA, 2021, DOI : 10.1073/pnas.2022200118



Artificial water channels-
AWC



AWC-Polyamide (PA)
composites



AWC-PA reverse-
osmosis RO membranes

Assessing the Influence of Mixed-Matrix Membrane Synthesis Parameters on CO₂/CH₄ Gas Separation Performance

Kulak, Harun - Main Author¹; Thur, Raymond - Co-Author¹; Vankelecom, Ivo - Co-Author¹
¹KU Leuven

Main topic: Gas separation

As traditional pure polymeric membranes for gas separation are limited by a trade-off between separation factor and permeability, mixed-matrix membranes (MMMs), which consist of inorganic fillers dispersed in polymer matrix, are considered as an emerging approach to overcome this constraint. However, the successful development of MMMs with minimum defects and high performance for the desired gas separations is still challenging as it depends on various synthesis parameters that need to be controlled during MMM synthesis process. In this study, we prepared 6FDA-DAM:DABA co-polyimide based MMMs using MOF-808 as filler to systematically examine the influence of five key synthesis parameters, including variation in polymer concentration, filler loading, dope solution volume, solvent type used, and solvent evaporation rate, on CO₂/CH₄ separation performance of the membranes. The pristine and MOF-808 incorporated membranes were investigated by SEM, XRD, FTIR, TGA, and DSC. Next, the membranes were assessed based on their visual appearance, mixed-gas CO₂/CH₄ separation factors, and CO₂ permeabilities. The results obtained indicate the relationship between high performance and visual appearance of the membranes is directly affected by the solvent evaporation rate as the most important synthesis parameter. While the fast evaporation of the solvent renders very brittle membranes, well-formed membranes could be obtained by slowing down the solvent evaporation. Furthermore, data illustrates that MMMs prepared with chloroform possess better performance improvement compared to other solvents studied. Without sacrificing the separation factor, 73% and 62% increase was observed in CO₂ permeabilities of chloroform-based MMMs upon 10 and 30 wt.% MOF-808 incorporation, respectively, compared to pristine 6FDA-DAM:DABA membrane. Although less dominantly influencing the MMM performance, the effect of polymer concentration and dope volume cannot be neglected to achieve an enhanced gas separation performance. The results demonstrate that the chosen synthesis parameters actively control the evaporation rate, dope solution viscosity, and particle agglomeration and settling rate, ultimately influencing the MMM performance. This study suggests that the improved separation strongly relies on the cumulative effect of these parameters rather than the individual impact and requires a system-specific design and optimization which is often overlooked and underestimated in the literature.

Asymmetric layer-by-layer polyelectrolyte nanofiltration membranes with tunable retention

Scheepers, Danielle - Main Author; Chatillon, Benjamin - Co-Author; Nijmeijer, Kitty - Co-Author; Borneman, Zandrie - Co-Author

Main topic: Nanofiltration/Reverse Osmosis

Layer-by-layer assembly of polycations and polyanions on a porous ultrafiltration support is a versatile method to produce nanofiltration membranes. The used polyelectrolytes determine the membrane structure and charge, thus determining the ion retention by size and charge exclusion. The frequently used polyelectrolyte couple polydiallyldimethylammonium chloride and poly(sodium-4-styrenesulfonate) (PDADMAC/PSS) has the disadvantage that the polyelectrolyte layers interdiffuse into each other. The diffusion mobility of PDADMAC is higher than that of PSS, which gives rise to an excess of positive charges resulting in positively charged membranes. This positive charge deteriorates the removal of negatively charged ions and makes the membranes more sensitive to fouling. To overcome this, we now use a polycation with a lower charge density i.e. poly(acrylamide-co-diallyldimethylammoniumchloride; P(AM-co-DADMAC)). We investigate the influence of this charge density on the membrane charge and performance of LbL coated membranes using the couples PDADMAC/PSS, P(AM-co-DADMAC)/PSS, or a combination of the two (Figure 1a and b). For PDADMAC/PSS, a pure water permeability of ~ 4 L/(m²hbar) and a slightly negative surface charge is measured (Figure 1c and d). The limited surface charge due to interdiffusion results in insufficient charge exclusion as seen by the low Na₂SO₄ retentions (Figure 1e). The opposite effect is visible for P(AM-co-DADMAC)/PSS, where the pure water permeability is extremely high, which indicates limited polyelectrolyte adsorption, caused by restricted charge overcompensation during layer-by-layer deposition. Consequently, size exclusion of membranes coated with solely P(AM-co-DADMAC)/PSS layers is limited; hence it is impossible to retain Na₂SO₄. Nevertheless, the use of P(AM-co-DADMAC) does form highly negatively charged membranes. For successful retention of Na₂SO₄, size as well as charge exclusion is necessary. We now show that by combining both polycations, we obtain pure water permeabilities in the nanofiltration range (~ 7 L/(m²hbar)). This is significantly higher than for PDADMAC/PSS membranes due to the hydrophilicity of P(AM-co-DADMAC). Additionally, a highly negatively charged membrane surface is produced. This results in outstanding Na₂SO₄ retentions of up to 95%, achieved by the necessary size and charge exclusion, which is in the top range compared to commercial membranes and other LbL membranes reported in literature.

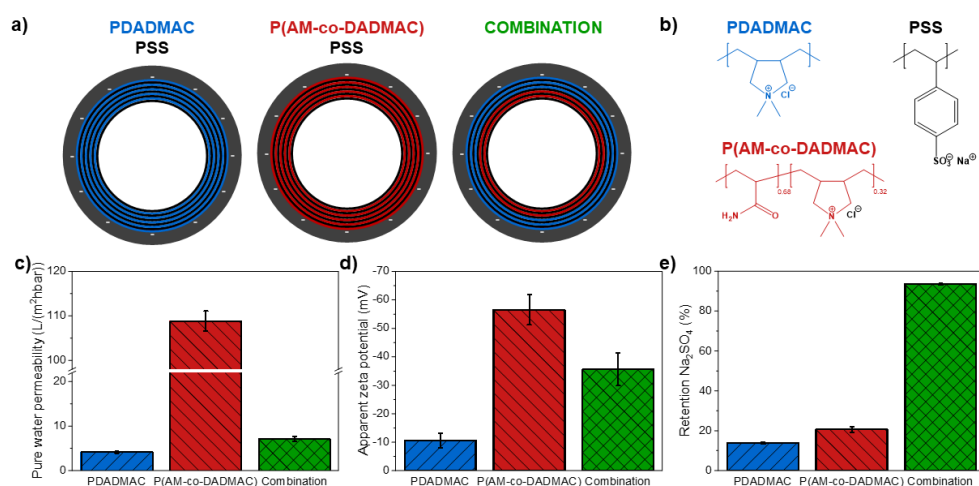


Figure 1: a) Schematic representation of asymmetric layer formation inside a hollow fiber support for (PDADMAC/PSS)₇, (P(AM-co-DADMAC)/PSS)₇ and (PDADMAC/PSS)₅+(P(AM-co-DADMAC)/PSS)₂ membranes b) Molecular structures of PDADMAC, P(AM-co-DADMAC) and PSS c) Pure water permeability d) Apparent zeta potential e) Na₂SO₄ retention.

Asymmetric polyelectrolyte multilayer membranes for highly efficient micropollutant removal

te Brinke, Esra - Main Author¹; Achterhuis, Iske - Co-Author¹; Reurink, Dennis - Co-Author²; de Grooth, Joris - Co-Author^{1,2}; de Vos, Wiebe - Co-Author¹

¹University of Twente, ²NX Filtration

Main topic: Novel membrane materials

There is growing awareness and concern about the presence of organic micropollutants in our surface water and drinking water. These small molecules (100-1000 Dalton) stem from industrial, medicinal and agricultural waste. They have the potential to cause long-term harm to humans and the environment, something especially true for micropollutants classified as endocrine disrupting chemicals, that can have a significant negative effect on health and environment even at very low concentrations.

Methods to remove micropollutants from surface and drinking water are available but are currently too costly and inconvenient for the treatment of large streams of water. An example of this is the current state of art reverse osmosis (RO) treatment. RO membranes are dense membranes that can remove micropollutants, but these membranes were designed for desalination and have significant drawbacks. RO membranes have a thick and dense active separation layer resulting in low permeabilities and thus a high energy demand.

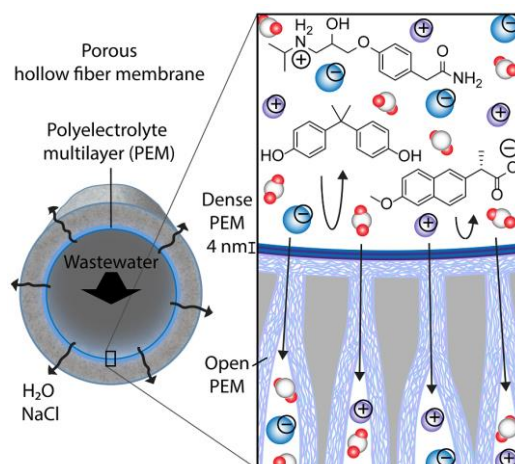
To circumvent this high energy demand, we aim to develop nanofiltration membranes for the removal of micropollutants. Polyelectrolyte multilayer (PEM) membranes have a lot of potential for such optimization because their properties can be controlled in multiple ways. The layer-by-layer assembly of a separation layer on top of a porous support, by alternatively exposing it to polycations and polyanions, provides control over layer thickness. Density, hydrophilicity and charge density can be fine-tuned by the type of polyelectrolytes and coating conditions such as ionic strength and pH. Here, we explore the coating of PEM membranes in an asymmetric fashion, where we first coat a low-density, high-permeability layer to close the pores of the support, to finally coat a thin, high-density layer to define the actual separation properties. This approach facilitates high micropollutant retentions, while significantly outperforming RO membranes in terms of water permeability. Interestingly, these membranes can be scaled up easily and show low salt retentions, which makes them particularly suitable for wastewater treatment and drinking water production.

Reference 1:

Esra te Brinke, Dennis M. Reurink, Iske Achterhuis, Joris de Grooth and Wiebe M.de Vos; Asymmetric polyelectrolyte multilayer membranes with ultrathin separation layers for highly efficient micropollutant removal; Applied Materials Today, 2020, 18:100471

Reference 2:

Esra te Brinke, Iske Achterhuis, Dennis M. Reurink, Joris de Grooth and Wiebe M.de Vos; Multiple approaches to the buildup of asymmetric polyelectrolyte multilayer membranes for efficient water purification; ACS Applied Polymer Materials, 2020, 2:715–724



Atomistic modeling of the formation of dynamic molecular polymers

Dupuis, Romain - Main Author^{1,2}; Maurin, Guillaume - Co-Author²; Barboiu, Mihail - Co-Author¹
¹IEM, ²ICGM

Main topic: Novel membrane materials

Capturing CO₂ is a major societal issue. Recently synthesized covalent molecular dynamic polymers (dynamers) show promising performances for the selective adsorption of CO₂ towards different gas molecules[1]. These polymers are formed by self-assembly of connector agents carrying aldehyde functions and macromonomers functionalized by amine groups (see Figure). They are dynamic due to the reversibility of their covalent bonds, which gives them a unique adaptive character. The free enthalpy of reaction to form a bond within these dynamers is of the order of a few $K_b T$, the association kinetics of the molecules is therefore governed by entropy and steric hindrance. The mechanisms of formation of this family of polymers and their structural properties remain unknown to this day due to their complexity and their evolutionary nature. To allow us to describe structural models of these assemblies for the first time, we developed a molecular simulation method integrating quantum and force-field approaches that makes it possible to account for the chemical reactivity of these systems.

During this presentation, I will outline the method that we have developed. First, the energy surface of the system is computed by quantum calculations to determine the energy activation of binding and dissociation of the amine group with the aldehyde group. Then, the energy barrier is used to define the bond formation/dissociation probability in a Monte Carlo method coupled with molecular dynamics. I will detail its interest in relation to recent developments of other methods, carried out with the aim of reproducing the formation of solids or colloids in solution[2], in which I have participated. These models allow us to study the formation of porosity and compare it with experimental data. On the other hand, the constructed atomic model makes it possible to simulate gas adsorption isotherms essential for understanding the mechanisms of selectivity and capture. Dynamers are of particular interest because the dynamic aspect could be used to control porosity and selectivity of adsorption during membrane use.

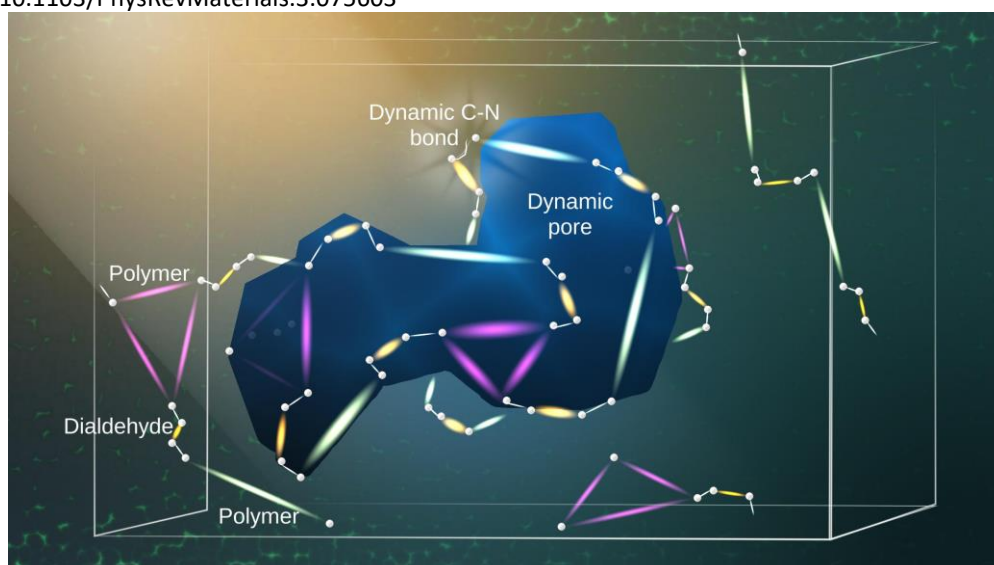
This work is supported by the LabMUSE Chimie of the University of Montpellier and benefited from state aid managed by the Agence Nationale pour la Recherche under the program Investissements d'Avenir with the reference ANR-16-IDEX-0006.

Reference 1:

[1] M. Barboiu, Constitutional Dynameric Networks for Membranes, Membrane Materials, Characterization, and Module Design, 2013, <https://doi.org/10.1002/9781118522318.emst054>

Reference 2:

[2] R. Dupuis et al. Molecular simulation of silica gels: Formation, dilution, and drying, Physical Review Materials, 2019, <https://doi.org/10.1103/PhysRevMaterials.3.075603>



Bio-based Fatty acid-derived membranes for carbon dioxide separation

Ettxeberria-Benavides, Miren - Main Author¹; Ślęczkowski, Marcin - Co-Author²; Ślęczkowski, Marcin - Co-Author²; David, Oana - Co-Author³; Bernaerts, Katrien - Co-Author²

¹TECNALIA, Basque Research and Technology Alliance (BRTA), ²Aachen-Maastricht Institute for Biobased Materials, Maastricht University, ³TECNALIA, Basque Research and Technology Alliance (BRTA),

Main topic: Gas separation

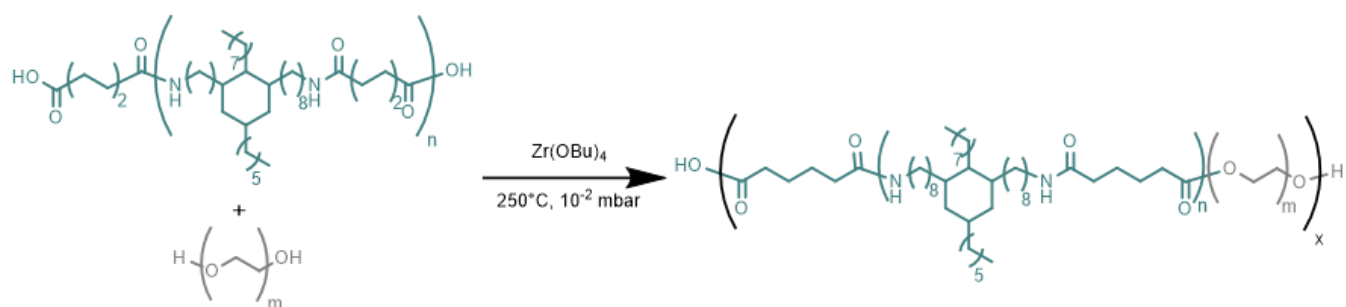
The recognition of greenhouse gas emissions as an important factor contributing to global warming was a turning point in international climate policy. Membrane separation technology of carbon dioxide, CO₂, considered as the largest contributor to the greenhouse gas emission, is of particular interest for scientists.

We investigate the synthesis of new and biobased, high-molecular weight polyamide-*b*-polyether (PEBA) segmented block copolymers as a part of the consortium BIOCOMEM, devoted to the development of biobased membranes for CO₂ separation. In past years, monomers derived from dimer fatty acids and furan dicarboxylic acid gained significant interest due to their high availability and low price as well as interesting material properties in different setups such as polyester, polyamides and polyimides. Interestingly, polyamides containing fatty-acid derivatives show semi-crystalline behavior, when copolymerized with linear 1,4-diaminobutane.¹ The synthesis and characterization of furan and fatty-acid derived polyamides and its block copolymers will be discussed. We show, how crystallinity of the polyamide block affects the thermal properties of block copolymers and how it reflects on membrane preparation process, which is key to produce membranes of the desired morphology. First synthesized copolymer was based on a polyamide labeled AdiPrA₃₂₀₀ and Polyethylene glycol (PEG₁₅₀₀). Polyamide block was prepared by the polycondensation of adipic acid with Priamine 1075® and in second step block copolymer was prepared by polycondensation of AdiPrA₃₂₀₀ and PEG₁₅₀₀ as depicted in **Figure 1**. First copolymer shows promising results in terms of membrane processability and gas permeation properties. Thin and dense films with good mechanical stability have been easily prepared by solution casting and solvent evaporation technique using dichloromethane as volatile solvent. CO₂ permeability was of 38,4 Barrer and CO₂/N₂ selectivity was of 36,9. Current work is focused on increasing the PEO content in the final polymer in order to improve CO₂ permeability and on increasing the molecular weight in order to fabricate monolithic and asymmetric hollow fiber membranes with stable structure and mechanical properties.

Figure 1: Reaction scheme for the synthesis of fatty acid derived copolymer

Reference 1:

[1] J. L. J. van Velthoven, L. Gootjes, B. A. J. Noordover, J. Meuldijk, *European Polymer Journal* 66 (2015) 57-66



Biobased PHA membranes fabrication using green solvent: tailoring the membrane microstructure

LOULERGUE, Patrick - Co-Author; Tomietto, Pacôme - Co-Author; Russo, Francesca - Co-Author; Galiano, Francesco - Co-Author; Paugam, Lydie - Co-Author; Audic, Jean-Luc - Co-Author; Figoli, Alberto - Co-Author

Main topic: Novel membrane materials

Commercial membranes are usually fabricated using fossil derived polymers and toxic solvents. There is thus a need for new strategies to develop greener membrane processes using renewable and non-toxic raw materials. Previous studies have demonstrated the potential of polyhydroxyalkanoates (PHA), a biobased and biodegradable polyesters, as eco-friendly alternatives for membrane fabrication [1–3]. However, in these studies toxic solvents (chloroform and NMP) were used. In the present study, we evaluated the use of green solvents as an alternative towards more sustainable membrane production. Based on a theoretical approach using the Hansen solubility parameters and empirical tests, Cyrene® (Dihydrolevoglucosenone), a bio-based and fully biodegradable solvent, was selected as the most promising candidate.

The membranes were fabricated using the phase inversion method and a 2-steps protocol including a first partial evaporation of the solvent (EIPS) followed by a water non-solvent bath (NIPS). The influence of the dope solution composition was studied. The mechanical properties and microstructure of the membranes were determined and linked to the separation performances.

It was observed that, by increasing the evaporation time, the membrane tensile strength was improved but the porosity decreased. Applying an evaporation time of 1.5 min and using PEG as an additive, porous membranes with typical pore size in the range of microfiltration (MF) membranes were obtained. For a time of 5 min dense asymmetric membranes suitable for pervaporation (PV) application were fabricated. Membranes performance were evaluated in terms of pure water permeability (MF) and for methanol/MTBE mixture separations (PV) (Fig. 1).

Figure 1: Cross section morphology and separation performances of PHA membranes fabricated using Cyrene as the solvent

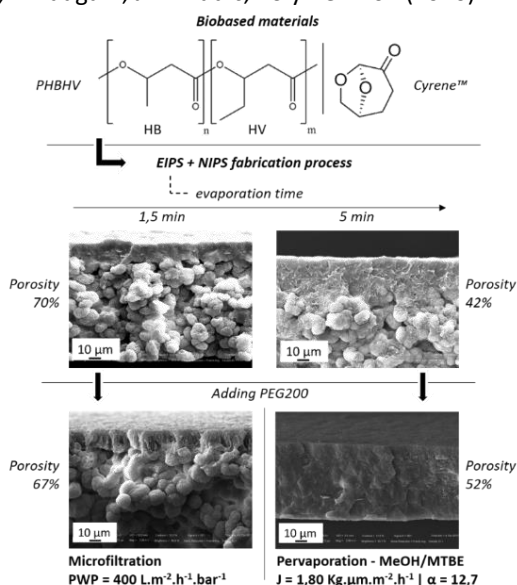
Acknowledgments: This study was carried out in the framework of the PHC GALILEO 2020-2021 funded by Campus France (project N°44342UM) and Università Italo Francese (project G20_335). Pacôme Tomietto acknowledges Rennes Métropole for providing the mobility grant making possible the collaboration between the two institutes involved in this work.

Reference 1:

[1] P. Tomietto, P. Loulergue, L. Paugam, J.-L. Audic, *Sep. Purif. Technol.* 252 (2020) 117419

Reference 2:

[2] P. Tomietto, M. Carré, P. Loulergue, L. Paugam, J.-L. Audic, *Polymer*. 204 (2020) 122813.



Biocatalytic composite membranes for CO₂ capture

Molina Fernández, Cristhian - Main Author¹; Luis, Patricia - Co-Author¹

¹UCLouvain

Main topic: Biomimetic and bioinspired membranes

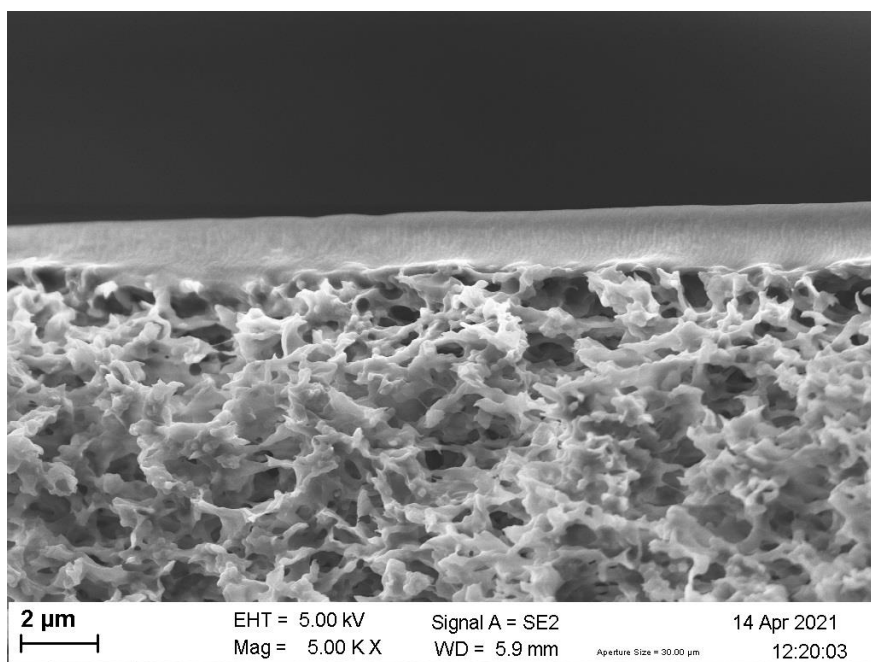
Nature has developed very active and specific catalysts that are critical for living organisms' existence. The application of some of such biocatalysts in CO₂ capture and utilization has recently attracted large interest from the research community and the industry [1,2]. For example, they have been applied to CO₂ absorption aiming to reduce the liquid side mass transfer resistance. This resistance is dominating the overall mass transfer and it can be reduced by catalyzing the slow CO₂ hydration reaction. Besides, they have also been incorporated in selective membranes. These membranes usually displayed improved permeability and selectivity due to the facilitated transport mechanism [2]. In addition, these biocatalysts are usually immobilized in/on a carrier to protect them from the harsh conditions in CO₂ capture and ensure long-term stability. Depending on the immobilization method, the immobilization results in different degrees of stabilization and activity loss. We report here the fabrication and characterization of novel composite membranes with immobilized biocatalyst for CO₂ bioconversion. These membranes were prepared by a novel method that ensured a good and straightforward biocatalyst immobilization. The membranes were structurally characterized by SEM while their activity in different conditions was evaluated using p-NPA hydrolysis. In addition, to demonstrate their applicability, the biocatalytic composite membranes were tested in a gas absorption set-up showing an increase in the overall mass transfer coefficient with respect to the pristine support. These membranes could also be interesting for other applications as the combination of a selective barrier and the biocatalyst leads to process intensification (reaction + separation in the same device).

Reference 1:

[1] P. Luis, V. Sang Sefidi, M. Sparenberg, M. Garcia Alvarez. (2021), continuous process and system for the production of sodium bicarbonate crystals, 20211693.5-1108, universite catholique de louvain. (Patent)

Reference 2:

[2] Molina-Fernández, C., & Luis, P. (2021). Immobilization of carbonic anhydrase for CO₂ capture and its industrial implementation: A review. *Journal of CO₂ Utilization*, 47, 101475.



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¹Institut Européen des Membranes

Main topic: Gas separation

CO₂ is believed to be a major contributor to greenhouse gases. CH₄ emissions also affect the concentration of atmospheric greenhouse gas, because of its 28 times higher global warming potential than carbon dioxide [1]. The dissolved methane (dCH₄) content in the anaerobic effluent could be between 10-25 mg L⁻¹, but the super saturation indices could go to as high as 6.9[2]. Other than environmental concerns, the dCH₄ loss in the effluent could result in a significant amount of economic loss. Hollow fiber membrane contactor (HFMC) desorption process could provide a safe and efficient way to recover these dissolved gases.

The present work focuses on the recovery of biogas from anaerobic membrane bioreactor (AnMBR) permeate using sweep and vacuum desorption technology in porous and dense HFMCs. Effluent from the AnMBR as well as synthetic effluents of pure and mixed (60% CH₄) CH₄ and CO₂ were used here. The AnMBR permeate is loaded from the outlet of the granular AnMBR operated at 25°C, which produces ~12 L/day of the effluent. Synthetic effluents were prepared at 25 °C, in a tank of 9.5 L by bubbling (for 60 minutes) the pure/mixed gas using a gas diffuser inside the tank. HFMC was operated in a counter current arrangement for effluent flow and sweep gas/vacuum, to recover the dissolved biogas from the effluent.

Porous HFMC was able to achieve a very high degassing efficiency of up to 95% for CH₄ and 78% for CO₂. Results revealed that increase in both liquid flowrate and gas flowrate enhances the degassing process by enhancing the transmembrane mass transfer flux and membrane mass transfer coefficient. The total highest biogas recovery after two hours was recorded to be up to 92% for CH₄ and 83% for CO₂. Experimental mass transfer coefficients of 1.99 10⁻⁰⁵ m s⁻¹ and 1.01 10⁻⁰⁵ m s⁻¹, were recorded for CH₄ and CO₂, respectively. Furthermore, an in depth investigations is being performed under the current work to analyze and characterize the porous and dense membrane fouling and its effect on the membrane performance. Moreover, a rigorous 2-D modelling approach will be used to extend the study and to make an approach toward possible scale-up.

Reference 1:

[1] R. Jiménez-Robles, C. Gabaldón, V. Martínez-Soria, and M. Izquierdo, "Simultaneous application of vacuum and sweep gas in a polypropylene membrane contactor for the recovery of dissolved methane from water," *J. Memb. Sci.*, vol. 617, no. June 2020, 2021.

Reference 2:

[2] J. Cookney et al., "Dissolved methane recovery from anaerobic effluents using hollow fibre membrane contactors," *J. Memb. Sci.*, vol. 502, pp. 141–150, 2016.

Biomimetic UF membranes with chemically fueled self-oscillating permeability

Pirkin-Benameur, Johanne - Co-Author

Main topic: Biomimetic and bioinspired membranes

Background

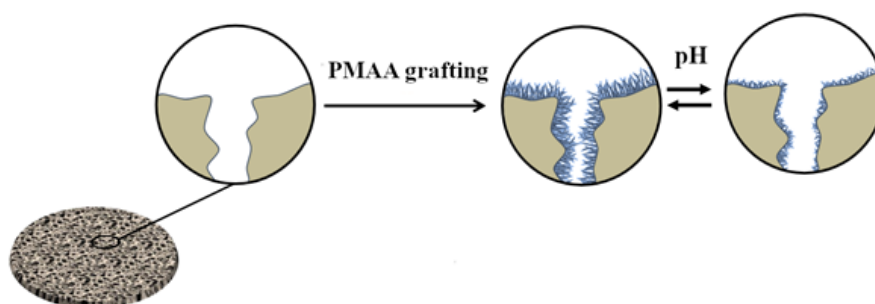
Soft matter materials research has considerably evolved the last decades mainly by promoting responsive polymer systems. Up to now, the dynamic behavior in materials was always reached by the action of an outside trigger (pH, light, etc.). To get free of this constraint, self-oscillating materials class have been created. In this work, the self-regulating pH cycles caused by chemical oscillator will make autonomous pH-sensitive polymer movements in the membrane interface, causing a pore size oscillation cycle and thus, a self-oscillating flow.

Results

This work involved the functionalisation of PES commercial membranes to achieve pore size oscillations. The pH-sensitive polymer, poly(methacrylic acid) (PMAA), was obtained by deprotection of poly(tert-butyl methacrylate) (PtBuMA) synthesized by RAFT polymerization. To adapt this functionalization to all types of commercial membranes, it was carried out by first depositing polydopamine (PDA) thin layer on the top of the membrane, which then allows a Michael-thiol reaction between PDA and functionalized PMAA, obtained by prior aminolysis of PtBuMA. The functionalization steps were characterized by XPS, SEM-EDX and by contact angle and permeability measurements. Then, membranes were placed in a filtration system containing a chemical pH oscillator to control the PMAA conformation through the pH cycle. Permeability analysis showed that there is indeed a dependence between permeability and PMAA conformation, leading to the conclusion that there is indeed a continuous oscillation in membrane pore size. Also, a preliminary test seems to show that oscillating permeability helps to reduce membrane clogging. This investigation will be the next part of the work.

Conclusions

In conclusion, a mild condition functionalization has turned a commercial filtration membrane into a biomimetic materials that showed self-oscillating permeability.



Biopesticides from tomato leaves biomass fractionated by membrane-assisted biorefinery

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Main topic: Bio-separations and bio-refinery

Plant protection from damage by pests is crucial for safe and sufficient agricultural production that meets the demands of a growing world population. Biopesticides are natural compounds, biodegradable and less toxic than synthetic pesticides that can be used to tackle plant diseases with the advantage of improving environmental safety and social acceptability.

Studies proved that plant defense can be triggered in response to 'damage-associated molecular patterns' – DAMPs. Aqueous tomato leaf extracts can be a rich source of biologically active molecules, such as the oligosaccharides called oligogalacturonides, that act as DAMPs for crop protection [1].

In this work, an enriched fraction of carbohydrates from a real complex matrix of tomato leaves was obtained using membrane operations. For this aim, a screening of commercial membranes with different physical-chemical properties was performed. Green extraction of bioactive compounds from tomato leaves was carried out using water. The obtained complex matrix was treated by a membrane cascade system based on loose ultrafiltration (UF, 30-50 kDa) and tight UF (polyethersulfone, 5 kDa) stage. Results showed that among the tested membranes for the first UF stage, the regenerated cellulose (RC) membrane was the most suitable to fractionate the carbohydrates and biophenols from proteins with a lower fouling tendency. In particular, 85% of proteins were retained by the RC membrane, while a sieving coefficient higher than 90% for carbohydrates and biophenols was obtained. The second stage of UF (5 kDa) with a sieving coefficient of 80% and 47% for carbohydrates and biophenols, respectively, permitted to obtain an enriched fraction of carbohydrates in the permeate. The different membrane selectivity towards similar molecular weight biomolecules can be explained by a synergistic effect of size exclusion and electrostatic interactions between the membrane and the biomolecules [2]. The biopesticide activity of the collected fraction enriched with carbohydrates demonstrated the suppression of the bacterial population growth when sprayed onto tomato leaves prior to inoculation with *Pseudomonas syringae*, the cause of bacterial speck disease. These preliminary evidences are supporting of a successful example of bio-protection using circular economy principles.

Acknowledgements

This work was supported by The Royal Society (IES\R2\192205).

Reference 1:

Ferrari S., Savatin D. V., Sicilia F., Gramegna G., Cervone F., De Lorenzo G., *Frontiers in plant science*, 4 (2013) 49.

Reference 2:

Conidi C, Drioli E., Cassano A., *Biomolecules*, 10 (2020) 935.

Biopolymers as a promising platform for biocatalyst immobilization in novel gas-liquid membrane contactor for carbon capture

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Main topic: CO₂ capture

Post-combustion carbon capture using membrane-based processes represents one of the potential technologies to mitigate the release of the greenhouse gases to the atmospheric. Gas-liquid membrane contactor (GLMC) utilizing porous hydrophobic membrane as a physical barrier to separate gaseous feed and liquid absorbent streams has a clear major advantage, i.e., excellent selectivity and lower energy requirement, over pressure-driven membrane gas separation at very low CO₂ concentration [1]. However, conventional GLMC suffers several major drawbacks, such as membrane wetting, toxic amine solvents and energy-intensive CO₂ desorption process. Recently, more benign solvents, such as carbonate salt solutions, have been used in place of amines to perform CO₂ capture in GLMC [2]. The slower absorption kinetics of these solvents, unfortunately, are not able to compete with the performance of conventional amines.

Incorporating biocatalysts that promote CO₂ hydration could accelerate the CO₂ capture rate of these solvents. In this work, we prepared novel biocatalytic membranes using biopolymer coating as an immobilization platform. The coating concentration, membrane coating method, immobilization parameters and process conditions were varied. The membranes were evaluated in an open-loop gaseous feed and a circulated liquid absorbent solution. Our work demonstrated that the membrane with the immobilized biocatalyst had a significant increase in the overall mass transfer coefficient: an increase of ~650% compared to the pristine membrane. In conclusion, our results clearly highlighted the impressive performance of novel biopolymer-coated membranes as a platform for biocatalysts immobilization in CO₂ capture process.

Reference 1:

U.W.R. Siagian, A. Raksajati, N.F. Himma, K. Khoiruddin, I.G. Wenten, Membrane-based carbon capture technologies: Membrane gas separation vs. membrane contactor, *J. Nat. Gas Sci. Eng.* 67 (2019) 172–195.

Reference 2:

X. Xu, G.J.O. Martin, S.E. Kentish, Enhanced CO₂ bio-utilization with a liquid–liquid membrane contactor in a bench-scale microalgae raceway pond, *J. CO₂ Util.* 34 (2019) 207–214.

Bipolar membrane design for high performance in (bi)carbonate electrolysis

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Main topic: Novel membrane materials

The use of bipolar membranes (BPMs) in liquid-feed (bi)carbonate electrolyzers emerges as a promising route to alleviate the energy constraints by coupling direct electrochemical carbon capture and reduction¹, unlike the classical gas-fed CO₂ electrolyzers. In (bi)carbonate flow cells configured with BPM in reverse bias, a continuous flux of H⁺ to the cathodic catalyst layer is maintained by the water dissociation (WD) reaction at the BPM interface. The supply of H⁺ drives an in-situ generation of catalytically active CO₂ for electrochemical CO₂ reduction (CO₂R) reaction.² As such, the chemistry of the CO₂R reaction over the cathodic catalyst layer is highly influenced by the kinetics of the WD and hence the structural compositions of the BPM interface (Fig 1.). Reverse bias membrane configurations are also limited by high overpotential and low selectivity. A potential solution to alleviate these problems involves the optimal tailoring of BPM and its interface structures, which allows tuning the membrane properties and reaction chemistries over the cathodic catalyst layer. Herein, an effort is done to vary the electrochemical properties of the cation exchange layer and catalytic composition of the interfacial layer in BPMs and correlate the structure-property-performance in (bi)carbonate electrolyzers with an ultimate goal of designing high-performance BPMs for combined electrochemical CO₂ capture and reduction.

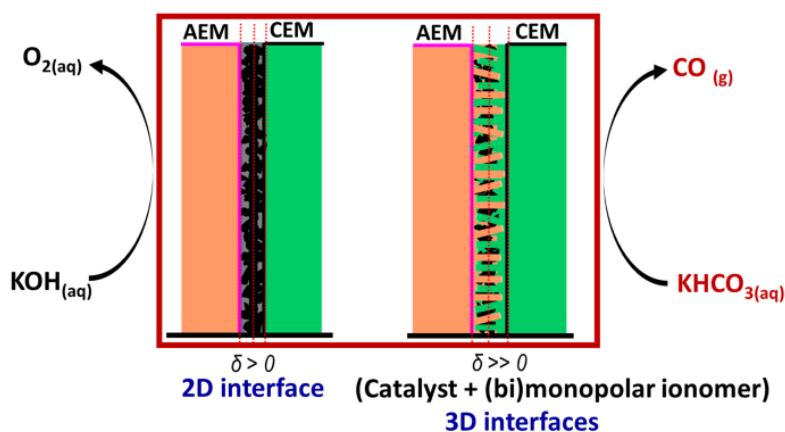
Reference 1:

Tufa, R. A.; Blommaert, M. A.; Chanda, D.; Li, Q.; Vermaas, D. A.; Aili, D., Bipolar Membrane and Interface Materials for Electrochemical Energy Systems. ACS Applied Energy Materials 2021, 4 (8), 7419-7439. doi: <https://doi.org/10.1021/acsaem.1c01140>

Reference 2:

Lees, E. W.; Mowbray, B. A. W.; Parlane, F. G. L.; Berlinguette, C. P., Gas diffusion electrodes and membranes for CO₂ reduction electrolyzers. Nature Reviews Materials 2021. doi: <https://doi.org/10.1038/s41578-021-00356-2>

Fig 1. BPM design for selective HCO₃⁻_(aq) reduction to CO.



Bipolar polymer electrolyte membranes for electrochemical conversion of CO₂

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¹Technical University of Denmark

Main topic: Electro-membrane processes

CO₂ electrolyzers based on bipolar polymer electrolyte membranes have been a popular research topic for CO₂ reduction reaction (CO₂RR) in flow cells as shown in Figure 1. Although anion exchange membranes seem to prevail over cation exchange membranes by transferring anionic species (HCO₃⁻, CO₃²⁻ and OH⁻) rather than H⁺, the parasitic CO₂ pumping results in CO₂-loss at the anode side under typical reaction conditions. Recent results have also shown that bipolar membranes (BPMs) can not only retain the unreacted CO₂ at the cathode side, but also maintain the pH values on both sides of the membrane, which shows great potential in enhancing the utilization efficiency of CO₂RR.¹ Most proof-of-concept studies of BPM in context with CO₂RR used BPMs prepared by simple lamination of arbitrarily chosen anion exchange layers and cation exchange layers (AELs/CELs). In this work, BPMs derived from styrene-ethylene-butylene-styrene (SEBS) AEL and CEL were obtained by installing alkyl halides as handles onto the styrene units of SEBS and then functionalized by trimethylamine (TMA) and sulfonate groups, respectively, as illustrated in Figure 2. The individual ionomers with different ion exchange capacity were cast into membranes and characterized. The overall ambition is to explore how the BPM junction morphology, thickness, composition and the presence of interfacial water dissociation catalysts relate to the polarization behavior of the membrane.

Reference 1:

Ma, M., Kim, S., Chorkendorff, I. & Seger, B. Role of ion-selective membranes in the carbon balance for CO₂ electroreduction: Via gas diffusion electrode reactor designs. *Chem. Sci.* 11, 8854–8861 (2020).

Reference 2:

Tufa, R. A. et al. Towards highly efficient electrochemical CO₂ reduction: Cell designs, membranes and electrocatalysts. *Appl. Energy* 277, 115557 (2020).

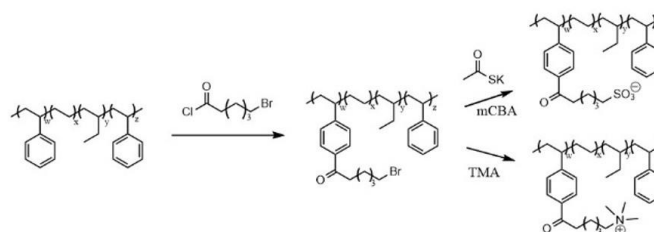
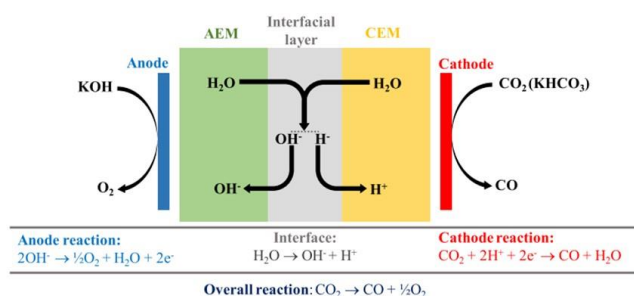


Figure 1. Configuration of a BPM-based CO₂ electrolyzer²

Figure 2. Synthetic pathway for SEBS-based CEL and AEL

Bringing ceramic membrane grafting close to market introduction.

Buekenhoudt, Anita - Co-Author¹; Borges, Pedro - Co-Author¹; Verheyden, Niels - Co-Author¹

¹VITO

Main topic: Industrial applications and scale-up

The European Open Innovation Test Bed INNOMEM gathers >20 recognised Membrane departments and technology transfer facilitators, providing breakthrough membrane manufacturing pilots, advanced characterization and modelling, as well as non-technical services. The main types of membrane materials, geometries and applications are covered. The existing 14 pilots are being upgraded for increased productivity, faster verification and standardization. And, innovative nanomembranes will be demonstrated in real life industrial problems (TRL7), facilitating their absorption in the market. Several (10) showcases, already defined are in progress. Potential clients will be able to access the INNOMEM services through a single entry point.

A decade ago VITO, together with University of Antwerp, developed an innovative grafting technology for ceramic membranes, based on Grignard chemistry. The method results in a unique, stable, carbon-metal bond, and offers great flexibility : different metal oxides and silicon carbide with a variety of pore sizes were successfully grafted. The resulting functionalised membranes demonstrated good performance in organic solvents, and strong anti-fouling effects in difficult wastewaters.

Development started grafting small-scale tubular membranes in stirred glass wear. Soon, we moved to grafting in filtration mode in a glove box. This was successfully scaled up to commercial size multichannel membranes (1,2 m long 19 to 163 channel membranes). Next, a closed-loop pilot system was build, able to graft 1 to 5 membranes simultaneously in one week. In the Atex set-up all three synthesis steps (pre-treatment, Grignard grafting, washing) and first quality control are performed without membrane manipulation. Moreover, the system is not limited to Grignard grafting alone.

Within INNOMEM, VITO will further upgrade and upscale this existing pilot line for increased production volumes (simultaneous grafting of 10 instead of 5 membranes) and improved production time (24h instead of one week). Moreover, a new pre-treatment was developed avoiding the high vacuum used up to now. Together with membrane supplier LiqTech, VITO will further demonstrate the beneficial use of the resulting grafted membranes for the purification of power-plant scrubber water. This contribution will highlight the efficiency of the upgraded pilot, and will clarify the preliminary results of the showcase.

Reference 1:

Acknowledgement: INNOMEM has received funding from the European Union's Horizon 2020 Research and Innovation Program under Grant Agreement N° 862330. <https://www.innomem.eu/>

Can Deep Eutectic Solvents (DES) be a replacement of Ionic Liquids for CO₂ separation?

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¹LAQV/REQUIMTE, NOVA School of Science and Technology, FCT NOVA

Main topic: Facilitated transport membranes

Deep eutectic solvents (DES) have been proposed in the last years as viable and more sustainable solvents when compared with ionic liquids (ILs), in a myriad of applications. CO₂ capture is one of those possible applications. ILs were seen as an interesting choice as solvents for CCS processes due to their affinity towards CO₂. Although ILs represent a major scientific breakthrough and are used in many different areas, they present some drawbacks, since they result from extensive synthetic reaction processes that use non-renewable products which makes them expensive and, in some cases toxic, hindering their large-scale applications. To overcome the gap left between the aqueous amine solutions for CO₂ capture, and the processes that use ILs, DES can have a role as alternative solvents. DES are formed by mixing two or more components, a hydrogen bond acceptor and a hydrogen-bond donor at an appropriate molar ratio, yielding a complex hydrogen bonded network which in turn results in a liquid mixture. They are often a combination of renewable chemicals, making their synthesis sustainable and simple.

In this work, different choline chloride DES were prepared, and CO₂ solubility and diffusivity coefficients were determined. The DES were immobilized in a PTFE porous support, and the pure gas permeability of 3 different gases (N₂, CO₂ and CH₄) was assessed, as well as DES supported liquid membranes ideal selectivity. An enzyme that is able to convert CO₂ into bicarbonate was also added to the DES, in order to increase the transport towards CO₂. The tested DES show solubility values in line with the ones reported in literature for related DES family and ILs. Solubility and diffusivity of CO₂ showed the best results in the DES composed of choline chloride and urea, showing even higher values when the enzyme was dispersed. The supported liquid membranes show higher permeability towards CO₂, especially in DES with choline chloride and urea. The membrane containing this DES also showed high selectivity for CO₂/CH₄, with values above the Robeson upper bound.

Case Studies of Nanofiltration and Membrane Distillation Membranes for Desalination Applications

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¹Department of Chemistry and Bioscience, Aalborg University

Main topic: Membrane contactors and membrane distillation

Clean water shortage is one of the most pressing issues for humankind. In this context, we tested two membrane technologies, namely nanofiltration (NF) and membrane distillation (MD), for desalination in two case studies. For each case study, the performances of commercial polymer membranes and lab-made inorganic membranes were investigated and compared to obtain information for the construction of pilot-scale facilities.

In the first case study, NF was used for the potabilization of the groundwater in a well from the Puglia Region, Italy [1]. This groundwater suffers from high salinity, the desalination performance of a commercial polymer membrane (Dow NF90) and a novel lab-made alumina-doped amorphous silica NF membrane were compared. The polymeric membrane modules could reduce the conductivity of the groundwater from 4.6 mS cm^{-1} to 1.3 mS cm^{-1} with an average permeability of $2.8 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$. Under the same filtration condition, the alumina-doped amorphous silica membrane module can reduce the permeate conductivity to around 2.4 mS cm^{-1} with an average permeability of $1.2 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}$. From these preliminary filtration tests, we calculated that both membranes can operate with a specific energy consumption of $0.2 \text{ kWh}\cdot\text{m}^{-3}$. Hence, a pilot plant (producing 1m^3 of drinking water/day) is under construction next to the well.

In the second case study, MD was used for the desalination of the effluent from an inland mariculture site located in Eilat, Israel. The effluent consists of seawater with high loading of organic residues from the fish tank. Desalination of such effluent was achieved by MD on a commercial polymeric hollow fiber membrane and with a newly developed inorganic membrane. The MD experiments showed that the polymer membrane can achieve almost complete desalination at 50°C with a permeate flux of around $1 \text{ L h}^{-1} \text{ m}^{-2}$. An inorganic MD membrane was specifically developed for this application. Compare with the traditional hydrophobically modified ceramic membranes used in MD, the new inorganic membranes are cheaper and have a lower thermal conductivity. Under the same testing condition, the new inorganic membrane had flux that is almost 3 times higher than the polymer membrane and maintained the same level of salt rejection.

Reference 1:

Ma, X.; Quist-Jensen, C.A.; Ali, A.; Boffa, V. Desalination of groundwater from a well in Puglia region (Italy) by Al_2O_3 -doped silica and polymeric nanofiltration membranes. *Nanomaterials* 2020, 10, 1–12.

Case-specific mass transfer correlations for concentration polarization minimization and fouling prevention

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¹CeFEMA/Instituto Superior Técnico/University of Lisbon, ²PPGE3M/Federal University of Rio Grande Do Sul (UFRGS)

Main topic: Transport models

In the present work, two case studies – ultrafiltration/nanofiltration of an atenolol solution and of a winery wastewater – are analyzed to obtain case specific correlations where mass transfer coefficients (k) besides being a function of Reynolds and Schmidt numbers are also dependent on a dimensionless number characteristic of the membranes' permeation properties. The solute rejection by ultrafiltration/nanofiltration membranes results in solute accumulation at the membrane/feed interface with a concentration adjacent to the membrane surface, C_{Am} , higher than the solute concentration in the bulk feed solution, C_{Ab} . An intrinsic and an apparent rejection coefficient are then defined as $f_{A'} = \frac{C_{Am} - C_{AP}}{C_{Am}}$ and $f_A = \frac{C_{Ab} - C_{AP}}{C_{Ab}}$, respectively, and related by $f_A = \frac{f_{A'}}{f_{A'} + \left(1 - f_{A'}\right) \exp\left(\frac{J_p}{\frac{D_{AW}}{\delta}}\right)}$, where J_p is the membrane permeation flux, C_{AP} is the concentration of solute A in the permeate, D_{AW} is the diffusivity of solute A in the feed boundary layer of thickness δ and k by the film theory is defined as $\frac{D_{AW}}{\delta}$.

Permeation experiments were conducted in total recirculation mode, in laboratory flat-cell units with 14.5 cm² of membrane surface area, using ultrafiltration/nanofiltration commercial membranes. In the first case study, 8 or 16 mg/L atenolol-containing solutions were processed using two nanofiltration membranes, NF90 & NF270 (DOW–Filmtec), at feed circulating velocities of 0.24–0.96 m/s and the pressures of 6–12 bar [1]. In the second case study, a winery wastewater previously treated by microfiltration was used as feed solution and presented 26.1, 10.1 and 4.2 mg/L of total polyphenols, polysaccharides and monomeric anthocyanins, respectively [2]. It was processed at feed circulating velocities of 0.48–0.96 m/s and pressures of 3–15 bar using an ultrafiltration membrane (ETNA01PP, from Alfa Laval, 1000 Da MWCO) and the NF270 membrane.

In general, the nanofiltration permeation fluxes increase linearly with pressure and tangential velocity; while the ETNA01PP showed typical behavior of ultrafiltration permeation fluxes, increasing linearly in low pressures and achieving a plateau (limiting flux) in higher pressures. The case-specific mass transfer coefficients, $Sh = \frac{kd_h}{D_{AW}} = 1.98 \times 10^4 \{Re\}^{0.5} \{Sc\}^{0.33} L_P^{+0.32}$ [1] and $Sh = 1.5 \times 10^4 \{Re\}^{0.47} \{Sc\}^{0.33} L_P^{+0.35}$ [2], allow the prediction of the concentration polarization phenomenon and thus enable an efficient design and operation of pressure-driven membrane processes.

Reference 1:

A. Giacobbo, E.V. Soares, A.M. Bernardes, M.J. Rosa, M.N. de Pinho, Water Sci Tech 81:2 (2020) 210–216.

Reference 2:

A. Giacobbo, A.M. Bernardes, M.J.F. Rosa, M.N. de Pinho, Membranes 8:3 (2018) 46.

Cellulose based membranes for energy storage applications

Lander, Sanna - Co-Author

Main topic: Novel membrane materials

Several of the most promising technologies for large-scale energy storage, such as redox flow batteries and fuel cells, rely on selective membranes for their function. Current state-of-the-art ion selective membranes have drawbacks such as poor barrier properties toward fuels and redox molecules, environmentally unfriendly production, as well as a high price limiting cost-efficient large-scale application.

In recent years, cellulose have gained attention as promising low-cost and environmentally benign starting materials for various membranes. Cellulose is of interest due to a combination of favorable properties: abundancy as a renewable material in nature, low cost, decent mechanical properties, ability to form porous networks at various scales, and high variability in possible functionalization routes. Cellulose is a biopolymer with abundant hydroxyl groups along the polymer chains, readily available for chemical modifications, for example the introduction of cationic or anionic functional groups. Cellulose has already been successfully used in energy storage systems in various ways: as porous separators for metal-ion batteries, as electrodes by its combination with conducting materials, and as proton conducting membranes for fuel cells.

In this work, membranes produced from chemically modified cellulose have been characterized and investigated in terms of their performance in a few energy storage systems.

Cellulose membranes in the treatment of spent deep eutectic solvent to purify the solvent and recover lignin

Ippolitov, Vadim - Main Author¹; Anugwom, Ikenna - Co-Author¹; Mänttäre, Mika - Co-Author¹; Kallioinen, Mari - Co-Author¹

¹LUT university

Main topic: Bio-separations and bio-refinery

Deep eutectic solvents (DESs) are promising possibility to recover biomass compounds. However, their use in industrial scale is still limited by the lack of efficient recycling processes. To enable the recycling, the solvents have to be purified. For instance, in a case, in which a mixture of choline chloride (ChCl) and lactic acid (LA), 1:10, is used to recover sulphur-free lignin selectively from wood biomass, recycling of solvent means that the water used to precipitate the dissolved lignin from the DES and the biomass originating impurities left in the DES have to be removed before the solvent can be used again. Our approach to solve the recycling of the spent DES is to utilise membrane filtration, because it makes it possible to concentrate and fractionate the lignin in the spent DES prior to precipitation with water. This approach helps us both to minimise the need to separate the antisolvent (water) from the spent DES and to produce sulphur-free lignin fractions in different molar masses. We have already shown in our earlier studies that the commercial RC70PP membrane (10 kDa, Alfa Laval) can be utilised in the treatment of the spent DES (Kallioinen et al., 2021). In this presentation we are presenting the results showing the possibility to use cellulose membranes having different cut-off values (RC70PP by Alfa Laval and Ultracel 5 kDa and 3 kDa UF Discs by Millipore) in the purification of the spent DES both in series and in parallel. Moreover, the stability of the membranes in the spent DES and their fractionation capability in production of purified lignin fractions will be discussed.

The authors thank Kymisäätiö for funding of this research.

Reference 1:

Kallioinen, M., Ippolitov, V., Anugwom, I. and Mänttäre, M., Ultrafiltration of deep eutectic solvent (DES) to recover lignin and purify the solvent, Presented in the conference "Renewable Resource and Biorefineries, 6.-8.9.2021, Aveiro, Portugal.

Cellulose-cellulose composite membranes for ultrafiltration

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¹Lehrstuhl für Technische Chemie II, Universität Duisburg-Essen, 45117 Essen, Germany

Main topic: Microfiltration/Ultrafiltration

Membranes made from cellulose were in history and still are important for the development of membrane technologies. Nevertheless, alternative fabrication methods for completely biopolymer-based separation membranes are of current interest with view on improved sustainability [1].

This project explores a new kind of composite membrane, with a thin selective cellulose layer on filter paper as porous support. Suited ionic liquids (IL) in combination with dimethylsulfoxide (DMSO) can be used to dissolve cellulose under mild conditions and subsequently to cast regenerated cellulose materials via shaping and phase separation [2].

The novel fabrication method of completely renewable and biodegradable cellulose-cellulose composite membranes for ultrafiltration (UF) is therefore based on film casting of a solution of cellulose in an IL/DMSO mixture on the filter paper as support and subsequent phase separation in water. Typical composite membranes have a cellulose film thickness of a few μm on filter paper with a pore size in the range of several μm . The separation performance of the obtained membranes can be specifically adjusted by fabrication parameters such as cellulose concentration, structure of IL and DMSO co-solvent content (Figure 1). However, the dry support is partially penetrated by the cellulose solution during the film casting, leading to too low permeability. The separation performance was improved by pre-wetting the support with various liquids to prevent pore penetration, but that can also weaken the membrane lamination as shown by adhesion tests. It was found that prewetting of the filter paper with DMSO can solve the problem, leading to composite membranes with a strongly attached cellulose film on the paper support and superior, tunable UF properties.

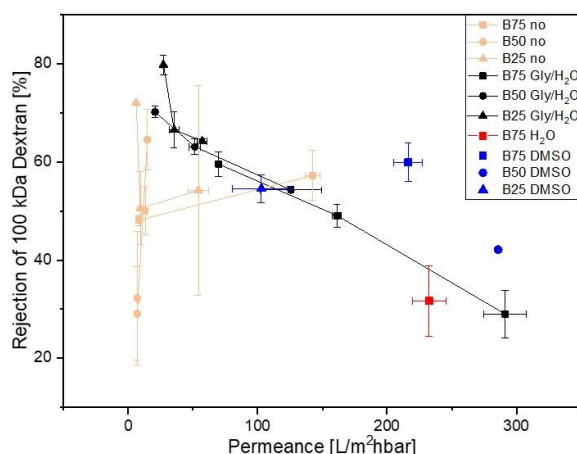
Figure 1: Relationship between dextran rejection in ultrafiltration and pure water permeance for cellulose-filter paper composite membranes prepared using different parameters. All casting solutions were prepared at different cellulose concentrations with butyl-methylimidazolium acetate as IL with a fraction of 75, 50 or 25% in its mixture with DMSO; pre-wetting conditions: “no” ... dry filter paper; “Gly/H₂O” ... with glycerine/water 40/60; “H₂O” ... with water; “DMSO” ... with DMSO.

Reference 1:

[1] S. P. Nunes, P. Z. Culfaz-Emecen, G. Z. Ramon, T. Visser, G. H. Koops, W. Jin, M. Ulbricht, Thinking the future of membranes: Perspectives for advanced and new membrane materials and manufacturing processes, *Journal of Membrane Science* 598 (2020) 117761.

Reference 2:

[2] A. S. M. Wittmar, D. Koch, O. Prymak, M. Ulbricht, Factors affecting the non-solvent induced phase separation of cellulose from ionic liquid-based solutions, *ACS Omega* 5 (2020) 27314-27322.



Cellulose-rich wood-based ultrafiltration membranes: introducing alkaline coagulation bath and studying applicability to real waste streams as an example of wastewater effluent purification

Lopatina, Anastasiia - Main Author¹; Liukkonen, Alma - Co-Author¹; Bec, Sabina - Co-Author¹; Anugwom, Ikenna - Co-Author¹; Mänttari, Mika - Co-Author¹; Kallioinen, Mari - Co-Author¹

¹LUT

Main topic: Microfiltration/Ultrafiltration

Regenerated cellulose membranes possess all the attractive properties of cellulose: relatively good thermal and chemical stability, great hydrophilicity, and sufficient mechanical stability. These membranes also often demonstrate low-fouling behavior and high capacity, which makes them an attractive instrument for the purification of water-based process streams. In the search for efficient and sustainable methods for the fabrication of regenerated cellulose membranes, the prospective approach is related to the exploration of both novel cellulose sources and improvements in the fabrication procedure. In our previous works, it was reported that hardwood biomass and cotton textile can be considered not a waste but prospective sources of cellulose, as an alternative to the commercially available cellulose fibers and powders (Lopatina et al., 2020, 2021).

The presented study was focused on the improvement of the cellulose-rich wood-based membranes' performance through the development of fabrication sequence. The DES-treated birch biomass was dissolved in the mixture of [Emim][OAc] and DMSO with 5 wt.% concentration until the formation of the homogeneous casting solution. The membranes were cast and subjected to a two-step coagulation process, particularly through the introduction of an additional coagulation bath filled with the alkaline solution with a concentration below the cellulose dissolution limit (Figure 1). The effect of NaOH concentration in the coagulation bath and coagulation time was studied.

The resulting membrane's pure water permeability is up to 450 L/m²·h·bar, the retention of CaCO₃ suspension is >95%, and above 70% removal of total phosphorus from the effluent of the wastewater treatment plant was achieved. Regardless of the coagulation bath parameters, membranes show negative surface charge within a wide pH range. However, a clear difference between values was observed and thus indicates a possibility to use an alkaline coagulation bath as a membrane's surface charge control tool.

(Figure 1 here)

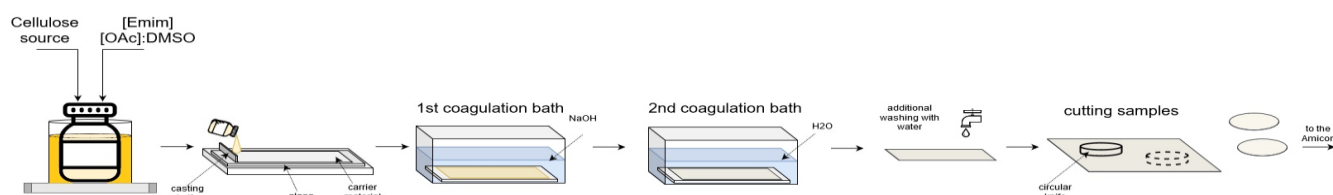
Figure 1. Modification of the membrane casting procedure via the introduction of an additional coagulation bath containing NaOH solution.

Reference 1:

Lopatina, A., Anugwom, I., Blot, H., Sanchez Conde, A., Mänttari, M., & Kallioinen, M. (2021). Re-use of waste cotton textile as an ultrafiltration membrane. *Journal of Environmental Chemical Engineering*, 9(4).
<https://doi.org/10.1016/j.jece.2021.105705>

Reference 2:

Lopatina, A., Anugwom, I., Esmaili, M., Puro, L., Virtanen, T., Mänttari, M., & Kallioinen, M. (2020). Preparation of cellulose-rich membranes from wood: effect of wood pretreatment process on membrane performance. *Cellulose*, 0.
<https://doi.org/10.1007/s10570-020-03430-0>



Ceramic membranes from dental zirconia waste

Messina, Giacomo - Co-Author¹; boffa, vittorio - Main Author¹; deganello, francesca - Co-Author²

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Main topic: Inorganic membranes

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Zirconia-based ceramics are the most used material for dental applications, due to their outstanding hardness, chemical stability and low toxicity. During the machining of zirconia blocks to prepare the various types of prosthesis, more than 50% of the material is lost in the form of nanopowder or lumps, and it cannot be recycled in teeth manufacturing. In this work, we used dental zirconia waste nanopowder to fabricate a ceramic membrane with high potential in the removal of oil residues in produced water. Dental zirconia waste was pulverized by dry milling, sieved over a micro-mesh, and sonicated in water together with a commercial binder and a dispersant, in order to form a dispersion used to coat some commercial ceramic supports. The filtration efficiency and fouling resistance of the new zirconia-based membranes were tested on model water by measuring the water permeability vs time, and the feed solution oil content/permeate.

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¹Nicolaus Copernicus University in Torun

Main topic: Advanced fabrication methods

Although membrane separation processes are well accepted in the industry and medicine for purification, concentration, fractionation, and distribution; there is an increasing search for the novel and modified materials widening the areas of membrane applications.

Ceramics are one of the most important materials possessing high ability to functionalization. The character of support is an important factor governing the enzyme immobilization, especially of lipases, due to the hydrophobic nature of their active sites [1,2]. The immobilization of enzymes can be implemented by physical adsorption or chemical (covalent) bonding. Nowadays, (3-aminopropyl) triethoxysilane (APTES) is commonly used as a modifier for the covalent attachment of enzymes. However, the short carbon chain of APTES limits the effectiveness of grafting and separation. Therefore, various hybrid inorganic-organic materials with controllable physiochemical properties can be generated.

Titania powders as well as ceramic titania membranes with MWCO of 15, 50, 150, and 300 kD were used as an inorganic support. Ceramic supports were subsequently modified with linkers of various chemistry. Finally, the chemical or physical immobilization of enzymes was performed. The resulting materials were characterized by implementing FTIR, AFM, TGA, contact angle measurements and determination of zeta-potential. 1-butyl-3-triethoxysilyl urea and 1-aminobutyl-3-triethoxysilyl urea were synthesized for the physical and chemical modification of TiO₂ support. In the case of chemical attachment, the glutaraldehyde was used as a coupling agent. The activity of *Candida antarctica* B (CALB) was monitored. Activity and stereoselectivity of immobilized CALB were determined in a model transesterification of a racemic alcohol with vinyl acetate as an acyl donor. The chemical attachment possessed higher stability. Enzyme on the membrane covalently functionalization maintained the initial activity of CALB 94% after 5 runs (24h each) of the process. However, for the sample treated via physical route in the last, 5th run only 53% of initial activity was seen. After each run the selected physiochemical factors were controlled as well, e.g., contact angle and roughness parameters.

Reference 1:

J. Kujawa, M. Głodek, I. Koter, B. Ośmiałowski, K. Knozowska, S. Al-Gharabli, L. F. Dumée, W. Kujawski, Molecular Decoration of Ceramic Supports for Highly Effective Enzyme Immobilization—Material Approach, *Materials* 2021, 14, 201

Reference 2:

J. Kujawa, M. Głodek, G. Li, S. Al-Gharabli, K. Knozowska, W. Kujawski, Highly effective enzymes immobilization on ceramics for separation processes: requirements for supports and enzyme, *Science of the Total Environment* 801 (2021) 149647

Characteristic dimensions of ion-exchange membranes studied by molecular sieving.

Slouka, Zdenek - Co-Author

Main topic: Electro-membrane processes

Ionic selectivity of ion-exchange systems (membranes, resin particles) plays an irreplaceable role in the directed transport of ions. This property, by its nature, gives the foundation not only for separation processes such as electrodialysis and electrodeionization but also electric energy-producing systems represented, e.g., by fuel cells or redox flow batteries. In a simplified view, the ionic selectivity results from electrostatic interactions between charged entities, namely mobile ions from processed solutions and a so-called fixed (bound) charge in/on the ion-exchange membranes. The polarity of the fixed charge stipulates the type of ions to be exchanged by the given membrane. This simple description becomes more complex when considering the characteristic length scales over which electrostatic interactions act. This length scale, being around 1 nm in water electrolytes, predetermines the size of internal structures of ion-exchange membranes, which, in turn, restricts the size of counterions exchanged by the given membrane.

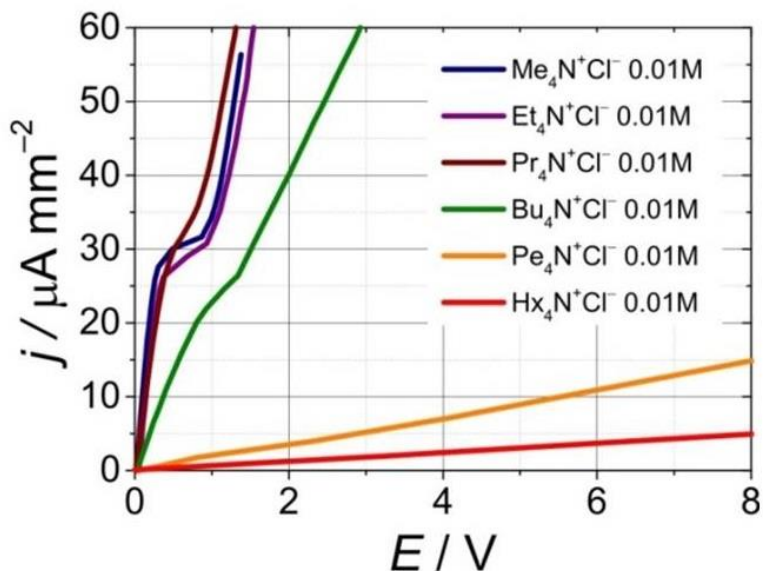
We undertook experimental studies with heterogeneous ion-exchange membranes and corresponding resin particles focused on identifying the counterions reflecting the size of membrane structures. We used homologous series of tetraalkylammonium cations when testing cation-exchange systems [1] and a series of alkyl sulfates for anion-exchange systems [2]. We determined the counterions of critical size (length) in both studies dividing the tested counterions into (i) smaller ones easily exchanged and (ii) larger ones blocking and fouling the membrane/resin particle. This counterion size division (around 1 nm in both studies) manifested itself in the overlimiting behavior of the studied systems. While electroconvection and water splitting dominated in cation- and anion-exchange systems, respectively, for the first group of counterions, almost no current passed through the system for the other group.

Reference 1:

Polezhaev, P., et al., Molecular sieving of tetraalkylammonium cations on cation exchange systems in DC electric field. Separation and Purification Technology, 2020. 241: p. 116691.

Reference 2:

Polezhaev, P., et al., Molecular sieving of alkyl sulfate anions on strong basic gel-type anion-exchange resins, accepted for publication in Separation and Purification Technology.



Current-voltage curves of a cation-exchange resin particle in solutions of tetraalkylammonium cations showing the effect of counterion size.

Characterization of (bio)fouling formation and the impact of cleaning solutions on unmodified and modified anion exchange membranes

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¹iBET - Instituto de Biologia Experimental e Tecnológica, ²LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, Universidade Nova de Lisboa, ³Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa

Main topic: Electro-membrane processes

Reverse electrodialysis is one of the sustainable technologies, which can be used to generate clean energy and thus, contribute to the 7th goal of the United Nation's 2030 Agenda for Sustainable Development (ensure access to affordable, reliable, sustainable, and modern energy for all). This technology generates electricity from salinity gradients sources (e.g. sea and river water) through the alternate use of cation and anion exchange membranes. Nevertheless, one of the main challenges that reverse electrodialysis faces is the formation of fouling on the ion exchange membranes [1].

Different solutions might be explored to mitigate the impact of fouling on ion exchange membranes, including membrane surface modification. In this study, a monolayer surface modification procedure, previously optimized by Merino-Garcia *et al.*, was performed to functionalize Ralex-anion exchange membranes (Ralex-AEM) with poly(acrylic acid) [2]. The resistance to organic and biofouling as well as to cleaning solutions was compared between the unmodified and modified Ralex-AEM.

Fouling experiments were conducted by immersing coupons of modified and unmodified membranes in river and sea water as well as in a cell suspension of *Aeromonas hydrophila*. After fourteen days, the membrane samples were analysed via Fourier-transform infrared spectroscopy (FT-IR), Scanning Electron Microscopy coupled with an Energy Dispersive Spectroscopy (SEM-EDS) and water contact angle measurements. The formation of biofouling was also evaluated by fluorescence microscopy, confocal laser scanning microscopy and by estimating the concentration of total microorganisms, total coliforms, and *E. coli* present on the top layer of the membrane samples.

Additionally, since sodium hydroxide and sodium hypochlorite are commonly used in the removal of organic and biofouling, respectively, the effect of different concentrations of these cleaning agents was evaluated. Briefly, samples of unmodified and modified Ralex-AEM were immersed in each cleaning solution during seven days. The membrane samples were then analysed via the same techniques previously described. Furthermore, the effect of these cleaning solutions to remove fouling was also assessed.

Reference 1:

S. Pawlowski, R.M. Huertas, C.F. Galinha, J.G. Crespo, S. Velizarov, On operation of reverse electrodialysis (RED) and membrane capacitive deionisation (MCDI) with natural saline streams : A critical review, *Desalination*. 476 (2020) 114183.

Reference 2:

I. Merino-Garcia, F. Kotoka, C.M. Portugal, J.G. Crespo, S. Velizarov, Characterization of poly (Acrylic) acid-modified heterogenous anion exchange membranes with improved monovalent permselectivity for RED, *Membranes* 10 (2020) 134.

Characterization of 3D printed spacers for electro dialysis in a lab-scale module

Bernardova, Eva - Main Author¹; Feher, Jakub - Co-Author¹; Tvrznik, David - Co-Author; Leskovjan, Martin - Co-Author¹; Safka, Jiri - Co-Author²; Tomek, Jan - Co-Author¹
¹MemBrain, ²The Technical University of Liberec

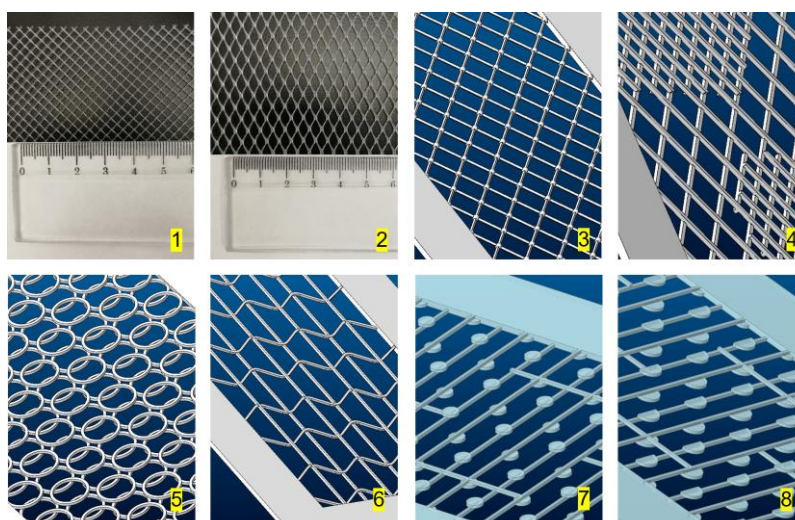
Main topic: Module design

Electrodialysis spacers are used to form flow compartments in an electro dialysis stack by maintaining a defined distance between membranes. In addition, they promote a turbulent flow of a liquid in the flow compartments reducing the effect of concentration polarization and thus facilitating mass transfer in the electro dialysis stack. On the other hand, they negatively affect the overall electrical resistance of the electro dialysis stack due to a screening (shielding) effect. In the present work, 6 different types (geometries) of 3D printed spacers were tested along with 2 standard extruded non-woven nets. All types of spacers had a thickness of 0.8 mm and were tested in a lab-scale electro dialysis stack with RALEX[®] heterogeneous membranes and 10 cell pairs. Volt-ampere (VA) characteristics were measured and batch tests were carried out for each type of spacer. VA characteristics were measured at two different flow rates. Dilute aqueous solutions of sodium chloride were used as a feed in the measurement of VA characteristics in order to minimize the effect of the membranes on the overall electrical resistance of the stack, to avoid back diffusion of the electrolyte, and nonideal selectivity of the membranes. The screening effect, the thickness of the diffusion layer, and degree of desalination were determined from VA characteristics [1]. From batch tests, the mass flux of salt, energy consumption, and current efficiency were obtained. 3D printed spacer with a lower mesh size showed a higher degree of desalination but also higher energy consumption, e.g. Spacer 4, 5. Optimized spacers, Spacer 7, 8, showed similar energy consumption as extruded nets but at a higher degree of desalination.

Acknowledgement: This work was carried out in the frame of the project ED3D - Development of novel components for electromembrane modules using additive technologies (FW01010292) supported by the Technology Agency of the Czech Republic.

Reference:

[1] Tvrzník, D.; Machuča, L.; Černín, A., Mathematical Model of Mass Transfer in an Electro dialyzer with Net-like Spacers. *Desalination and Water Treatment* 2010 (14), 174–178. <https://doi.org/10.5004/dwt.2010.1024>.



Tested spacers: (1-2) – extruded non-woven, (3-8) – geometries made by 3D print

Characterization of the selective layer of PAN and PES polymeric filtration membranes using 3D FIB/SEM and flux calculation.

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Main topic: New characterisation methods

Membrane filtration processes have recently been adapted for microalgae valorization, where filtration employing nanoporous polymer membranes is used to separate and recover lipids and proteins from ground microalgae aqueous extracts. The biomolecules recovered can be used in pharmaceutical industry, cosmetics, food supplements or biofuel industry as biodiesel. The performance of the membrane is related to the size and density of its pores, but also to the selective layer thickness, as shown by Poiseuille's law [1]. During filtration, the unwanted accumulation of biomolecules at the surface and in the pores, termed fouling, hampers membrane performances. A detailed characterization of the pore structure, firstly in clean membrane, is essential to understand and help minimize the fouling.

Scanning electron microscopy (SEM) coupled with a focused ion beam (FIB) allows characterizing the 3D nanoporous structure of the material with a few nanometers resolution [2]. Data acquisition is particularly challenging with polymer membranes constituted of amorphous materials presenting little contrast and a strong sensitivity to the electron and ion beams. Moreover, 3D reconstructions of porous media present a common issue: the shine-through artefact, leading to a pores deformation in the FIB-milling direction.

We have characterized two polymer membranes in dry conditions: PAN (polyacrylonitrile) and PES (polyethersulfone), with a nominal pore size of their selective layer, as provided by the manufacturers, of 30 nm and 100 nm, respectively. We have developed a 3D FIB/SEM method to obtain quality 3D reconstructions with a 5 nm voxel size and overcoming beam sensitivity and artefact difficulties.

In this presentation, the sample preparation as well as the optimization of acquisition and reconstruction parameters will be described. We will present a method for identifying the selective layer in polymer filtration membranes using serial FIB/SEM. The quantitative analysis of pore size distribution, porosity, connectivity and tortuosity (figure 1) will be discussed. The properties-structure relationships will be analysed, by linking these results with the theory of Hagen-Poiseuille on the porous media flux calculation.

In perspectives, The use of cryogenic conditions would permit directly observing lipids or protein fouled hydrated membranes while minimizing damage and maintaining the native structure of both: the organic material and biomolecules.

Reference 1:

[1] AIMAR et al., Text. Ref : TIP452WEB - « Op  rations unitaires. G  nie de la r  action chimique ». Editions T.I. | Techniques de l'Ing  nieur (2010).

Reference 2:

[2] Sundaramoorthi et al., Industrial & Engineering Chemistry Research 55 (2016).

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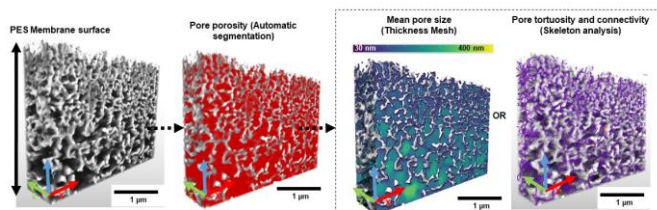


Figure 1: Illustration of the main 3D analysis steps. Here for PES membrane pores were segmented in order to extract quantitative analysis of the volume, the mean pore size (thickness mesh) and the pore tortuosity and connectivity (skeleton)

Chemistry in a spinneret – antifouling hollow fiber membranes through in-situ microgel functionalization

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¹RWTH Aachen University, ²DWI - Leibniz-Institute for Interactive Materials, ³AVT.CVT, RWTH Aachen University, ⁴ITMC, RWTH Aachen University, ⁵AMIBM, Maastricht University

Main topic: Membrane fouling and cleaning

New membrane functionalities and performance improvements often result from chemically and procedural complex post-modification steps. Microgels are highly functional colloidal macromolecules. Due to their hydrophilicity, switchability and functionalizable structure, the post-modification of membranes with microgels has been widely investigated [1]. The resulting membranes show improved or novel properties. Still, the post-modification of membrane surfaces and pores with microgels consists of multiple steps: microgel synthesis, membrane formation, and a subsequent immobilization step of the microgels on the membrane.

Here, we present two routes to directly fabricate functional hollow fiber membranes with microgels using our platform technology chemistry in a spinneret [2]. The procedural most complex, but single step route is the synthesis of microgels in the lumen fluid during hollow fiber spinning. The lumen fluid additionally contains the components for microgel synthesis - monomer, crosslinker and initiator. In the tubing before the spinneret and in the lumen of the forming hollow fiber, microgel particles evolve and immobilize on the lumen surface of the membrane.

Further, we present a simpler variation of this approach. In this case, fully synthesized microgels are added to the lumen fluid and/or polymer solution.

All presented routes successfully generate hollow fiber membranes with immobilized microgels.

We chose poly(N-vinylcaprolactam) (PVCL) as base microgel system which is highly functionalizable and biocompatible. Furthermore, we apply zwitterionic microgels containing sulfobetaine groups.

The resulting hollow fiber membranes exhibit unique porous structures with embedded microgels and are in the ultrafiltration range. Flux stepping experiments with bovine serum albumin solution prove the exceptional antifouling characteristics of the hollow fiber membranes containing pure as well as zwitterionic microgels. Additionally, the unique responsiveness to ionic strength of the zwitterionic functionalized membranes proves the effect of the two different microgels on the membrane performance.

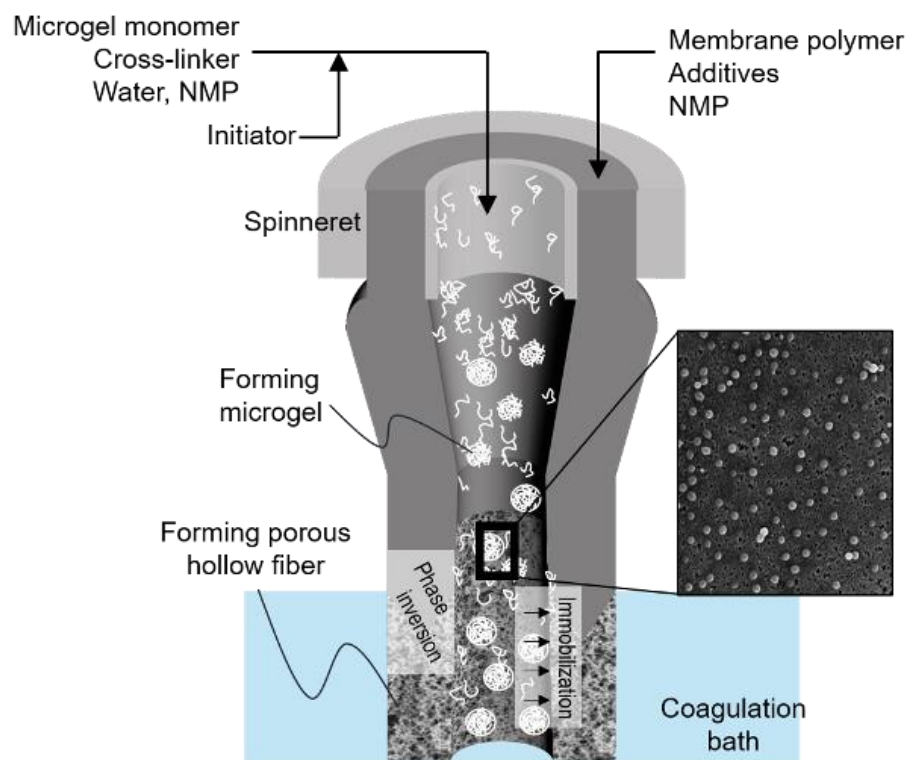
The proposed spinning methods promise to become a technology base for the design of microgel functionalized hollow fiber membranes. By varying the microgel materials and purposefully providing functional groups, we envision the emersion of functional membranes for all imaginable areas of application.

Reference 1:

Saha, P., Santi, M., Emondts, M., Roth, H., Rahimi, K., Großkurth, J., Ganguly, R., Wessling, M., Singha, N. K., & Pich, A. (2020). Stimuli-Responsive Zwitterionic Core-Shell Microgels for Antifouling Surface Coatings. *ACS Applied Materials and Interfaces*, 12(52), 58223–58238. <https://doi.org/10.1021/acscami.0c17427>

Reference 2:

Roth, H., Luelf, T., Koppelman, A., Abel, M., & Wessling, M. (2018). Chemistry in a spinneret – Composite hollow fiber membranes in a single step process. *Journal of Membrane Science*, 554(November 2017), 48–58. <https://doi.org/10.1016/j.memsci.2018.02.051>



Cleaner, better and cheaper use of chemicals in RO membrane filtration systems

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Main topic: Nanofiltration/Reverse Osmosis

Water scarcity can be a regional phenomenon around the world, but water reuse is a global trend that has increasingly grown over the first decade of 2000. The preferred technology for desalination is with no doubt reverse osmosis (RO). The International Desalination Association reports close to 18,500 desalination plants in operation, however the number can be “doubled” by including system with sizes in the range 20 to 1000 m³/d. The installed reuse capacity (130 million m³/day) has passed the installed high brackish water, seawater desalination capacity (89 million m³/day). Membrane fouling is a known problem in RO and nanofiltration (NF) that impact and deteriorate membrane performance. A reduced membrane performance will translate into higher operational costs.

Previous research (Antony et al., 2011) refers to the mechanisms of crystal formation when scaling occurs. It has been known about the role of anti scaling chemicals from early boiler applications. That knowledge has been in principle adapted to membrane filtration, where effects of concentration polarization and the willingness to achieve high system recovery will definitely have consequences of membrane scaling. The problem is that dosing of antiscalants and water treatment has been a practice only understood by some experts and chemical providers that have applied extra margins of safety to control precipitation. The current practice is to maintain the dosage of a recommended blend of chemicals to target certain types of scaling. Scaling is a precipitation phenomena that is dependent in many other conditions apart from water chemistry. Overdosing of the chemical will impact the filtration process and so do will underdosing of the chemical. In some cases, the dosing will be manually adjusted based on experience of the operator and history of operation of the plant. In the best cases, dosing may be performed with proportional dosing to the feed flow water stream. The present work builds upon a smart filtration control algorithm that based on the system response measured by key standard sensors will dynamically adjust the chemical dosing (e.g. antiscalant. pH adjustment). Optimization of two pilot systems (Denmark, Netherlands) are presented, where reduced chemical and energy consumption have demonstrated that the dosing control can be implemented.

Reference 1:

Antony, A., Low, J. H., Gray, S., Childress, A. E., Le-Clech, P. & Leslie, G. 2011. Scale formation and control in high pressure membrane water treatment systems: A review. *Journal of Membrane Science*, 383, 1-16.



CoFe₂O₄-Peroxymonosulfate based Catalytic UF and NF Polymeric Membranes for Naproxen Removal: The Role of Residence Time and pH

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¹University of Twente

Main topic: Membrane reactors

Small organic micropollutants pose a significant threat to water quality, aquatic and public health. Unfortunately, current treatment methods like coagulation-flocculation, activated carbon adsorption, and bioreactors cannot provide efficient and sufficient elimination of the micropollutants [1]. A catalytic membrane, combining membrane filtration and peroxymonosulfate (PMS) activation provides an alternative and promising option for this treatment [2].

In this study, CoFe₂O₄ based catalytic particles were added to a PES dope solution, to obtain catalytic UF membranes. For part of the membranes, layer-by-layer assembly of poly-(diallyl dimethylammonium chloride) (PDADMAC) and poly(styrenesulfonate) (PSS) was performed on the surface of the catalytic UF membrane to build a catalytic NF membrane. We studied these catalytic UF and NF membranes in full-recycling mode and single-pass mode to reveal the influence of residence time on the treatment efficiency of catalytic membranes. The naproxen rejections for the catalytic UF and NF membranes indicate that in full recycling mode, a longer residence time enhances the degradation efficiency, improving the effective naproxen rejection/removal. In single-pass mode, both catalytic UF and NF membranes showed high and stable naproxen removals which were higher than 80%. Moreover, by prolonging the residence time to 18.6 seconds, the catalytic UF membrane exhibited an 87.7% naproxen removal at just 0.1 bar pressure, which shows great potential in the treatment of micropollutants due to its low energy consumption. The effects of pH on the naproxen adsorption on the membrane and degradation efficiency were also investigated using the UF membranes. The naproxen adsorption capacity of the UF membrane increased from 0.23 to 14.33mg/g when the pH decreased from 10 to 4. By controlling the pH of the solution to 8 after the addition of PMS, the degradation kinetic constant dramatically increased from 1.54×10^{-2} /min to 5.4×10^{-1} /min.

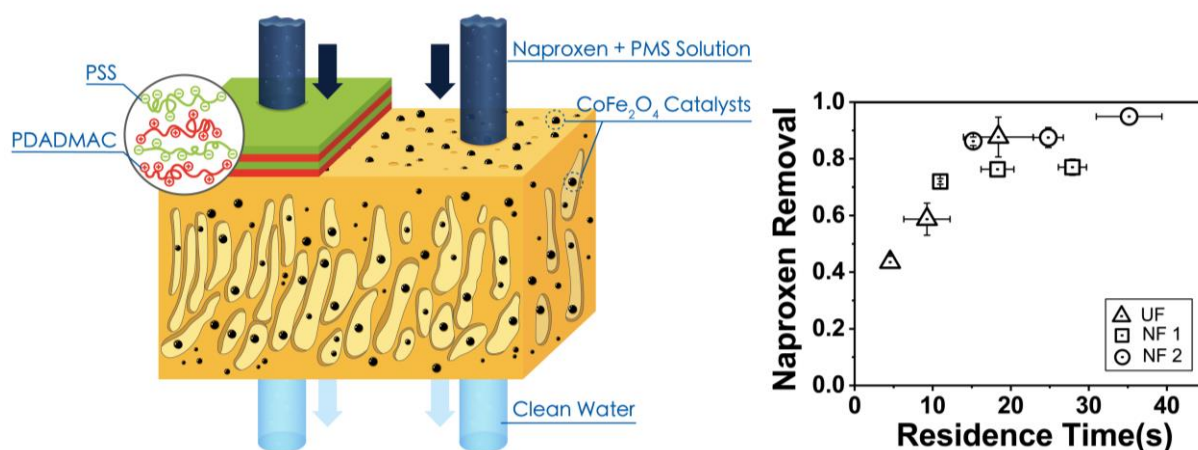
Our study provides a new strategy for fabricating catalytic membranes and reveals the significant influences of residence time and pH on the treatment efficiency of micropollutants by catalytic membranes. The fabricated catalytic UF membrane is promising due to the low required pressure, showing the possibility of treating MPs in a high-efficiency and energy-friendly way.

Reference 1:

.P. Westerhoff, et.al, Environ. Sci. Technol. 39 (2005) 6649–6663.

Reference 2:

W. Qing, et.al, J. Memb. Sci. 583 (2019) 118–138.



Comparison of chloride and sulfate transport in an anion exchange membrane

Kuldeep, Kuldeep - Co-Author

Main topic: Electro-membrane processes

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Electrodialysis processes may be used for desalination and recovery of acids and bases through the splitting of inorganic salts. In order to improve these processes, a basic understanding of species transport mechanisms in ion exchange membranes is needed. Sodium and proton transport in cation exchange membranes (CEM) and chloride transport in anion exchange membranes (AEM) are extensively studied and quite well understood. In dilute aqueous solutions, these processes can be modelled by the Nernst-Planck equation and by applying the Donnan equilibria at the membrane surfaces. However, the transport of sulfuric acid through an AEM is much more complicated due to the incomplete dissociation of bisulfate to sulfate. Moreover, experimental data indicates that sulfate is the only mobile anion in the AEM although bisulfate is the main anion in dilute aqueous solutions. Furthermore, AEMs in contact with dilute sulfuric acid show much higher proton leakage than those in contact with hydrochloric acid of the same concentration[1].

Ionic diffusion coefficients in the membrane are needed for the Nernst-Planck modelling of the ion transport in AEMs. We will approximate the ionic diffusion coefficients of Na^+ , H^+ , Cl^- , SO_4^{2-} and HSO_4^- based on diffusion of dilute NaCl, HCl, Na_2SO_4 and H_2SO_4 solutions through the AEM and the AEM conductivity in contact with these solutions[2]. Finally, we will apply these parameters to a COMSOL Multiphysics based AEM model.

[1] Y. Lorrain, G. Porcelly, C. Gavach, Desalination 109 (1997) 231-239.

[2] J. Kamcev, D.R. Paul, G.S. Manning, B.D. Freeman, Macromolecules 51 (2018) 5519-5529.

Reference 1:

Y. Lorrain, G. Porcelly, C. Gavach, Desalination 109 (1997) 231-239.

Reference 2:

J. Kamcev, D.R. Paul, G.S. Manning, B.D. Freeman, Macromolecules 51 (2018) 5519-5529.

Comparison of membrane technologies using superstructure optimization: case of desalination

Martinez Triana, Alvaro - Co-Author^{1,2}; KANNICHE, Mohamed - Co-Author³; NEVEUX, Thibaut - Co-Author³; CASTEL, Christophe - Co-Author¹; FAVRE, Eric - Co-Author

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Main topic: Industrial applications and scale-up

Performance evaluation of different membrane technologies is a key task for scale up in different industries. To do so, mathematical models have been proposed by different authors (e.g. Li et al., 2021) to account for mass transfer phenomenon through polymeric membranes used in reverse osmosis (RO) and membrane distillation (MD) technologies, including limitations by (concentration and/or temperature) polarization effects. Nowadays, process simulation for RO at industrial scale has evolved conducting to propose hybrid systems between RO and non-membrane technologies like thermal distillation. However, MD mathematical models are not widely employed at process simulation using commercial software solutions.

This work aims to present a modified method from (Zhao et al., 2018) to obtain a membrane process adapted to various conditions of aqueous solution to treat (solute concentrations and feed temperature on intake). Thus, Computer aided process simulation is used to achieve the results; the mathematical model was coded in FORTRAN and added to a commercial software (PROSIM) as external subroutine to simulate the membrane processing units. Then, a superstructure is defined in (PROSIM) and optimized within an ant colony algorithm (MIDACO). Operational conditions (pressure and in-process temperature) and specific number of modules in series and in parallel are obtained because of the superstructure optimization.

This methodology was applied to desalination as a case study, giving as a result a number of modules, a configuration to set them up as well as operative conditions to achieve an objective of fresh water flowrate. The geometry and material parameters included in the mathematical model were taken from a RO commercial module; besides, polarization phenomena and drop pressure due to each module were taken into account.

As a main result, a comparative chart of vacuum membrane distillation (VMD) and RO is presented in terms of energy consumption and recovery ratio for desalination. Then, the effect of solute concentration is calculated with a sensitivity analysis for a constant membrane area. These comparisons will allow further studies to create hybrid solution among MD technologies, as it is done today with RO.

Reference 1:

Li, F., Fang, C., Liu, W., Yang, L., Guo, B., Zhang, S., 2021. High recovery, energy efficient wastewater desalination. *J. Membr. Sci.* 631, 119317. <https://doi.org/10.1016/j.memsci.2021.119317>

Reference 2:

Zhao, Q., Neveux, T., Mecheri, M., Privat, R., Guittard, P., Jaubert, J.N., 2018. Superstructure optimization (MINLP) within ProSimPlus Simulator, in: *Computer Aided Chemical Engineering*. Elsevier, pp. 767–772. <https://doi.org/10.1016/B978-0-444-64235-6.50135-2>

Competing effects of electrostatic double layer and hydrophilic interaction on membrane filtration and backwash

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¹DWI - Leibniz Institute for Interactive Materials e.V., ²RWTH Aachen University, AVT.CVT - Chemical Process Engineering

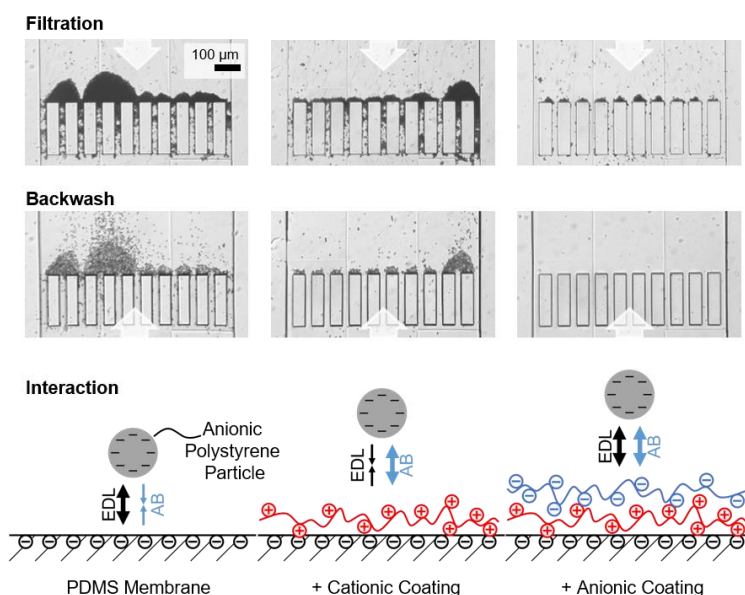
Main topic: Membrane fouling and cleaning

Colloidal fouling is a notorious limiting factor in many membrane processes. Although intensely studied in the past in mostly macroscopic systems, the underlying phenomena of complex fouling events are not yet fully understood. Especially the competing effects arising at different membrane charges and hydrophilicity remain unknown, even though a trend of decreased fouling with increased membrane hydrophilicity is reported. To shed light on these microscopic competing effects of electric double layer and hydrophilic interactions, we systematically investigate fouling and backwashing of anionic polystyrene particles in microfluidic structures with tailored surface charge and hydrophilicity. We evaluate the observed phenomena with the extended Derjaguin-Landau-Verwey-Overbeek (xDLVO) theory on interaction potentials as a sum of Van-der-Waals-, electrostatic double layer-, and acid-base-interaction potentials.

By tailoring the structure's surface properties, we investigate particle-membrane interactions in first, hydrophobic structures with negative zeta potential, second, hydrophilic structures with positive zeta potential, and third, hydrophilic structures with negative zeta potential. Comparing membrane-mimicking systems with these three different types of surfaces in their filtration and backwash behavior allows us to conclude the qualitative changes of membrane-particle interaction potentials regarding their hydrophilic and electrostatic double-layer interactions. While observing a strong attraction between particles and hydrophobic structures, the competing effects of electrostatic double layer and acid-base interactions lead to similar particle deposition and removal in hydrophilic cationic structures. In contrast, strong electrostatic repulsion leads to little fouling and full reversibility during backwash in hydrophilic anionic structures.

Further, we compare the resulting overall interaction potential and its impact on particle deposition and removal at a broad range of applied shear during backwash. We confirm the macroscopic trend described in the literature of decreased particle deposition and enhanced reversibility during backwashing with increasing hydrophilicity. However, we show that hydrophilicity alone is an insufficient measure to estimate a membrane's particle deposition and removal behavior. More importantly, the combination of a hydrophilic membrane with a tailored surface charge is promising for optimal membrane design to achieve a low-fouling membrane that can be cleaned with pure flow reversal during regular backwashing.

Impact of competing electrostatic effects in particle-membrane interaction



Computer tomography for 3D analysis of swollen heterogenous ion-exchange membranes

Slouka, Zdenek - Co-Author; Vobecká, Lucie - Main Author; Svoboda, Miloš - Co-Author; Beneš, Jan - Co-Author

Main topic: Electro-membrane processes

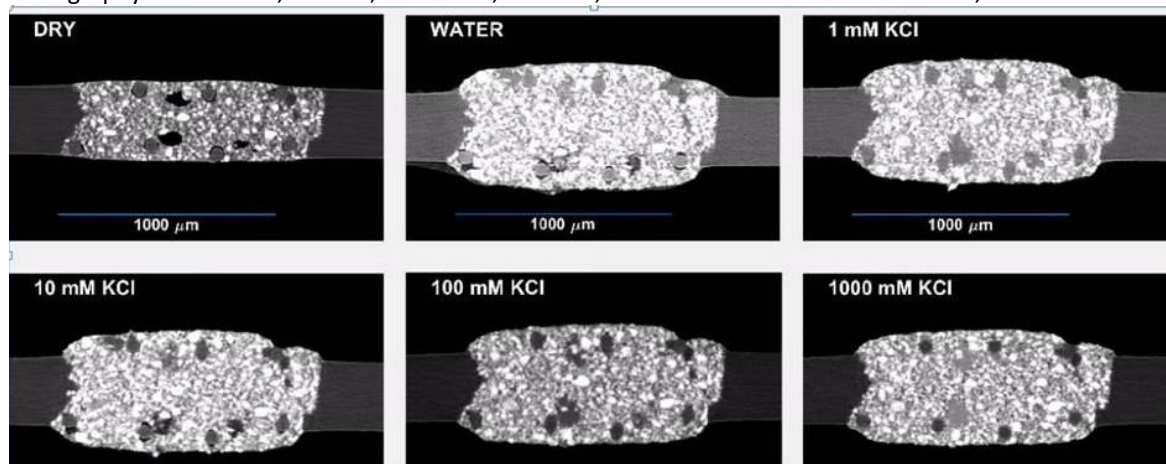
Heterogeneous ion-exchange membranes are composites of three major components: (i) finely ground ion-exchange resin, (ii) polymeric binder, and (iii) polymeric fibers. The ground resin provides for the required selectivity of the membranes, and the other two nonconductive components impart the membrane with mechanical strength. Their manufacturing is based on blending the resin and binder followed by rolling the blend in a softened state between two heated cylinders leading to the continuous production of a membrane sheet. The sheet is eventually laminated with fibers. Although such manufacturing is cheap and robust, the control over the spatial distribution of resin and the final quality of the membrane is limited. For example, air pockets are often trapped in these membranes. They can later either increase the membrane resistance or, if filled with the electrolyte, create shortcuts leading to the decreased permselectivity. To analyze the 3D structure of heterogeneous ion-exchange membranes, we employed micro-computed tomography [1, 2]. We developed a cell that allows scanning the membranes in the swollen state in which they find when applied in real applications. This state is dramatically different from the dry one due to the immense swelling forces. Our analysis of the membranes showed that the ground resin is surprisingly evenly distributed within the binder, although their size distribution is wide. The air pockets trapped in the membranes almost uniquely fill with the water solution as the membranes swell. Our further studies confirmed that swelling is dependent on the concentration of the electrolyte solution. Water causes the largest changes in the membrane volume and any addition of salt results in membrane shrinkage. Both shrinkage and swelling are driven by the resin particles, and the associated structural changes are history-dependent. Membrane swelling to its maximum in water followed by partial shrinkage due to addition of salts makes the membrane “leaky” since the binder cannot follow the resin volume decrease. These processes may have profound effects on the permselectivity of the membranes, and therefore, on the process performance.

Reference 1:

Heterogeneity of heterogeneous ion-exchange membranes investigated by chronopotentiometry and X-ray computed microtomography. L Vobecká, M Svoboda, J Beneš, T Belloň, Z Slouka, *Journal of Membrane Science* 559, 127-137

Reference 2:

Swelling induced structural changes of a heterogeneous cation-exchange membrane analyzed by micro-computed tomography. M Svoboda, J Beneš, L Vobecká, Z Slouka, *Journal of Membrane Science* 525, 195-201



Computer-aided characterisation of porous open-pored membranes using pore network modeling

Kunz, Willfried - Main Author¹; Laqua, Matthieu - Co-Author²; Altschuh, Patrick - Co-Author³; Bremerich, Marcel - Co-Author⁴; Selzer, Michael - Co-Author³; Nestler, Britta - Co-Author³

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Main topic: New characterisation methods

The demand for rapid and easy-to-use medical diagnostic devices, referred as Point-of-Care-Testing (POCT), has increased over the last years. Especially in lateral flow assays (LFAs) the benefits of POCT-devices are evident due to their user-friendliness and cost-efficiency. The working principle of LFAs is based on the capillary driven liquid transport of a fluid to a test line using polymeric highly porous and open-pored membranes.

Even though LFAs such as the currently widespread COVID-19 rapid tests, are produced and used on a large scale, the interaction mechanisms of the liquid transport and the microstructural properties in the integrated porous membrane, as indicated in Fig. 1, are still not fully understood. In order to improve the test design, it is necessary to reveal microstructural properties at the pore-scale (μm -scale) of the porous membranes and investigate their impact on the macroscopic wetting behavior (cm-scale).

A pore network model (PNM) represents an abstraction of a fully resolved porous structure by pores and throats. Once the network is established, the data obtained will allow data science algorithms to be run for structural characterisations and flow simulations at the meso-scale (mm-scale) to determine correlations between porosity and permeability. At this scale a sufficient amount of information for capturing microstructural topological properties, such as connectivity, is still available while the observable spatial volume reaches the macro-scale. This allows the extraction of effective parameters at the micro- and meso-scale, which can be passed on to macroscopic models, as illustrated in Fig. 1.

In the present study, a PNM extraction algorithm using a marker-based watershed segmentation, based on the work of Gostick [1], was implemented in the simulation framework Pace3D [2]. Subsequently, the implemented extraction methods are validated by applying a powerful generation algorithm. The algorithm thereby allows to generate porous 3D membrane structures with defined and locally varying microstructural properties. Furthermore by using imaging techniques, such as computed tomography, the methods were applied on digital twins of real reconstructed membranes.

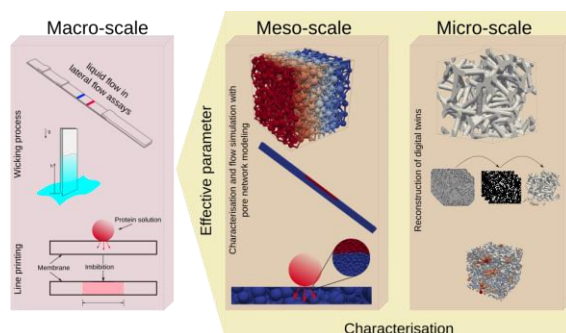
The performed characterisations and flow simulations based on a pore network model are presented, while discussing both benefits and challenges in using PNMs in the context of highly porous open-pored membranes.

Reference 1:

GOSTICK, Jeff T. Versatile and efficient pore network extraction method using marker-based watershed segmentation. *Physical Review E*, 2017, 96. Jg., Nr. 2, S. 023307

Reference 2:

HÖTZER, Johannes, et al. The parallel multi-physics phase-field framework Pace3D. *Journal of computational science*, 2018, 26. Jg., S. 1-12



Concentration of skim milk by forward osmosis using delactosed permeate as an innovative draw solution

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Main topic: Forward osmosis/Pressure retarded osmosis

Forward osmosis has found limited application in the food industry due to challenges surrounding recovery of draw solutions and migration of undesirable solutes from the draw to feed stream. In this study, the potential of delactosed permeate (11800 kPa osmotic pressure), a dairy waste stream, was assessed as a draw solution for concentration of skim milk (649 kPa osmotic pressure) from 9 to 18 % dry matter when osmotic equilibrium was reached. The effect of the temperature of the feed and draw solutions on filtration performance was assessed, whereby average water fluxes of 0.06 and 0.08 kg·min⁻¹·m⁻² were obtained at 10 and 30°C, respectively, along with a 86 % higher initial flux at 30°C due to a lower product viscosity and higher water diffusivity. In average for both temperatures, 4.5 kg of water was removed from the feed per kg of delactosed permeate at osmotic equilibrium (1427 or 1454 kPa at 10 or 30°C, respectively). Clean water flux measurements indicated that negligible fouling, if any, had occurred during the time frame investigated. This study demonstrated an energy saving of 58 % or 84 % per mass of water removed compared to reverse osmosis or evaporative concentration processes, respectively, if operated throughout its optimised range of osmotic pressure difference. Using delactosed permeate as a draw solution overcomes the challenges associated with migration of non-dairy components to the feed, making it auspicious for the concentration of a wider variety of high-value dairy products.

Could membrane contactors save the use of physical solvent in gas-liquid absorption ?

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Main topic: Membrane contactors and membrane distillation

For the last decades, much effort has been made to investigate CO₂ capture for storage or application. In the membrane contactors field, numerous studies focused on gas-liquid processes based on chemical solvent, making these processes well-known with several pilot units tested with real flue gases.[1]

Surprisingly, the same situation does not hold for gas liquid absorption processes based on physical solvents. However, this kind of process could offer advantages for some applications where the chemical pump is not required, such as CO₂ removal from a pressurized gas mixture (hydrogen purification or precombustion carbon capture).

Many parameters, from the selected solvent to the operating conditions, could have an influence on the volume reduction on the one hand, and energy requirement on the other hand. Figure 1 shows a membrane contactor and the associated parameters related to the membrane, the contactor, the solvent and the operating conditions.

In a previous study case, we demonstrated that membrane contactors offer promising intensification possibilities compared to a classical packed column with volume reduction ratios. [2]

In light of these results, we can push further our investigation with the following subjects:

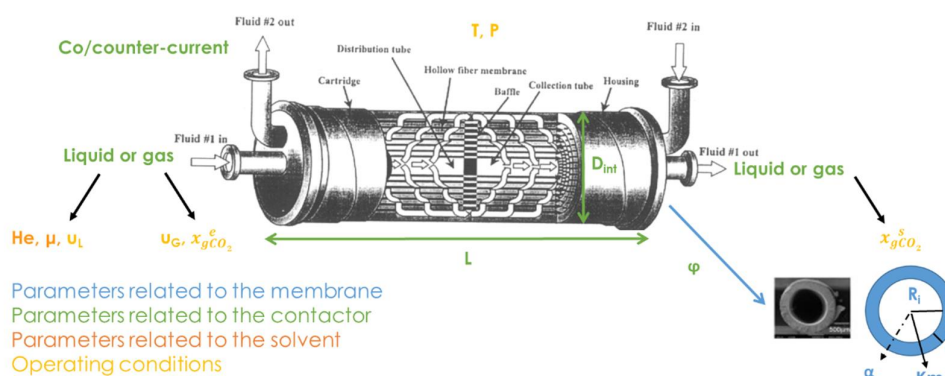
- Solvent properties obviously have huge influence on the separation, which make us ask ourselves what solvents can be used for future improvement. Indeed, new kinds of solvents (ionic liquids and deep eutectic solvents) appeared lately with great interest and their use in membrane contactor is a question that needs to be asked.
- Temperature influence is also worth the investigation because of its antagonist effect on transfer phenomena and thermodynamics. Depending on the chosen {solvent/gas} pair, win-win or lose-lose situations can be achieved.
- Gas mixture and compositions make us face different challenges and we can wonder what are the ranges of composition and gas mixture where physical solvents can still be efficient ?

Reference 1:

E. Favre, H.F. Svendsen, Membrane contactors for intensified post-combustion carbon dioxide capture by gas-liquid absorption processes, *Journal of Membrane Science*. 407–408 (2012) 1–7. <https://doi.org/10.1016/j.memsci.2012.03.019>.

Reference 2:

L. Cesari, C. Castel, E. Favre, Membrane contactors for intensified gas-liquid absorption processes with physical solvents: A critical parametric study, *Journal of Membrane Science*. 635 (2021) 119377. <https://doi.org/10.1016/j.memsci.2021.119377>.



Coupling Cahn-Hilliard equation, hydrodynamics and external transfers to simulate the membrane formation dynamics

Bouyer, Denis - Co-Author; Manzanarez, Hervé - Co-Author; Mericq, Jean-Pierre - Co-Author; Guenoun, Patrick - Co-Author

Main topic: Transport models

One of the most important challenges in the membrane formation field concerns the control of the formation mechanisms, which will have a great impact on the final membrane structure and thus on the functional properties such as the permeability and the selectivity. The elementary formation mechanisms can be optimized and monitored with use of computational simulation to describe the structuration dynamics once the phase inversion starts.

A numerical model was developed to simulate the formation dynamics of polymeric membranes by phase inversion. A phase field model based on Cahn-Hilliard equation was coupled to Navier-Stokes equations [1, 2]. Furthermore, the phase separation model was coupled to transfer equations to simulate the evaporation during membrane formation.

We developed 2 and 3D models using the Flory-Huggins-De Gennes theory to describe the thermodynamic potential and we solved the NS equations to simulate the coupling with hydrodynamics. The patterns were analyzed with Fourier transform and Minkowski functionals, exhibiting the influence of hydrodynamics on growth laws during phase separation.

Then, we coupled the phase separation with transfer phenomena occurring at the upper interface of the system to simulate the solvent evaporation that could occur during the process. The formation of a dense skin was exhibited depending on the evaporation rate, which increased during time due to continuous solvent loss by the system at the upper boundary. The simulations were launched at different initial composition to simulate different demixing dynamics that could lead to bicontinuous structures or droplets of rich phase into continuous phase of solvent.

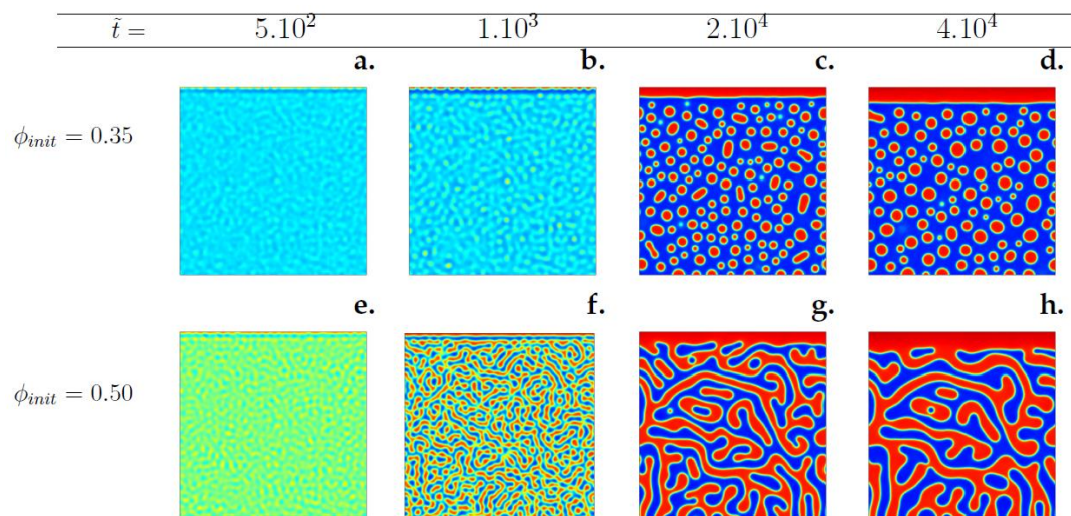
This work show great potential for better understanding the dynamics of membrane formation by phase inversion and to predict the final membrane morphology that depends on the formulation and the process parameters.

Reference 1:

J. W. Cahn and J. E. Hilliard, Free Energy of a Nonuniform System. I. Interfacial Free Energy, J. Chem. Phys. 28, 258 (1958).

Reference 2:

V.E. Badalassi, H.D. Cenicerros, S. Banerjee, Computation of multiphase systems with phase field models, J. Comput. Phys. 190 (2003).



CO₂ capture properties of a Zn(II)-based MOF by Monte Carlo simulations

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Main topic: CO₂ capture

Metal-organic frameworks (MOFs) are a class of highly ordered materials which consist of metal ions or clusters and organic ligands connected to each other to form an extended 3-D or 2-D network. MOFs with versatile pore structures can be synthesized. In addition to their large surface area and tunable functionality MOFs are generally robust enough to allow the removal of guest species resulting in permanent porosity, and are therefore promising for adsorption-related applications, among others [1]. CO₂ capture is one of the most active and attractive research areas in MOF's applications. Molecular simulations have greatly contributed to the development of MOFs for gas separation and capture by providing insight into the microscopic phenomena that occur during adsorption.

In this work, grand canonical Monte Carlo simulations were applied to a Zn(II)-based MOF [2] with the aim of understanding the mechanisms that govern the adsorption of those gaseous molecules in the MOF. This MOF was obtained in the literature by introducing the 1,2,4-triazole ligand in a tetracarboxylate system, forming the anionic MOF [(CH₃)₂NH₂][Zn₂(ABTC)(Tz)]·3DMF (being ABTC = 2,2',5,5'-azobenzene tetracarboxylic acid, Tz = 1,2,4-triazole and DMF = N,N-dimethylformamide) [2].

The adsorption isotherms for CO₂, CH₄, C₂H₆ and C₃H₈ were first computed as a means of validating our force field, and after that, the preferential adsorption sites of the gas molecules were analyzed. As next steps, our models were applied for studying the CO₂, C₂H₆ and C₃H₈ adsorption, and the guest-host radial distribution functions and adsorption enthalpies were analyzed in order to gain insight into the interactions at the origin of the adsorption phenomenon.

Acknowledgements

Funding from Juan de la Cierva IJCI-2016-30776 (B.Z.) program is acknowledged. Ayuda PID2019-104009RB-I00 financiada por CIN/AEI/10.13039/501100011033.

Reference 1:

[1] G. Maurin, C. Serre, A. Cooper, G. Férey, *Chem. Soc. Rev.*, 2017, 46, 3104-3107.

Reference 2:

[2] L. Zou, J. Yuan, Y. Yuan, J. Gu, G. Li, L. Zhang, and Y. Liu, *CrystEngComm*, 2019, 21, 3289-3294.

CO₂ separation via Zr-MOFs/Pebax mixed matrix membranes

BOUTSIKA, LAMPRINI - Main Author¹; BRATSOS, IOANNIS - Co-Author¹; CHARALAMBOPOULOU, GEORGIA - Co-Author; STERIOTIS, THEODORE - Co-Author

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Main topic: Gas separation

Mixed matrix membranes (MMMs) containing metal organic frameworks (MOFs) have attracted significant attention due to the combined advantages of high performance and easy processability [1]. The aim of this work is to evaluate the CO₂ separation properties of Pebax[®] MH1657 membranes after incorporating different concentrations of a series of Zr-based MOF fillers, namely UiO-66, UiO-67 and two UiO-66 analogues with linker and cluster defects [2]. The latter were developed by adding monocarboxylic acid modulators during UiO-66 synthesis, specifically formic (UiO-66_F) and acetic (UiO-66_Ac) acid. The chemical structure, morphology and thermal properties of the synthesized MOFs were studied by X-ray diffraction (XRD) analysis, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and TGA/DSC measurements. The permeability of pure gases (CO₂, CH₄, H₂) in a neat Pebax[®] MH1657 membrane and Pebax/MOF MMMs was determined by the constant volume/variable pressure approach. The incorporation of MOFs into the Pebax[®] MH1657 matrix led to a steady increase of CO₂ permeability for all the membranes reaching 148 Barrer for 20 wt% UiO-66_F. Moreover, CO₂/CH₄ and CO₂/H₂ selectivities increased with increasing MOF loading. The best separation performance was observed for 20 wt% UiO66_F loading reaching a CO₂/CH₄ selectivity of 25 and a CO₂/H₂ selectivity of 18. The results of this study showed that the synthesized MMMs are very promising to be utilized in gas separation processes.

Reference 1:

S. Meshkat, S. Kaliaguine, D. Rodrigue, *Sep. Purif. Technol.* (2018), 200, 177–190.

Reference 2:

J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, and K. P. Lillerud, *J. Am. Chem. Soc.* (2008), 130, 42, 13850–13851.

CO₂/CH₄ separation performance in polymeric membranes involving physical tightening, thermal-oxidation and carbonatization

Xu, Xiaoyan - Main Author; Thür, Raymond - Main Author; Vankelecom, Ivo - Main Author

Main topic: CO₂ capture

Thermal treatment of polymer membranes often results in enhanced separation characteristics of the membrane. Four well-studied polymer membranes, including three polyimides (6FDA-DAM, Matrimid®5218 and P84) and one polymer of intrinsic microporosity (PIM-1) were subjected to a thermal treatment from 100 °C to 400 °C in air atmosphere. Three changes in the membrane structure were observed during the heat treatment. XRD and density experiments demonstrated a physical tightening of all polymer matrices with higher annealing temperature. ATR-FTIR showed that for all polyimides thermo-oxidative oxidation and crosslinking occurred between 300 °C and 350 °C, while (partial) carbonization of the polymer backbone set in at 300 °C for PIM-1. Characteristic polyimide peaks for all polyimides only disappeared at 400 °C.

Higher annealing temperatures induced higher CO₂/CH₄ separation factors as a result of the densification of the polymer matrix. The polyimide membranes systematically showed an upward trend in separation factor till 350 °C (+385% for 6FDA-DAM, +279% for Matrimid and +540% for P84). At the same time their permeability dropped severely and steadily (-99% for 6FDA-DAM, -93% for Matrimid and -74% for P84) during annealing from 100 °C till 350 °C, in correspondence with a loss in fractional free volume, as determined by density experiments. PIM-1 on the other hand, showed a low selectivity between 7 and 8 with a CO₂ permeability of 5845 Barrer when annealed below 300 °C. Compared to the PI membranes, PIM-1-300 showed a very strong selectivity improvement with a CO₂/CH₄ separation factor over 114 at 5 bar feed pressure. When further increasing the temperature to 400 °C, vaporization of functional groups and interchain crosslinking caused the gas separation performance of the (partially) carbonized Matrimid, 6FDA-DAM and P84 membranes to even surpass the 2008 Robeson upper bound as a result of a strong permeability enhancement compared with 350 °C treated membranes (+233% and +900%, +245% respectively).

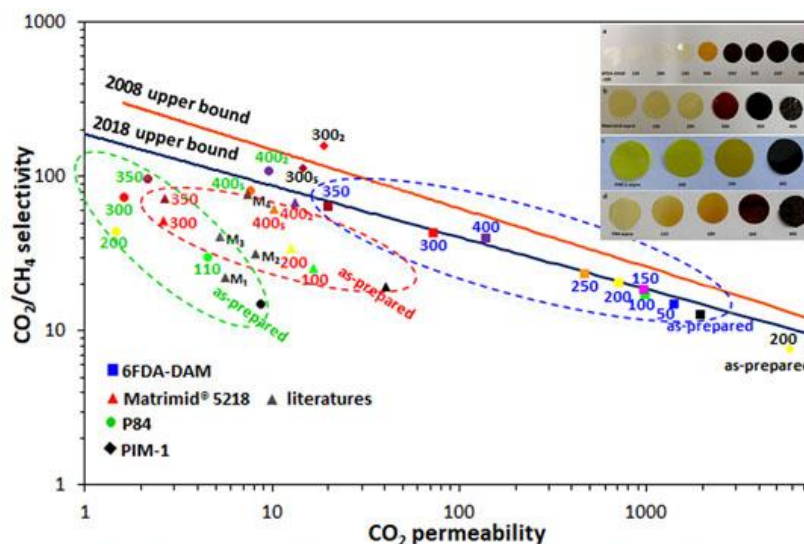


Figure 1: Overview of obtained data and state-of-the-art in a selectivity-permeability plot. Literature reference is added for comparison, Matrimid is referred to in the legend.

Cross-Linked Isoporous Ultrafiltration Membranes with High Thermal and Chemical Stability

Appold, Michael - Main Author; Rangou, Sofia - Co-Author; Filiz, Volkan - Co-Author

Main topic: Microfiltration/Ultrafiltration

Membranes are today the basic media for filtration, separation or purification processes based on the relative size of the materials processed, in either gas or liquid phase separations. They offer a bright range of application in fields of gas separation (separation through solution/diffusion), and liquid separation (from reverse osmosis, nano-, ultra-, up to micro-filtration) like water purification, waste water treatment, the food industry, the chemical and pharmaceutical as well as in the medical sector. Due to these interdisciplinary fields of applications, there is a number of different requirements on the membrane performance. Polymer based materials are due to their unique and wide spread characteristics promising candidates for membrane applications. In this regard, significant progress has been made in the development of polymer and block copolymer membranes having higher selectivity, sharp molecular weight cut-off and permeability.

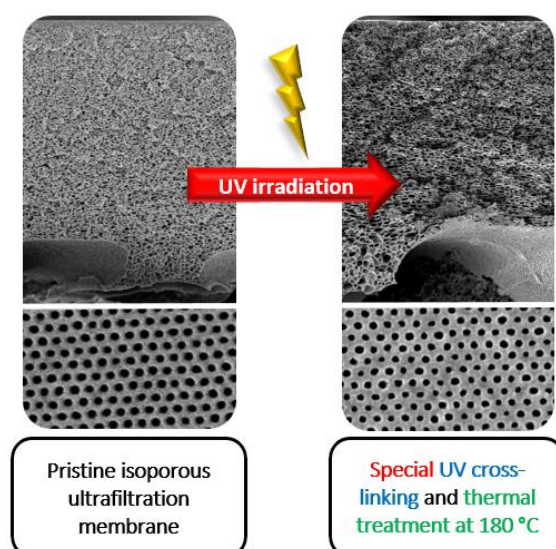
In this context, we present a new and convenient way of fabricating cross-linked isoporous integral asymmetric block copolymer-based membranes. They were prepared by combining the self-assembly of the block copolymers with the solvent non-solvent induced phase separation (SNIPS) process. Afterwards the membranes were completely cross-linked by UV irradiation in a special process while perceiving their integral asymmetric structure. While the membrane initial construction is responsible for high selectivity and permeability the cross-linking induces high temperature and chemical stability. On the one hand, the cross-linking allows this type of membranes applications for high temperature (in the range of -20-350 °C) and high-pressure ultrafiltration with pressure differences up to 150 bar like wastewater treatment. On the other hand, these membranes show high chemical stability in organic solvents, acidic and basic media making them interesting for applications in the chemical, pharmaceutical and medical sector like dialysis. Additionally the membranes show good long-time performance and long lifetime due to the cross linking process. Normally the lifetime of a membrane is very limited due to fouling processes also effecting the membrane performance in terms of selectivity and permeability by time. The cross-linked block copolymer membranes can be sterilized and regenerated thermally as well as chemically paving the way for sustainable materials.

Reference 1:

K.-V. Peinemann, V. Abetz, P. F. W. Simon, nature materials 2007, 6, 992-996.

Reference 2:

S. Rangou, V. Filiz, B. Lademann, K. Buhr, European Patent Application EP3772370A1 2021.



Cross-sectional Preparation of Energy Devices and their Microscopic Characterization

Hepp, Marco - Co-Author¹; Wiktor, Christian - Co-Author²; Nürnberg, Edward - Co-Author³; Peinecke, Volker - Co-Author³; Radev, Ivan - Co-Author³; Ruhkopf, Jasper - Co-Author⁴; Plachetka, Ulrich - Co-Author⁴; Zubkova, Tatiana - Co-Author; Baumann, Reinhard - Co-Author⁵; Lemme, Max - Co-Author⁴; Butz, Benjamin - Co-Author¹

¹University of Siegen, Micro- and Nanoanalytics Chair, ²University of Siegen, Micro- and Nanoanalytics Chair, ³ZBT GmbH, ⁴AMO GmbH, ⁵TU Chemnitz

Main topic: Fuel cells

Energy devices are commonly assembled from multiple functional components. To gain fundamental understanding of the microstructure-property relations between individual components, their degradation and failure mechanisms and to enable characterization/optimization cycles through microscopic studies, it is desirable to prepare (electron transparent) cross sections of entire devices or of as large sections of a device as possible. Since most specimen preparation techniques are optimized for specific material classes, preparing samples of devices consisting of different materials may be difficult. Therefore, sample preparation is often preceded by the disassembly of a device down to individual components rendering an investigation of relations between the individual components impossible. Ultramicrotomy as a cross-sectioning technique can solve these problems as it can generate (electron transparent) cross sections with sizes typically larger than the structure sizes in modern, micro- and nanostructured devices. As no ionizing radiation is used, artifacts due to beam damage are avoided.

We demonstrate the capabilities of ultramicrotomy in conjunction with microscopic characterization over the length scales, when high quality samples are provided. Examples include the investigation of complex devices like PEM fuel cells by OM, SEM and TEM, each providing their unique contrasts. Besides that, the application of various spectroscopic mapping techniques, ideally suited to investigate the interfaces of individual layers and components in terms of their morphology and contact as well as the systematic identification of their composition, is applied.

– Part of this work was performed at the Micro-and Nanoanalytics Facility (MNaF) of the University of Siegen –

Computer-aided characterisation of porous open-pored membranes using pore network modeling

Wang, Tao - Co-Author¹; de Vos, Wiebe - Co-Author; de Grooth, Joris - Co-Author

¹University of Twente

Main topic: Membrane reactors

Small organic micropollutants pose a significant threat to water quality, aquatic and public health. Unfortunately, current treatment methods like coagulation-flocculation, activated carbon adsorption, and bioreactors cannot provide efficient and sufficient elimination of the micropollutants [1]. A catalytic membrane, combining membrane filtration and peroxymonosulfate (PMS) activation provides an alternative and promising option for this treatment [2].

In this study, CoFe_2O_4 based catalytic particles were added to a PES dope solution, to obtain catalytic UF membranes. For part of the membranes, layer-by-layer assembly of poly-(diallyl dimethylammonium chloride) (PDADMAC) and poly(styrenesulfonate) (PSS) was performed on the surface of the catalytic UF membrane to build a catalytic NF membrane. We studied these catalytic UF and NF membranes in full-recycling mode and single-pass mode to reveal the influence of residence time on the treatment efficiency of catalytic membranes. The naproxen rejections for the catalytic UF and NF membranes indicate that in full recycling mode, a longer residence time enhances the degradation efficiency, improving the effective naproxen rejection/removal. In single-pass mode, both catalytic UF and NF membranes showed high and stable naproxen removals which were higher than 80%. Moreover, by prolonging the residence time to 18.6 seconds, the catalytic UF membrane exhibited an 87.7% naproxen removal at just 0.1 bar pressure, which shows great potential in the treatment of micropollutants due to its low energy consumption. The effects of pH on the naproxen adsorption on the membrane and degradation efficiency were also investigated using the UF membranes. The naproxen adsorption capacity of the UF membrane increased from 0.23 to 14.33mg/g when the pH decreased from 10 to 4. By controlling the pH of the solution to 8 after the addition of PMS, the degradation kinetic constant dramatically increased from $1.54 \times 10^{-2}/\text{min}$ to $5.4 \times 10^{-1}/\text{min}$.

Our study provides a new strategy for fabricating catalytic membranes and reveals the significant influences of residence time and pH on the treatment efficiency of micropollutants by catalytic membranes. The fabricated catalytic UF membrane is promising due to the low required pressure, showing the possibility of treating MPs in a high-efficiency and energy-friendly way.

Reference 1:

P. Westerhoff, et.al , Environ. Sci. Technol. 39 (2005) 6649–6663.

Reference 2:

W. Qing, et.al, J. Memb. Sci. 583 (2019) 118–138.

Covalent organic frameworks: study of the synthesis conditions for membrane preparation

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Main topic: 1D- and 2D-materials for membranes

Mixed matrix membranes (MMMs) comprises molecular sieves such as porous crystalline solids (dispersed filler) embedded in a porous polymer (continuous matrix). Among the different porous materials stand out the zeolites, MOF (metal-organic frameworks), and the most recently synthesized COF (covalent organic frameworks). While MOF particles are a class of porous polymeric material consisting of metal ions linked together by organic bridging ligands (a combination of inorganic and organic counterparts), COFs are only synthesized by organic materials where building blocks are linked by strong covalent bonds [1]. They are made entirely from light elements (H, B, C, N, and O) providing covalent frameworks that could be functionalized for diverse applications ranging from gas storage to catalysis.

Giving the premise of the good performance of MOFs embedded in MMMs for gas separation, this work evaluates the COF candidates that could be successfully used as filler materials in a membrane attending to different synthesis procedures, pore structure and particle sizes. Promising separation performance relies on a proper contact between filler and continuous polymer matrix, as interfacial defects between both phases are undesired.

In general, harsh experimental conditions (e.g., reaction in a sealed pyrex tube, inert atmosphere, suitable solvents, longer time for crystallization, etc.) are required during COF synthesis to form well-ordered crystalline frameworks [2]. The selection of COF particles with low pore size will allow molecular sieving transport of separating molecules. Two synthesis routes such as mechanochemistry [2] or via dynamic covalent bonding, synthesizing the COF in water, emerge of considerable interest. This will allow the construction of bonds through a simple, economical, and environmental friendly route for MMM fabrication.

Acknowledgements: Ayuda PID2019-104009RB-I00 financiada por CIN/AEI/10.13039/501100011033.

Reference 1:

Diercks, C. S.; Yaghi, O. M. *Science* 2017, 355, 1585.

Reference 2:

Biswal, B.P.; Chandra, S.; Kandambeth, S.; Lukose, B.; Heine, T. Banerjee, R. J. *Am. Chem. Soc.* 2013, 135, 5328–5331.

Cyclomatrix polyphosphazene membranes for hot hydrogen separation

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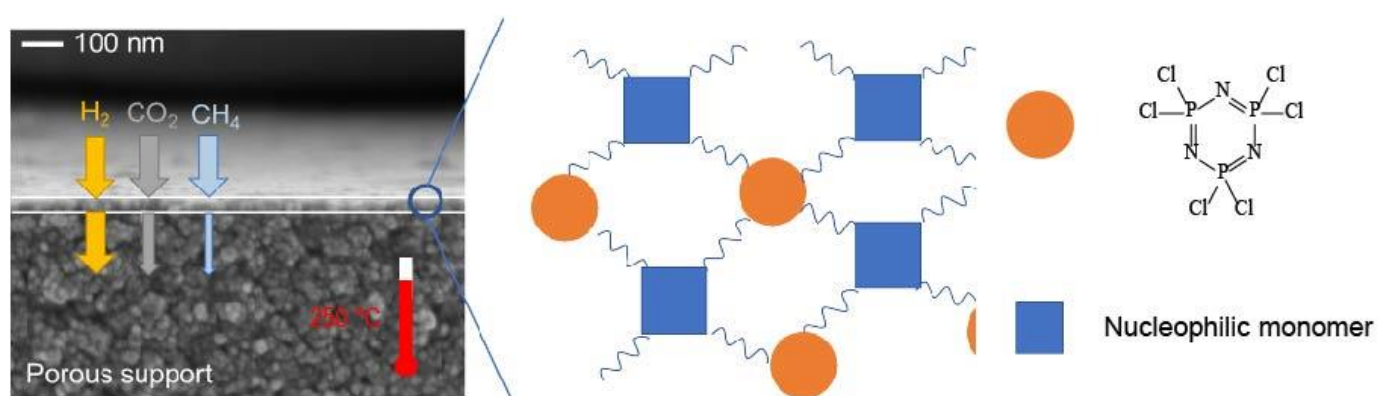
Main topic: Gas separation

Gas separation membranes are beneficial for various industrial gas separation processes, particularly in H₂ recovery at high temperatures. The high temperatures of these processes limit the applicability of the polymeric membranes, especially due to their low thermal stability and high macromolecular dynamics. Therefore, finding new approaches that can overcome or diminish the drawbacks of the existing polymeric membrane for hot gas separation is important. One way to address this issue is to increase the crosslinking degree of polymers by introducing a rigid and compatible building block to the macromolecular backbone. Hexachlorocyclotriphosphazene (HCCP) with six chlorine functionalized groups provides this possibility. The reaction of HCCP with di- or trifunctional compounds results in a hyper crosslinked network: cyclomatrix poly(phosphazene) (PPz). These structures are of interest for their high thermal stability and fire retardancy.

A diverse group of organic molecules can substitute the chlorine in HCCP and form PPz with N and O linking atoms which broaden the properties of these structures. Extremely thin selective cyclomatrix PPz membranes are prepared by interfacial polymerization reaction between HCCP and various nucleophilic monomers.

The formed networks are indeed highly crosslinked and thermally stable up to temperatures in the range of 400-450 °C. At temperatures between 50-270 °C, the membranes show interesting molecular sieving behavior; at 50 °C, the permselectivities of H₂/N₂ and H₂/CH₄ are both around 60, at temperatures as high as 270 °C, the membranes preserve the molecular sieving behavior and show still permselectivities of H₂/N₂ (25), H₂/CH₄ (25-31) and H₂/CO₂ (4.5-12).

Compared to polyimide membranes (polyPOSS imide), these new chemistries allow for a more facile and economical technique for fabrication, higher selectivities (H₂/N₂ and H₂/CH₄), at similar permeances. The extremely high thermal and chemical resistance showed by these new materials will undoubtedly be beneficial to increase the applicability of polymeric membranes under very harsh process conditions.



DCMD operation optimization for maximal selectivity and lowest thermal consumption in the production of ammonium sulphate from wastewaters.

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¹AEE - Institut für Nachhaltige Technologien

Main topic: Membrane contactors and membrane distillation

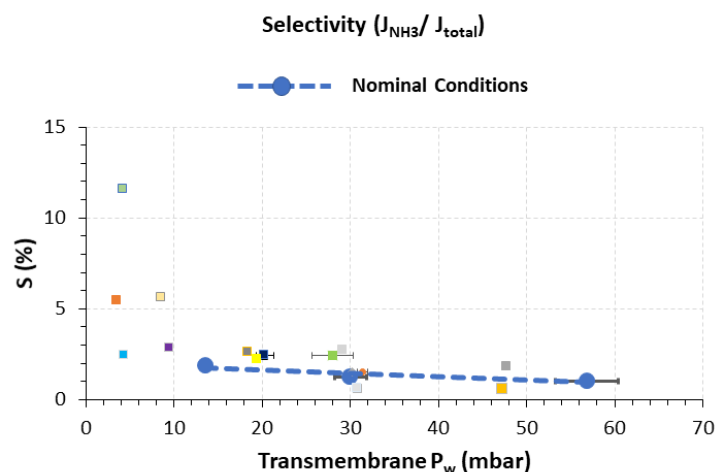
Ammonia (NH₃) is the world's second most produced chemical. It is produced via the Haber-Bosch process which is responsible for a 3-5% of the global annual NG consumption. The main use of the NH₃ is as N-fertilizer in agriculture. The increasing food demand has resulted into an excessive production of agricultural, animal and industrial ammonia-rich waste streams. Only in the EU, between 2-5 Mt of N₂ per year are not recovered¹ and represent 18 – 46% of the mineral N₂ applied annually. Moreover, NH₃ causes eutrophication in water bodies and it is toxic at very low concentrations.

In the state-of-the-art nitrification/denitrification process, NH₃ is lost in the form of N₂ and 1/3 of the electrical consumption of the waste water treatment plants (WWTPs) is used. Membrane Distillation (MD) is a thermally driven technology that can recover this NH₃ for further use and eventually close the N-cycle. MD uses low grade waste heat available at WWTPs. When used for NH₃ recovery and because of its volatility, even lower temperatures could be employed. However, the amount and quality standards of the current NH₃ applications are challenging.

Within the ThermaFlex project we have explored the NH₃ recovery for ammonium sulphate (a fertilizer) production via MD at a pilot scale with a focus on product quality and techno-economics. In a first stage, we applied the RSM methodology to optimize the operation parameters of a DCMD commercial module (2,3 m² membrane area) towards a maximized selectivity towards NH₃ (for highest product quality) and minimized thermal consumption without compromising NH₃ flux and removal. The present work shows the results of the DoE and the optimization methodology. The experiments were performed with an artificial feed solution simulating the expected NH₃ concentration in the WWTP stream (i.e., < 1g l⁻¹). The optimization results showed a major breakthrough when a 100% selectivity without reduced flux and a thermal consumption <7 kWh/kg NH₃ was achieved. The optimized parameters were used in the operation of the pilot plant at the WWTP in Gleisdorf (Austria) and the results are discussed in a second work presented also in this conference.

Reference 1:

1 Buckwell, A., & Nadeu, E. J. B. R. F. (2016). Nutrient Recovery and Reuse (NRR) in European agriculture. A review of the issues, opportunities, and actions.



Deep eutectic solvent as greener alternative for sustainable membrane fabrication

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Main topic: Novel membrane materials

Deep eutectic solvents (DES) have invoked a new class of low-cost, greener and biorenewable solvents and additives for wide variety of applications. In this research, a novel family of DES was introduced for the first time as a solvent for membrane fabrication. The formation of different DESs were first confirmed experimentally and theoretically (using molecular dynamic simulations). Membranes were fabricated by employing DES solvent into polyvinylidene fluoride (PVDF) polymer. The effect of polyvinylpyrrolidone (PVP) concentration as a pore former in PVDF/DES-1 solution was first studied to find the optimum concentration of additives for the polymeric system. Then, the membranes were fabricated with three different solvents based on the optimized PVP concentration. The resulting membranes were characterized in terms of morphology, pore size, mechanical strength, porosity, contact angle, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Their performances were evaluated by pure water flux and bovine serum albumin (BSA) separation test. The PVDF/DES-1 membrane with 2 wt% PVP exhibited good water flux (94.23 L/m².h) and obtained good separation efficiency with 96.23% of BSA rejection. As the conclusion, PVDF membranes have been successfully prepared using a novel family of solvents that offers the possibility to replace commonly used toxic solvents in the membrane manufacturing industry.

Deep eutectic solvents (DESs) for polyvinylidene fluoride (PVDF) and polyacrylonitrile (PAN) porous membranes preparation

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Main topic: Novel membrane materials

Membrane technology fulfils most of the 17 objectives of the Sustainable Development Goals (SDG) aiming to a global sustainable development by 2030. One of the recent trends is the sustainability related to the membrane preparation. Generally, the preparation of membranes involves the use of toxic solvents such as N, N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), N-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF) and polymeric materials deriving from fossil sources. These substances may pose several issues for both human health and environment. In this contest, new alternative solvents attracted great interest according to the Green Chemistry design [1]. The aim of this work is to study and develop new highly sustainable membranes, using deep eutectic solvents (DESs). They are well known as environmentally friendly solvents for their properties such as low or absent toxicity, high recycle and reuse capability, chemical and thermal stability and non-flammability. Natural deep eutectic solvents (NADES) and sulfobetaine based DES were used for the first time in the preparation of poly (vinylidene fluoride)-PVDF and polyacrylonitrile-PAN based membranes via non-solvent induced phase inversion (NIPS). The thermodynamic aspects (i.e. solubility and polymer-solvent distance) and kinetic parameters in term of viscosity were deeply investigated. The Hansen parameters of solvents were also calculated. The effects of the selected DESs, the affinity with non-solvent (water or/and water-isopropanol) and the interaction with co-solvent (polarclean[®], triethyl phosphite and dimethyl sulfoxide) on the morphology and performance of prepared membranes were also studied. All the prepared membranes were fully characterised in terms of morphology (SEM), wettability (contact angle), chemical composition (FT-IR), pore size and pore distribution. The membrane morphology confirmed the possibility to obtain finger-like and sponge-like structures with spherulitic surfaces. The pore size ranged from 0.08 μm to 0.3 μm with a porosity value above 80%. Pure water permeability (PWP) ranged from 800 to 2600 $\text{L}/\text{m}^2\text{hbar}$ and confirmed the potential application of the produced membranes in microfiltration (MF) and ultrafiltration (UF) processes.

Reference 1:

A. Figoli, T. Marino, S. Simone, E. Di Nicolò, X.-M. Li, T. He, S. Tornaghi, E. Drioli, Towards non-toxic solvents for membrane preparation: a review, *Green Chem.* 16 (2014) 4034.

Degradation of organic micropollutants in water using a novel thermocatalytic membrane

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Main topic: Inorganic membranes

The increasing amount of organic micropollutants in our wastewater and surface water, caused by the industrialization, is a great risk to the environment and human life. Current biological treatments show minor efficiency for organic micropollutants removal, while advanced oxidation processes look more promising [1]. One viable solution in removing organic micropollutants is membrane filtration, e.g. nanofiltration. However, the water recovery by nanofiltration is limited due to the buildup of osmotic pressure caused by contaminants in the water, which results in large amounts of retentate with micropollutants to be handled [2]. In this context, it is important to continue improving the state-of-the-art technologies and developing new technologies to overcome this environmental threat. As an innovative alternative, novel thermocatalytic microfiltration membranes have been developed in this study, to be used in wastewater treatment for continuous degradation of organic pollutants. Ceramic membranes were functionalized with a perovskite and showed remarkable degradation of endocrine disruptor bisphenol A, which was shown to accelerate when heating the membrane and feed stream from 22 to 60 °C. The membranes were characterized regarding pore size, gas and water permeability, degradation efficiency as well as their mechanical performance. As the perovskite is incorporated, the porosity and pore size increases, thus, increasing the permeability of the membrane, but still within the microfiltration range. On the contrary, the increased porosity and pore size reduces the mechanical strength of the membranes. The amount of perovskite incorporated in the membrane shows limited effect on the catalytic activity. Therefore, the thermocatalytic membranes were compared based on their characteristics to suggest the optimal composition and procedure for the fabrication of this new type of membranes for continuous micropollutant degradation based on the current knowledge.

Reference 1:

S. Giannakis, F.A.G. Vives, D. Grandjean, A. Magnet, L.F. De Alencastro, C. Pulgarin; Effect of advanced oxidation processes on the micropollutants and the effluent organic matter contained in municipal wastewater previously treated by three different secondary methods; *Water Research* 84 (2015) 295-306

Reference 2:

A. Azaïs, J. Mendret, E. Petit, S. Brosillon; Influence of volumetric reduction factor during ozonation of nanofiltration concentrates for wastewater reuse; *Chemosphere* 165 (2016) 497-506

Design of a membrane-based solvent exchange process for pharmaceutical nanosuspensions

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¹Laboratory of Thermodynamics, Department of Biochemical and Chemical Engineering, TU Dortmund University

Main topic: Pharmaceuticals and biotechnology

Nanocrystal suspensions of active pharmaceutical ingredients (API) have gained popularity over common formulation strategies offering benefits such as modified pharmacokinetic properties, better intermuscular penetration and higher patients' convenience [1]. However, one major challenge during their production is the removal of organic solvents used during the manufacturing process. Removal of these solvents (required due to strict limitations regarding human exposure) with conventional separation techniques is time- and cost-intensive or even not possible. One very promising process alternative is a membrane-based purification process which offers benefits such as: fulfilling residual solvent content requirements, low thermal treatment, minimized energy and chemical requirements [2].

Within this work, we investigated the feasibility of diafiltration (selected from several alternative membrane-based process concepts) with commercially available organic solvent nanofiltration (OSN) membranes for the removal of ethanol from a (nano)crystal suspension. Membrane screening experiments were performed in a crossflow filtration unit using different OSN membranes with water-ethanol mixtures at various concentrations. Afterwards, diafiltration trials were performed in a dead-end filtration cell with water as diluent. To mimic nanocrystal API's effect on the membrane performance, model particles were utilized.

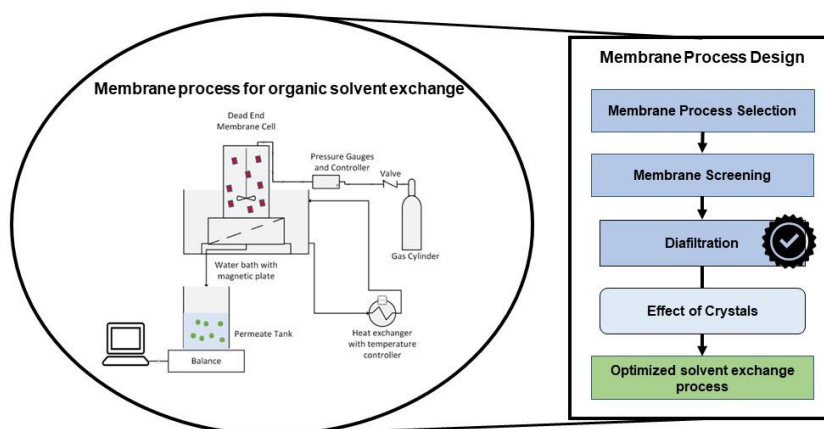
The selected membrane (DuraMem 300 by Evonik Industries) provides a three times higher flux compared to the (excluded) other membranes and shows long-term stability in water/ethanol mixtures. Moreover, the fluxes increase as the water content of the feed increases with no significant reduction in the separation factor between water and ethanol, providing an additional benefit for subsequent diafiltration experiments. Diafiltration with 20 wt% ethanol and 0.1 wt% model particles in the water-ethanol feed mixture (total feed: 200 g) was completed in 6 stages. The filtration time was 92 minutes with complete retention of the model particles and a final concentration of less than 0.5 wt% ethanol in the retentate. Concluding, this study demonstrates that membrane-based diafiltration is an effective solvent exchange method and can pave the way for a continuous manufacturing/purification of commercial nanocrystal-based injectables.

Reference 1:

Liu, M., Hong, C., Li, G., Ma, P. and Xie, Y., 2016. The generation of myricetin–nicotinamide nanocrystals by top-down and bottom-up technologies. *Nanotechnology*, 27(39), pp.395601.

Reference 2:

Marchetti, P., Jimenez Solomon, M., Szekeley, G. and Livingston, A., 2014. Molecular Separation with Organic Solvent Nanofiltration: A Critical Review. *Chemical Reviews*, 114(21), pp.10735-10806.



Design of an integrated downstream process to purify bio-based succinic acid from anaerobic fermentation

Garcia, Jorge - Co-Author

Main topic: Industrial applications and scale-up

Succinic acid is the most important multifunctional chemical platform for the industry with several applications in industrial sectors such as petrochemistry, pharma, food, chemistry, and agriculture, amongst others. Succinic acid can be produced either petrochemically or fermentatively by using different types of bacteria and yeasts. However, due to the depletion of crude oil and the need for moving from the current linear economy to a more sustainable development, the biological production of succinic acid (bio-based succinic acid, bioSA) from renewable resources has attracted wide attention over the recent years [1]. However, the use of downstream separation and purification processes are indispensable to achieve the global bio-based market and compete with the existing petrol-sourced succinic acid [2].

The EU-funded NEOSUCCESS project has found a way to use biogas plants as a beneficial platform to reduce the environmental footprint of the industry by simultaneously producing biomethane and bio-based succinic acid (bioSA) in a single integrated plug&play technology.

Experiments were focused on separating, isolating and purifying the bioSA formed during anaerobic fermentation into a product in powder form. Several separation technologies were proposed with the purpose of removing the impurities that accompany the target compound, including solid-liquid separation, liquid-liquid separation based on membrane technologies, adsorption and product formation by spray drying. The study was specially focused on their synergies and drawbacks to find the best solution in terms of production and purity of bioSA in the final product.

After developing several trials at lab and pilot scale, the final product obtained shows from moderate (79,3 %) to excellent purity (87,9 %) of bioSA content, achieving recovery efficiencies up to 71,9 %. Results therefore demonstrated the successful adaptation and implementation of different technologies into a synergetic integrated separation system. Further developments will focus on upscaling and optimising such results in order to satisfy the Key Performance Indicators of the NEOSUCCESS project.

Reference 1:

[1] Dai Z. et al. (2020). Bio-based succinic acid: an overview of strain development, substrate utilization, and downstream purification. *Biofuels, Bioprod. Bioref.* 14, 965-985.

Reference 2:

[2] Sosa P.A. et al. (2016). Membrane assisted recovery and purification of bio-based succinic acid for improved process sustainability. *J. Membr. Sci.* 501, 236-247.

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Design of membrane-based gas-liquid absorption units: a fast, efficient, high throughput batch to continuous methodology

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¹Université de Lorraine, CNRS, LRGF

Main topic: CO₂ capture

Membrane contactors offer promising perspectives for intensified gas-liquid absorption processes. A rational design of a membrane-based absorption process ideally requires evaluation of membrane material/solvent compatibility, and key thermodynamics and kinetics data. More specifically, impact of gas and liquid velocities, and solvent loading, on effective mass transfer performances are of major importance for design purposes [1]. Classical, time consuming membrane gas absorption tests with different inlet solvent loadings are most often separately performed to determine these different data sets. A fast, compact, easy to use method has been developed to assess, through one experiment, both thermodynamics and mass transfer data based on a batch to continuous approach. The set-up can easily be used for studies of membrane and solvent performance.

These aspects will be shown and discussed, based on experiments performed with chemical solvents for CO₂ absorption from a gaseous mixture.

Materials and Methods

The key concept of the method is to extract solvent capacity and mass transfer coefficients from a breakthrough curve obtained by a set-up combining a solvent recirculation loop circulating in a membrane contactor module exposed to a constant composition gas mixture at the inlet (Figure 1.a). Starting from the differential solute mass balance, the instantaneous effective mass transfer coefficient is extracted the breakthrough curve.

Different operating conditions can be tested before solvent saturation. Breakthrough curve integration enables then thermodynamics data to be determined.

Results

Commercial lab-scale dense skin (PMP) and porous membrane (PP) contactors have been tested with different solvents (amines, amino acids...). Solvent solubility, effective mass transfer coefficient (K_a) as a function of gas/liquid velocities and solvent loadings have been determined (Figure 1.b).

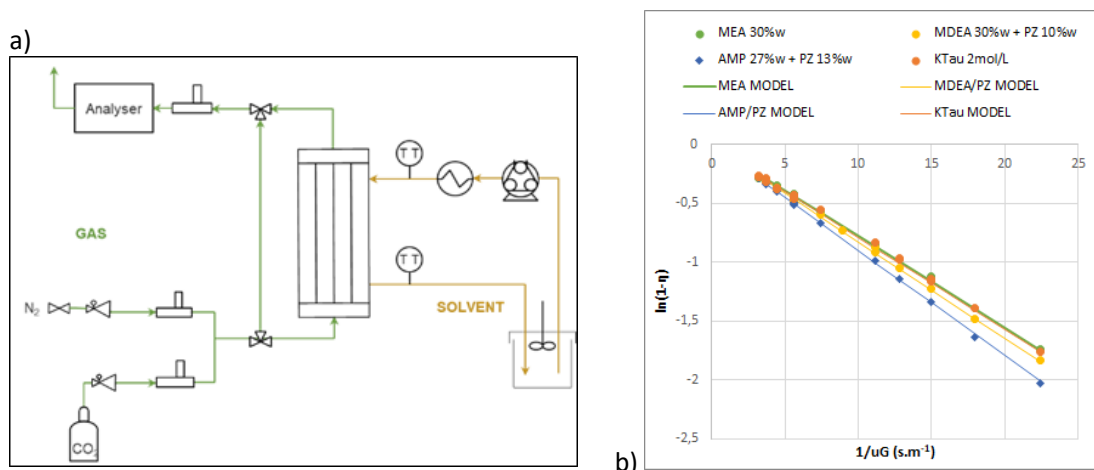


Figure 1

a) Sketch of lab set-up.

b) Examples of validation of the methodology for different solvents: comparison between simulated (line) and experimental (dots) data for: MEA 30%w, MDEA/PZ 30%w/10%w, AMP/PZ 27%w/13%w, potassium taurate 2mol/l.

Conclusions

The method is reproducible and reliable information can be quickly obtained. The interest of the technique for minimum size, automated, high throughput membrane and solvent screening will be discussed.

Acknowledgements

C2FUEL project - Agreement **No 838014**.

B. Wegman (ENGIE) is gratefully acknowledged.

Reference 1:

[1] Favre, E., Svendsen, H.F. Membrane contactors for intensified post-combustion carbon dioxide capture by gas-liquid absorption processes (2012) *Journal of Membrane Science*, 407-408, pp. 1-7

Determination of the limiting current density for boundary layer separation in electro dialysis of multi-component mixtures

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²Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), ³Department of Chemistry, Norwegian University of Science and Technology (NTNU)

Main topic: Electro-membrane processes

In producing elemental zinc from ores, the depletion of the raw material forces producers to accept ores of lower quality, i.e., with a higher degree of impurities. In hydrometallurgical zinc production, the ore is leached in sulfuric acid before electrolysis. Increased halogenide concentrations (Cl^- and F^-) are problematic in the process, as they reduce the cathode lifetime. Therefore, it is highly relevant to develop a technology to efficiently separate low levels of halogenides from concentrated sulfuric acid solution.

Electrodialysis (ED) is an electric potential-driven process. Several cation- and anion-exchange membranes are alternated to concentrate all ions in every second compartment while every other compartment is desalinated. For selective removal of the monovalent anions chloride and fluoride, ED with monovalent-selective anion-exchange membranes (AEMs) is studied. In many applications for multi-ionic mixtures, the concentration of the target ions is comparatively low. To ensure the most efficient ratio between the transport of monovalent (Cl^- and F^-) and divalent (SO_4^{2-}) anions during ED, we determine the limiting current density (j_{lim}) for the target anions and adjusting the operating current to the limiting value for those ions. We refer to this operation mode as *boundary layer separation*. To determine the membrane-specific j_{lim} of target anions, we record current-voltage characteristics of an ED stack and find the current density at which the ion concentration is zero at the membrane surface through the cell potential and the Nernst-Planck equation.

We obtained j_{lim} for chloride and fluoride for different membranes and at different process conditions and use this to evaluate the most efficient conditions for removing low concentrations of chloride and fluoride from concentrated sulfate solutions. The results are validated by performing desalination experiments. The research gives valuable insight into the viability of electro dialysis for selective removal of monovalent anions in multi-ionic mixtures and optimal process design.

Development and investigation of novel chitosan succinate composite membranes modified with Fe-BTC for pervaporation of isopropanol

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Main topic: Advanced fabrication methods

Novel nanocomposite chitosan succinate (ChS)/Fe-BTC membranes on polyacrylonitrile ultrafiltration membrane-support for isopropanol dehydration were developed via the formation of selective layer in dynamic mode (dead-end ultrafiltration). The effect of Fe-BTC concentration (5-40 wt.% with respect to ChS in the aqueous solution) in the selective layer on membrane structure and pervaporation performance was investigated. For nanocomposite membranes the selective layer thickness was found to increase with increase in Fe-BTC concentration in the ChS solution. It was revealed that the selective layer thickness of nanocomposite membrane with 40 wt.% Fe-BTC in ChS solution is 4.65 μm compared to 0.44 μm of ChS/PAN composite membrane. It was shown that increase in Fe-BTC concentration in the selective layer leads to increase in surface roughness of nanocomposite membranes. Introduction of Fe-BTC into the selective layer resulted in formation of large globular aggregates of Fe-BTC that can be observed on the surface of the membrane selective layer. It was found that the water contact angle increases slightly with addition of Fe-BTC into the selective layer. An increase in the water contact angle indicates the hydrophobization of the selective layer surface of thin composite membranes. Thus, addition of 40 wt.% Fe-BTC caused increase in water contact angle to 41° compared to 30° for the reference ChS/PAN composite membrane. Nanocomposite membrane performance was studied in the pervaporation of isopropanol/water mixtures with water content 12, 20 and 30 wt.%. It was found that increase in Fe-BTC concentration results in significant increase in membrane flux during separation of 88 wt.% isopropanol/ 12 wt.% water mixture. Rise of water content in the feed solution was revealed to yield the increase in the permeation flux of both reference and Fe-BTC modified composite membranes. The water content in permeate increased with an increase in Fe-BTC concentration in the selective layer. It was found that Fe-BTC modified membranes possessed higher swelling stability and characterized by significantly higher values of pervaporation separation index compared to the reference ChS/PAN composite membrane.

DEVELOPMENT OF A MOBILE, COMPACT DESALINATION PLANT OPERATED BY MUSCLE POWER

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¹TU Wien, Department of Engineering Design and Product Development, ²TU Wien, Institute of Chemical, Environmental and Bioscience Engineering

Main topic: Drinking water

Supplying the world population with clean drinking water will be one of the greatest challenges for our society in the coming decades. Reverse osmosis is the state of the art for desalination of seawater, but due to the high pressure requirement it is currently only used in large energy-intensive industrial plants, which also produce high amounts of waste brine [1]. Reverse osmosis with a pedal drive has so far only been used for the treatment of fresh water [2], which is technically easier due to the low operating pressures.

Aim of this work was the development of a mobile, compact, inexpensive and robust desalination plant based on a reverse osmosis process operated by muscle power with an adapted commercially available bicycle.

Figure 1: Schematic of the bicycle based desalination plant.

The desalination unit is mounted on the rack of the bicycle (Fig. 1) or pulled like a trailer, so that the bike remains fully functional. Sea water is sucked in, filtered accordingly and pressed through the membrane package by means of a hydraulic piston, whereby around 10% of the water passes through the membrane as fresh water and is removed, the remaining water is used for pressure recovery in the second chamber of the reciprocating piston, to reduce the power that is needed to generate the high pressures (55-60 bar) required in the reverse osmosis process. The translatory thrust for the hydraulic piston is generated via the bicycles' crank drive at a rotational speed of 70 rpm and a maximum of 75W pedaling power. The sprocket set at the rear wheel is modified so that part of the pinions do not propel the back wheel but transmit the applied torque to the desalination unit. When the chain is lifted onto these sprockets by the normal bicycle gearshift, the desalination plant is operated.

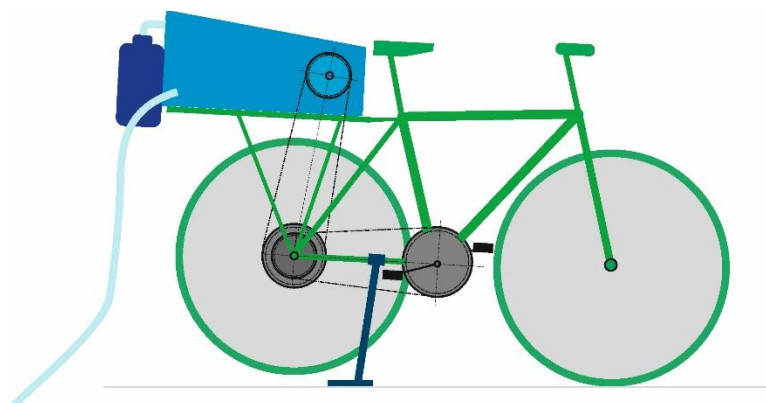
Due to the overall concept of the presented system including pressure recovery, the mobile desalination plant enables the extraction of fresh water from salt water in a small space and with comparatively low forces. The system is specifically suited for the use in remote areas or after disasters.

Reference 1 (Max 50 words):

[1] Ghalavand et al. (2014), DOI: 10.1080/19443994.2014.892837

Reference 2 (Max 50 words):

[2] Gidwani et al. (2016), IJSART,2,(5),10–13.



DEVELOPMENT OF COMPOSITE POLYSULFONE/ POLYTETRAFLUOROETHYLENE MEMBRANES FOR WATER-OIL EMULSION ULTRAFILTRATION

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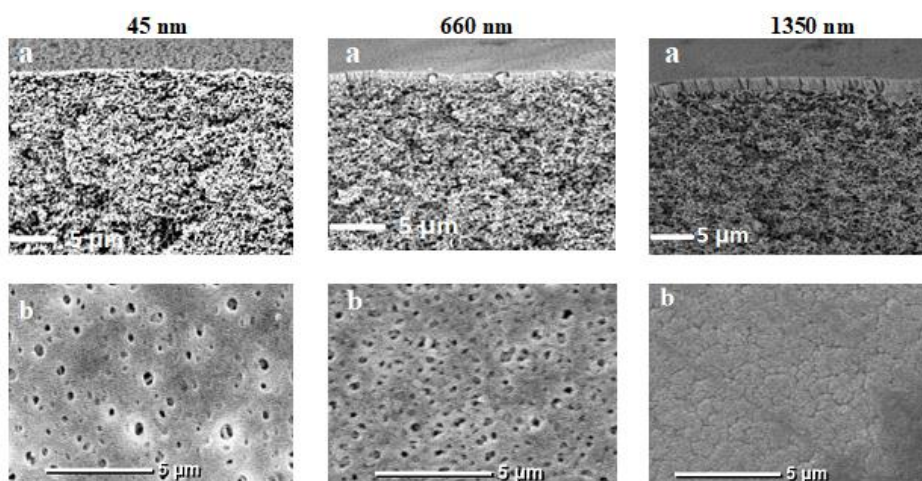
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Main topic: Novel membrane materials

Modification of commercial ultrafiltration polysulfone membrane PSf-300 (manufactured by Institute of Physical Organic Chemistry of the National Academy of Sciences of Belarus) was carried out. A low energy electron-beam deposition technique was applied for membrane modification by using of polytetrafluoroethylene (PTFE) as targets material to improve hydrophobic properties of the reference membranes. A low energy electron-beam deposition was performed at the following process parameters: an energy of 800–1600 eV, a current density of 0.01–0.03 A/cm², pressure of residual gases in a vacuum chamber of $\approx 4 \times 10^{-3}$ Pa, the average distance “electron gun - target” of 150 mm. The thickness of the layer was controlled with a quartz crystal microbalance device. The successful deposition of PTFE in the selective layer was confirmed by the appearance of the absorption band observed in the frequency range of 1300-1000 cm⁻¹, responsible for valence vibrations of C - C and CF₂ groups in FTIR spectra. The thickness of the PTFE layer was reached 45, 660, and 1350 nm that was proved using SEM (Fig 1). Moreover, it was found that a significant thickness of the coating layer doesn't lead to the complete pores overlapping, leaving microcracks and breaks on the surface. Modification led to increase in water contact angle from 56° to 99-115°. Surface roughness was found to increase with the rise of PTFE layer thickness. Separation performance and fouling resistance were evaluated by ultrafiltration of the cutting fluid (CF). It was established that the flux for initial and modified membranes in optimal modes was in the range of $10 \pm 2 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, while rejection of oil significantly differed: 20% for pristine membrane, 81%, 83% and 96% for modified PSf-300 membrane with PTFE layer thickness 45 nm, 660 nm and 1350 nm respectively. The developed PSf-PTFE membranes were found to be highly efficient in oil-water emulsion purification.

Figure. Modified PSf membrane with PTFE layer: (a) cross-section, (b) skin-layer

This work was supported by Belarusian Republican Foundation for Fundamental Research, grant No. X21M-009.



Development of a planar ceramic membrane module for high temperature oxygen separation in industrial processes

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Main topic: Module design

Oxygen transport membranes (OTMs) are widely studied as an alternative technology for the separation of pure oxygen. Several studies demonstrated the feasibility of the production of pure oxygen at high temperature with high efficiency and lower energy demand, with respect to standard techniques. The most promising applications of OTMs are related to the integration of a membrane module in high energy intensive processes (e.g. glass manufacturing or steel production) or the production of chemical commodities and energy vectors through membrane reactors.

A membrane module consists of a metallic container where one or more membranes are placed and joined by using a proper sealing technique. An OTM module can be based on different membrane geometries (planar, tubular, hollow fiber, etc.).

The objective of this work is the design and development of a planar LSCF membrane module. The planar configuration has been chosen because it can be easily scaled up and the presence of free flow channels in the membrane structure allows the feeding of a sweep gas, making the technology more flexible. Another advantage of this configuration is the high mechanical resistance of the ceramic assembly, thanks to the presence of an intermediate porous structure.

LSCF membrane element has been designed based on the mechanical characterization of the ceramic material associated with a stress analysis study. The multi-layered components have been manufactured from powders following a scalable approach that involved several steps: tape casting of ceramic slips, shaping of the flow channels, lamination and sintering. The size of the final membrane element is approximately 60 x 60 mm, as reported in the following picture (Figure 1).

Figure 1 Planar LSCF membrane element with flow channels.

The metallic container consists of two shells forming a housing for the membrane and its sealing material, while lateral channels allow the feeding of the air and the sweep gas in cross flow mode.

Moreover, starting from experimental permeation results, a model has been developed in order to study the fluid dynamic regime inside the module and to optimize the membrane permeation rate according to the identified process operating conditions.



Development of high-performance membranes for CO₂ capture: from polymer to module

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¹EMI Twente, University of Twente, ²SINTEF Industri, ³Leitat Technological Center

Main topic: CO₂ capture

Process intensification and carbon capture technology are crucial actions to be taken in order to reach the climate targets set by the IPCC (i.e. ensuring global warming to stay below 2°C). In that sense, the importance of membrane technology is expected to increase exponentially. For instance, the use of membrane technology in post-combustion carbon capture is recognized as a promising alternative to the only large scale available technology today; chemical absorption, which is costly and there are concerns about potential chemical emissions to the environment.

Numerous materials are reported with great potential for CO₂ capture. However, just a few materials are actually being converted into an actual membrane and scaled up. In this work we present the development and scale up of a very promising material concept and demonstration it in a relevant post-combustion application to achieve at least 90% of CO₂ recovery at a cost of 15€/MWh in one carbon intensive industry.

The identification of the key steps of the process besides of the control of the processing parameters are crucial. Here, we show how to control the development and scale up of a thin-film composite hollow fiber membrane with high separation performance in post combustion CO₂-capture. A multilayer approach was taken in order to obtain a very thin separation layer (<200 nm thick) and thus high CO₂-permeance². A dope recipe and spinning for a porous support hollow fiber membrane procedure was developed in-house that allowed the application of a very thin gutter layer with minimum gas transport resistance. The fiber is post-treated in-line and collected on a spool and could be directly used in a semi-continuous coating machine to apply the gutter and separation layer. The resulting membrane has been tested under real process conditions and has shown very promising stable separation performance for post-combustion CO₂-capture.

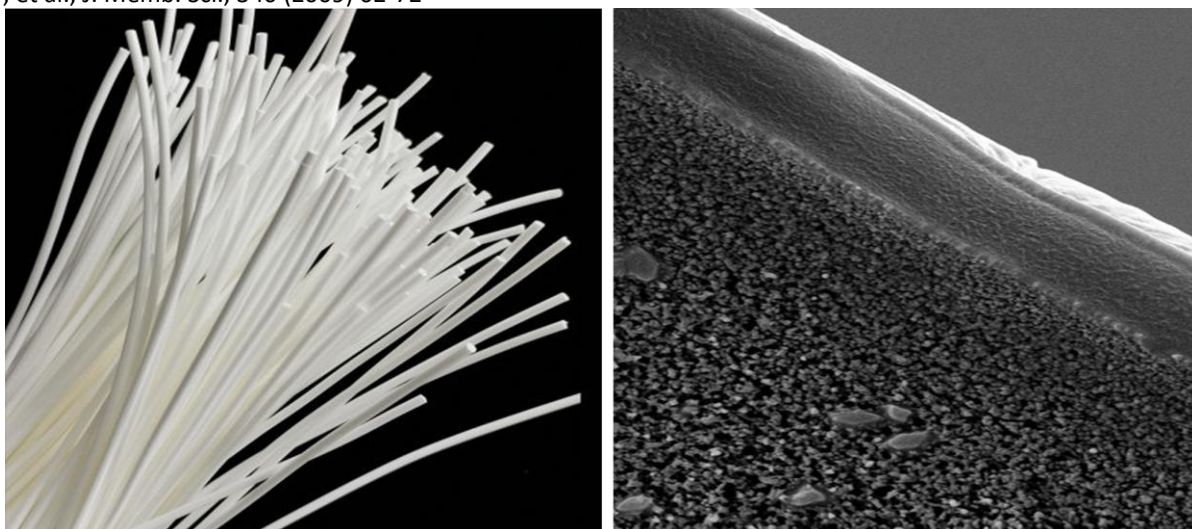
Acknowledgement: This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760899. This publication reflects only the author's views and the European Union is not liable for any use that may be made of the information contained therein.

Reference 1:

Bui et al., Energy & Environmental Science 11 (2018) 1062

Reference 2:

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Development of hydrophilic Poly(vinylidene fluoride)-based membrane by chemical modification with Alkali Lignin

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Main topic: Novel membrane materials

The aim of this work was the development of a polyvinylidene fluoride (PVDF)-based membrane with improved water wettability and, therefore, permeability. The strategy used was a chemical reaction between PVDF and alkali lignin (AL), a biomass material with antiradical and antibacterial properties [1]. The reaction was conducted in an acidic environment, in which the nucleophilic hydroxyl groups of AL and electrophilic carbons of PVDF formed new covalent C-O bonds. The viscosity of the PVDF/AL (15/5) dope solution was much lower (893 ± 4 cP) than that of the PVDF (20 wt.%) alone (1593 ± 7 cP). Membranes were prepared by non-solvent induced phase separation method. Dimethyl sulfoxide and deionized water were used as solvent and non-solvent, respectively. FTIR analysis confirmed the presence of the AL in the membrane. The PVDF/AL membranes showed a decreased water contact angle (50 vs 81°) and a smoother surface compared to unmodified PVDF membrane. The high hydrophilicity and low surface roughness contribute to fouling mitigation. The water permeance of PVDF/AL membrane was more than 7 times higher than that of PVDF membrane (530 vs 70 L/hm²bar, respectively).

Membranes were tested for the separation of oil droplets from water. Emulsion was prepared using 1% sodium dodecyl sulphate and 1% vegetal oil dispersed in aqueous continuous phase. A complete separation of oil droplets (retentate) from water (permeate) was obtained using the PVDF/AL membrane. A full recover of pure water permeance after oil/water emulsion separation was obtained.

Acknowledgement

The work was carried out within the RAVEL project funded within the POR CALABRIA FESR-FSE 2014-2020.

Reference 1:

[1] Kai, D., Tan, M. J., Chee, P. L., Chua, Y. K., Yap, Y. L., & Loh, X. J. (2016). Towards lignin-based functional materials in a sustainable world. *Green Chemistry*, 18, 1175.

Development of Membranes for the Separation of Valeraldehyde in the Hydroformylation reaction in Membrane Reactors

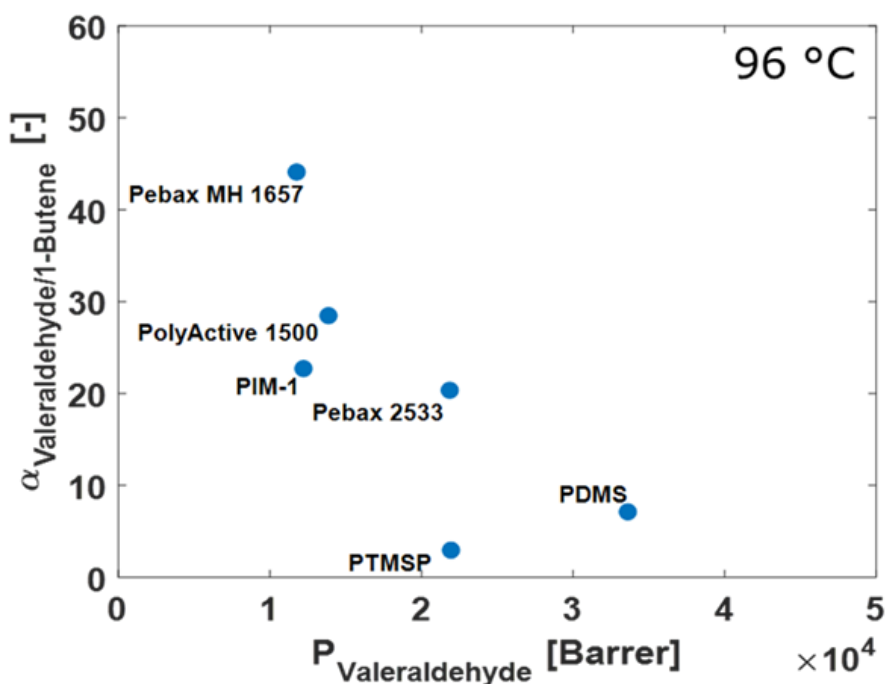
Weigelt, Fynn - Co-Author¹; Shishatskiy, Sergey - Co-Author¹; Filiz, Volkan - Co-Author¹; Brinkmann, Torsten - Co-Author¹

¹Helmholtz-Zentrum Hereon

Main topic: Gas separation

In the hydroformylation reaction, alkenes react with syngas to aldehydes. The hydroformylation reaction is one of the most energy-intensive processes in the chemical industry. Membrane reactors are a possible way to intensify this process, by combining the reaction with a separation step. The EU-Project MACBETH (Membranes And Catalyst Beyond Economic And Technological Hurdles) investigates, among other things, the hydroformylation reaction in a membrane reactor concept.

This work shows the development and investigation of polymeric membranes, which are suitable for the in-situ separation under reaction conditions. In the studied hydroformylation reaction, syngas (H_2 and CO) reacts with 1-Butene to Valeraldehyde. In the membrane reactor Valeraldehyde should be separated from the reaction zone ($T = 90 - 120^\circ C$ and $p_{Feed} = 17 \text{ bar}$) to enhance the reactor performance. For this, different polymers were investigated. The Figure shows the single gas permeation of different polymers for the separation of 1-Butene/Valeraldehyde at $96^\circ C$ and for a feed activity $\rightarrow 0 \text{ mbar}$. Poly(dimethylsiloxane) (PDMS) and Pebax[®] MH 1657 were used further to investigate mixed-gas performances. These polymers were coated onto porous SiC monolithic supports, which could be used in a membrane reactor setup. These membranes were further analyzed for their mixed gas separation performance under reaction conditions.



Development of monovalent selective ion exchange membranes for the separation of halogenides from sulfate solution

tekinalp, onder - Co-Author

Main topic: Electro-membrane processes

In hydrometallurgical processes, electrolysis of an aqueous zinc sulfate solution is performed to produce elemental zinc. In many cases, the aqueous zinc sulfate solution contains halogenides after the production which reduce the lifetime of process equipment. Hence, an improved technology for the removal of halogenides (F^- , Cl^-) from highly concentrated sulfuric acid solution (SO_4^{2-}) is an urgent need. Ion exchange membranes (IEMs) are the materials used in the removal of such ions from aqueous solutions by electrodialysis (ED). Conventional IEMs offer low selectivity between ions of the same charge. Monovalent selective ion exchange membranes (MSIEMs) are of special utility for the separation of monovalent ions from multivalent ions. One way of developing MSIEMs is the surface modification via layer by layer (LbL) deposition of polyelectrolytes which is a promising strategy to achieve an effective separation between ions of the same sign and/or charge. The LbL method is a facile method to synthesize such membranes due to controlling the membrane surface properties such as swelling, top-layer tightness, and surface charge of membrane coatings, thereby favoring the transport of ionic species of smaller charge and size while repelling bigger ones. This study, therefore, intends to prepare MSIEMs by LbL polyelectrolyte deposition on tailor-made anion exchange membranes to separate fluoride (F^-) and chloride (Cl^-) ions from sulfate (SO_4^{2-}) ions in a ternary mixture solution. Different tailor-made membranes were produced with different properties using a variety of nucleophiles. Considering the flexibility offered by LbL technology, the influence of the number of layers, pH and salt concentration in polyelectrolyte solution on the monovalent selectivity of the membranes were investigated using different polyelectrolyte pairs. ED experiments of LbL-modified membranes were performed with feed solutions of a ternary mixture of fluoride, chloride and sulfate at a concentration range of 0.01 M to 1 M. A monovalent selectivity of 11.02 was determined after only 5 number of layer deposition.

Development of photocatalytic membranes for surface water disinfection

Martínez Sosa, Santiago - Co-Author¹

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Main topic: Microfiltration/Ultrafiltration

Increase in the exploitation of water resources has led to the deterioration of their quality. Diverse pollutants are easily found in surface water and effective treatment requires a combination of systems. These techniques must keep improving to meet the challenges that new pollutants, demand, and stricter regulations will bring. Membranes are attractive for water treatment, but limitations like fouling and the production of a concentrated retentate affect their full-scale implementation. Combining membrane filtration with photocatalysis provides the opportunity to integrate self-cleaning membranes, tackle problems of the individual technologies, and improve the system operation.

In this work, we first studied two approaches to combine membrane filtration with zinc oxide photocatalysis (catalyst in suspension and immobilized) activated by L.E.D's, emitting at 365 nm. Systems were compared in terms of catalyst concentration in the permeate stream (below the limit of detection) and their recovery after five filtration assays (recovery higher than 74%). The system's capability to retain and inactivate target bacteria (total coliforms and *E. coli*) was tested with samples of real surface water. Both configurations showed an improved performance in comparison to the membrane treatment alone, without bacteria detected in the permeate and enhanced degradation of compounds held in the retentate.

For the modified membranes, different catalyst concentrations and thermal treatments were also tested. The performance of all the processes was evaluated in terms of retention, permeate flux and degradation of compounds in the retentate.

Modified membranes showed an efficient retention of bacteria, with higher performances than the unmodified membrane (96.2% for total coliforms and 94.9% for *E. coli*). Remarkable retention and treatment were achieved with a catalyst load of 75 g/m² and 2-hour treatment at 300 °C. This modification leads to a performance higher than the system with the catalyst in suspension, which usually shows a better performance. During operation, the permeate flux reduction is lower with the modified membranes which might lead to longer operation times without further cleaning or replacement.

The combined system using ceramic membranes modified with zinc oxide and UV-A light emitting diodes proved to be effective to retain and disinfect aqueous streams with target bacteria from surface water.

Development of polysulfone ultrafiltration membranes with enhanced antifouling performance for the valorisation of side streams in the pulp and paper industry

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Main topic: Advanced fabrication methods

One-stage method of polysulfone (PSf)/polyethylene glycol (PEG, $M_n = 400 \text{ g}\cdot\text{mol}^{-1}$) membrane modification by the addition of polyacrylic acid (PAA, $M_n = 250\cdot 10^3 \text{ g}\cdot\text{mol}^{-1}$) to the coagulation bath during membrane preparation *via* non-solvent induced phase separation was proposed. It was found that addition of PAA into coagulation bath resulted in decreasing pore size and porosity of the selective layer as well as the formation of a thicker and denser selective layer that was confirmed by scanning electron microscopy. Water contact angle of the modified membranes was found to decrease significantly from 65° for reference PSF/PEG to 16° for PSF/PEG/2.0 wt.% PAA membranes. Zeta potential of the selective layer was shown to become more negative in the studied pH range 3-10, all compared to the reference membrane. It was revealed that pure water flux decreased in 2.2 times for PSF/PEG/2.0 wt.% PAA membrane compared to the reference membrane. This is the result of the formation of a denser selective layer and a decreasing of the selective layer pore size and porosity. Lysozyme and polyvinylpyrrolidone K-30 retention was shown to increase with the increase in PAA concentration in the coagulation bath. It was found that membranes modified with PAA demonstrated better antifouling stability in ultrafiltration of humic acid solution and thermomechanical pulp (ThMP) process water. Modified membranes were found to have higher flux in ThMP process water ultrafiltration: from 17 to $82 \text{ L m}^{-2} \text{ h}^{-1}$ for reference PSF/PEG and PSF/PEG/1.5 wt.% PAA membranes, correspondingly, at transmembrane pressure of 1 bar. It was shown that PAA modified membranes are characterized by higher flux recovery ratio compared to the reference membrane both after distilled water rinsing ($\text{FRR}_{\text{rinse}}$) and cleaning with alkaline agent ($\text{FRR}_{\text{clean}}$). For instance, for PSF/PEG membrane $\text{FRR}_{\text{rinse}}$ and $\text{FRR}_{\text{clean}}$ were 13 and 34% respectively, and for PSF/PEG/1.5 wt.% PAA membrane — 54 and 96%. The developed membranes were found to be more effective for the concentration of hemicellulose due to the smaller pore size of the selective layer compared to the reference membrane. Thus, it is possible to use developed membranes for the valorization of hemicelluloses from the ThMP process water in pulp industry.

Development of silicon carbide-titanium dioxide membranes at low temperature for water treatment

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¹DTU Energy, ²LiqTech Ceramics

Main topic : Microfiltration/Ultrafiltration

This study reports the development at relatively low temperature of silicon carbide membranes to be potentially applied in ultrafiltration. Silicon carbide macroporous supports were coated with allylhydridopolycarbosilane (AHPCS) by spin-coating or dip-coating and submitted to pyrolysis at 750 °C. Upon pyrolysis, polycarbosilane was converted to silicon carbide, thus forming a thin and porous layer. The decomposition of AHPCS was accompanied by volume shrinkage and release of gases, which led to the formation of cracks on the deposited film [1]. As the shrinkage of the preceramic polymer can be reduced by introducing a filler [1], fine powders of titanium dioxide (TiO₂) were added to AHPCS mixed with n-hexane. Besides helping to avoid the formation of cracks, TiO₂ could also introduce photocatalytic properties to the membrane. Several parameters were investigated, such as speed of deposition of the suspension, amount of TiO₂ added and number of depositions. Samples developed by spin-coating with multi-depositions or dip-coating exhibited thicker membrane layers, which increased the formation of cracks. On the other hand, membranes developed by spin-coating with addition of TiO₂ by one-deposition exhibited a considerable reduction of micro-cracks. The results of this study thus indicate that TiO₂ could be beneficial to reduce the formation of cracks upon pyrolysis of AHPCS films.

Reference 1:

[1] P. Colombo, G. Mera, R. Riedel, and G. D. Sorarù, "Polymer-derived ceramics: 40 Years of research and innovation in advanced ceramics," *J. Am. Ceram. Soc.*, vol. 93, no. 7, pp. 1805–1837, 2010, doi: 10.1111/j.1551-2916.2010.03876.x.

Development of ultra-robust fabric embedded PVDF membranes by NTIPS method and their applications in membrane distillation

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Main topic: Membrane contactors and membrane distillation

Membrane distillation is a thermally-driven process involving the transport of water vapor across a microporous hydrophobic membrane, driven by transmembrane vapor pressure gradient induced by temperature difference [1]. It is considered a promising alternative to existing solute recovery methods [2]. Most currently used hydrophobic membranes (e.g., PVDF) in MD were adopted from other processes such as microfiltration (MF) and hence may not meet the MD requirements, such as wetting resistance and mechanical strength [3]. The unsupported/pure PVDF membranes reported in MD literature exhibited tensile strength in the range of 0.8 MPa to 3.5 MPa, which was not sufficient to withstand the intense hydraulic pressure and flow disturbance under industrial conditions [3]. Most the industrial scale membrane casting is directly done on non-woven fabric supports to enhance mechanical stability, which however still pose potential challenges in MD due to the simultaneous contact with hot and cold solutions. Thus, the choices of the supporting fabrics and the integration methods with membrane substrates are critical factors for producing robust MD membranes.

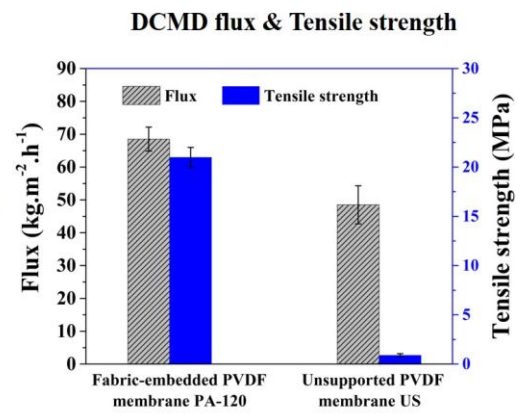
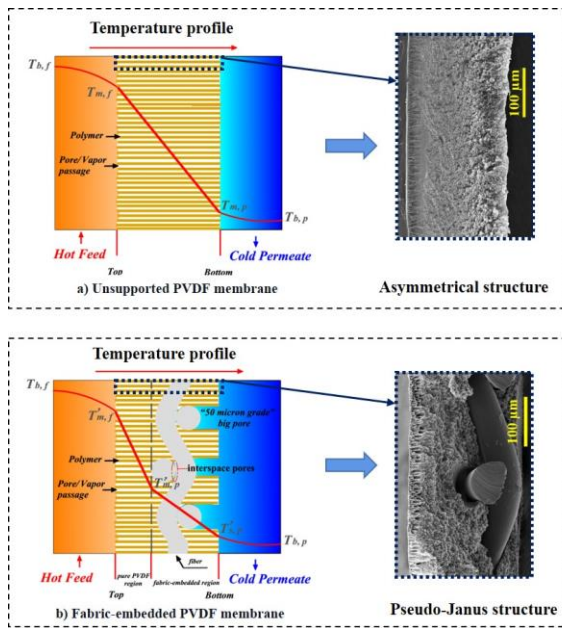
This study proposed a novel strategy to fabricate highly permeable and robust supported PVDF membranes for membrane distillation, via a nonsolvent thermally induced phase separation method. Different from the traditional supported membranes casted on non-woven fabrics, a well-integrated fabric-embedded PVDF (FE-PVDF) membrane was successfully obtained using polyamide 66 (PA) gauze supports. The optimal FE-PVDF membranes PA-120 exhibited desirable bicontinuous pore network and an interesting structure with pseudo Janus function, resulting in a DCMD flux of $68.5 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 70°C with synthetic saline solution and exceptional tensile strength of 21 MPa (lateral) / 21 MPa (longitudinal), which was 1.4-fold and 23-fold higher than that of the unsupported benchmark, respectively. The PA-120 membrane was further evaluated via the concentration of 10 wt% monosodium glutamate solution at 70°C up to 55 wt% when crystallization was observed, with an initial flux of $64.6 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (10 wt%), followed by a minor decrease by 16.3% until 40 wt% and a subsequent decline towards 55 wt%. Repeated concentration cycles were successfully conducted with intermediate membrane rinsing by fresh feed, demonstrating highly recoverable performance. This preliminary study brings new perspectives towards pushing the limits of current lab-made MD membranes, showing promise for applications in solute harvesting.

Reference 1:

[1] Peng Wang, Tai-Shung Chung, Recent advances in membrane distillation processes: Membrane development, configuration design and application exploring, *Journal of Membrane Science*, 474 (2015) 39-56. [2] K.W. Lawson, D.R. Lloyd, Membrane distillation, *Journal of Membrane Science*, 124 (1997) 1-25.

Reference 2:

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Differences between polyvinyl difluoride membrane ageing by sodium hypochlorite single soaking and at full-scale MBR

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Main topic: Ageing of polymeric membranes

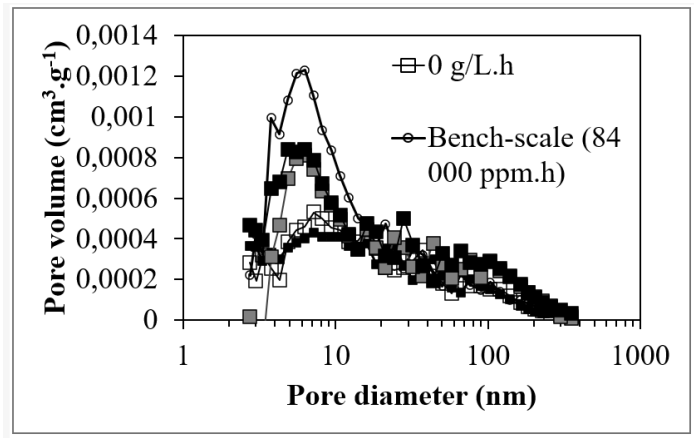
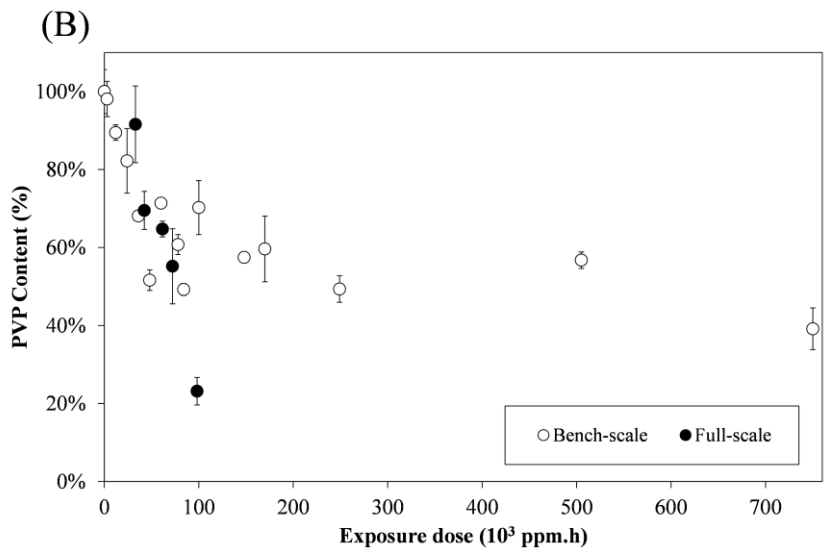
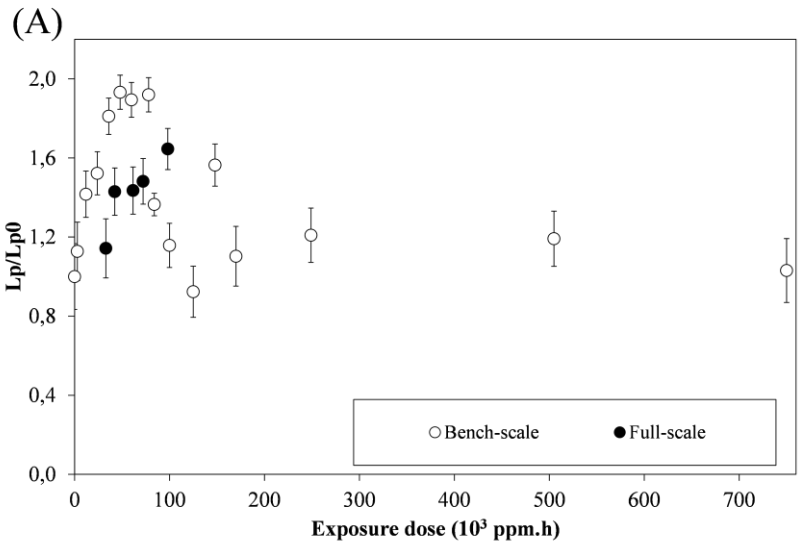
Membrane bioreactors (MBR) experienced exponential growth driven by stricter legislation in effluent quality, discharge to sensitive water body and space limitations. Despite that, this technology still presents higher costs than conventional ones. Membrane replacement is one of the reasons as it can account for over 25% of the total membrane plant cost (1). Besides there is environmental concerns about their production and discharge. Studies about polyvinyl difluoride (PVDF) membrane ageing mainly soaked membranes in NaOCl solutions as it is believed to be the main ageing propellant. The present study aims to address the representativeness of this approach regarding full-scale ageing. Zeeweed® 500D membranes were aged at bench-scale by sole hypochlorite action and at full-scale in a municipal wastewater MBR operating since 2014. Samples were characterized for water permeability, hydrophilic agent content, i.e. polyvinyl pyrrolidone (PVP), by infra-red analysis (ATR-FTIR), porometer by nitrogen adsorption. Membranes exposed to 84,000 ppm.h (5.25 operating years equivalent) at bench-scale presented a 2.3-fold increase in water permeability, followed by a sudden decline (Figure 1.A). Meanwhile, full-scale aged membranes had a 1.6-fold increase over the period (100,000 ppm.h exposure). Physical-chemical properties were characterized to assess these evolutions. Both sets presented a decline in PVP content (Figure 1.B), which was expected as these species are highly reactive to hypochlorite (2). Actually, the main difference between bench and full-scale ageing relied on changes of pore size distribution and PVP degradation, which was the driver for the permeability changes (Figure 2). At bench-scale, membranes increased porosity as a result of increasing the quantity of small pores (<20 nm diameter) until 84,000 ppm.h, then the structure collapsed, decreasing porosity. At full-scale, besides higher amounts of small pores, higher quantities of large pores (>50 nm) appeared, which may lead to integrity issues in future. According to ATR-FTIR analysis, MBR conditions were also responsible to changes in PVP degradation mechanism. Ageing membranes at bench-scale can be a practical tool to assess chemical ageing such as PVP content but it presents limitations regarding full-scale MBR ageing. Thus, filtration/aeration conditions and sludge presence play major roles in membrane ageing.

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Reference 2:

Robinson S J, Bérubé P R. Seeking realistic membrane ageing at bench-scale. (2021) *Journal of Membrane Science* 618:118606.



Differentiating biofilm growth on the spacer and on the membrane using optical coherence tomography

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Main topic: Membrane fouling and cleaning

In cross-flow membrane separation processes biofouling can lead to a severe permeability decline, by forming a layer on the membrane surface and causing a pressure drop along the module. In the present study a new method was developed to separately quantify both biofilm growth on the spacer and on the membrane surface. Thereby their influence on membrane performance can be evaluated individually. Optical coherence tomography (OCT) was performed to acquire 3D pictures of the feed channel during a 26 days experiment, in which a low-pressure reverse osmosis (LPRO) membrane was operated at 25 bar and 37 °C. Experiments were carried out using flat sheet membrane units (FMU), simulating spiral wound modules. The dissolved organic carbon (DOC) of the feed solution was as high as 10 g/L. An ImageJ macro was written and used to process the OCT datasets, allowing for a time and space resolved biomass quantification until the end of the experiment, when the permeability dropped. Two additional parameters: SP (spacer), indicating fouling in the spacer area and ME (membrane), indicating fouling on the membrane surface area were developed. Although biofilm predominantly grew on the spacer during the first 15 days (Chart), no significant decline of the permeability was observed in this stage. The fact that the biofilm first accumulates on the spacer filaments is in accordance with previous studies [1,2]. From day 16 biofilm attachment on the membrane surface started playing a role (Chart). The pressure drop along the membrane module increased during the whole period, whereas the permeability stabilized on day 3 at one value and then dropped on day 22.

Results showed that the accumulation of biofilm on the spacer region is the main responsible for the pressure drop in the feed channel. However, the biofilm on the spacer and the one on the membrane surface, both, contributes clearly to fouling and to the final permeability decline.

Caption

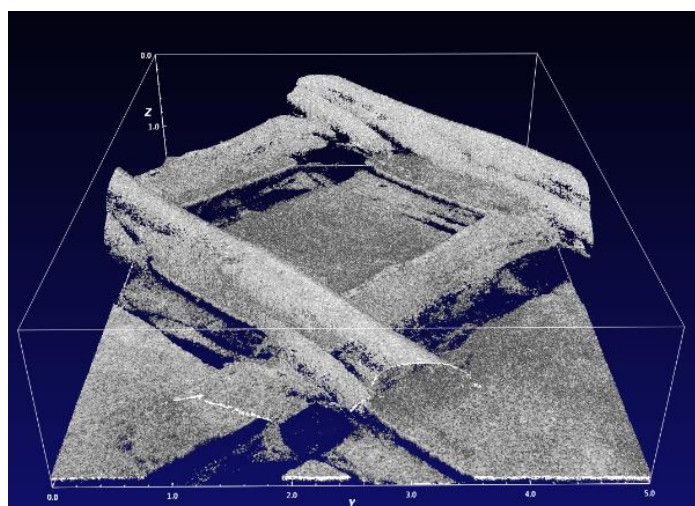
OCT rendering of the feed channel (26 days) (Picture) and development of the fouling layer for SP and ME (Chart).

Reference 1:

Fortunato L., Jeong S., Leiknes T. (2017). Time-resolved monitoring of biofouling development on a flat sheet membrane using optical coherence tomography. *Scientific Reports*. 7 (1)

Reference 2:

West S., Wagner M., Engelke C., Horn H. (2016). Optical coherence tomography for the in situ three-dimensional visualization and quantification of feed spacer channel fouling in reverse osmosis membrane modules. *Journal of Membrane Science*. 498 pp. 345-352



Direct membrane filtration - Investigating fouling and antifouling in wastewater treatment

Lipnizki, Frank - Main Author¹; Khalid, Omer - Co-Author¹; Gidstedt, Simon - Co-Author; Rudolph, Georg - Co-Author¹
¹Department of Chemical Engineering, Lund University, Sweden

Main topic: Wastewater treatment

Direct membrane filtration (DMF) has received a lot of attention in recent years because of its ability to treat low-strength and low temperature wastewater where biological based treatments are inefficient. Compared to conventional wastewater treatment processes, DMF can be operated with less energy and requires a smaller footprint, lower capital cost and has less environmental impact. Additionally, it provides high resource recovery and the permeate obtained from this single step operation can comply with discharge/reclamation requirements. The main aim of this study is to investigate membrane fouling, its mitigation approaches and influence on organic/nutrient retention during DMF of municipal wastewater in crossflow mode. It was observed that physicochemical pre-treatment of wastewater with polyaluminum chloride (PACl) and polyamide (PAM) significantly retards membrane fouling and improves organics/nutrient retention. From short-term physicochemically pre-treated wastewater concentration studies, with microfiltration (MF) and ultrafiltration (UF) operating under different conditions, it was revealed that (i) increasing crossflow velocity (CFV), from 1 to 2 m/s, improves filtration performance by reducing irreversible fouling (ii) elevating transmembrane pressure (TMP), from 0.18 to 0.4 bar, increases both reversible and irreversible fouling (iii) periodic permeation relaxation increases the extent of irreversible fouling and contributes to higher overall fouling in UF. Operating DMF continuously with wastewater for 192 h, UF showed higher filtration performance and organics retention in comparison to MF. The combination physicochemical wastewater pre-treatment and microsieveing (100 μm) with direct ultrafiltration produced superior quality permeate with approximate removal of 92% chemical oxygen demand (COD), 91% total organic carbon (TOC), 95% total phosphorus (TP) and 100% suspended solids (SS). Almost the complete permeability of the fouled membrane was resorted with in-line alkaline cleaning, using Ultrasil-10 at 1 m/s and 50°C. Overall, this study shows that with optimized operating and cleaning protocol, long-term sustainable DMF process for wastewater treatment with controlled membrane fouling and improved resource recovery can be devised for up-scale.

Direct observation with a high speed camera for particle track and trace during membrane fouling

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¹Aalborg University

Main topic: Membrane fouling and cleaning

Membrane fouling is a significant challenge in membrane operation, as fouling reduces performance, while being difficult to monitor and control. Fouling monitoring methods can potentially lead to increased understanding of mechanisms of fouling formation during filtration and removal during cleaning. Existing in-situ fouling monitoring methods count ultrasonic reflectometry, laser triangulometry and fluid dynamic gauging, which can characterize the fouling layer in terms of thickness, rate of formation and cohesive strength (Rudolph et al., 2019). On the other hand, direct observation techniques have been developed to monitor the filtration process by recording the formation of fouling layers through a microscope.

In this study, the records of a hollow fiber microfiltration membrane observed through a microscope using a high-speed camera were studied by the application of advanced MATLAB scripts. The membrane was fouled with synthetic core-shell particles with a mean diameter of 1.6 μm . The scripts were developed to track and trace particles and from that calculate the velocity profiles of particles moving towards and away from the membrane (Fig. 1). The measured velocities of particles along the membrane were according to theoretical velocities calculated by computational fluid dynamics modelling. However, the measured velocities of particles moving towards the membrane in a region of 3–80 μm from the membrane showed to be higher than expected from the measured water flux. Hence, permeation drag underpredicts the actual rate of transport of particles towards the membrane surface. In addition, it is observed that particles shift direction as they approach the membrane, which suggests a region of high turbulence near the membrane surface.

Hence, the methodology of combining direct observation through a microscope with MATLAB analysis of particle behavior proposed in this study can serve as a valuable tool to understand particle behavior during membrane filtration.

Reference 1:

Rudolph et al., J. Membr. Sci. (2019) 117221

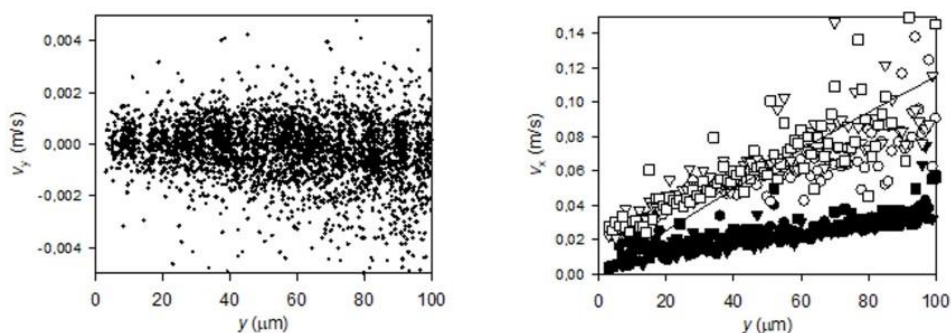


Figure 1: Particle velocities towards (left) and along the membrane surface (right) plotted against distance from the membrane.

Diverse and abundant antibiotic resistance genes removal by nanofiltration from pig manure and biogas digestate of Germany

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Main topic: Environmental applications

Antibiotic resistance genes (ARG) monitoring is one of the crucial objectives of the World Health Organization global action plan due to its potential threat to the worldwide human health. In particular, intensive livestock farming and the resulting biogas digestate slurries are among the major contributors of ARGs¹. Recent studies have highlighted the ARG retention efficiency of membrane filtration from water and wastewater². However little information is available regarding the ARG removal efficiency by nanofiltration (NF) from pig manure and biogas digestate slurry. Here we report the detection of diverse and abundant ARGs from pig manure and biogas digestate of Germany and their treatment by NF270 membrane. We show that, total 189 ARGs were detected and quantified in raw manure and digestate, among which 70 ARGs were unique. These ARGs confer resistance most dominantly to tetracycline (51.9%), aminoglycoside (15.3%) and MLSB (14.8%) followed by sulfonamide (6.3%), other groups (4.8%), β -Lactam (3.7%), taxonomic (1.6%) and MDR (1.6%). The total ARG copies was found highest in pig manure of site 2 ($1.15\text{E} \times 10^8$ copies/100 μL), which was one and two order of magnitude higher than pig manure of site 1 (3.74×10^7 copies/100 μL) and digestate of site 3 (7.61×10^6 copies/100 μL) respectively. Absolute concentrations of 37 unique ARGs were found above 10^5 copies/100 μL . The log retention value (LRV) of ARGs by NF270 were noticed mostly above 3. However, the LRV of ARGs from digestate, in particular conferring resistance to aminoglycoside were between 1 to 2. We show that NF270 membrane is highly efficient of retaining most of the ARGs above 99%. Size exclusion and charge repulsion were identified as the main retention mechanisms. However, lower ARG concentration in feed resulted in relatively lower retention by NF. This is mainly due to the hair like formation of ARGs which made them able to pass through NF270, especially at a working pressure above 3 bar.

Reference 1:

Zhu, Y.-G. et al. Diverse and abundant antibiotic resistance genes in Chinese swine farms. Proceedings of the National Academy of Sciences 110, 3435-3440 (2013).

Reference 2:

Slipko, K. et al. Removal of extracellular free DNA and antibiotic resistance genes from water and wastewater by membranes ranging from microfiltration to reverse osmosis. Water Research 164, 114916 (2019).

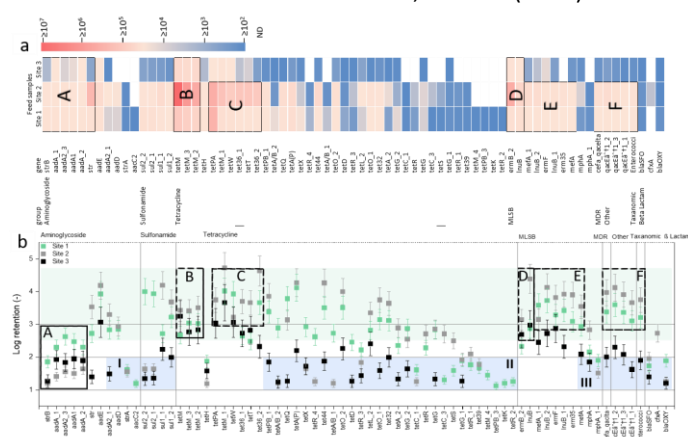


Figure 1. (a) ARG concentration (per 100 μL) profile resistance to different antibiotic groups profile in each sampling site. Zone (A), (B) and (D) are enriched in all of the sampling sites; (C), (E) and (F) are enriched in site 1 and site 2 but not in site 3. [ND: Not detected] and (b) Log retention of individual ARGs of pig manure and digestate samples from site 1, 2 and 3.

Donnan Dialysis for drinking water production: a circular process for increased water recovery and remineralization

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Main topic: Industrial applications and scale-up

In the Netherlands and many other countries, drinking water is produced from groundwater reservoirs and surface water sources. However, the availability and quality of water sources keep decreasing due to inadequate disposal of wastewater, increased presence of organic micropollutants, and rising salinity due to the intrusion of seawater and intensified fresh water use. Because of this, reverse osmosis (RO) is being applied to ensure that the drinking water is free of micropollutants and excess salts. However, RO has two negative aspects: 1) limited recovery due to scaling occurring on the membranes, and 2) the treated water is not ready for consumption as it needs to be re-mineralized (see Figure 1A). This means that calcium and magnesium ions need to be supplied to achieve the adequate water hardness, frequently involving the transport of the minerals and extra costs. However, both problems could be tackled by pre-treating the feed water with Donnan dialysis (DD), as will be further explained.

The **Donnan Dialysis ReMineralization (DoReMi)** process is a recently patented scheme designed to tackle the previously mentioned problems. As shown in Figure 1B, DoReMi uses Donnan dialysis (DD) as pretreatment for the RO process, where divalent cations (Ca^{2+} , Mg^{2+}) from the feed water are exchanged with the monovalent ions present in a draw solution. Later, these divalent cations are recovered using nanofiltration (NF), which separates these ions from the sodium (Na^+), and used to remineralize the drinking water.

In this work we present the DoReMi process, explain the initial experiments at laboratory-scale, and describe its implementation onto pilot scale. The pilot, consisting of a DD, a NF and a RO unit was designed and operated to treat onsite 100L/h of fresh groundwater in a continuous form. During the operation, parameters like temperature, conductivity, ionic composition and concentration of micropollutants were monitored for the different streams. These values allowed to calculate the transport rates of salts and micropollutants under different process conditions. Ultimately, we analyze the economy of the process with the improved water recovery and the retrieval of minerals from the groundwater, and present our suggestions for future developments in the field.

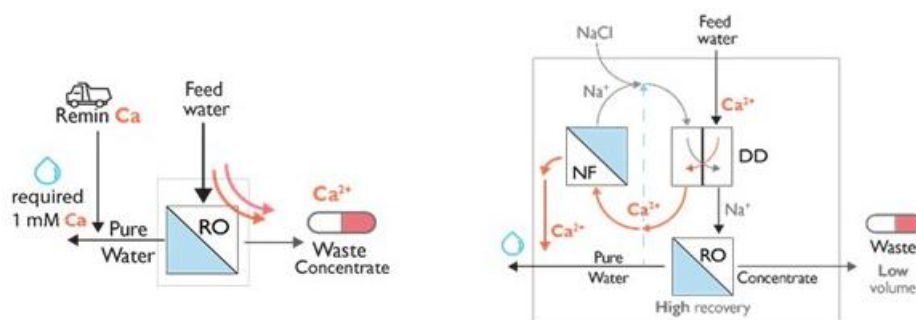


Figure 1. A) Current status of drinking water production. B) DoReMi process for drinking water production (Dutch patent NL2021733). The feed water is pre-treated with Donnan dialysis and the hardness minerals are recovered with a nanofiltration unit.

Donnan Dialysis to recover ammonium from waste water: towards a more circular fertilizer (N₂) cycle.

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Main topic: Wastewater treatment

Food production in the world is heavily dependent on the energy intensive production of ammonia from N₂ via the Haber-Bosch process. The ammonia is converted to fertilizer and used in agriculture to produce crops for human and animal consumption. Eventually, this bound nitrogen ends up in municipal waste water treatment plants. Here it is converted back to ammonia, via energy intensive steps, back to N₂ to prevent eutrophication of surface waters.

Recovery of ammonia from wastewater is potentially much more resource efficient and would save a lot of energy but is severely limited by the low concentration. An energy efficient concentration process is needed to pre-concentrate ammonia after which it can be stripped and recovered in an economically viable way. Donnan Dialysis is a very energy efficient candidate and would overcome these limitations to allow further concentration[1] of the ammonia by stripping[2]. The resulting stream can be catalytically converted to ammonium-nitrate in a simple aqueous oxidation step.

Here we present Donnan Dialysis to concentrate ammonia from dilute solutions. The process requirements and main governing separation characteristics for mass-transfer will be treated. The measured ion transport rate and selectivity will be shown and discussed both from a theoretical and practical point of view. Besides these important factors the membrane characteristics as ion exchange capacity and permselectivity were also shown to play an important role for the removal efficiency. To complete the circular approach of the project, the catalytic conversion of ammonia into ammonium-nitrate will be shown both from an experimental as theoretical point of view.

The integration of these technologies is believed to partially disrupt the world-wide linear approach to fertilizer production making it much more circular. It allows for an easy integration into anaerobic waste water treatment plants that also produce biogas, rather than consume large amounts of energy for the complete destruction of nitrogen and carbon compounds.

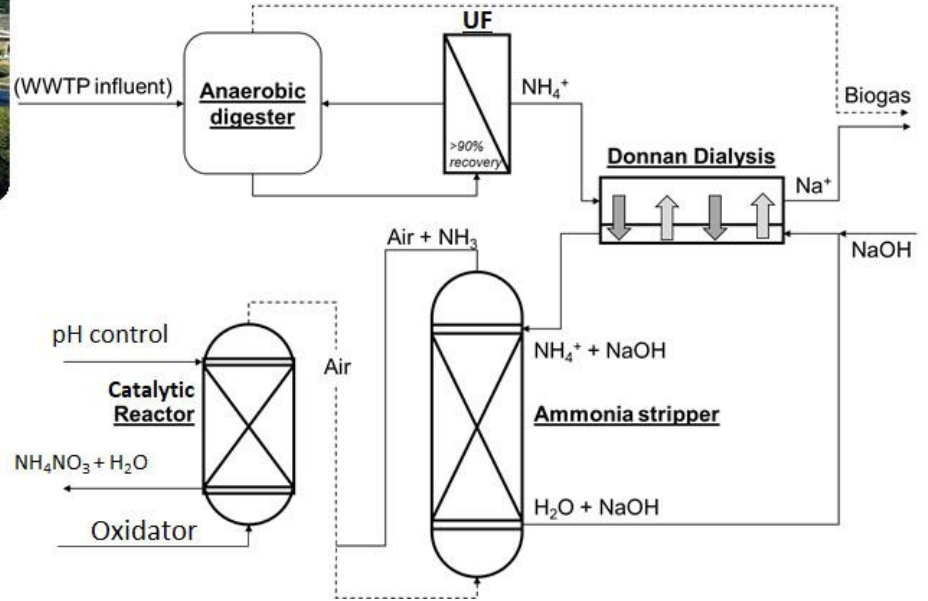
Figure 1. *A more circular approach towards world wide fertilizer use: CAS replacement by anaerobic digesters producing biogas and ammonia. Subsequent preconcentration by Donnan Dialysis, stripping and catalytic oxidation to ammonium-nitrate allows for the recovery instead of decomposition of this resource.*

Reference 1:

R.M. Wallace, Concentration and separation of ions by donnan membrane equilibrium, Ind. Eng. Chem. Process Des. Dev. 6 (1967) 423–431.

Reference 2:

S. Guštin, R. Marinšek-Logar, Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent, Process Saf. Environ. Prot. 89 (2011) 61–66.



Downstream processing of a novel sweet protein produced by precision fermentation

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Main topic: Food processing

Fermentation is a method used by humans since the Neolithic age to produce foods and drinks. Up to date, it is the underlying process for making alcoholic drinks and dairy products such as cheese or yoghurt.

This very old method can be improved by so-called precision fermentation, which uses engineered microorganisms to produce proteins and other biomolecules highly efficiently. The product molecule can be fine-tuned to have specific and improved features, such as being hypoallergenic, stable, product-fit, healthier, and better-tasting. Precision fermentation is a cost-effective, and environmentally friendly process, and it has the ability to increase sustainability of the food sector.

The EIT Food project “Precision Fermentation: From Biotechnology to Sustainable Nutrition” has the aim to develop and optimise a process for the production of a novel sweet protein by precision fermentation. The protein will have the sensory profile of sugar but will be much healthier than sweeteners and refined sugars because it is as quickly digested by the body similar to other proteins.

Once the proteins are produced by the microorganisms, they are secreted into the fermentation broth, and have to be separated, purified, and concentrated subsequently. This task has to be highly selective, low-energy demanding, and cost efficient. The pressure driven membrane processes microfiltration and ultrafiltration are suitable unit operations for this task, and have been successfully established in the food industry since the 1970's. The challenge lies in using the best membrane and identifying the optimal operation conditions to reach the fine balance between selectivity, product flux, and fouling.

The focus of this work is on the downstream processing of the proteins and will present the current status of the process development, results from membrane screening, and will give an outlook on how a scale-up of the production process could look.

Reference 1:

EIT Food iVZW, Brussels, Belgium
Amai Proteins, Rehovot, Israel
VTT Technical Research Centre of Finland, Espoo, Finland
Aarhus University, Aarhus, Denmark
Maspex, Wadowice, Poland

Drastic change in performance of NF-membranes after contact with water/solvent-mixtures

El Fadil, Abdelhakim - Co-Author

Main topic: Nanofiltration/Reverse Osmosis

This presentation will describe how polymeric nanofiltration membranes fail in treating water/solvent-mixtures. The four NF chemistries studied in this work are crosslinked PI, PVDF and epoxy-based solvent resistant nanofiltration (SRNF) membranes, as well as PA-based NF-membranes originally designed for aqueous applications. All NF-membranes showed a very significant water and solvent permeance decrease by more than 40% after exposure to water/solvent-mixtures. In the experiments, the feed solution consisted of a mixture of either DMF, DMSO or acetonitrile with water. Existing literature transport models were not able to describe this permeance drop phenomenon and an empirical model was developed in this study.

Effect of alginate viscosity on combined alginate-humic acid fouling mechanism and mitigation during microfiltration

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¹University of Iceland

Main topic: Membrane fouling and cleaning

In membrane-based water and wastewater treatment processes, understanding the interactive effect of various types of organic components on membrane fouling is crucial in order to identify effective fouling mitigation strategies. In this study, two types of alginate (low viscosity and medium viscosity) and humic acid were selected as model foulants. The membrane fouling behaviours of combined alginate-humic acid solution were monitored under constant flux conditions in both dead-end and crossflow microfiltration (MF) membrane filtration systems. The membrane fouling mechanisms were illustrated by fitting the experimental data with the reported membrane fouling models. The effects of operation conditions (intermittent interval, cleaning protocols) on the fouling potential of combined alginate-humic acid were examined.

The results revealed that the presence of humic acid (100 mg/L) appeared to accelerate alginate fouling under both dead-end and crossflow filtration conditions, following cake layer filtration mechanism (dead-end) and a combined intermittent pore blocking and cake layer filtration mechanism (crossflow) respectively. Under the crossflow filtration condition, the fouling mechanism of the alginate-humic acid mixture was dependent with the permeate flux and alginate nature, e.g., less pore blocking with more cake layer fouling were present at a higher permeate flux during filtration medium viscosity alginate-humic acid mixture. When intermittent relaxation was employed during crossflow filtration, the presence of humic acid could alleviate medium viscosity alginate fouling. This was attributed by a significant shift of irreversible fouling to reversible cake layer fouling, which was readily removed by shear force during relaxation. A comparison of membrane performance during intermittent filtration with periodical flushing using clean water, NaClO (5%), and persulfate (100 mg/L) at 50 °C indicates that high temperature clean water flushing was effective in maintaining membrane performance during filtrating alginatehumic acid complex, which majorly contributed to a reduction of reversible cake layer fouling.

Effect of concentration and membrane ageing on virus removal by ultrafiltration in drinking water production

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¹Aix Marseille Univ., CNRS, Centrale Marseille, M2P2 UMR 7340, Equipe Procédés Membranaires (EPM), ²Eau de Paris – Direction de la Recherche du Développement et de la Qualité de l'Eau

Main topic: Microfiltration/Ultrafiltration

During drinking water (DW) production, removal of pathogen microorganisms is an important issue. Regarding human enteric viruses, membrane producers of ultrafiltration (UF) membranes announce 4 log virus removal, using MS2 phage as enteric virus surrogate. The conditions of laboratory tests and plant production can vary, especially regarding viral feed concentration. Evaluate the real UF efficiency regarding enteric viruses in DW production plants is then needed. A comparison of two enteric viruses (ADV41 and CV-B5) with the MS2 phage has been conducted regarding UF removal to understand the retention mechanisms and evaluate the MS2 phage as surrogate. The virus concentration in the feed water can affect aggregation and retention mechanisms, causing changes in removal efficiency. Indeed, laboratory studies usually used artificially high virus concentrations due to analytical methods detection limits and practical considerations ($> 10^6$ viruses.L⁻¹), but concentrations in the water resources used to produce DW are smaller ($< 10^4$ viruses.L⁻¹) [1]. Effect of feed concentration has been studied in order to validate laboratory experiments to assess the virus removal in DW production. After experiments of virus removal on native UF membrane, the modifications on membrane material with chemical ageing have been considered. Membrane chlorine exposure during the membrane cleaning causes membrane modifications (pore size, changes in hydrophilic properties, etc...) [2]. This chlorine ageing has been studied regarding membrane permeability and changes in virus removal efficiency. First results showed that the increase of virus feed concentration leads to an increase in virus removal. Thus, laboratory experiments with high virus concentrations could cause an overestimation of the removal efficiencies achieved in DW plants with resources containing low viral content, especially groundwaters. The comparison of MS2 phages and enteric viruses removal allows to consider the MS2 phage as a potential good “worst case” surrogate, as the removal of this phage is similar or lower than the two studied enteric viruses. Membrane chlorine exposure leads to modifications of membrane material causing an increase of membrane permeability. Despite this membrane ageing, virus removal is not affected.

Reference 1:

P. Waldman, « Conséquences des interactions entre les virus entériques humains et la matière organique sur la persistance virale, l'efficacité de traitements de désinfection et l'évolution des populations virales . », <http://www.theses.fr>, nov. 25, 2019. <http://www.theses.fr/s162237>

Reference 2:

W. Fu et W. Zhang, « Chemical aging and impacts on hydrophilic and hydrophobic polyether sulfone (PES) membrane filtration performances », *Polymer Degradation and Stability*, vol. 168, p. 108960, oct. 2019, doi: 10.1016/j.polymdegradstab.2019.108960

Efficiency of membrane technology in the removing of phytotoxicity from soybean oil refineries wastewater for safe and sustainable reuse

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¹Water Research and Technologies Centre (CERTe), ²Laboratoire de Mécanique, Modélisation et Procédés Propres (M2P2-CNRS-UMR 7340-EPM)

Main topic: Wastewater treatment

One of the most hazardous industrial effluents is wastewater generated during the vegetable oil refining process. The vegetable oil refinery wastewater (VORW) are mostly being discharged either without any treatment or with partial treatment for oil removal. This effluent has alkaline pH, high organic and inorganic dissolved solids, COD, BOD and oil, requires adequate treatment before discharge into inland surface water or for land use to conform effluent discharge standards prescribed by the regulatory agencies. The membrane processes are high effective in the removal of pollutants from aquatic solutions. However, even after membrane treatment, VORW can be still toxic for environment. One of the ways to assess the degree of toxicity of wastewater, apart from the determination of the physico-chemical indicators, is the toxicity test [1]. Currently, tests based on plant bio-indicators are often recommended as an effective and affordable method of assessing the toxicity of environmental samples with a sensitivity similar to tests using mammalian cells [2]. The aim of this study is to highlight the efficiency of the membrane treatment of Soybean VORW (Tunisia) for safe and sustainable reuse in irrigation using the phytotoxicity test. Membrane filtration experiments were conducted under the Dead-End Filtration mode using Amicon stirring cell. Several flat membranes have been tested with pore size ranged from 0.22 to 5 μm for microfiltration (MF) and molecular weight cut off (MWCO) varied between 10 kDa and 100 kDa for ultrafiltration (UF). Seed germination were carried out on distilled water, raw and MF/UF treated VORW. Water samples were pipetted into a sterilized plastic Petri dish lined with a Whatman filter paper. 20 seeds of lettuce (*Lactuca sativa*) were scattered on the filter paper and incubated at 25°C during 7 days. The number of germinated seeds was then counted, and the length of roots was measured. The responses were evaluated by calculating the germination index (GI).

The present study highlights the efficiency of UF to completely remove the phytotoxic effect from Soybean VORW showing a GI of 100% regardless of the MWCO used, and then UF-treated water can be safely reused for irrigation.

Reference 1:

[1] Da Costa Filho B. M., da Silva V. M., de Oliveira Silva J., da Hora Machado A. E., & Trovó A. G. (2016). Coupling coagulation, flocculation and decantation with photo-Fenton process for treatment of industrial wastewater containing fipronil: biodegradability and toxicity assessment. *Journal of environmental management*, 174, 71-78.

Reference 2:

[2] Rora, A., Kachamakova-Trojanowska N., Jozkowicz A., Kruk J., Cocquerelle C., Vandebulcke F., & Plytycz B. (2014). Coelomocyte-derived fluorescence and DNA markers of composting earthworm species. *Journal of Experimental Zoology Part A: Ecological Genetics and Physiology*, 321(1), 28-40.

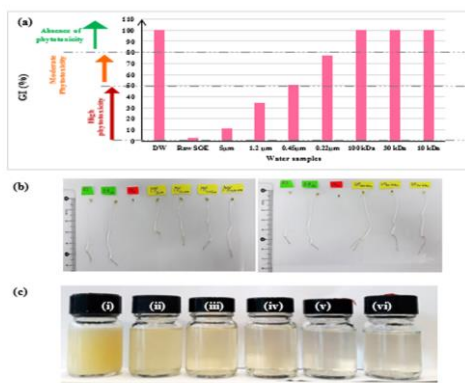


Fig 1. (a) Germination index after 7 days of incubation of lettuce seeds using raw and treated Soybean VORW using MF and UF treatments. (b) Phytotoxic effect of raw and treated Soybean VORW using MF and UF treatments on the length of *Lactuca sativa* roots. (c) Performance of DEF in the treatment of VORW (i) using different membrane sizes: 1.2 μm (ii), 0.45 μm (iii), 0.22 μm (iv), 500 kDa (v) and 100 kDa (vi).

Efficient and sustainable membrane platform development for microfiltration applications

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¹Sartorius Stedim Biotech GmbH

Main topic: Advanced fabrication methods

Most porous polymeric membranes are made from polymer solutions (casting solutions) where membrane formation is based on phase separation. There are four main mechanisms for phase separation: vapor-induced phase separation (VIPS), non-solvent-induced phase separation (NIPS), evaporation-induced phase separation (EIPS) and thermal-induced phase separation (TIPS). Often, the precipitation casting process mainly consists of a combination of the two mechanisms VIPS and NIPS. This combination provides the possibility to vary the resulting membrane structures and thus the membrane properties in many ways.

In addition to the specified process parameters, the resulting membrane properties are also dependent on the composition of the casting solution. To influence the thermodynamics and kinetics of membrane formation, various solvents and additives are part of the casting solution in addition to the membrane-forming polymer.

In this investigation the phase diagram of the casting solution is used to efficiently develop a new platform. [1] A series of suitable casting solution compositions can be derived from these phase diagrams.

These casting solutions are then used for the process development of membranes (VIPS+NIPS) on a laboratory scale casting line. Here the most important process parameters can be investigated and a pre-development for production scale is conducted efficiently.

With this equipment (phase diagram and lab casting line) at hand, deeper insight into the formation of membrane is gained, which will in turn lead to a more efficient process development.

One target is to develop a sustainable cellulose acetate-based microfiltration platform including high-performance membranes with tailored structures. Another goal is to create of casting solutions with sustainable and green solvents.

Reference 1 :

[1] C. Kahrs, M. Metze, C. Fricke, J. Schwellenbach, J. Mol. Liq. 2019, Thermodynamic analysis of polymer solutions for the production of polymeric membranes.

Elaboration of novel thin film bicontinuous cross-linked polymer material from acrylates microemulsions using commercial non-polymerizable surfactants for enhanced membrane filtration

Guzelot, Chloé - Main Author; Lahitte, Jean-François - Co-Author; Remigy, Jean-Christophe - Co-Author

Main topic: Advanced fabrication methods

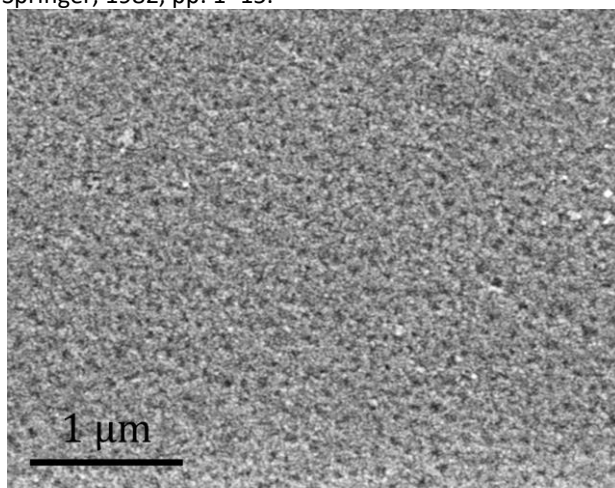
The use of bicontinuous structures has been shown useful to create nanostructured thin-films on top of mechanical supports, allowing to reach a high flux coupled with a good selectivity. It has however been commonly agreed that bicontinuous microemulsion can be used to enhance membrane filtration [1] but can only be obtained using polymerizable surfactants. Those chemicals have however one major disadvantage which is the synthesis step prior to their use, contrary to a lot of non-polymerizable surfactants that are commercially available. Therefore, a process using non-polymerizable surfactants would save time and facilitate the transition to industrial scale. Our findings suggest that using non-polymerizable surfactants can actually lead to cross-linked bicontinuous microstructures. Our works assume that some rearrangement of the structure during polymerization takes place, as already shown by some researches [2], in contrast to polymerizable surfactants which seem to retain the initial structure. Our statement is supported by various analyzes of the liquid and polymerized samples. Using Small-angle X-Ray scattering (SAXS) analyzes we obtained curves that follow the Teubner-Strey model and therefore highlight the appearance of a nano-scale bicontinuous (i.e. 4-6 nm range) structure upon polymerization, whereas no such structure existed in the liquid state. The resulting microstructure is also demonstrated by SEM images which suggest the existence of nanoscaled channels. SAXS analyzes also proved that the liquid formulation is stable over a wide range of easily accessible temperatures, e.g. between 10°C and 40°C, which would benefit the industrialization of the process by limiting production costs. Our findings also brought out that a polyacrylate film as thin as 50 µm can be handled, which offers large perspectives for the deposit on support membranes and also potentially for solvent filtration.

Reference 1:

F. Galiano et al., "UV-LED induced bicontinuous microemulsions polymerisation for surface modification of commercial membranes – Enhancing the antifouling properties," *Sep. Purif. Technol.*, vol. 194, pp. 149–160, 2018, doi: 10.1016/j.seppur.2017.10.063.

Reference 2:

C.-U. Herrmann, G. Klar, and M. Kahlweit, "On the Phase Inversion in H₂O—Oil—Nonionic Surfactant Systems and Related Phenomena," in *Microemulsions*, Springer, 1982, pp. 1–15.



SEM surface of the polymerized microemulsion

Electro-membrane separation of heavy metals and natural organic matter from surface water

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Main topic: Electro-membrane processes

The presence of heavy metals (HM) and natural organic matter (NOM) in surface water is problematic in terms of water treatment. NOM is represented by humic substances like fulvic acids (FA) and humic acids (HA), polysaccharides, and proteins [1]. These compounds have different properties in terms of molecular weight and size, presence of functional groups, charge at different pH-values, and their solubility in water [2]. In this study, separation of HM (Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} and Ni^{2+}) and NOM with customized bipolar membrane electrodialysis (BMED) was investigated. Different feed samples from a brown water lake (original sample of lake Hohloh (HO), and FA and HA as XAD isolates of the lake Hohloh) were used. The results showed, that more than 95 % of all HM were removed from the feed solution in all cases. Cu^{2+} was found to interact stronger with FA compared to HA. The binding of Cu^{2+} to HA is higher in comparison with Cr^{3+} . NOM was preferably bound to Cu^{2+} and Cr^{3+} compared to Cd^{2+} , Co^{2+} , and Ni^{2+} . The mass balance and SEM-EDX images revealed that a big portion of removed HM and organic carbon (OC) was accumulated on ion exchange membranes (IEMs). The accumulation of OC on IEMs increased linearly with the concentration of HM. Despite the HM and OC accumulation on IEMs, the desalination rate (with respect to sodium chloride) was not compromised. SEM-EDX analysis of the cleaned IEM showed the presence of chromium species specifically on anion exchange membranes. The separation of HM and NOM by the proposed process is greatly influenced by the type and concentration of HM, and the nature of NOM. HM constitutes the bridge, which enhances the binding of NOM on IEMs. These findings show, that a BMED design can produce process streams free of HM and NOM by inducing stronger interactions between HM, NOM and IEMs.

Reference 1:

Leenheer, J.A.; Croué, J.-P. Peer Reviewed: Characterizing Aquatic Dissolved Organic Matter. *Environ. Sci. Technol.* 2003, 37, 18A–26A

Reference 2:

Zhang, Y.; Zhao, X.; Zhang, X.; Peng, S. A review of different drinking water treatments for natural organic matter removal. *Water Sci. Technol. Water Supply* 2015, 15, 442–455

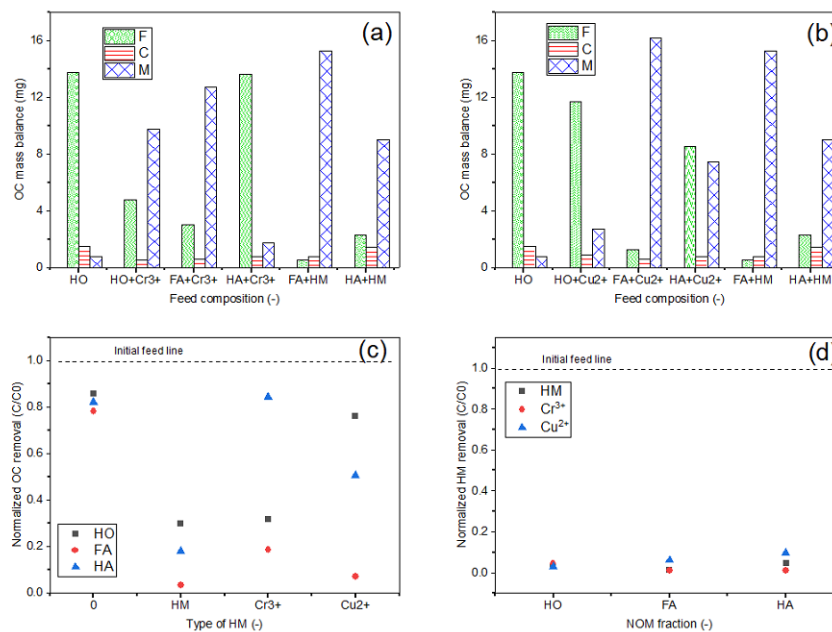


Figure 1: (a) and (b) OC mass balance as a function of the feed composition. (c) Normalized OC removal as a function of the type of HM. (d) Normalized HM removal as a function of the type of NOM.
Operational conditions: feed solution $V = 1$ L: OC (as DOC in mg/L): 15 mg/L of HO, FA and HA; NaCl: 0.5 g/L; HM: 0 and 10 mg/L; concentrate solution $V = 1$ L: NaCl: 0.5 g/L; electrode rinse solution: 50 g of Na₂SO₄/L; applied voltage: 15 V; process time: 120 min and flow rate: 20 L/h

Abbreviations:

- F: OC dissolved in dilute (feed stream) at the end of process time
- C: OC dissolved in concentrate (concentrate stream) at the end of the process time
- M: Calculated OC deposit on the membrane at the end of the process time
- HO: Original brown water of lake Hohloh
- FA: Fulvic acid
- HA: Humic acid

Bobák, Marek - Co-Author

Main topic: Electro-membrane processes

One of the frequent requirements in waste water treatment (WWT) projects is to achieve a zero liquid discharge (ZLD) system. The fundamental drawback of most ZLD processes is a fact that they produce no other valuable products except water for reuse. Big effort is spent in academic and commercial R&D of ZLD systems in order to generate valuable products targeting circular economy approach and higher economical revenues. The presented paper summarizes several selected projects, demonstrating the benefits of efficient electrodialysis (ED) application. For ED in ZLD and similar applications, MemBrain developed new type of industrial scale stack EDR-IF bringing heterogeneous ion-exchange membranes close to their limits. The main feature is significantly increased current density up to 400 A.m^{-2} , increased concentrate conductivity up to 220 mS.cm^{-1} and improved efficiency. EDR-IF stack is now commercially available and its typical application benefits will be presented as a short case study for brine processing with 2 variants: (i) minimum liquid discharge with water recovery of 96-97% and (ii) near ZLD with 98-99%. Nevertheless, further effort in R&D was spent in order to find practical limits and verify performance in two typical cases – Na_2SO_4 based and NaCl based waste water concentration. Experiments were performed in the industrial scale for 1000 hours. ED unit confirmed stable operation with average Na_2SO_4 concentration 220 g.kg^{-1} , salt flux $750 \text{ g.m}^{-2}.\text{h}^{-1}$ and electrical efficiency 81%. Results from processing of NaCl based on real feed are actually not available in industrial scale yet but they will be presented as well.

The objective of another project was to find out how to concentrate chlorides from the real mixture of ion-exchange waste eluates with TDS of 43.7 g.l^{-1} and Cl^- concentration 23.3 g.l^{-1} . Three process variants were experimentally compared in lab scale: (i) 2-stage precipitation + ED; (ii) 2-stage precipitation + NF + ED and (iii) 1-stage precipitation + NF + ED. The most promising is the second variant achieving concentration of Cl^- 71.6 g.l^{-1} and high sulphate reduction by approx. 97%.

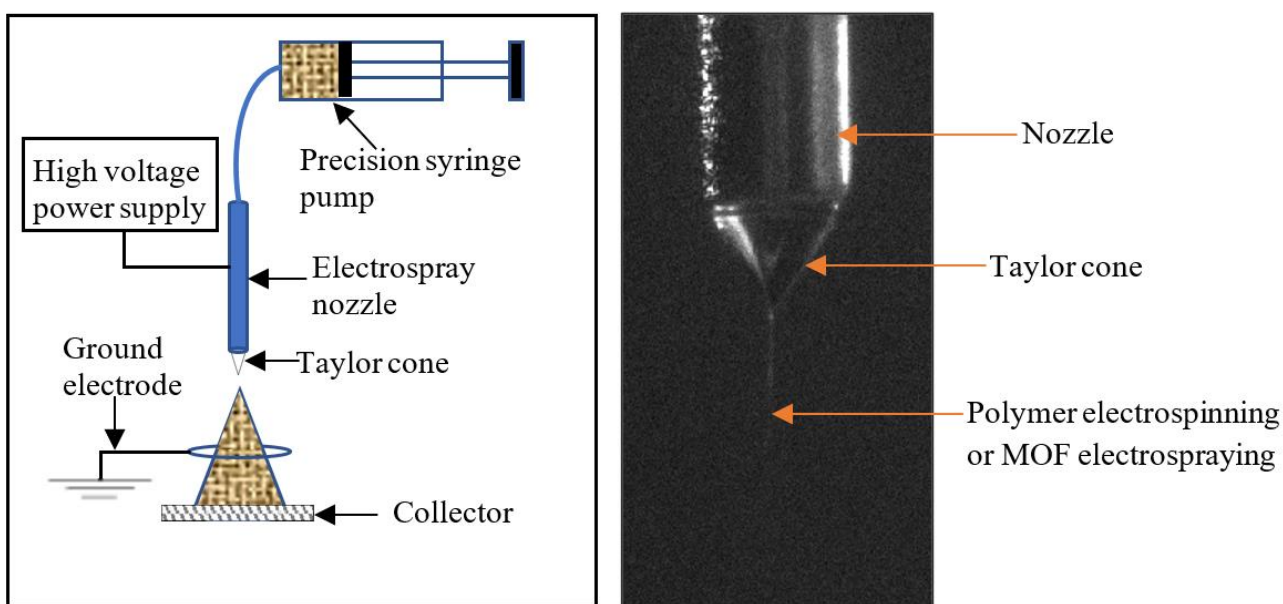
Presented results clearly show that efficient ED process is useful in various process schemes targeting efficient WWT reducing the liquid discharge.

Electrohydrodynamic Emission as a Manufacturing Technology for the Fabrication of Mixed Matrix Membranes

Alkandari, sharifah - Co-Author

Main topic: Advanced fabrication methods

In this study, we explored the features of electrohydrodynamic emission (EHE) as an advanced manufacturing technology for the fabrication of gas separation microporous mixed matrix membranes (MMM) composed of cellulose acetate (CA) and/or polysulfone (PSF) and zeolite imidazole framework (ZIF-67). EHE can generate polymer nanofibers (electrospinning) or MOF nanoparticles (electrospraying), leveraging the presence of strong electric fields applied upon a precursor solution to form 2D structures such as membranes. The functionality of conventional membrane is defined by two vital factors: flux and selectivity. While the selectivity is controlled by the surface properties of the membrane that distinguish the type of species that can be transported across the membrane, the flux defines the rate at which it is transported. Interestingly, the EHE possesses a unique characteristic which allowed controlling the dispersion and particle size distribution of MOF nanoparticles, supramolecular structure of the MOF crystal, surface topography, morphology, orientation, thickness and other properties which determines selectivity and flux of the resultant MMM. The EHE offers the opportunity to tune these membrane attributes by controlling the operating conditions of the process including the voltage, temperature, pressure and concentration of electrospun polymer and/or MOF solution. In a nutshell, numerous merits of EHE have been exploited in this investigation to fabricate a novel, thin, asymmetric MMM with a reliable potential for functionalization due to the high surface area of the nanofibers, high pore interconnectivity and comparatively homogeneous pore size distribution, all of which contributed to the overall high performance of the membrane in gas separation.



Electron beam engineering of polymer membranes: high performance, antifouling, long-term stability

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Main topic: Novel membrane materials

Membrane separation systems have gained increasing importance for many different applications, e.g., in waste and surface water treatment, seawater desalination, sterilizing filtration, beverage production, or hemodialysis. Today, porous polymer membranes are predominantly fabricated from synthetic membrane materials, such as poly(ethersulfone), poly(sulfone), or poly(vinylidene fluoride).

The diverse applications necessitate the modification of the polymer in order to avoid any fouling on the hydrophobic membrane surfaces or to achieve a functionalized membrane for specific applications. When using the named polymers in water-based applications in particular, fouling is the greatest challenge. Regarding water treatment, hydrophobic interactions of the hydrophobic membrane polymer surfaces with the hydrophobic backbone of biomolecules (e.g. proteins) are a typical problem. As a result, membranes lose their permeability and energy consumption increases in order to maintain a steady flux of the membrane-based filtration system.

In order to improve the antifouling properties of micro- and ultrafiltration membranes, surface hydrophilization is a common strategy. The necessary chemical and physical properties of the polymer bulk are thus retained. Contrary to other physical activation methods such as plasma treatment or UV irradiation with UV light, electron beam treatment allows a great depth of penetration of the electrons into the polymer material (up to several cm). Since the entire surface of porous membranes affects the inner pore walls, the electron beam method shows great potential here. In addition, no photoinitiators, catalysts or other toxic reagents are required.

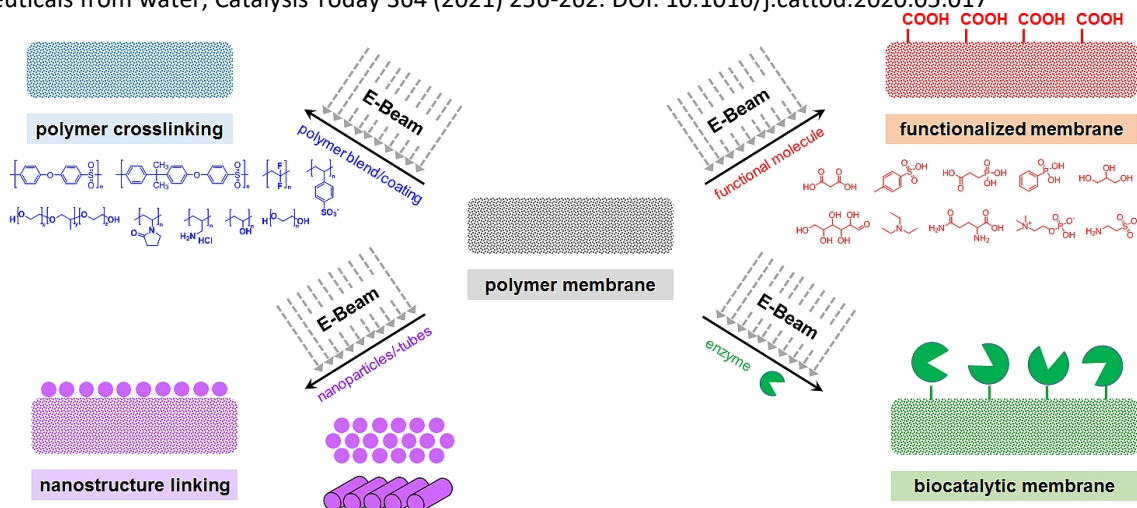
This presentation will summarize a comprehensive investigation of membrane surface engineering using electron beam irradiation. This includes permanent surface hydrophilization [1], functionalization, and catalyst immobilization [2] on different porous membrane types and polymers (see Figure 1). The resulting membranes are analyzed and characterized in detail and used in various functional tests including upscaling of the method in order to evaluate the resulting properties for possible applications in water treatment. Furthermore, theoretical calculations and simulations were carried out in combination with experimental studies to understand the underlying reaction mechanism. As a result, the electron beam engineering of membrane surfaces is now comprehensively understood in order to enable the preparation of tailored membrane surfaces.

Reference 1:

A. Schulze, B. Marquardt, S. Kaczmarek, R. Schubert, A. Prager, M. R. Buchmeiser, Electron Beam-Based Functionalization of Poly(ethersulfone) Membranes, *Macromol. Rapid Comm.* 31 (2010) 467-472. DOI:10.1002/marc.200900666

Reference 2:

J. Becker-Jahn, P. Langowski, S. Nieß, J. Griebel, A. Schulze, Photoactive polymer membranes for degradation of pharmaceuticals from water, *Catalysis Today* 364 (2021) 256-262. DOI: 10.1016/j.cattod.2020.05.017



Elucidating the effect of aliphatic molecular plugs on ion-rejecting properties of polyamide membranes

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¹Technion - Israel Institute of Technology, ²Israel Atomic Energy Commission (IAEC), ³Nuclear Research Centre - Negev

Main topic: Nanofiltration/Reverse Osmosis

Polyamide membranes are the key element of seawater desalination technology. However, further development is hampered by insufficient understanding of their complex irregular structure and rejection mechanism. Recently, we reported exposure of polyamide RO membranes to 10- and 12-carbon long aliphatic amines (“molecular plugs”) enhances the boron and salt rejection [1, 2]. The present study aims at clarifying the mechanism of plug immobilization as well as the effect on the rejection properties of polyamide. We applied electrochemical impedance spectroscopy (EIS), quartz crystal microbalance (QCM), and surface stress analysis to polyamide films, isolated from genuine RO membranes. Change in membrane conductivity, measured by EIS, was used to monitor ion-rejection properties, while molecular plug uptake was quantified by QCM. Surface stress data provide additional information on stresses developed within the film.

We observed that exposure of the film to n-decylamine solution led to up to a 10-fold irreversible decrease of membrane conductivity (Fig. 1). However, from the effect of the solution pH we concluded that irreversible uptake is mainly controlled by charge attraction, rather than hydrophobic interactions. Washing decylamine using a clean buffer led to increase in the conductivity, more significant for lower pH. For alcohols the initial drop in conductivity was subsequently reversed (Fig. 1). In turn, larger surfactant molecules produced only a monotonic decrease in conductivity, most pronounced for positively charged surfactant DTAB (Fig. 1). We hypothesized that uptake of short amphiphilic molecules within the film via hydrophobic interactions resulted in a temporary change of surface properties due to initial stresses, but could also induce plasticization of the polyamide that led to relaxation and restoration of the initial rejection properties. This was confirmed by surface stress measurements. Apparently, the effect was possible for molecules 8-10 carbons large, while longer molecules simply adsorbed on the surface and did not show this effect. Assisting plug uptake with charge interactions varying pH, significantly enhanced the mass uptake, as confirmed by QCM, and produced a stronger and partly irreversible effect of rejection properties.

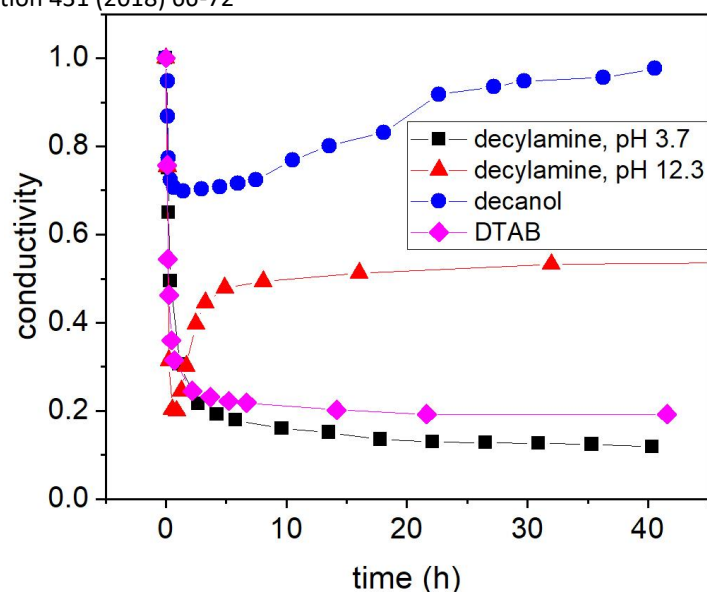
In conclusion, there still exists significant room for improving and tuning the selectivity of polyamide membranes via the insertion of appropriate plug molecules in the polyamide structure using different types of molecular interactions.

Reference 1:

S. Shultz et al., J. Mem. Sci. 546 (2018) 165–172

Reference 2:

S. Shultz & V. Freger, Desalination 431 (2018) 66-72



Enantioselective Sorption and Separation of Racemic D,L - Tryptophan on Resilient Functionalized Polyimide Membrane

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Main topic: Facilitated transport membranes

Since the discovery of chiral nature of many biological molecules and the associated selectivity of human body towards the individual enantiomers, separation of racemic mixtures has been very important, yet still difficult and expensive to achieve for large number of substances. It is of great interest for food and pharmaceutical industry to reduce the costs of food additives, supplements and enantiomeric-pure, safe drugs, and membrane processes are great candidates to do so. In this work, we examined enantioselectivity of a resilient polyimide (commercially available Matrimid) membrane in pure form and functionalized with an addition of optically active polyimide based on 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and (+)- or (-)-1,2-diaminocyclohexane (DACH) as a chiral selector. In series of pertraction (dialysis) experiments, we investigated interactions and transport of D, L - Tryptophan through the Matrimid membrane with and without the chiral selector. We found that, while the contribution of the chiral selector to the preferential sorption of L-Tryptophan increases the selectivity (for both (+)- and (-)-1,2-diaminocyclohexane), the polyimide structure itself preferentially interacts with L-Tryptophan. This observation agrees with results of simulations using molecular dynamics and the three-point interaction model. We show that selectivity and permeability of the membrane is a function of thickness of the self-standing film, where films thinner than 100 microns allow Tryptophan permeation with selectivity up to 99 %. Other experimental conditions we discuss are the temperature and choice of solvent.

Acknowledgement: This work was supported by grants of Czech Science Foundation No. 20-06264S

Enhanced stability of polyvinyl alcohol-based membranes using pectin as green crosslinker

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Main topic: Novel membrane materials

In this work, two highly water-soluble biopolymers were used to develop very stable hydrophilic membranes: these are polyvinyl alcohol (PVA) and pectin (PEC). So far, pectin was used as a blending additive in membrane production [1]. Here, it was first used as a bioderived crosslinking agent. It was hypothesized that the presence of numerous carboxyl groups would make it a good crosslinker. Neat PVA and PVA/PEC blended membranes were also prepared to compare their performance. The produced membranes were chemically, thermally, and functionally characterized. With a degree of crosslinking of about 86%, the PVA/PEC membrane with mass ratio 1:1 showed a very high stability in boiling water and in water at different acidity (pH 3 - 11). A higher Young's modulus (300%), a reduced water uptake (58%), and a resistance to degradation under the soil suggest that the structure of the PVA/PEC crosslinked membrane is more orderly compared to bare PVA membrane, due to the formation of new ester bonds pointed out by FTIR profile. The interaction between PVA/PEC crosslinked membrane and bacteria (in both solid and liquid media) blocked bacteria growth; on the contrary PVA membrane was unable to inhibit bacteria growth. Similar trend was also observed in scavenging free radical solution. PVA/PEC 1:1 crosslinked membranes with a thickness of 18 (± 2) μm were prepared by evaporation induced phase separation. They showed a stable water vapor permeability ($1.34 \cdot 10^{-4}$ ($\pm 2.15 \times 10^{-5}$) $\text{g m/h m}^2 \text{ bar}$) for 190 days of observation. Characterization in liquid phase indicated a dextran 670 kDa rejection of about 90%. The lecture will illustrate morphological and structural properties (measured by AFM and SEM) as well as it will discuss the performance in various application, including food packaging and water purification.

Acknowledgements

The authors gratefully acknowledge for the financial support the project P.O.R. Calabria FESR-FSE 2014-2020 [Project RAVEL].

Reference 1:

[1] Mohanapriya, S., Rambabu, G., Bhat, S. D., & Raj, V. (2018). Pectin based nanocomposite membrane as green electrolytes for direct methanol fuel cells. *Arabian J. Chem.*, 13, 2024–2040.

Enhancing physics-based model with machine learning to predict fouling in electro dialysis.

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¹Ghent University, ²Flemish Institute for Technological Research (VITO)

Main topic: Electro-membrane processes

To facilitate the transition to a bio-based economy, there is a need for efficient and selective separation technologies. Membrane separation technologies play a critical role in fractionating, purifying and the recovery of complex bio-based process streams and can effectuate a circular economy by closing cycles. Electrodialysis is an electro-membrane separation process where the separation of the components is based on charge characteristics and due to its selective nature and energy efficiency, it plays an important role as a separation technology. The selective extraction of amino acids and organic acids during the upstream and downstream processing steps and the detoxification of biomass during the pretreatment steps are promising applications of electrodialysis in the bio-based industry.

The major hurdle for all membrane-based separation processes is the fouling of the spacer channels and membranes. This is also valid for electrodialysis where fouling of the ion-exchange membranes during the process can be quite severe, especially when treating the complex mixture of inorganic and organic compounds and colloids in bio-based process streams. This contribution focuses on the colloidal fouling of electrodialysis. A model is developed to control the operational parameters and reduce the fouling severity, reduce cleaning frequency and, ultimately, reduce the cost of membrane replacements that make a considerable part of the operational expenses of electrodialysis treating bio-based process streams. A physics-based description of the transport processes is augmented with a machine learning model to describe the complex phenomena of colloidal aggregation and gel formation on the ion-exchange membranes. This hybrid model can predict the growth of a colloidal fouling layer, along with its effect on the electrodialysis process and quantifies the influence of the operational parameters and stack design on the fouling rate.

The model was validated with fouling experiments using a brine containing anionic polyacrylamide as a colloidal fouling component. The validation showed that by combining physics-based models with machine learning one can improve the predictive power of the model considerably while reducing the need for experimental data. This research also shows that machine learning can complement mechanistic models where fundamental knowledge on the process is lacking or computational resources are limiting.

Reference 1:

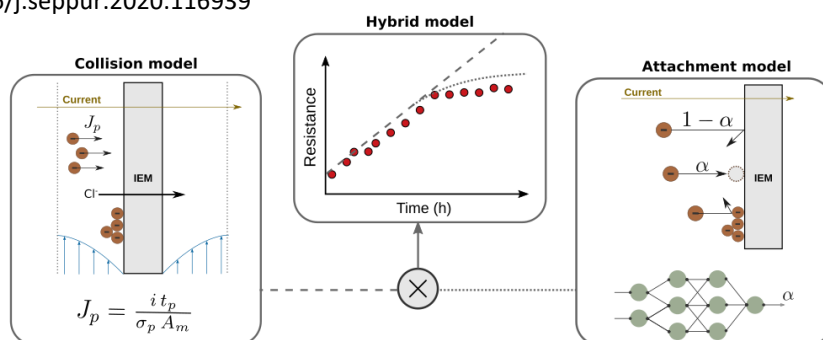
De Jaegher, B., De Schepper, W., Verliefdde, A., & Nopens, I. (2021). Enhancing mechanistic models with neural differential equations to predict electrodialysis fouling. *SEPARATION AND PURIFICATION TECHNOLOGY*, 259.

<https://doi.org/10.1016/j.seppur.2020.118028>

Reference 2:

De Jaegher, B., Larumbe, E., De Schepper, W., Verliefdde, A., & Nopens, I. (2020). Colloidal fouling in electrodialysis : a neural differential equations model. *SEPARATION AND PURIFICATION TECHNOLOGY*, 249.

<https://doi.org/10.1016/j.seppur.2020.116939>



Entanglement-enhanced water dissociation in bipolar membranes with 3D electrospun junction and polymeric catalyst

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¹European centre of excellence for sustainable water technology, Wetsus

Main topic: Electro-membrane processes

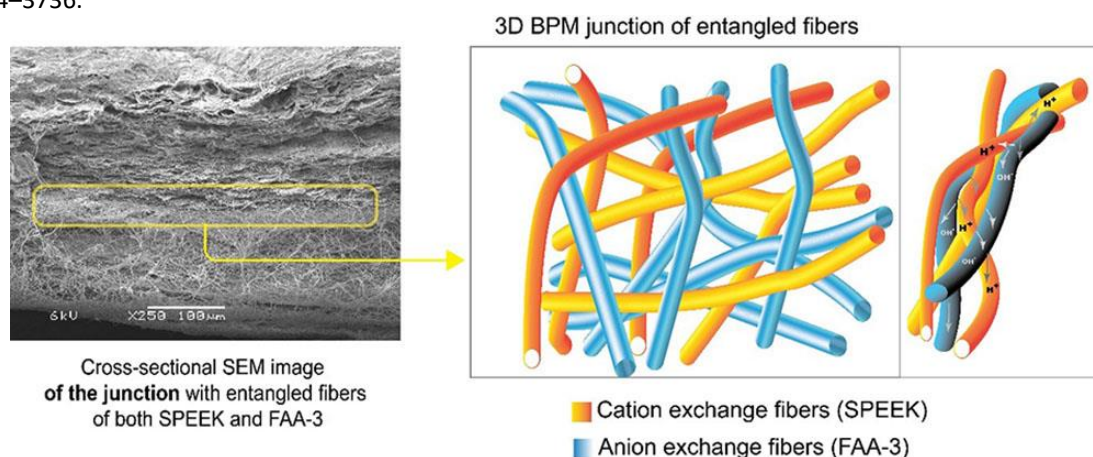
As bipolar membranes (BPMs) are increasingly used for a wider variety of applications, there is an urgent need to understand and improve the catalytic performance of BPMs for water dissociation, as well as to increase their physical and chemical stability. In this regard, electrospinning has been suggested as a promising route to produce high-performance BPMs with 2D and 3D junction structures [1]. In this work, we investigate the effect of entangling anion and cation exchange nanofibers at the junction of bipolar membranes on the water dissociation rate. In particular, in a single/double continuous electrospinning process, we have fabricated customized BPMs with a 2D (laminated) and 3D (electrospun) junction, thus modifying the BPM interface morphology while keeping the same polymeric composition [2]. The bipolar membrane with a 3D entangled junction shows enhanced water dissociation rate compared to the bipolar membrane with laminated 2D junction, with more than a 50% reduction in the membrane potential. In addition, we explored the use of poly(4-vinyl-pyrrolidone) (P4VP) as water dissociation catalyst at the junction. The bipolar membrane with incorporated P4VP catalyst and 3D junction shows a higher water dissociation rate (by a factor of 10) than the BPM with the same catalyst but a laminated 2D-junction. Moreover, the effect of 3D junction thickness on the BPM water dissociation performance and selectivity has been studied by examining different BPMs with various 3D junction thicknesses. Finally, this work demonstrates that the entanglement of the anion exchange polymer with P4VP as water dissociation catalyst in a 3D junction is promising to develop next-generation bipolar membranes with enhanced water dissociation performance.

Reference 1:

[1] C. Shen, R. Wycisk, P.N. Pintauro, High performance electrospun bipolar membrane with a 3D junction, *Energy Environ. Sci.* 10 (2017) 1435–1442.

Reference 2:

[2] E. Al-Dhubhani, H. Swart, Z. Borneman, K. Nijmeijer, M. Tedesco, J.W. Post, M. Saakes, Entanglement-Enhanced Water Dissociation in Bipolar Membranes with 3D Electrospun Junction and Polymeric Catalyst, *ACS Appl. Energy Mater.* 4 (2021) 3724–3736.



Enthalpic and Entropic Selectivity of Water and Small Ions in Polyamide Membranes

Shefer, Idit - Main Author¹; Peer-Haim, Ophir - Co-Author¹; Leifman, Olga - Co-Author¹; Epsztein, Razi - Co-Author¹
¹Technion

Main topic: Nanofiltration/Reverse Osmosis

Background

While reverse osmosis and nanofiltration polyamide membranes have been extensively utilized in water purification and desalination processes, the molecular details governing water and solute permeation in these membranes are not fully understood¹. Elucidating new transport mechanisms is a crucial step to design selective membranes for more sustainable water desalination and purification processes².

Materials and Methods

In this study, we explore water, cation (i.e., Li^+ , Na^+ , K^+ , Cs^+ , and Mg^{2+}), and anion (i.e., F^- , Cl^- , Br^- , I^- , and SO_4^{2-}) selectivity trends and transport mechanisms in loose and tight polyamide nanofiltration membranes. Applying transition-state theory, we systematically break down the intrinsic permeabilities of these species into enthalpic and entropic components by measuring their Arrhenius energy barriers and pre-exponential factors, respectively. We analyze trends in these parameters to elucidate molecular phenomena that induce water-salt, monovalent-divalent, and monovalent-monovalent selectivity at different pH values.

Results

Our results suggest that the thermal activation of ions in the form of ion dehydration is less likely in pores that are either too small or contain a charged mouth, resulting in entropically-driven selectivity with steric exclusion of hydrated ions. Alternatively, ion dehydration in larger uncharged sub-nm pores is more feasible, inducing enthalpic selectivity that is driven by differences in the ion hydration properties. The dehydration phenomenon is further emphasized by the opposite rejection trends observed for monovalent cations ($\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$) compared to monovalent anions ($\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$) with respect to the ion bare size, as well as by the opposite cation rejection trends observed in the loose ($\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$) and tight ($\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$) polyamide membranes. We also demonstrate that electrostatic interactions between cations and intrapore carboxyl groups hinder salt permeability, increasing the enthalpic barrier of the transport.

Conclusions

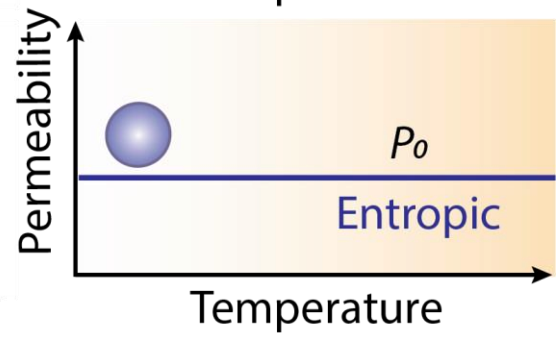
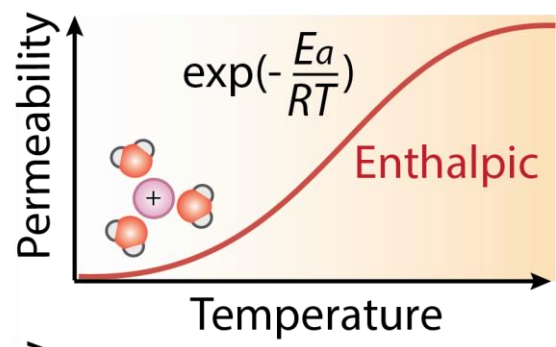
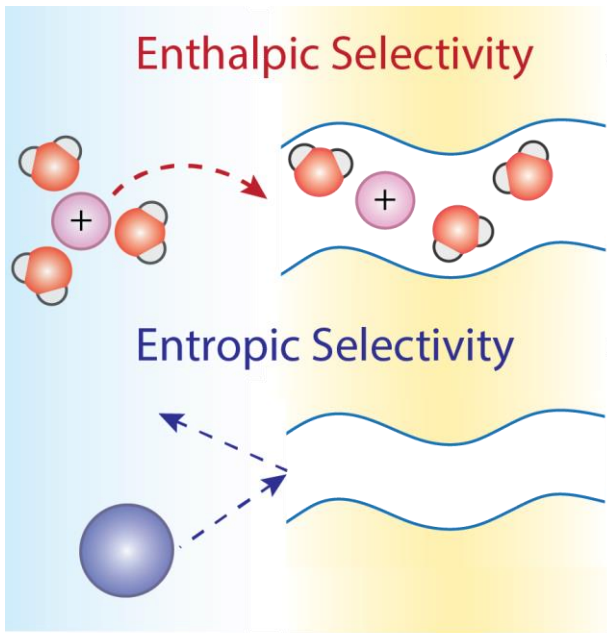
Transition-state theory can shed light on the transport of water and solutes through dense membranes and explain selectivity trends between akin ions, highlighting the role of molecular dehydration. Overall, fundamental insights from this study can strengthen the foundations required for designing membranes with improved water-solute and solute-solute selectivity for various applications.

Reference 1:

Epsztein R, DuChanois RM, Ritt CL, Noy A, Elimelech M. Towards single-species selectivity of membranes with subnanometre pores. *Nat Nanotechnol.* 2020;15(6):426-436. doi:10.1038/s41565-020-0713-6

Reference 2:

Zhao Y, Tong T, Wang X, Lin S, Reid EM, Chen Y. Differentiating Solutes with Precise Nanofiltration for Next Generation Environmental Separations: A Review. *Environ Sci Technol.* 2021;55(3):1359-1376. doi:10.1021/acs.est.0c04593



ENVIRONMENTAL IMPACTS REDUCTION OF H₂-SELECTIVE Pd MEMBRANES FABRICATED BY ELECTROLESS PORE-PLATING: THE ROLE OF INTERMEDIATE LAYERS AND SCALE-UP

ALIQUE, DAVID - Co-Author¹; Martinez Diaz, David - Co-Author; Leo, Pedro - Co-Author; Calles, José Antonio - Co-Author; Sanz, Raúl - Co-Author

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Main topic: Inorganic membranes

The production of ultra-pure hydrogen from a wide variety of feedstock through Pd-based membranes is attracting great attention due to the possibility to use a process scheme based on independent chemical reactors and separators or combining both equipment in intensified membrane reactors. The membrane fabrication has been significantly improved during the last few years, reaching very thin Pd-films onto porous substrates with excellent H₂-selectivity, high permeation capacities and mechanical stability [1]. However, their commercialization and penetration in the industry are still scarce due to the limited knowledge about their lifespan and associated economic and environmental issues. The study of the last implications during their fabrication are of key relevance to detect possible bottlenecks and select the best fabrication strategy if considering the wide variety of alternatives proposed in the specialized literature. In this context, the current study expands the first life cycle assessment focused on the preparation of Pd-based composite-membranes by Electroless Pore-Plating (ELP-PP) recently published elsewhere [2]. Based on the interesting results reached in this first work, now the use of doped CeO₂ particles with Pd nuclei as intermediate layer has been considered for the fabrication of the composite membranes onto tubular porous stainless steel with 0.1 μm media-grade, also analyzing the influence of scaling-up the fabrication process. All the associated environmental impacts for each case were estimated through ReCiPe methodology by using the software Simapro 8.5. The results evidence that climate change (CC), human toxicity (HT), acidification (AC), freshwater ecotoxicity (FWE), metal depletion (MD) and fossil fuel resources depletion (FD) are the most relevant environmental impacts generated during the manufacturing of Pd-based membranes by ELP-PP. In this context, it should be noted that these impacts were reduced up to around 50% respect to a conventional ELP-PP membrane in which no ceramic intermediate barrier was considered between the porous support and the Pd-film. Moreover, the incorporation of previously doped CeO₂ particles as intermediate layer provided a further improvement of the environmental impacts respect raw commercial ceramic particles probably due to the necessity of a minor number of ELP-PP recurrences during the synthesis procedure and the lower final Pd-thickness. Finally, an additional reduction of the environmental impacts was also achieved by scaling-up the process for the fabrication of longer membranes.

Reference 1:

D. Alique, D. Martinez-Diaz, R. Sanz, J.A. Calles, Review of supported Pd-based membranes preparation by electroless plating for ultra-pure hydrogen production. *Membranes* 8(1) (2018) 5

Reference 2:

D. Martinez-Diaz, P. Leo, R. Sanz, A. Carrero, J.A. Calles, D. Alique, Life cycle assessment of H₂-selective Pd membranes fabricated by electroless pore-plating. *Journal of Cleaner Production* 316 (2021) 128229.

Enzymatic cascade reaction by using Switchable pH-responsive membrane to produce phytotherapeutic

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Main topic: Biomimetic and bioinspired membranes

Microenvironment plays a significant role in enzymatic catalysis, which in biological membrane is strictly regulated by biomolecule compartmentalization. The artificial compartmentalization is possible by enzyme immobilization using artificial membranes. However, the co-immobilization of several enzymes, to catalyze multi-enzymatic cascade reactions in the same membrane is highly difficult, since it needs to spatially localize the enzymes in the different membrane compartments (e.g.: membrane surface, within the pores). In this work, a new biocatalytic membrane, in which two different enzymes (pectinase and β -glucosidase) in two separate membrane compartments (membrane surface and within membrane pores) were immobilized, using switchable pH-responsive membranes. The membrane pores opening and closing are regulated by pH, e.g within the range of pH 2-4.5, the pores are closed, while from 4.5 to 10 the pores are open. Besides, the membranes were functionalized with NH_2 groups to promote the enzyme immobilization based on covalent or ionic interaction.

Before immobilization, the enzymes were firstly characterized in solution by circular dichroism, light scattering and zeta potential measurements to carry out membrane biofunctionalization in conditions of low enzyme aggregation, without substantially modifying the enzyme secondary structure. Considering all the mentioned aspects, pectinase was covalently immobilized on the surface of the membrane to control membrane fouling due to pectin accumulation (pH optimum around 4), while β -glucosidase (pH optimum 6.5) was mainly immobilized within the membrane pores of the same membrane to hydrolyze oleuropein and to produce the phytotherapeutic oleuropein aglycone [1,2]. Before and after membrane biofunctionalization, the used switchable pH-responsive membranes were characterized by TEM, FESEM and FTIR. The prepared biocatalytic membranes were then tested in a biocatalytic membrane reactor, by which it is possible to hydrolyze pectin (pH 4, closed pore configuration) on the membrane surface and then to hydrolyze oleuropein (pH 6.5, open pores configuration), by using a simulated solution containing both substrates. Preliminary results demonstrated that the best immobilization procedure for β -glucosidase is adsorption (conversion: 80%), while for pectinase is covalent bond (conversion: 85%).

The authors would like to thank POR Calabria FESR-FSE 2014/2020 for the financial support to the SmartMatter project in the M-ERA.NET Call 2019 and KAUST.

Reference 1:

Gebreyohannes, A.Y., Mazzei, R., Curcio, E., ...Drioli, E., Giorno, L Study on the in situ enzymatic self-cleansing of microfiltration membrane for valorization of olive mill wastewater,. *Industrial and Engineering Chemistry Research*, 2013, 52(31), pp. 10396–10405.

Reference 2:

Mazzei, R., Yihdego Gebreyohannes, A., Papaioannou, E., Nunes S., Vankelecom, I.F.J., Giorno, L., Enzyme catalysis coupled with artificial membranes towards process intensification in biorefinery- a review, *Bioresource Technology*, 2021, 335, 125248.

Enzyme immobilization on membranes: designing methods for high enzyme loading and tunable enzyme micro-environment

Sigurðardóttir, Sigyn Björk - Co-Author

Main topic: Membrane reactors

Enzyme catalysis provides an environmentally friendly alternative to the more conventional thermochemical processes. Enzymes are easily available, biodegradable, and safe catalysts and enzymatic processes are generally operated under mild process conditions, such as at moderate temperature and pressure and in aqueous solvents. These factors, together with the exceptional catalytic efficiency, specificity, and selectivity of enzymes, make enzyme catalysis highly relevant in the development of future sustainable processes.

Enzyme catalysis may be conveniently operated in an enzymatic membrane reactor (EMR), where the main goal is to reuse the enzymes by retaining them inside the reactor while the substrates/products can freely pass through the membrane. The EMR can accommodate both free and immobilized enzymes.

In an EMR, the membrane may be applied as a support for enzyme immobilization, in addition to its function as a selective barrier. Thus, the reaction occurs in flow-through mode as the substrate passes through the membrane. This set-up aids mass transfer and the reaction equilibrium. However, a high enzyme loading and stable enzyme immobilization must be ensured to allow high reaction efficiency and minimal loss of enzymes.

We have investigated enzyme immobilization methods that meet the abovementioned design objectives; high enzyme loading and stability.

First, we applied fouling-induced enzyme immobilization for the immobilization of glycerol dehydrogenase in a membrane support layer. By filtering the enzyme feed solution through the membrane in reverse mode, the enzymes are trapped inside the pores, which ultimately creates multiple parallel enzymatic microreactors with ultra-high enzyme loading. Different support sealing methods and their effects on enzyme stability and the performance of the system were investigated.

Moreover, we introduced different polyelectrolytes and nanoparticles to the enzyme immobilization systems and investigated the ability to control the microenvironment of the enzymes using such methods.

Estradiol Removal by Adsorptive Coating on a Microfiltration Membrane

Niavarani, Zahra - Main Author; Breite, Daniel - Co-Author; Abel, Bernd - Co-Author; Schulze, Agnes - Co-Author

Main topic: Microfiltration/Ultrafiltration

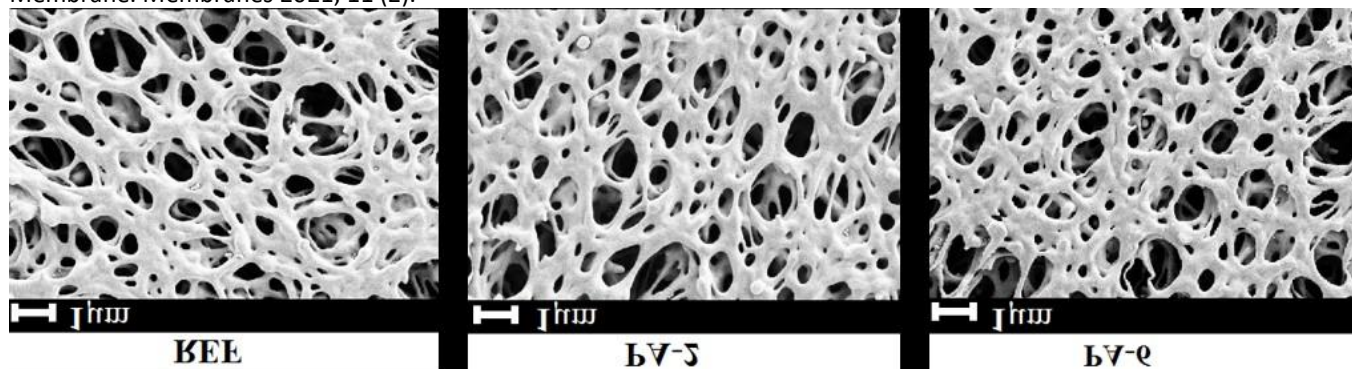
Humans and aquatic species are frequently exposed through the water to substances that cause disruption of the endocrine system, called endocrine-disrupting chemicals (EDC). This exposure has become a serious environmental and health problem worldwide [1]. In this study, the removal of a highly potent EDC, 17 β -Estradiol (E2) in water using adsorber membrane is achieved. The Polyethersulfone (PES) membranes were modified with a hydrophilic coating functionalized by amide groups. The modification was performed by the interfacial reaction between an amine monomer and an acid monomer on the surface of the membrane using electron beam irradiation. The results showed that the adsorption capacities of modified PES membranes toward E2 are >60%, while the unmodified PES membrane had an adsorption capacity up to 30% for E2 under similar experimental conditions, i.e., an enhancement of a factor of 2. The X-ray Photoelectron Spectroscopy (XPS) analysis revealed that the application of the thin amide layer changed the chemical composition measured at the membrane surface, and a significant increase in nitrogen on the surface of the membrane was detected. Since the reference PES membrane does not contain any nitrogen, this effect indicates that amide functionalities were formed on the membrane surface. It can rather be discussed that the successful formation of hydrogen bonds between E2 and amide coating is responsible for such high adsorption capacities of the modified membranes toward E2. Adding toluene enhances the uptake further by swelling the membrane and possibly providing higher active surface area with an adsorption capacity of 0.82 $\mu\text{g cm}^{-2}$ [2]. The modified membranes also had a slightly higher water wettability and water permeance compared to those of the unmodified PES membranes. The pore structure on the other hand was not changed which indicates a very thin or even monomolecular layer of the amide modification.

Reference 1:

Yager, J. D.; Davidson, N. E., Estrogen Carcinogenesis in Breast Cancer. *New England Journal of Medicine* 2006, 354 (3), 270-282

Reference 2:

Niavarani, Z.; Breite, D.; Prager, A.; Abel, B.; Schulze, A., Estradiol Removal by Adsorptive Coating of a Microfiltration Membrane. *Membranes* 2021, 11 (2).



Evaluating sustainable materials for membrane separations through molecular simulations: the case of Polyhydroxyalkanoates (PHA)

Papchenko, Kseniya - Main Author¹; Ricci, Eleonora - Co-Author²; De Angelis, Maria Grazia - Co-Author¹

¹University of Edinburgh, ²University of Bologna

Main topic: Novel membrane materials

Polyhydroxyalkanoates (PHA) are a family of linear optically active semi-crystalline polyesters produced by bacterial fermentation, known for their overall sustainability, including biodegradability and biocompatibility. PHA are also characterized by thermoplasticity and good mechanical properties, comparable to those of commercially relevant standard polymers.

The gas transport properties of these materials are still scarcely characterized experimentally, and their determination is complicated by a number of uncertainty sources, such as a time-dependent degree of crystallinity. In this study we aim at evaluating the physicochemical and transport properties of such materials with molecular simulations, to gain information about their applicability in the membrane gas separation field. In order to draw correlation between the molecular structure and the performance of these materials, three homopolymers and two copolymers of the PHA family were considered:

- poly(3-hydroxybutyrate) (P3HB);
- poly(3-hydroxyvalerate) (P3HV);
- poly(4-hydroxybutyrate) (P4HB);
- poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV);
- poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (PHBB).

Molecular models of each material were simulated using Molecular Dynamics (MD), obtaining amorphous density and solubility parameter values, that were successfully validated with experimental data found in literature. The simulated values of radius of gyration, accessible free volume, density, cohesive energy and elastic modulus of the amorphous phase of different copolymers were correlated to their chemical composition.

Sorption and diffusion in the polymers were then analysed for two gases, CH₄ and CO₂, by means of Widom insertion method and MD simulations. The results were compared with experimental values, obtained through sorption tests at different temperatures, performed on PHBV with 8% of 3-hydroxyvalerate monomers purchased from Merck-Sigma.

Reference 1:

H. Mitomo, N. Morishita, Y. Doi, "Structural changes of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) fractionated with acetone-water solution", *Polymer*, 1995, 36, 2573-2578.

Reference 2:

H. Mitomo, W.-C. Hsieh, K. Nishiwaki, K. Kasuya, Y. Doi, "Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) produced by *Comamonas acidovorans*", *Polymer*, 2001, 42, 3455-3461.

Evaluation of different ultrafiltration membranes as possible pre-treatment in view of future recovery of phenolic compounds from olive oil washing wastewater

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¹University Research Institute for Industrial, Radiophysical and Environmental Safety (ISIRYM), Universitat Politècnica de València, Spain, ²Department of Chemical and Nuclear Engineering, Universitat Politècnica de València, Spain

Main topic: Microfiltration/Ultrafiltration

The production of olive oil generates wastewater with a high organic load and toxicity due to the high concentration of phenolic compounds. In recent years, the study on the treatments of these wastewaters has been intensified together with the search for a process to recover the phenolic compounds due to their outstanding antioxidant potential [1,2]. Seven ultrafiltration membranes of different MWCOs (4, 5, 10, 15 and 50 kDa) and materials (PES; PESH, RCA and ZrO₂-TiO₂) were assessed as a possible pre-treatment of an olive oil washing wastewater. The evolution of permeate flux over time and the rejection of chemical oxygen demand (COD) and phenolic compounds were evaluated to find the best operating conditions to obtain a permeate with low organic matter but rich in phenolic compounds, to then be treated with another membrane process (nanofiltration and/or forward osmosis). The samples were taken from a two-phase continuous centrifugation olive oil milling plant located in the Valencian Community (Spain). The working conditions were crossflow velocities (CFV) between 1.5 to 4.0 m·s⁻¹ and transmembrane pressures (TMP) between 1 to 3 bar at 25°C.

The membranes with lower MWCO showed stable permeate fluxes without significant changes over time. All the membranes were able to effectively reduce the turbidity (average over 95 %) and colour (average over 65%). All the membranes enriched the permeate in phenolic compounds (fig. 1), with UP005 being the one that presented the best performance.

With the exception of UH050, all organic membranes were regenerated with a simple water rinsing with osmotic water at 35 °C. However, the ceramic membranes and the UH050 required a chemical cleaning (1% v/v of P3 Ultrasil 115). Modelling was carried out to determine the predominant fouling mechanism for each membrane. Fouling was produced by the combination of several mechanisms. For the organic membranes, complete pore blockage was the predominant mechanism, while for the ceramic ones it was cake formation.

The UP005 membrane was selected as the optimal for the pre-treatment of this type of water for a further recovery of phenolic compounds.

Abbreviations: MWCO: molecular weight cut-off; PES: Polyethersulfone; PESH: Permanently hydrophilic polyethersulfone; RCA: Regenerated cellulose acetate.

Reference 1:

A. El-Abbassi, H. Kiai, J. Raiti, and A. Hafidi, "Application of ultrafiltration for olive processing wastewaters treatment," *J. Clean. Prod.*, vol. 65, pp. 432–438, 2014, doi: 10.1016/j.jclepro.2013.08.016.

Reference 2:

M. Volpe et al., "One stage olive mill waste streams valorisation via hydrothermal carbonisation," *Waste Manag.*, vol. 80, pp. 224–234, 2018, doi: 10.1016/j.wasman.2018.09.021

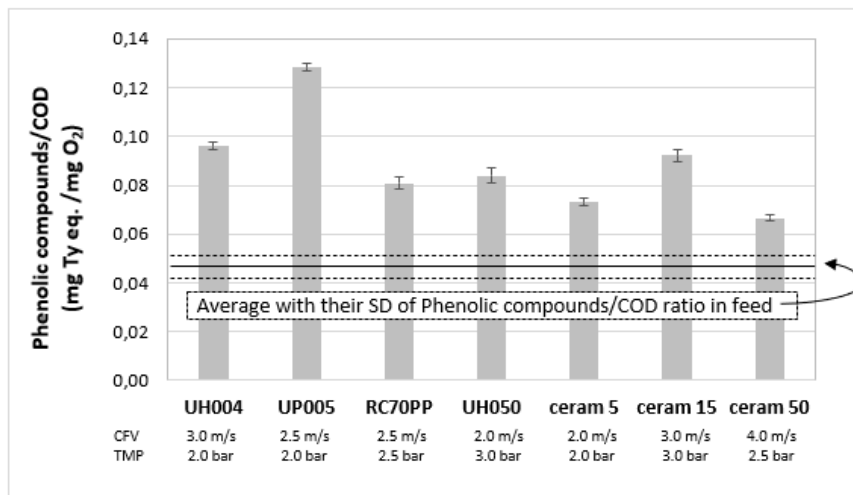


Fig. 1. Phenolic compounds/chemical oxygen demand (COD) ratio in the permeate streams at the best operating conditions for each membrane

Abbreviations: TMP: transmembrane pressure; CFV: cross flow velocity; UH004: PESH membrane with MWCO of 4kDa (Microdyn Nadir); UP005: PES membrane with MWCO of 5kDa (Microdyn Nadir); RC70PP: RCA membrane with MWCO of 10kDa (Alfa Laval); UH050: PESH membrane with MWCO of 50 kDa (Microdyn Nadir); ceram 5: ZrO₂-TiO₂ ceramic membrane with MWCO of 5 kDa (Tamy Industries); ceram 15: ZrO₂-TiO₂ ceramic membrane with MWCO of 15 kDa (Tamy Industries); ceram 50: ZrO₂-TiO₂ ceramic membrane with MWCO of 50 kDa (Tamy Industries).

Evaluation of the toxicity removal by osmotic membrane bioreactor coupled to membrane distillation to treat sewage containing pharmaceutically active compounds

Santos, Carolina - Main Author; Arcanjo, Gemima - Co-Author; Oliveira, Caique - Co-Author; Santos, Lucilaine - Co-Author; Amaral, Míriam - Co-Author

Main topic: Membrane bio-reactors

Recent studies have constantly discussed the partial removal of micropollutants in conventional wastewater treatment plants (WWTPs) since pharmaceutically active compounds (PhACs), and other recalcitrant contaminants are found in raw and treated wastewater, surface water, and drinking water worldwide. PhACs can be toxic to aquatic organisms even at low concentrations, in the range of ng L^{-1} and $\mu\text{g L}^{-1}$, which several studies have demonstrated. This fact shows the importance of advanced technologies to remove these contaminants, such as membrane bioreactors, which have shown satisfactory efficiencies in removing several micropollutants. In addition, ecotoxicological tests during wastewater treatment are essential to measuring the risks promoted to the aquatic environment from the release of contaminants. These tests, in general, are laboratory analyzes that use living organisms exposed for established periods to quantify or qualify the toxic effect of a sample. However, despite the importance of ecotoxicological tests, few studies have evaluated the toxicity removal by membrane bioreactors for treating wastewater with PhACs. In this context, the study aimed to evaluate the removal of toxicity from sewage fortified with seven PhACs (17 α -ethinylestradiol, ketoprofen, fenofibrate, fluconazole, loratadine, prednisone, and betamethasone) with a concentration of $2 \mu\text{g L}^{-1}$ each, when treated by an osmotic bioreactor coupled with membrane distillation (AnOMBR-MD). For this, the bioreactor was operated for 32 days. The collected samples (feed solution: sewage with PhACs; mixed liquor: bioreactor supernatant; and distillate: final effluent) had their toxicity evaluated through tests using the bacteria *Aliivibrio fischeri*, according to ABNT NBR 15411-3. The results showed that the feed solution was not toxic for the organism, while the mixed liquor was classified as toxic, with an effect concentration (EC_{50}) of 19.9% (for an exposure time of 30 min), due to the accumulation of micropollutants in the reactor since the membranes present high rejection to dissolved compounds. The distillate was not considered toxic to *A. fischeri*, with effects above 100%. The results indicate that AnOMBR-MD was efficient in removing toxicity to the bacteria. However, tests with other organisms are also needed.

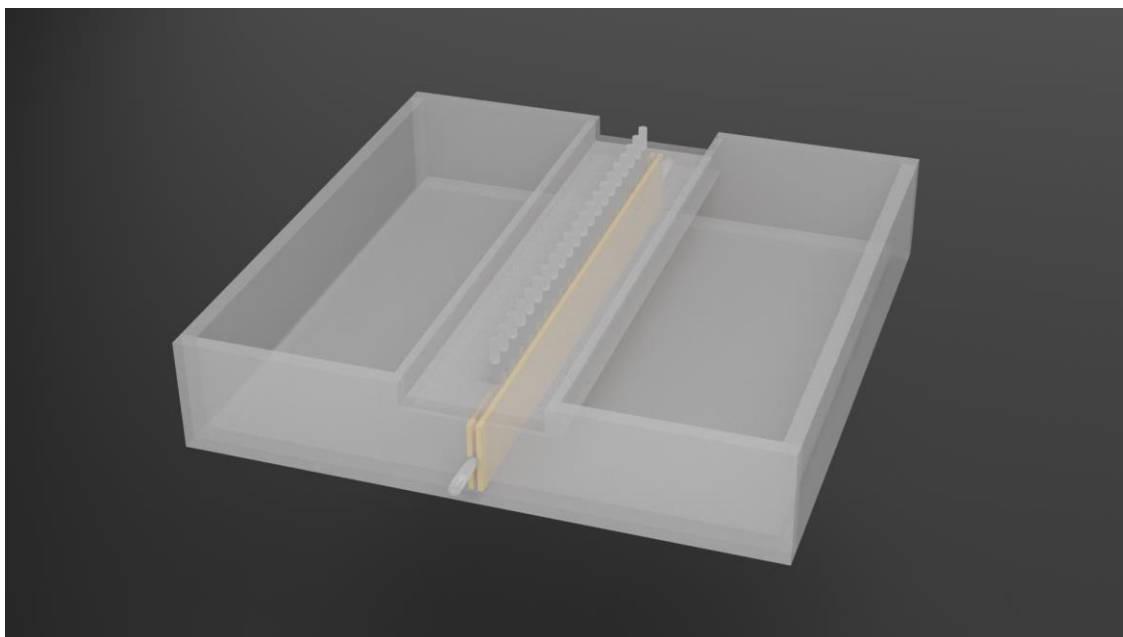
Experimental analysis of electrodialysis in milifluidic flow-through systems

Kovář, Petr - Co-Author¹

¹University of Chemistry and Technology, Prague

Main topic: Electro-membrane processes

Electrodialysis is an electro-membrane separation process traditionally used to remove small ions from processed water solutions. Desalination of the sea or brackish waters is a typical application of electrodialysis. Ion-exchange membranes constitute a significant part of the electrodialysis units because they provide selectivity toward the transport of the ionic components. DC voltage connected to a stack of membranes drives the movement of ions through the respective membranes, which produces two output water solutions. The solution characterized by a high ionic concentration is referred to as concentrate. The solution of low ionic concentration is denoted as diluate. This work focuses on the experimental analysis of the electrodialysis in self-constructed milifluidic flow-through systems. The constructed milifluidic electrodialysis units contain specific ports that allow us to withdraw solution samples from the desalination channel and therefore measure the concentration and pH of the samples. We performed an in-depth experimental study investigating the effect of the applied processed solution flow rate and the connected electric current load on the overall desalination efficiency and the differential decrease in the ionic concentration along the same channel. We reconstructed a 3D profile of ionic concentration in the channel for different values of the applied electric current. We observed that (i) the concentration of the desalted solution changes both in the lateral and vertical direction (with respect to the channel), (ii) interestingly, only minor differences in the concentration were seen in the transverse direction, (iii) the concentration profile suggest an essential role of natural convection in the ionic transport from solution bulk to membrane surfaces, (iv) the averaged concentration profile along the channel is approximately linear until reaching a critical current density, (v) nonlinear concentration profiles establish for current densities larger than the critical one. The conducted research is to deepen the understanding of quite complex reaction-transport processes occurring in electrodialysis units.



Experimental investigation of direct contact membrane distillation for gold mine wastewater treatment

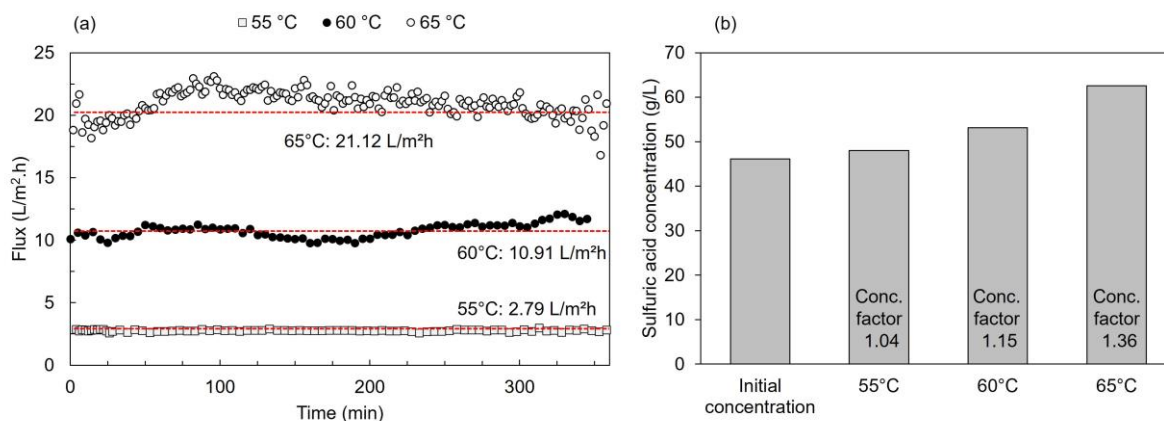
Ramos, Ramatisa - Main Author¹; Lebron, Yuri - Co-Author¹; Moreira, Victor - Co-Author¹; Foureaux, Ana - Co-Author¹; Santos, Lucilaine - Co-Author¹; Amaral, Míriam - Co-Author

¹Universidade Federal de Minas Gerais (Brazil)

Main topic: Membrane contactors and membrane distillation

Direct contact membrane distillation (DCMD) is an alternative to conventional membrane separation processes (MSPs) when considered for the treatment of wastewater produced at high temperatures. Unlike MSPs, whose operation has a temperature limit to ensure membrane integrity, DCMD benefits from the residual heat of these wastewaters to promote its driving force. An example of wastewater produced at a high temperature is the one derived from the gold processing industry. To achieve a higher recovery of gold, most industries adopt a process of pressure hydrometallurgy that occurs at a high temperature (~210°C) and pressures (~20 atm), and the ultimate result is wastewater with an outlet temperature of 60°C. The same temperature was considered in our DCMD experiments (in addition to 55 and 65°C; permeate temperature: 25°C), which aimed for water recovery and wastewater concentration. The system was operated for 300 min in which both feed and permeate flow rates were kept at 0.55 L/min. The increment in permeate mass was monitored at regular intervals of 5 min. It was used a commercial polymeric membrane made of polytetrafluoroethylene (PTFE) with an effective area of 0.0042 m². The results demonstrated that there was no flux decay during the tests (Figure 1(a)), which led to higher recovery rates at higher temperatures (from 3.81 to 26.26%). Regardless of the temperature, the DCMD was capable to achieve rejections greater than 99.86% for all ions in the feed (including Fe, Ca, Al, Cu, Mg, Ni, As, Mn, Co, and SO₄²⁻), demonstrating the system robustness in the treatment of the mining wastewater. The increase in sulfuric acid concentration in the concentrate (Figure 1(b)) allows its recovery at higher efficiency by other technologies such as solvent extraction and ion exchange resins. Furthermore, the calculated temperature polarization coefficient was 0.807-0.714 showing that both mass and heat transfer resistance played a role in the total resistance. Finally, the physical and chemical cleanings were able to recover upwards of 96.7 and 99.4 of the initial water flux respectively.

Figure 1. (a) MD permeate flux and (b) sulfuric acid concentration in MD concentrate.



Experimental Measurement and Modelling of Sorption of Ternary Gas Mixtures of CO₂, CH₄ and C₂H₆ in PIM-1

Ricci, Eleonora - Co-Author¹; Benedetti, Francesco Maria - Co-Author^{1,2}; Noto, Antonella - Co-Author; Jin, Jianyong - Co-Author³; Merkel, Timothy - Co-Author⁴; De Angelis, Maria Grazia - Co-Author^{1,5}

¹University of Bologna, ²Massachusetts Institute of Technology, ³The University of Auckland, ⁴Membrane Research & Technology Inc., ⁵University of Edinburgh

Main topic: New characterisation methods

Background

Gas separation with dense polymeric membranes follows the solution-diffusion mechanism. In the case of mixtures containing gases with high solubility differences, such as CH₄ and CO₂, **solubility plays a predominant role** compared to diffusivity [1]. However, often only pure-gas solubility is measured, and the very few measurements of solubility of gas mixtures in polymers reported are for the case of binary mixtures. In applications such as natural gas upgrading, however, the presence of other components and contaminants can significantly alter the performance of the membrane, due to **plasticization** and **competitive exclusion**.

Materials and Methods

To characterize these effects, we measured the **sorption isotherms** of C₂H₆, CO₂, and CH₄ in PIM-1, in binary and ternary conditions, using a pressure decay apparatus, working at constant composition and variable pressure of the gas phase. A **new measurement protocol** was designed to measure sorption of **ternary gas mixtures** for the first time [2]. The Non-Equilibrium Lattice Fluid (**NELF**) model (Doghieri, Sarti G.C., *Macromolecules* 24,7885-7896, 1996) was applied to predict binary and ternary sorption isotherms, using only pure-gas parameters as input.

Results

The results show strong competitive sorption effects in all binary and ternary cases analyzed. In the binary cases, both CO₂ and C₂H₆ have a strong exclusion power over CH₄, whereas the effect of CH₄ on the two gases is limited. Surprisingly, **C₂H₆ has a strong exclusion power** over CO₂ as well, even though these gases have very similar condensability and pure-gas sorption in PIM-1. In the ternary case, the superposition of the effects highlighted in binary tests is observed: both CO₂ and CH₄ are excluded due to the presence of C₂H₆, while C₂H₆ solubility is barely altered compared to pure-gas conditions. Overall, **the effect of C₂H₆ on CO₂/CH₄ solubility-selectivity is modest**, compared to the corresponding binary case. The **NELF model predictions are in good agreement** with the data, indicating that the model is a reliable tool to study mixed-gas sorption, even in complex scenarios.

Reference 1:

1. Ricci E., Benedetti F.M., Dose M.E., De Angelis M.G., Freeman B.D., Paul D.R., Competitive sorption in CO₂/CH₄ separations: the case of HAB-6FDA polyimide and its TR derivative and a general analysis of its impact on the selectivity of glassy polymers at multicomponent conditions, *J. Membr. Sci.* 612, 118374, 2020.

Reference 2:

2. Ricci E., Benedetti F.M., Noto A., Merkel T.C., Jin J., De Angelis M.G., Enabling Experimental Characterization and Prediction of Ternary Mixed-Gas Sorption in Polymers: C₂H₆/CO₂/CH₄ in PIM-1, *Chemical Engineering Journal*, 130715, 2021.

Effect of C₂H₆ on CO₂/CH₄ solubility in PIM-1

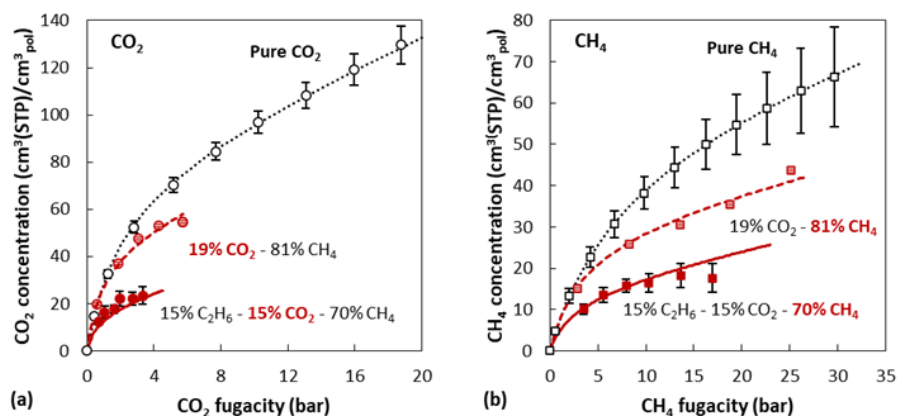


Figure 1. Third component (C₂H₆) effects on CO₂ and CH₄ solubility in PIM-1 at 35 °C. Lines represent NELF model predictions of pure- and mixed-gas sorption isotherms. Binary 19-81% CO₂/CH₄ mixed-gas sorption test: [Vopička et al. J. Membr. Sci. 459, 246-276, 2014.](#)

CO₂/CH₄ solubility-selectivity in PIM-1 for CO₂/CH₄/C₂H₆ mixtures

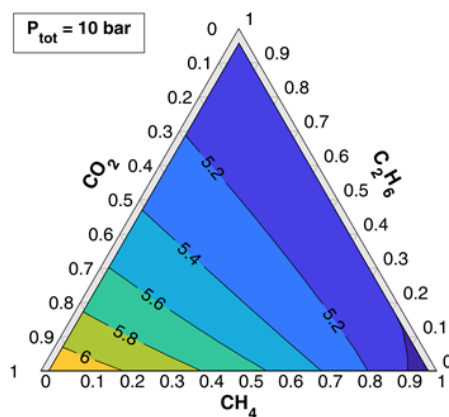


Figure 2. Ternary diagrams of CO₂/CH₄ solubility-selectivity as a function of the composition of the CO₂/CH₄/C₂H₆ mixtures in PIM-1 at 35 °C and 10 bar total pressure, calculated with the NELF model. The axes represent the molar fraction of each component in the gas mixture.

EXPLORING THE PERFORMANCE OF ORGANIC MEMBRANES FOR THE ORGANIC-SOLVENT ULTRAFILTRATION OF AN ETHANOL-BASED EXTRACT FROM TWO-PHASE OLIVE MILL WASTEWATER

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¹Research Institute for Industrial, Radiophysical and Environmental Safety (ISIRYM), Universitat Politècnica de València,

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Main topic: Microfiltration/Ultrafiltration

The major residue of the olive oil industry is the two-phase olive mill waste (TPOMW) (or *alperujo*). Despite its large environmental impact, it has been demonstrated its potential as a source of bioactive compounds, such as polyphenols.

Through an ultrasound-assisted solid-liquid extraction, it is possible to recover a high concentration of phenolic compounds from TPOMW (near 7 g/kg). According to our results, the best recoveries can be obtained by using ethanol/water 50:50 (v/v) as an extractant [1]. However, the alcoholic character of this extract hinders the purification of the obtained polyphenols by membrane technology.

Considering the advantages of membrane processes, such as ultrafiltration, to separate biophenols from the concomitant organic matter, it is of high interest to develop a methodology to ultrafiltrate TPOMW extracts, even if ethanol is present at considerable percentages.

In this contribution, our ongoing experiments to achieve satisfactory rejection and permeate flux values to purify phenolic compounds will be discussed. First, the effect of different conditionings to prepare the membranes for their contact with ethanol has been investigated. One promising approach consists on submitting the membrane to a gradual increase of the ethanol percentage. An increase of a 10% was performed after 24 hours of solvent-membrane contact, until the achievement of the 50%. Alternatively, a direct immersion in 50% ethanol for 2 hours was considered. Polymeric membranes, such as UP005 (Microdyn Nadir), UF010104 and UF010801v3 (SolSep) were tested. When the best pre-treatment was selected, the membranes were used to ultrafilter a TPOMW extract. A dead-end stirred cell was employed. Three operating pressures were studied for each membrane, in the range of 1-5 bar.

All permeates were subjected to liquid chromatography coupled to mass spectrometry to obtain the distribution of the phenolic profile and calculate the rejection of each molecule. Their purity was increased, as color and total dissolved solids were rejected in a range of 70 - 100 % and 50 - 99 %, respectively, whereas the polyphenols were hardly retained and were recovered in the permeate.

These results suggest that an adequate pre-conditioning permits the recovery of bioactive compounds contained in TPOMW by solid-liquid extraction followed by ultrafiltration.

Reference 1:

[1] C.M. Sánchez-Arévalo, H. Ellicott, M.-C. Vincent-Vela, S. Álvarez-Blanco, Assesment of several organic and inorganic membranes to ultrafilter a phenolic extract from two-phase olive mill wastewater, in: II Int. Congr. Water Sustain., Barcelona, 2021.

Fabrication of functionalized hollow fiber membranes for aqueous applications

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¹EMI Twente, University of Twente

Main topic: Industrial applications and scale-up

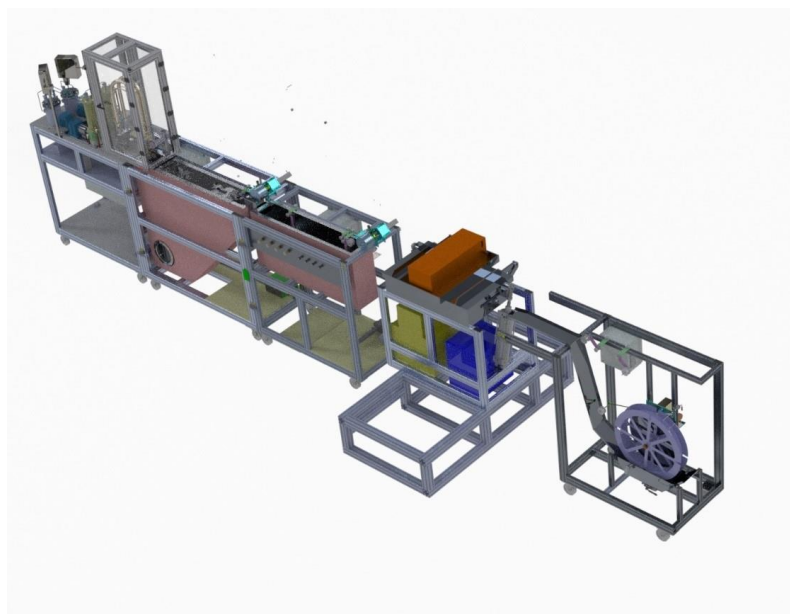
The EU-project INNOMEM develops and organizes a sustainable open innovation test bed (OITB) for innovative scale-up of nano-enabled membrane products. Potential clients can access the services of various service providers through a single entry point (SEP) to develop, test and adopt, novel high-performance membranes to their specific needs. Within the project 14 pilot lines are upgraded/upscaled and 10 showcases carried out to validate the OITB-concept.

We will present the upgrade of our pilot hollow fiber spinline (Figure 1) and first results of the showcase we carry out together with NX Filtration. The pilot spinline is equipped with a winder to allow fabrication of larger bundles of hollow fiber membranes with sufficient length to allow making full scale modules. Consistent quality is achieved by proper in-line dope preparation (mixing, degassing and filtration) and precise control of the area around the air gap/chimney where the most crucial step of the membrane formation process takes place. Furthermore, most solvent can be removed prior to collecting the fiber by making multiple passes in the rinsing bath.

Within INNOMEM the pilot line will be equipped with integrated in-line surface modification technology by means of electro-beam, which will be used to develop a next generation of water purification membranes. Often the performance of hollow fiber membranes is enhanced by modifying the surface off-line batch-wise in one or several post-treatment steps. The purpose of such a modification is to obtain e.g. better chemical stability, higher rejection or reduced fouling. Its off-line nature makes the process time-consuming, cost-ineffective and prone to errors. It would be a major improvement if these modifications can be applied in-situ during the initial fabrication of the membranes.

Treatment by E-beam can improve the stability and potentially enhance the selectivity of the separation layer. Furthermore, the penetration depth of the E-beam allows for modifications not only at a visible surface (as with UV) but also within a porous structure or at the inner side of the membrane. Moreover, modifications (e.g. crosslinking) can be achieved without the addition of chemical agents.

Acknowledgement: INNOMEM has received funding from the European Union's Horizon 2020 Research and Innovation Program under Grant Agreement N° 862330. <https://www.innomem.eu/>



Fabrication, characterization and gas transport in films of poly(hydroxyalkanoate)s casted from different solvents

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¹University of Edinburgh, ²University of Bologna

Main topic: Novel membrane materials

Poly(hydroxyalkanoate)s (PHA) are a family of linear optically active polyesters produced by bacterial fermentation and known for their overall sustainability, including fully renewable origin, biodegradability in many environments and physiological biocompatibility. Because of their thermoplasticity and good mechanical properties, somehow similar to those of commercially relevant standard polymers, a study aimed at correlating their molecular structure to their behaviour in terms of transport properties was initiated.

The case study is a random poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) copolymer (experimental grade) containing approx. 75% mol of 3-hydroxybutyrate and approx. 25% mol of 3-hydroxyvalerate (HV) units. Compared to pure homopolymer poly(3-hydroxybutyrate) (PHB), the simplest and most diffused polymer of the PHA family, PHBV is more flexible, transparent and less crystalline.

Several solvents, namely chloroform (CHCl₃), dimethylcarbonate (DMC), dimethylformamide (DMF), formic acid (HCOOH), and acetic acid (CH₃COOH), were chosen for membrane production. The solvent casting protocol was optimized for each solvent in order to produce self-standing membranes, suitable for further characterization.

The thermal properties of PHBV-based membranes were investigated by differential scanning calorimetry (DSC), their structure and physical properties were investigated by Fourier Transform Infrared Spectroscopy (FT-IR), by Gel Permeation Chromatography (GPC), and by Scanning Electron Microscopy (SEM). Ultimately, the transport properties were analysed through permeability and sorption tests.

The choice of solvent and of the casting protocol affects significantly both structural and thermal properties of the material. In addition, the presence of HV monomeric units destabilises the crystalline structure, typical of PHB, causing the on-set of melting at low temperatures and accelerated secondary crystallisation.

From the point of view of transport properties, PHBV presents a mixed behaviour. It is characterized by the solubility-driven selectivity and reduced size-sieving ability although a direct dependence of permeability from the kinetic diameter of penetrants is observable.

The ultimate purpose of this project is to promote industrial sustainability through the analysis of potential applicability of bio-based polymers in typical industrial applications.

Reference 1:

Sudesh, K., Abe, H. & Doi, Y. Synthesis, structure and properties of polyhydroxyalkanoates: Biological polyesters. *Prog. Polym. Sci.* 25, 1503–1555 (2000)

Reference 2:

Galiano, F. et al. Advances in biopolymer-based membrane preparation and applications. *J. Memb. Sci.* 564, 562–586 (2018)

Fast water transport through biomimetic reverse osmosis membranes embedded with peptide-attached (pR)-pillar[5]arenes water channels

Lim, Yu Jie - Co-Author¹

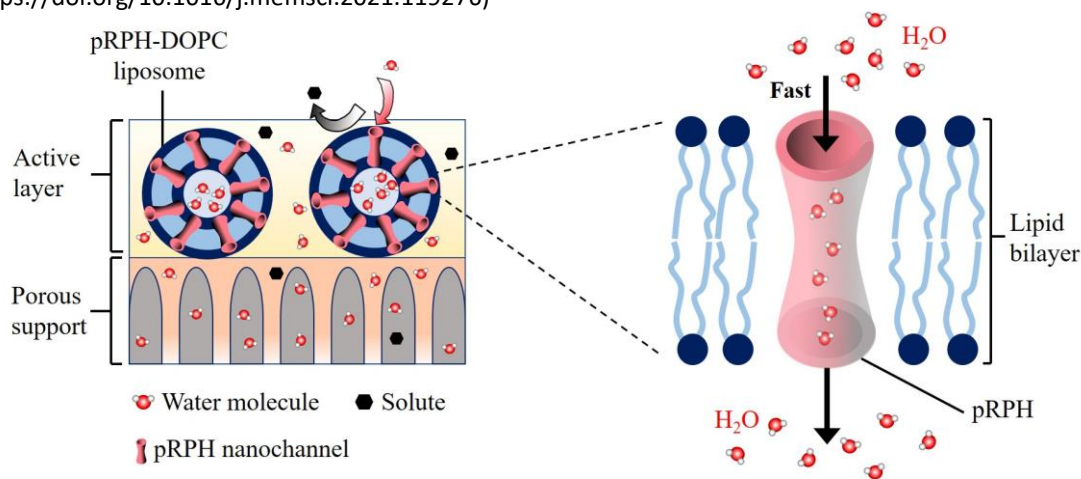
¹Singapore Membrane Technology Centre (SMTC)

Main topic: Biomimetic and bioinspired membranes

This study examined the feasibility and performance of a nanochannel-based biomimetic membrane (NBM) for brackish reverse osmosis (RO) desalination. Two types of peptide-attached synthetic nanochannels, (pR)-pillar[5]arenes (pRPH) and (pS)-pillar[5]arenes (pSPH), were incorporated into liposomes. pSPH is a diastereomer of pRPH and was used as a negative control (*i.e.* mutant) to pRPH in this work. The nanochannel-containing liposomes (*e.g.* pRPH-liposomes) were then immobilized into the active layer of the RO membranes via *in situ* interfacial polymerization on the top of a polysulfone support membrane to form NBM-pRPH membranes. To maximize the potential and benefits of the NBM-pRPH membrane, the physical characteristics of the polyamide layer was further tuned using some additives and the eventual membrane was named as NBM-pRPH-A. The NBM-pRPH-A membrane exhibited a water permeability of $6.09 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and 98.2% NaCl rejection under a 15.5 bar applied pressure using 2000 mg L^{-1} as feed solution. The 62% flux increment with respect to the pristine control is postulated to arise from a thinner, less cross-linked (more free volume) and more hydrophilic active layer as well as the possible supplementary transport pathways of the pRPH-liposomes. The performance of the NBMs under differential feed pressures and temperatures further exemplifies the water permeation property of the pRPH nanochannels. Accordingly, the NBM-pRPH-A gave a water permeability higher than commercial RO membranes tested in this work (DuPont BW30 and Hydranautics ESPA2) as well as other RO membranes reported in the literature. This study provides a tangible foundation for the development of NBMs for brackish RO desalination.

Reference 1:

Lim, Y. J., Goh, K., Lai, G. S., Ng, C. Y., Torres, J., & Wang, R. "Fast water transport through biomimetic reverse osmosis membranes embedded with peptide-attached (pR)-pillar[5] arenes water channels." *Journal of Membrane Science* (2021): 119276. (<https://doi.org/10.1016/j.memsci.2021.119276>)



Flexible Diamond Fibers: From Fabrication to Application

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Main topic: Advanced fabrication methods

The combination of different materials classes for membrane applications offers the unique possibility to take advantage of different materials properties. The fabrication of such hybrid materials is therefore an aspired path to add new functionalities to a membrane. For instance, membranes or woven meshes that are able to conduct an electrical current or selectively attract ions from a liquid phase through an electrical potential are of great interest for desalination, membrane fouling mitigation, energy storage applications or even catalysis. However, a high electrical conductivity is often only found in brittle non-flexible inorganic materials which limits their utilization for membrane applications.

In this contribution, flexible diamond fibers, the components of diamond cloths, are produced through overgrowing conductive carbon fibers (CF) with a thin boron-doped diamond (BDD) film as a shell using a microwave plasma enhanced chemical vapor deposition process [1]. To improve the adhesion of the BDD film on CF, an interlayer of TiC is introduced between the BDD film and the CF surface. This interlayer also impedes significant H₂ etching of the CFs during the diamond deposition process. Finally, the as-grown diamond coated fibers are treated by an O₂ plasma to increase the hydrophilicity (or wettability) of the diamond fibers. The resultant fibers combine the flexibility and good conductivity of CFs with the wide electrochemical potential window, long-term stability and environmental harmlessness of BDD.

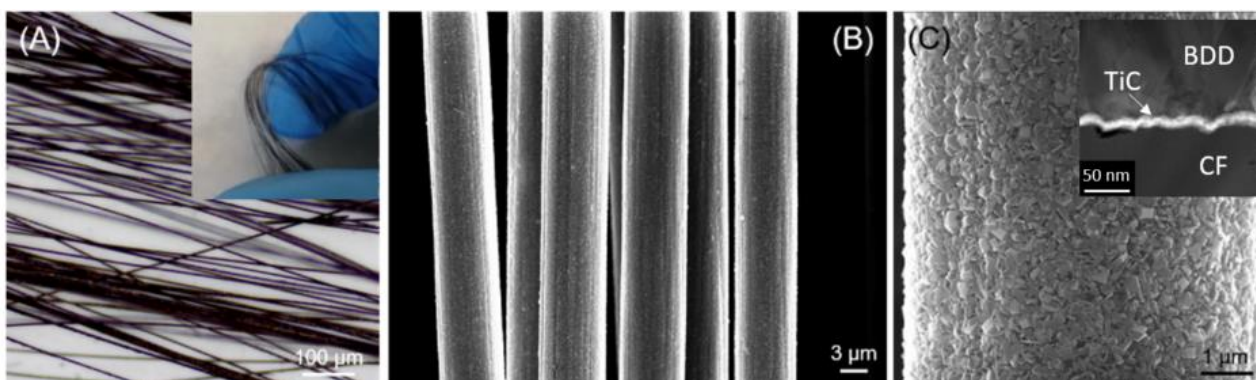
In order to characterize the fiber coating, scanning electron microscopy, high-resolution transmission electron microscopy, X-ray diffraction structure analysis as well as X-ray photoelectron spectroscopy have been carried out. The flexibility of these diamond fibers was examined under different bending conditions.

Such flexible fibers are well-suited for making woven meshes or integrating them into other membrane materials. For a test application, these diamond coated fibers have been employed as the cathode membrane in the fabrication of zinc-ion supercapacitors. Together with an anode fabricated from zinc nanosheet coated diamond fibers, this diamond supercapacitor delivers a high and stable specific capacitance. More importantly, it delivers high gravimetric and volumetric energy and power densities, even under severe bending states.

Image caption: (A) Photograph and (B) and (C) SEM images of the diamond coated fibers.

Reference 1:

[1] Z. Jian et al, Adv. Energy Mater. 2020, 2002202 (DOI: 10.1002/aenm.202002202)



Flow-electrode Capacitive Deionization from Lab to World: Control of Osmosis and pH at high Concentrations

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¹RWTH Aachen University, Chemical Process Engineering, ²DWI - Leibniz Institute for Interactive Materials

Main topic: Electro-membrane processes

Selective water desalination using electrochemical technologies receives vital attention since it gives an energy-efficient solution to the treatment of effluent streams containing valuable or harmful salts. Electrodialysis and Flow-electrode Capacitive Deionization (FCDI) are known technologies for continuous desalination and concentration by electric ion removal, and present solutions for the need. Both technologies deploy a special compartment in the module setup, which contains an electroactive liquid and transfers electric to ionic charge. In ED, this solution is called the rinse solution, and in FCDI, it is the flow electrode.

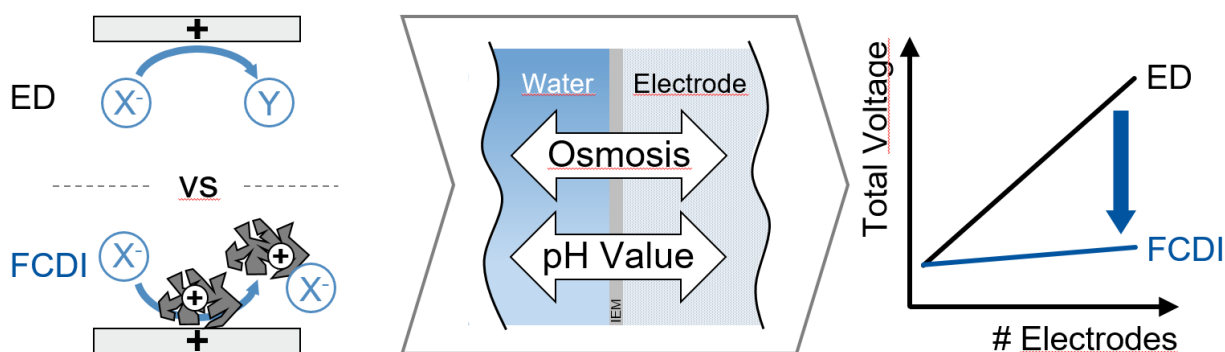
In this work, we show the unique developments and capabilities of FCDI especially on control of the diffusive fluxes within the cell and their impact to large-scale application. To achieve high salt concentrations, it is vital to understand all processes, which involve the electroactive compartment. Focusing on FCDI, we show that the salt content in the flow electrode controls the diffusive fluxes.

Small changes in the flow electrode's composition by unwanted diffusive fluxes need to be counteracted to ensure a long-term stable desalination performance. An investigation of all water fluxes across the membranes resulted in an optimal salt concentration for the flow electrode to balance out all fluxes.

Exchange of hydroxide and hydronium ions is also part of the diffusive fluxes. Since most ion-exchange membranes are pH-sensitive, the pH change is a critical factor in long-term stable desalination using FCDI. Hence, we present the first approach to describe the pH values evolving in the FCDI module. Here, the salt content of the flow electrode has a vital role in determining the pH of treated water solution.

Concluding from this work, we describe that the composition of the electroactive liquid has a significant effect on desalination and concentration. Better control of all diffusive processes within a large stack would be possible by adding more compartments containing a flow-electrode or rinse solution in FCDI or ED, respectively. However, the ion-electron conversion accruing in all these compartments acquires more potential in an ED setup than FCDI. Thus, FCDI is the more energy efficient technology for controlled ion concentration and desalination.

Control by Electrode Composition



Flux-Step Test Using Model Foulant on UF PES Membranes Coated with Novel Low-Fouling Coating

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Main topic: Membrane fouling and cleaning

Ultrafiltration membranes are widely used in membrane bioreactors (MBRs) for municipal and industrial wastewater treatment to eliminate suspended particles. Deposition of submicron particles on the membrane surface during MBR operation makes membrane fouling inevitable and more pronounced with passage of time. Since it is a pressure-driven membrane filtration process, membrane fouling implies consequent increase in energy consumption and potential decline in membrane life-span. Commercially available polyethersulfone (PES) membrane was enhanced by spray-coating anti-fouling layer of polymerisable bicontinuous microemulsion (PBM) materials, followed by 1 minute of ultraviolet (UV) light exposure to complete the polymerisation process. The modified membrane surface was characterised by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and the hydrophilicity was studied by sessile drop measurement of contact angles. Flux-step tests were conducted to identify the onset of critical fouling and compare the fouling propensity of commercially available PES membranes with PBM-coated membranes. Based on three key parameters – permeate flux, transmembrane pressure (TMP) and permeability, the fouling behavior of membranes was investigated in a side-stream cross-flow membrane module using 100 mg/l humic acid solution as model foulant for feed. Critical flux characterised by a rapid substantial increase in TMP was found to be about 39% higher accompanied with 25% lesser decline of permeability for PBM spray-coated membrane than commercial PES membrane. This exhibits the potential of PBM spray-coated membrane over commercial PES membranes to be used in MBR with lesser maintenance over prolonged operation time. Further studies will be conducted to study the performance of spray-coated PBM layer in contrast to casting coated PBM layer on PES membranes.

Reference 1:

F. Galiano, S. A. Schmidt, X. Ye, R. Kumar, R. Mancuso, E. Curcio, B. Gabriele, J. Hoinkis, A. Figoli, "UV-LED induced bicontinuous microemulsions polymerisation for surface modification of commercial membranes — Enhancing the antifouling properties", *Separation and Purification Technology*, 2018, 194, pp. 149-160

Reference 2:

E. Ranieri, V. Goffredo, M. Campanella, M. W. Falk, "Flux-step method for the assessment of operational conditions in a submerged membrane bioreactor", *Water Science & Technology*, 2016, 73, pp. 2222-2230

Forward osmosis optimization: system-scale analysis and environmental sustainability at the water-energy nexus

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Main topic: Forward osmosis/Pressure retarded osmosis

Forward Osmosis (FO) is widely recognized as one of the most promising treatment technologies for the recovery of water from contaminated sources. Thanks to its low fouling propensity, FO results specifically suitable for wastewater treatment. However, the scale-up of FO systems in real applications still presents some challenging limitations, mostly ascribed to the lack of data presenting the technological transfer of FO in real-scale scenarios.

This study aims at tackling these limitations, by studying the different parameters involved in real-scale FO applications, presenting new potential FO configurations and their suitability when combined with different draw solute post-recovery processes. Firstly, the traditional co-current and counter-current mode were analyzed through FO system-scale modeling. Results predicted larger performance in counter-current, however, highlighting also the low flexibility of this configuration when high recovery rates or variation of the influent draw solute osmotic pressure are required. Similar performance with better adaptability was determined with innovative co-current FO configurations. The new filtration systems were designed in different stages, where “recharge” or “split” of the draw solution is intentionally carried out to enhance the water productivity. These configurations result in simpler membrane module configurations and wider operating conditions, differently from the counter-current mode, which requires stringent operative limits. The FO configurations were further analyzed by performing an energy assessment as a function of the desalination post-recovery system, i.e., thermal- or membrane-based. The results suggest that when thermal units are needed, significant energy savings may be achieved by adopting more flexible FO configurations, i.e., in co-current mode. Instead, working in counter-current mode results more feasible in FO systems combined with pressure-driven membrane processes of draw solution recovery.

Finally, the environmental sustainability of potential real-scale FO scenarios was studied. Different draw solutes were analyzed, comprising fertilizers, inorganic, organic and thermolytic draw solutions. Results suggest that the influent draw osmotic pressure plays a key role in the design of the FO systems and in turn its environmental sustainability. The environmental impacts of potential FO real-scale scenarios may be governed by a trade-off between the energy required by the regeneration step and the draw solution management.

Formulation and characterization of biodegradable arabinoxylan films from corn fiber

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Main topic: Novel membrane materials

Corn fiber is a by-product of the corn starch industry, produced in great amounts, mainly used for low-value animal feed applications. However, corn fiber contains valuable components, especially ferulic acid and arabinoxylan, where the arabinoxylan polysaccharide, with known film-forming properties, is present in high concentrations in corn fiber. This polysaccharide can be extracted with a mild alkaline extraction and further purified with membrane processes, leading to a dark-colored rich arabinoxylan biopolymer fraction in the end. In this work, a purified rich arabinoxylan extract was used as raw material for film formulations, envisioning food packaging applications. Due to the intense brownish color of the extract, decolorization was attempted with hydrogen peroxide as the decolorizing agent. Decolorization was somewhat achieved with this method and films cast with this formulation exhibited a light-yellow color, more appealing than their respective non-decolorized films. For the formulation of arabinoxylan films, glycerol was chosen as a plasticizer and citric acid as a cross-linker. While the cross-linking reaction was not successful, films exhibited water vapor permeability values similar to their respective non-decolorized films and other polysaccharides and contained significant antioxidant activity and favorable mechanical properties for their application as packaging materials of low-water-content food products.

Reference 1:

Weng, V.; Brazinha, C.; Coelho, I.M.; Alves, V.D. Decolorization of a Corn Fiber Arabinoxylan Extract and Formulation of Biodegradable Films for Food Packaging. *Membranes* 2021, 11, 321. <https://doi.org/10.3390/membranes11050321>

Fouling of ion-exchange membranes by food and bio-based industrial streams: characterization and impacts

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¹Ghent University, ²Vlaams Instelling voor Technologisch Onderzoek (VITO)

Main topic: Electro-membrane processes

Background

Ion-exchange membranes (IEM) are extensively used in food and bio-based industries to selectively separate charged compounds of interest that can be further reused in other processes. However, fouling severely impacts the performance of anion exchange membranes (AEM), as negatively-charged organics present in the feed stream adsorb on the membrane surface, leading to a decrease in their selectivity, increase in electrical resistance, loss of ion-exchange capacity (IEC), and increase in operating costs. The study of different compounds from industrial feed streams adsorbing on AEM's is still a black box and has not been researched in detail. The goal of this work is to characterize the different foulant matrices adsorbed on the AEM surface by various industrial feeds, as well as the irreversibility of the adsorption.

Materials and methods

An initial feed characterization of the stream revealed the presence of glycerol, tartaric, lactic, acetic, formic, propionic acids, in addition to ethanol. A by-product of industrial citric acid was used as feed and re-circulated from the same tank into the diluate and concentrate channels at a flow velocity of 6 cm/s, using 40 % of the limiting current density (LCD) value. The fouled AEM's were then characterized using water permeability (WP), perm-selectivity (PS) and IEC tests. ATR-FTIR, and SEM-EDX techniques were used to identify the presence of different foulant matrices.

Results and conclusion

WP, PS and IEC tests with pristine and fouled AEM's revealed an increase of 33.37 %, a decrease of 10.95 % and a decrease of 38.88 % respectively, thereby indicating a higher water transport, lower degree of selectivity and IEC caused due to fouling. Opposed to pristine membranes, ATR-FTIR results of both AEM types revealed the presence of glycerol in fouled membranes. As glycerol is a major compound present in the feed, its adsorption on the surface of the IEM indicates either the presence of electrostatic interaction or hydrogen bonding. To further support these results, SEM-EDX results reveal an increase in the oxygen content (from 8.6 to 19.7 wt%) on AEM surface which can be due to the presence of glycerol.

Acknowledgement

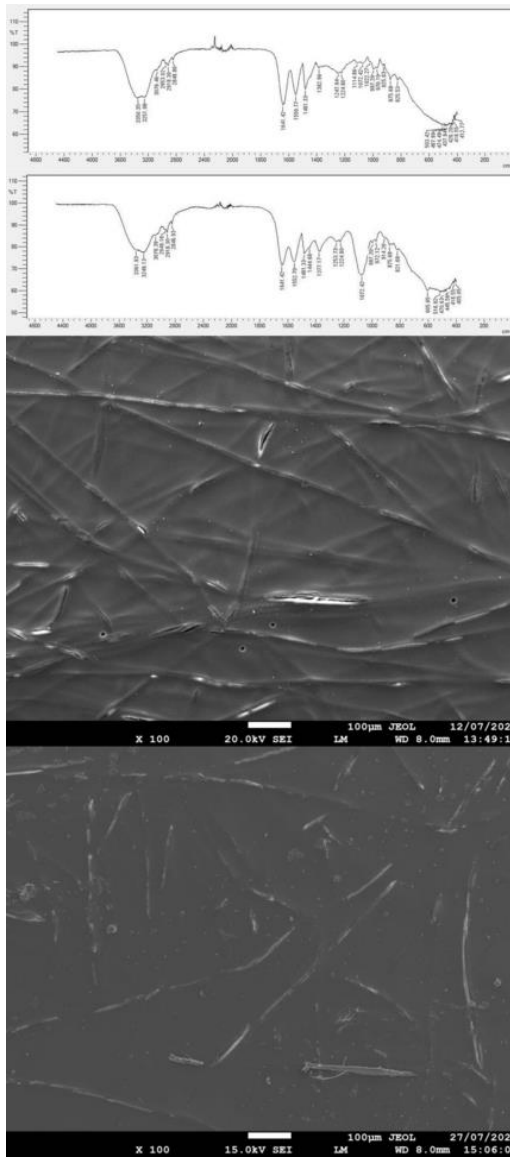
This project has been funded by the FWO-SB PhD scholarship in Belgium.

Reference 1:

Y. Wang, C. Jiang, L. Bazinet, and T. Xu, *Electrodialysis-based separation technologies in the food industry*. Elsevier Inc., 2018.

Reference 2:

S. Mikhaylin and L. Bazinet, "Fouling on ion-exchange membranes: Classification, characterization and strategies of prevention and control," *Adv. Colloid Interface Sci.*, vol. 229, pp. 34–56, 2016.



From lab to pilot scale: Lignin recovery with nanofiltration in the kraft pulping process

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¹Department of Chemical Engineering, Lund University, ²Department of Food Technology, Engineering and Nutrition, Lund University, ³SunCarbon AB

Main topic: Paper and pulp industries

Lignin is one of the main components of wood and can be found in high amounts in the black liquor stream of the kraft pulping industry. Kraft black liquor is usually incinerated in the recovery boiler to generate heat and power for the mill. However, lignin is also a very promising renewable raw material that has the potential to replace fossil carbon sources and can be used in biofuel production. Lignin can be recovered by membrane filtration, which is an environmental and economically viable technology. In particular, the use of ultrafiltration for recovery of lignin from kraft black liquor has been widely studied (Holmqvist et al., 2005; Wallberg et al., 2003). The focus in this study is on a potential sub-sequential step recovering lignin from ultrafiltration permeate by nanofiltration to increase the overall lignin yield of the process. To achieve this both laboratory and pilot scale experiments were conducted. On laboratory scale two concentration studies were performed with the polymeric nanofiltration membranes: MPS 36 (Koch Separation Solutions, USA) and NF090801 (SolSep, Belgium). The conditions during the studies were (A) 50°C and 35 bar, and (B) 70°C and 15 bar. The lignin retentions for NF090801 and MPS 36 under condition (A) were 94% and 92%, respectively; and under condition (B) 91% and 83%, respectively. Based on these results the NF090801 was selected for the on-site pilot scale experiments in spiral wound configuration. The on-site pilot was located at an integrated pulp and paper mill in the north of Sweden. Pressure and temperature conditions during the pilot tests were adjusted based on the laboratory experiments. Lignin retention at 50°C and 25 bar was 82%, and at 70°C and 15 bar it reached 81%. Hence, both pilot scale conditions resulted in a volume reduction of 0.8 with similar lignin concentrations. Overall, the pilot scale experiments demonstrated that high lignin yields from kraft black liquor can be achieved using a membrane cascade of ultrafiltration followed by nanofiltration.

The authors would like to acknowledge the financial support of the Swedish Energy Agency, project No. 47504-1. The project is further associated to the IETS Annex XVII "Membranes in Biorefineries".

Reference 1:

Holmqvist, A., Wallberg, O., & Jönsson, A. S. (2005). Ultrafiltration of kraft black liquor from two Swedish pulp mills. *Chemical Engineering Research and Design*, 83(8 A), 994–999. <https://doi.org/10.1205/cherd.04204>

Reference 2:

Wallberg, O., Jönsson, A. S., & Wimmerstedt, R. (2003). Fractionation and concentration of kraft black liquor lignin with ultrafiltration. *Desalination*, 154(2), 187–199. [https://doi.org/10.1016/S0011-9164\(03\)80019-X](https://doi.org/10.1016/S0011-9164(03)80019-X)

Full scale demonstration of osmotic power in high salinity

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¹SaltPower, ²TOYOBO CO., LTD., ³Nobian, Dansk Salt A/S, ⁴Semco Maritime

Main topic: Forward osmosis/Pressure retarded osmosi

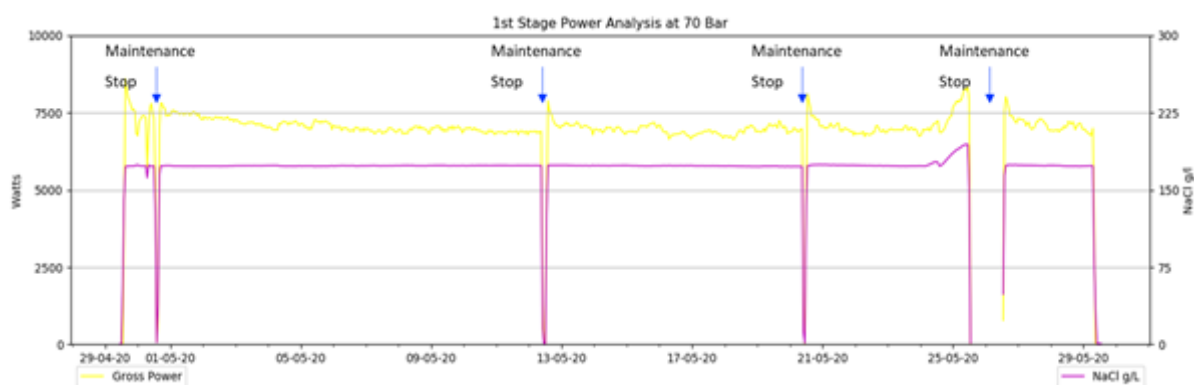
Osmotic power can be generated by pressure retarded osmosis (PRO) aided by semi-permeable media. Where two different salt concentration aqueous solutions are separated by membrane barrier, meanwhile water from low saline phase penetrates through connected membrane pores to meet and dilute high saline solution, leading to salinity gradient, which can be further converted into electricity, so called blue energy. Although the idea itself is highly attractive especially in application of seawater desalination, research work of PRO for power generation has been retarded several times in the past two decades due to the insufficient efficiency. Positive results seems only available in lab-scale with prototype membranes. So far there is not a commercialized full scale PRO plant even Mega-ton claimed their project successfully achieved 17 W/m² power density [1].

Monumentation of full-scale PRO for power generation was revived at Europe, by Jørgen M. Clausen in 2015, after failure of Statkraft project. The founder of SaltPower believes a success of high power output using high salinity brines instead of seawater [2]. This concept is further confirmed by scientific research [1]. Today, resources of high brine solutions are more versatile and richer than oil, and makes it possible to be alternative power solution for green energy generation. SaltPower is therefore striving for developing a technical solution to transform salt into power.

Solution mining is the process of extracting salts by leaching from underground deposits. When doing this, a valuable high saline solution is extracted and used for salt production and simultaneously an underground cavern is formed which is ideally suited for large scale storage of gas, like natural gas or hydrogen from renewable sources. Such solution mining forms the basis for the salt production at Nobian, Dansk Salt A/S where a full scale demonstration PRO plant is designed and built-up by SaltPower and Semco Maritime.

This article presents a long-term test with above demonstration unit using Toyobo proprietary 10-inch hollow fiber membrane module with hypersaline draw solution at pressure up to 70 bar. Initial results show relative stable membrane performance and power output within 2000 hrs duration by hypersaline PRO process, as predicted.

Figure 1 Power generated from salt by PRO



Reference 1:

H. T. Madsen, T.B. Hansen, T. Nakao, S. Goda, E.G. Sjøgaard. Energy Conversion and Management 226 (2020) 113504.

Reference 2:

<http://saltpower.net/applications/>

Functionalized graphene oxide (GO)-based nanocomposite facilitated transport membranes for CO₂/H₂ separation

Xu, Wenqi - Main Author; Lindbråthen, Arne - Co-Author; Deng, Liyuan - Co-Author

Main topic: Gas separation

H₂ is widely recognized as the most promising non-carbon-based fuel and clean energy carrier. Currently, hydrogen is mainly obtained through steam reforming of hydrocarbons (e.g., natural gas, coal) followed by the water-gas shift reaction. A large amount of CO₂ is emitted at the same time as the process producing H₂. Pressure swing adsorption (PSA) and amine absorption are the main H₂ purification processes in today's industry. Membrane separation can be a promising alternative to traditional PSA and amine absorption due to its lower energy consumption, much smaller footprint, lower capital and operating costs, higher energy efficiency, operation simplicity, and high modularity.

CO₂/H₂ separation commonly uses H₂-selective membranes and keeps CO₂ in the retentate side (high-pressure side) but the selectivity is usually very low since H₂ has a higher diffusivity, but CO₂ has a higher solubility. However, it is beneficial to better transportation and storage to save energy if H₂ is retained at the high-pressure side, and uses CO₂-selective membranes.

In this work, a CO₂-selective membrane is developed. Functionalized GO-embedded polyvinylamine (PVAm)-based nanocomposite facilitated transport membranes are prepared and optimized for CO₂/H₂ separation. Having the highest content of primary amino groups, PVAm is widely used in facilitated transport membranes for CO₂ separation. Functionalized-GO nanosheets have the potential to improve the selectivity of CO₂ over H₂ because of their "block property" as a gas barrier in the membrane and high tortuosity. The modified surface of the GO with higher CO₂ affinity also benefits the competition of CO₂ transport over H₂. GO-, PVA-GO- and porous GO-based membranes are prepared. The prepared membranes were characterized to evaluate physical, chemical, and separation properties by using SEM, FTIR, TGA, and gas permeation tests. Comparing with a neat PVAm membrane, the CO₂/H₂ selectivity of the three membranes, as mentioned before, increase ~25%. More different functionalized-GO should be optimized to further improve the CO₂/H₂ selectivity.

Functionalized graphene oxide membrane for lithium recovery from water

Baudino, Luisa - Main Author^{1,2}; Pedico, Alessandro - Co-Author¹; Periolatto, Monica - Co-Author¹; Lamberti, Andrea - Co-Author^{1,2}; Pirri, Candido Fabrizio - Co-Author^{1,2}

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Main topic: Environmental applications

Lithium has become a crucial element in today's economy due to its many appealing properties and thus applications. Its use in both primary and secondary batteries has doubled in the last years and now represents about 60% of its market share [1]. Unfortunately, recycling methods are still in the cradle and while mineral ores are diminishing the demand is ever increasing. Several alternatives to the mining technology, like evaporation of salt lakes, have been proposed but they are time and water consuming. More viable alternatives under study are the adsorption by ion sieves and supramolecular systems which can be easily integrated in membrane technologies.

Graphene oxide (GO) is widely studied for membrane applications like water treatment due to the easiness of functionalization and characteristics like its hydrophilic channels that ease the targeting of ions in water streams. A nanocomposite crown ether functionalized GO membrane is here reported to selectively harvest lithium from water resources during pressure filtrations. The GO flakes were functionalized following the procedure of [2] via carbodiimide esterification and a polymeric binder was then added before obtaining the membrane by vacuum filtration on a polymeric support. The nanocomposite membrane was tested in a dead-end pressure setup under nitrogen gas with different solutions. Morphological characterizations were carried out on pure GO membranes, functionalized GO and nanocomposite ones to assess which polymeric binder was best suited for this application. The selectivity towards lithium ions was tested by successively filtrating monovalent and bivalent chloride salts and diluted HCl solutions as stripping agent. Conductivity tests were performed on NaCl, LiCl, KCl, MgCl₂ and CaCl₂ solutions, as well as HCl stripping solutions. ICP mass measurements were performed to verify the reliability and reproducibility of the conductivity measurements.

Reference 1:

[1] United States Geological Survey. Mineral Commodity Summaries 2020. 2020.

Reference 2:

[2] Sun D, Meng M, Lu Y, Hu B, Yan Y, Li C. Porous nanocomposite membranes based on functional GO with selective function for lithium adsorption. *New J Chem* 2018;42:4432–42. <https://doi.org/10.1039/C7NJ04733A>

Functionalized membrane bio-interface to control blood protein behavior: polyelectrolyte-protein interaction investigated using Small Angle X-ray Scattering (SAXS)

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Main topic: Bio-medical applications

Proteins interaction with polymeric materials are key phenomena to understand and control responses of body fluids and tissues towards medical devices [1]. These interactions maybe either unwanted or wanted to enhance a specific affinity. For that, the membrane biointerface is often customized at the nanoscale by grafting on it some functional groups such as poly(acrylic acid) **PAA**.

With the purpose of designing a membrane advanced technology allowing the concentration of the growth factors stored inside platelets and expressed after their capture and activation, we coated a PVDF membrane with different copolymers such as Polystyrene-block-Poly(acrylic acid) (PS-PAA), and Polystyrene-block-Poly(ethylene glycol) (PS-PEG). FTIR (Fourier-transform infrared spectroscopy) mapping of this modified membrane before and after the filtration of Human Serum Albumin (**HSA**) through reveals a specific affinity with PS-PAA. Hence, a fine command of interactions between grafted moieties and biomolecules as HSA is a prerequisite to get the best yield of these surface modifications.

In the present work, we study interactions between HSA and PAA (100kDa) using Small Angle X-ray Scattering (SAXS) combined to chromatography. The SAXS spectra analysis reveals the binding of HSA molecules to PAA chains. The investigation of ionic strength-pH combined effects shows that HSA-PAA complexation takes place only at pH 5 and low ionic strength (0.15M). Otherwise, for higher pH and salts concentration (0.75M) the HSA-PAA complex tends to dissociate showing the reversibility of the complexation. The assessment of HSA/PAA molar ratio influence on the complex size (radius of gyration and Porod volume) evinces that 4 HSA molecules would bind to each PAA chain. This stoichiometry is supported by an all atom SAXS model calculated using BUNCH program and found to fit well the complex scattering data. This model allows to portray the complex as a pearl-necklace assembly with 4 HSA on each PAA chain [2].

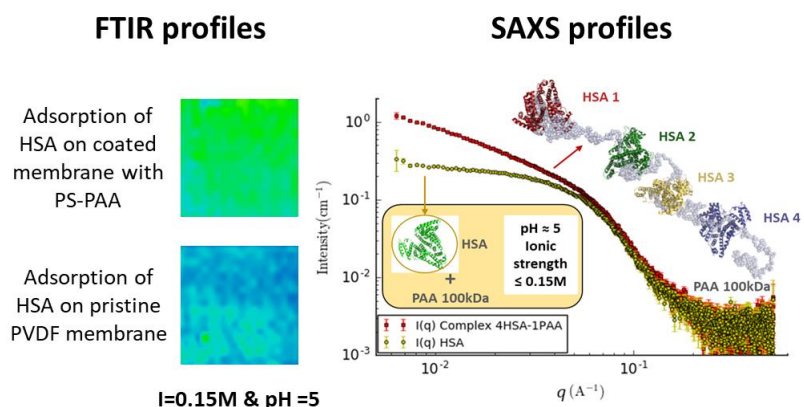
These findings are used to shed light on our data of HSA adsorption on membranes coated with PS-PAA at various pH and Ionic Strength.

Reference 1:

Q. Wei, T. Becherer, S. Angioletti-Uberti, J. Dzubiella, C. Wischke, A. T. Neffe, A. Lendlein, M. Ballauff and R. Haag, Protein Interactions with Polymer Coatings and Biomaterials, *Angew. Chem., Int. Ed.*, 2014, 53(31), 8004–8031.

Reference 2:

C.Merzougui, P.Roblin, P.Aimar, A.Venault, Y.Chang, C.Causserand, P.Bacchin. Pearl-Necklace Assembly of Human Serum Albumin with the Poly(Acrylic Acid) Polyelectrolyte Investigated Using Small Angle X-Ray Scattering (SAXS). *Soft Matter* 2020, 16, 9964–9974.



HSA-PAA binding as showed by SAXS experiments in solution and by FTIR mapping on PVDF coated membrane

Gas permeation applied to CO₂/CH₄ separation using chitosan-based and polydimethylsiloxane membranes

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¹Universidad de Cantabria

Main topic: Gas separation

Membrane separation processes are considered of great potential to address the drawbacks of the conventional-based amine processes for CO₂ capture and for natural gas sweetening or biogas upgrading where the effective separation of CO₂ and CH₄ is essential. However, commercially available membranes still face challenges regarding water and chemical resistance [1]. Chitosan (CS) is a non-toxic, hydrophilic, functional, biodegradable and biocompatible polymer from abundant natural sources, with good adhesive and film forming properties. The primary amine and hydroxyl groups of the biopolymer exhibit strong affinity towards CO₂, especially in humid conditions. Different concepts of CS-based membranes have been developed, which include material blending and composite and mixed matrix membranes with non-toxic fillers, in order to promote the use of more environmentally friendly products [2].

The present work evaluates the gas permeation performance CS-based composite membranes for the separation of CO₂/CH₄ mixtures, to identify the optimal design and operation conditions that maximize the technical performance, given in terms of purity and recovery of components, by proposing an optimization methodology as a useful tool to advance in parallel in the implementation of the membrane separation systems and the development of membrane materials [2]. The performance of commercial polydimethylsiloxane composite membranes was used as reference.

IL-CS/PES membranes were prepared by coating CS layer hybridized by 5 wt% [emim][acetate] non-toxic ionic liquid (IL) on porous polyethersulfone hydrophilic support. The permeance and selectivity parameters were measured in a laboratory scale setup and introduced to the membrane unit model, where the material balances and components permeation were solved.

The influence of the main design and operation variables was studied by means of sensitivity analyses. The effects of increasing the stage cut are highlighted in the **Figure 1** from using a IL-CS/PES composite membrane. The results give a clear idea on the counterbalance between the different objectives for the technical optimization of the separation process. If the two components are considered design targets, the multi-objective optimization can be used to the minimization of the normalized distance for all the objectives (purity and recovery).

Reference 1:

G.S. Cerveira, C.P. Borges, F. de A. Kronemberger, J. Clean. Prod. 187 (2018) 830–838.

Reference 2:

C. Casado-Coterillo, A. Garea, A. Irabien, Membranes. 10 (2020) 1–12.

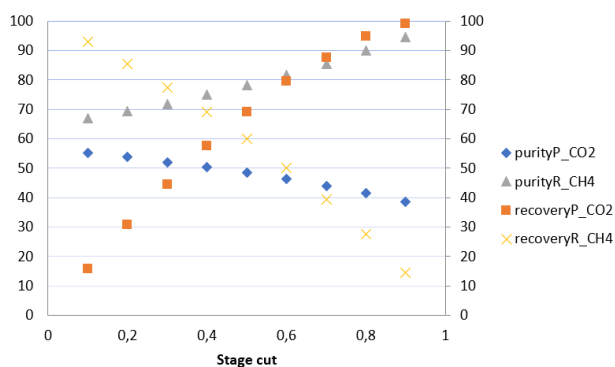


Figure 1.- Evolution of the permeate and retentate purity and recovery through an IL-CS/PES membrane for different stage cut values.

Gas Separation in MOFs Materials by Flexible Force Field Simulation

Zhao, Hengli - Co-Author¹; Ghoufi, Aziz - Co-Author¹; Maurin, Guillaume - Co-Author²

¹Institute of physics of Rennes, ²Institute Charles Gerhardt Montpellier

Main topic: Gas separation

A series of Metal-Organic Frameworks (MOFs) was systematically explored to predict their ability to separate hexane isomers of vital importance in the field of petrochemical industry.^{1,2} An Hybrid osmotic Monte Carlo scheme based on the use of a flexible force field for both MOFs enabled to identify two promising MOFs, the Zeolitic Imidazole Framework-8 (ZIF-8) cage-like MOF and the di-carboxylate triangular channel-like MIL-140B(Zr) that show attractive performance to separate linear from mono and di-branched isomers. This was further confirmed by experimental breakthrough experiments. As a further stage, we envisaged an innovative strategy to boost the selectivity of these materials by combining the guest stimulus with an applied external mechanical pressure.

Typically, we demonstrated that the application of a mechanical pressure of 1 GPa was predicted to boost the linear hexane/2-methylpentane and 2-methylpentane/2,3-dimethylbutane selectivity of ZIF-8 by 40% and 17%, respectively. In the case of MIL-140B, we highlighted a gain of selectivity of hexane isomers up to 68% under 1 GPa of mechanical pressure.

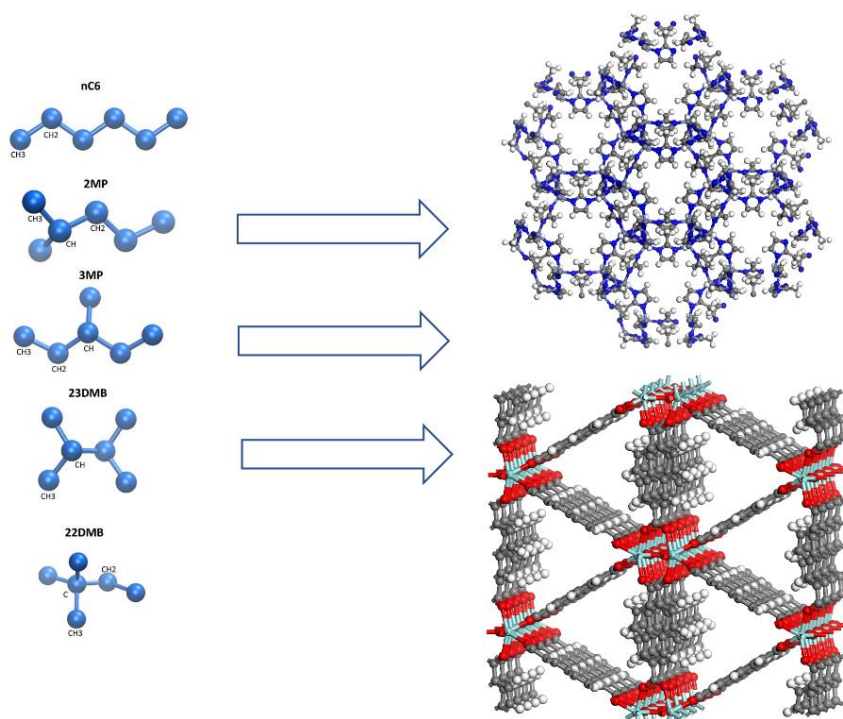
This work highlights the crucial role of tiny tilting of the organic linkers of narrow-pore MOFs in their sorption properties.

Reference 1:

Hengli Zhao, Guillaume Maurin, Aziz Ghoufi, J. Chem. Phys. 2021, 154, 084702

Reference 2:

Adriano Henrique, Tanmoy Maity, Hengli Zhao, Pedro F. Brantuas, Alirio E. Rodrigues, Farid Nouar, Aziz Ghoufi, Guillaume Maurin, Jose A. C. Silva, Christian Serre. J. Mater. Chem. A, 2020, 8, 17780-17789



Granular Anaerobic Membrane Bioreactor for energy positive domestic wastewater treatment

Sanchez, Lucie - Main Author; Lesage, Geoffroy - Co-Author; Héran, Marc - Co-Author; Sohaib, Qazi - Co-Author

Main topic: Membrane bio-reactors

Granular anaerobic membrane bioreactor (G-AnMBR) is an emerging intensive hybrid bioprocess that has a great potential to compete conventional aerobic treatment for domestic wastewater treatment (DWWT) at ambient temperature by providing a high-quality effluent and energy recovery. Among the biggest challenges, biological activity upgrading, membrane fouling mitigation, process design and dissolved methane recovery still need to be investigated. This study first aims to highlight that membrane submerged directly into a granular anaerobic bioreactor improves the anaerobic treatment efficiencies while keep a compact design reactor. Then, it provides a better understanding of the impact of the submerged membrane separation through the anaerobic granular sludge activity. Lastly, it proves that G-AnMBR can achieve organic removal efficiencies as high as aerobic treatment for DWWT at ambient temperature while producing renewable energy.

A G-AnMBR and an UASB were operated with the same operating conditions during 120 days at 25°C with low-strength synthetic wastewater (HRT=13h, OLR=0.8kgCOD.m⁻³.d⁻¹). Treatment efficiencies were evaluated in terms of tCOD, sCOD, DOC, nutrients and MLSS removals. AGV, pH, ORP, 3DEEM, TMP and fouling mechanisms were followed to track biological and separation process stability. Sludge characteristics were observed through specific methanogenic activity, settleability, particle size distribution (PSD) and zeta potential. The methane generated was quantified in gaseous and aqueous phases by GC. Finally, a complete COD mass balance was performed.

Following the experiment it has been demonstrated that:

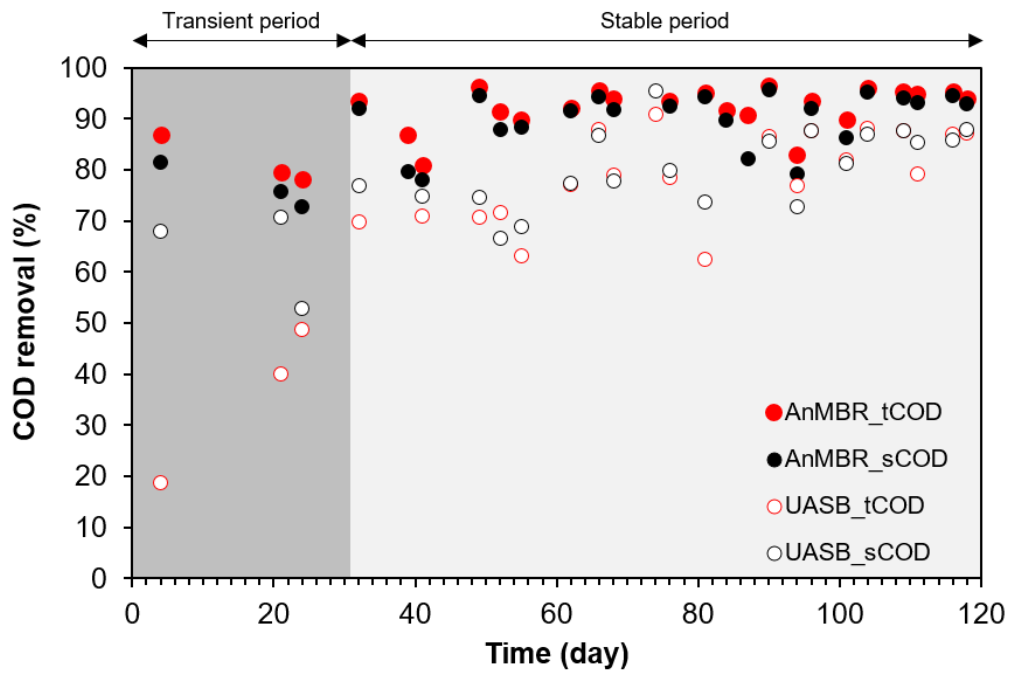
1. G-AnMBR was stable and efficient almost from the beginning whereas a transient period of 1 month was observed for UASB.
2. G-AnMBR performed higher organics and suspended solids removal (93%-tCOD, 1mgMLSS_{effluent}/L) in comparison to the UASB (79%-tCOD, 11mgMLSS_{effluent}/L) due to the UF membrane separation that retains all particulate and colloidal matter and macromolecules.
3. Higher quantity of gaseous methane was produced in the G-AnMBR (0.82 vs 0.72 NL-CH₄/day) highlighting that the matter retained by the membrane is later converted into biogas thanks to a longer biomass-pollutant contact time.
4. The membrane separation allows to maintain the PSD tendency of the granular sludge within the G-AnMBR while large granules became predominant in UASB sludge bed.
5. Biomass growth was three-times higher in the G-AnMBR, due to biomass loss in the UASB.

Reference 1:

Srinivasa Raghavan, D. S.; Qiu, G.; Song, Y.; Ting, Y.-P. (2017) 12 - Anaerobic Treatment of Low-Strength Wastewater. In: Current Developments in Biotechnology and Bioengineering (D.-J. Lee, V. Jegatheesan, H. H. Ngo, P. C. Hallenbeck & A. Pandey, eds.), 293–320; Elsevier.

Reference 2:

Smith, A. L.; Stadler, L. B.; Love, N. G.; Skerlos, S. J.; Raskin, L. (2012) Perspectives on anaerobic membrane bioreactor treatment of domestic wastewater: A critical review. *Bioresource Technology*, 122, 149–159.



Graphene Oxide Membranes for Reverse Electrodialysis Applications

Aixalà Perelló, Anna - Main Author^{1,2}; Pedico, Alessandro - Co-Author¹; Laurenti, Marco - Co-Author^{1,2}; Fontananova, Enrica - Co-Author^{3,4}; Bocchini, Sergio - Co-Author²; Ferarri, Ivan - Co-Author²; Lamberti, Andrea - Co-Author^{1,2}
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Main topic: 1D- and 2D-materials for membranes

Energy issues and environmental problems are forcing the researchers to investigate new ways to harvest energy from renewable sources. Reverse electrodialysis (RED) arises as an alternative technology which converts the Nernst potential between two water streams at different salt concentration into electricity. Nevertheless, the feasibility of this technology depends on the performance of the ion-exchange membranes (IEM), main actors of this process. 2D materials show promising properties to be applied in IEM for RED due to their great transport properties, low resistance, impressive mechanical strength, and antifouling characteristics [1]. Graphene oxide (GO) membranes have been proposed in this study as they are naturally negatively charged thanks to their oxidized functional groups, have good mechanical strength, low cost, and facile synthesis [2]. One of the novelties of this project is the use of doctor blade technique as a scalable method for GO membranes production for RED application.

This work focuses on the study of the properties of GO membranes in terms of permselectivity and electrical resistance. GO membranes presented good ion selectivity and size exclusion towards monovalent cations, being Na⁺ and K⁺ the most performant ones. In addition, UV light irradiation has been proposed as an alternative green reduction method. GO reduction increased permselectivity of membranes by 10% due to a decrease of the nanochannels in the GO structure and a reduction of the swelling degree of the membranes. The addition of different binders has also been proposed in order to strengthen the mechanical resistance of membranes, showing no significant differences on the permselectivity measurements.

Electrical impedance spectroscopy was proposed to measure electric resistance of the membranes. Results show a dominant effect of the solution inside the membranes pores. Instead, membranes with binders and treated with UV-light presented a lag in the solution permeation.

Reference 1:

Macha, M., Marion, S., Nandigana, V. V. R. & Radenovic, A. 2D materials as an emerging platform for nanopore-based power generation. *Nat. Rev. Mater.* 4, 588–605 (2019)

Reference 2:

Ji, J. et al. Osmotic Power Generation with Positively and Negatively Charged 2D Nanofluidic Membrane Pairs. *Adv. Funct. Mater.* 27, 1–8 (2017)

Grass! A delicious plant where tasty protein can be recovered by membrane filtration and used for food

Holt, Christian - Main Author; Lübeck, Mette - Co-Author¹; Lübeck, Peter - Co-Author¹; Heilskov Veje, Malene - Co-Author¹; Kjær Jørgensen, Anders - Co-Author¹; Jørgensen, Mads - Co-Author¹

¹Department of Chemistry and Bioscience, Aalborg University

Main topic: Food processing

Before clover grass can be used as ensiled feed for cows, it must be cut and then lie on the field before the farmer can collect it. The cut starts a plethora of biochemical processes which leads to water seeping from the grass. This water not only contains nutrients, but also a high amount of protein. The most abundant protein in grass is the enzyme RuBisCO, which facilitates CO₂ fixation. RuBisCO has a favorable nutritional amino acid profile, making it an ideal non-animal protein source in food.

By utilizing both micro- and ultrafiltration (MF and UF), we are interested in recovering the grass protein in grass juice before microbial degradation. The microfiltration membrane will remove microorganisms and larger particles and water-soluble proteins are collected in the MF-permeate. For efficient transmission of proteins through the MF membrane it is crucial to avoid fouling, as the fouling layer acts as a secondary membrane. Accordingly, our studies have shown that selecting a properly high crossflow velocity and type of MF membrane is crucial to avoid fouling and ensure protein transmission, to obtain high yields of RuBisCO protein. With UF we have seen that we are both able to concentrate the protein containing MF-permeate and wash out salts, small molecules, and peptides by diafiltration. The UF retentate thus contains a high amount of protein but without salts and the off- flavor tasting peptides. On the other hand, the UF permeate still has a good nutritional value which can be used as fermentation substrate or as fertilizer.

Gravity-driven Membrane Filtration of Municipal Wastewater for Irrigation Reuse

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¹University of Iceland, ²Nanyang Technological University

Main topic: Environmental applications

The gravity-driven membrane (GDM) filtration process utilizes hydrostatic force and naturally-developed biofilm, combining microfiltration(MF)/ultrafiltration (UF) membrane separation to obtain superior permeate water (Pronk et al. 2019), offering an alternative solution for municipal wastewater treatment (Lee et al., 2021). In this study, three GDM systems packed with Icelandic lava stones at different packing densities were operated to treat secondary municipal wastewater and the external-located UF membrane modules experienced periodical cleaning protocols (physical and chemical-enhanced physical cleaning at various durations). The reactor performance, membrane filterability, and water quality were examined. The GDM permeate was employed to culture different model plants (*Solanum lycopersicum*, *Lycopersicon lycopersicum*, *Ocimum basilicum*). The plant growth was recorded and heavy metal uptake by plants and soils were analysed, as a comparison with those irrigated with tap water and commercial fertilizer.

The results revealed that the GDM systems could achieve higher organic removals ($BOD_5 >94.5\%$; $COD >75.3\%$) regardless of absence and presence of lava stones. While, the lava stones packed GDM reactors displayed more nitrogen removal (51.2-56.6% vs. 37.6% without biocarriers), possibly relating to enhanced denitrification and released MnOx particulates from lava stones. The GDM (without lava stones) experienced dominant pore blocking during the initial stage, but combined pore constriction and cake fouling was predominant in the GDM with lava stones. The flux stabilization was associated with both decreasing pore constriction and cake fouling coefficients, regardless of lava stone packing ratios. The NaOCl-based cleaning (0.5% in 50 °C geothermal water, 10 min per 3-4 days) was more effective in improving flux recovery (~46-79%) and overall water permeability compared to non-cleaning or geothermal water-/persulfate-based cleaning. Meanwhile, the plants irrigated with the GDM permeate showed the similar time-related growth profiles as those with tap water or commercial fertilizer. The metal element analysis revealed slightly higher uptake of Al, Cd, Fe, Mg, Mn, V, or Zn by the plants with the permeate compared to those with tap water or commercial fertilizer under two planting conditions. The detected non-essential heavy metal levels in the plants and soils were lower than the maximum allowable concentrations proposed by WHO and EU, indicating negligible human health risk.

Reference 1:

Pronk, W., Ding, A., Morgenroth, E., Derlon, N., Desmond, P., Burkhardt, M., Wu, B. and Fane, A.G. (2019) Gravity-driven membrane filtration for water and wastewater treatment: A review. *Water Research* 149, 553-565.

Reference 2:

Lee, S., Badoux, G.O., Wu, B. and Chong, T.H. (2021) Enhancing performance of biocarriers facilitated gravity-driven membrane (GDM) reactor for decentralized wastewater treatment: Effect of internal recirculation and membrane packing density. *Science of the Total Environment* 762.

Green pharmaceutical chemistry: solvent regeneration using pervaporation

Magne, Adrien - Main Author^{1,2}; Le Hir, Morgane - Co-Author²; Clair, Thomas - Co-Author²; Carretier, Emilie - Co-Author¹; Moulin, Philippe - Co-Author¹

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Main topic: Pervaporation and vapour permeation

Pharmaceutical industry's objective is to use greener chemistry by working on the implementation of innovative processes such as flow chemistry but also by better valorizing effluents and especially solvents. These fluxes contain complex solvent mixtures sometimes with chemical compounds or by-products. Recycling them has major environmental and economic interests due to the high quantities of solvents used and their possible toxicity. However, treatment issues are frequent due to the complexity of the mixture (azeotrope between solvents, chemicals' solubility...) and to the high quality and regulatory required for the regenerated solvents in the pharmaceutical field. This work describes an efficient dichloromethane (DCM) regeneration process from a methanolic effluent by coupling distillation and membrane pervaporation process. Distillation alone was impossible for recovering DCM due to the presence of an azeotrope (methanol / DCM / water). A water washing was inefficient as a purification step of the azeotrope because too much residual water was recovered in the organic phase, meaning that the quality specifications of recovered DCM were not reached. Pervaporation was found to be a solution to the DCM purification from the azeotrope collected by distillation. Hydrophilic HybSi[®] membrane were used, letting methanol and water pass through while retaining DCM. Feasibility had been proven at laboratory scale, with a membrane area of 0.15 m². Then, a semi-industrial pervaporation pilot plant has been used to study various parameters in order to optimize the process: the membrane area of 1.05m² enabled the industrial scale-up. During the experiments, near infrared (NIR) probes were implemented. This process analytical technology (PAT) tool enabled an online and real-time monitoring. A DCM purity of 99.9 %w/w for the regenerated solvent was obtained. The whole process (distillation + pervaporation) reached a global DCM recovery yield of 90% according to ProSim modeling and 80% proven experimentally. This modeling yield was limited by the presence of methylal, a compound from the chemical waste distilled just after the azeotrope, and retained by the pervaporation membrane.

Oliveira, Caique - Main Author¹; Viana, Marcelo - Co-Author¹; Paula, Eduardo - Co-Author¹; Amaral, Miriam - Co-Author¹

¹Federal University of Minas Gerais

Main topic: Membrane reactors

Process intensification is a concept focused on developing equipment and methods that result in cleaner, more compact, and more energy-efficient technologies. Meanwhile, Photocatalytic Membrane Reactors (PMRs) prefigure as prominent exponents, as they integrate reaction and separation in only one equipment [1]. The benefits achieved in this configuration overcome limitations and operational problems of using catalysts or membranes separated to treat effluents. One of the advantages obtained is the reduction of membrane fouling due to the photodegradation of pollutants in the feed by the catalyst, ensuring the stability of the permeate flow, and the reduction of energy consumption. Moreover, the association provides the maintenance of nanometric catalysts in the reaction medium, enabling its further separation from the treated solution without using chemicals necessary in conventional processes. Furthermore, catalyst reuse is allowed, and the residence time of the pollutants molecules in the reactor can be controlled, generating a better quality permeate [2]. In this work, the association of a PMR with a membrane bioreactor (MBR) was investigated to treat oil refinery effluent. The MBR comprised a 3.36 L biological reactor, in which a hollow fiber UF membrane (average pore diameter: 0.04 mm, area: 0.047 m²) was submerged. Suspensions of titanium dioxide (TiO₂) nanoparticles, synthesised by a cleaner route assisted by microwave radiation, and recycled membrane, an end-of-life reverse osmosis membrane converted to an ultrafiltration membrane by oxidation (area: 119 cm²), were prepared for use as a PMR. COD analyzes revealed that around 60% of the MBR permeate recalcitrant organic matter was degraded by the PMR, which contributed to the fouling mitigation. In PMR, the membrane fouling resistance was 7.3 times lower than that of the system operated in the absence of the catalyst. The green catalyst exhibited a better performance in maintaining the stability of the flux compared to a commercial one (P25 Degussa). Reuse tests demonstrated the system's stability by maintaining high rates, even in the second reuse, of COD removal (around 50%) and ABS254 removal (around 40%), as well as flow stabilization (Fig. 1). Therefore, the system is stable and promising for polishing refinery effluent treated by MBR.

Reference 1:

O. Iglesias, M.J. Rivero, A.M. Urtiaga, I. Ortiz, Membrane-based photocatalytic systems for process intensification, Chem. Eng. J. 305 (2016) 136–148. <https://doi.org/10.1016/j.cej.2016.01.047>.

Reference 2:

C.P.M. de Oliveira, M.M. Viana, G.R. Silva, L.S. Frade Lima, E. Coutinho de Paula, M.C.S. Amaral, Potential use of green TiO₂ and recycled membrane in a photocatalytic membrane reactor for oil refinery wastewater polishing, J. Clean. Prod. 257 (2020) 120526. <https://doi.org/10.1016/j.jclepro.2020.120526>.

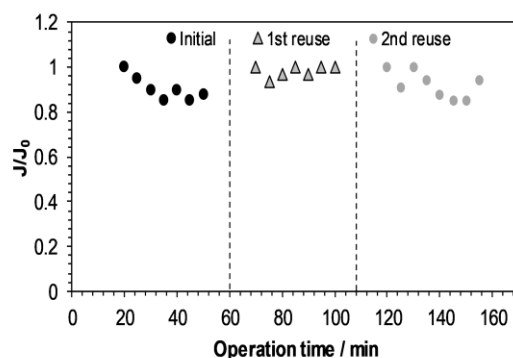


Figure 1: Permeate flux over time in the PMR with the catalyst reuse.

Heat to hydrogen by RED

Solberg, Simon Birger Byremo - Main Author¹; Zimmerman, Pauline - Co-Author¹; Wilhelmsen, Øivind - Co-Author¹; Lamb, Jacob - Co-Author¹; Burheim, Odne - Co-Author¹; Bock, Robert - Co-Author²

¹Norwegian University of Science and Technology, ²Federal Institute for Materials Research and Testing of Germany

Main topic: Electro-membrane processes

The negative Gibbs energy of mixing a concentrated electrolyte solution with a more dilute solution of the same salt may be exploited through the process of reverse electrodialysis (RED) [1]. Ion exchange membranes (IEM) separate alternating concentrate and dilute solutions creating emf. With an appropriate selection of electrodes, a stack of such repeating units may be used as a flow battery or to produce hydrogen [2]. The spent electrolytes may then be restored to the initial concentrations by thermal processing, e.g. by evaporation of excess water from spent concentrate which is then added to the spent dilute [2]. We use non-equilibrium thermodynamics in a numerical model of the transport processes perpendicular to the IEMs [1]. The model highlights the influence of coupled water and salt transport on membrane permselectivity, and the expected hydrogen production rate is calculated for a KCl electrolyte. Furthermore, we investigate a case where the electrolyte regeneration is carried out with waste heat at reduced pressure, and the heating duty is estimated. This integrated system could serve as an alternative to conventional water electrolysis, where waste heat is the input rather than electricity.

Reference 1:

D. Bedeaux, S. Kjelstrup, *Non-Equilibrium Thermodynamics of Heterogeneous Systems*, World Scientific, 2008.

Reference 2:

K. W. Krakhella, M. Morales, R. Bock, F. Seland, O. S. Burheim, K. E. Einarsrud, *Electrodialytic Energy Storage: Permselectivity Stack Measurements and Life-Cycle Analysis*, *Energies* 13, 2020.

Heparinized in-situ functionalized chitosan membranes

Rose, Ilka - Main Author^{1,2}; Roth, Hannah - Co-Author^{2,1}; Klimosch, Sascha N. - Co-Author³; Wessling, Matthias - Co-Author^{2,1}; Schmolz, Manfred W. - Co-Author³; Kather, Michael - Co-Author^{1,2}

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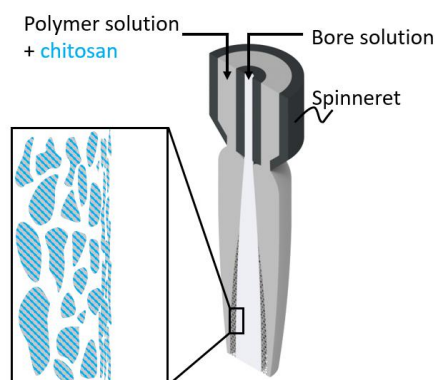
Main topic: Bio-medical applications

In recent years, the modification of membrane surfaces has become increasingly important. In this field, chitosan, formed by deacetylation of chitin, is often used in medical applications due to its anti-fouling properties, along with the hydrophilic effect, antibacterial property, non-toxicity, and non-allergic effect. In addition, these chitosan-functionalized membranes are often used for heparinization due to their charge differences. Subsequent heparinized surfaces are a promising alternative to the anticoagulation of human blood, otherwise achieved by high amounts of injected heparin. However, in almost all membrane processes that use chitosan as a coating for heparinization, chitosan is immobilized after membrane fabrication. Thus, the membrane undergoes additional, complex, and usually costly post-treatment steps to accomplish the final membrane product.

In this work, we present the successful in situ modification of membranes with chitosan for subsequent heparinization. Here, our chemistry in a spinneret technology serves as a basis for the fabrication of chitosan-modified membranes. Pretests with chitosan-modified flat sheet membranes show promising anti-fouling properties. Heparinization of these chitosan-functionalized membranes shows a significant improvement in hemocompatibility based on human blood tests. Finally, using the dry-jet wet spinning process, chitosan-immobilized polyethersulfone hollow fiber membranes are produced. The in situ modified chitosan membranes show an influence on the pure water permeance of the fibers. These hollow fiber membranes and the pretested flat sheet membranes are suitable for dialysis and enable applications in other membrane processes.

We highlight our chitosan-functionalized membranes using our chemistry in a spinneret approach, which turns a multi-step chitosan coating into a single-step in situ chitosan immobilization. As a result, we eliminate time-consuming post-treatment steps without adversely affecting the properties of the membranes.

In-situ chitosan functionalization via chemistry in a spinneret technique



Hierarchical ion exchange membranes as versatile materials for application in water treatment and energy storage

Deboli, Francesco - Co-Author^{1,2}; Van der Bruggen, Bart - Co-Author; Donten, Mateusz - Co-Author³

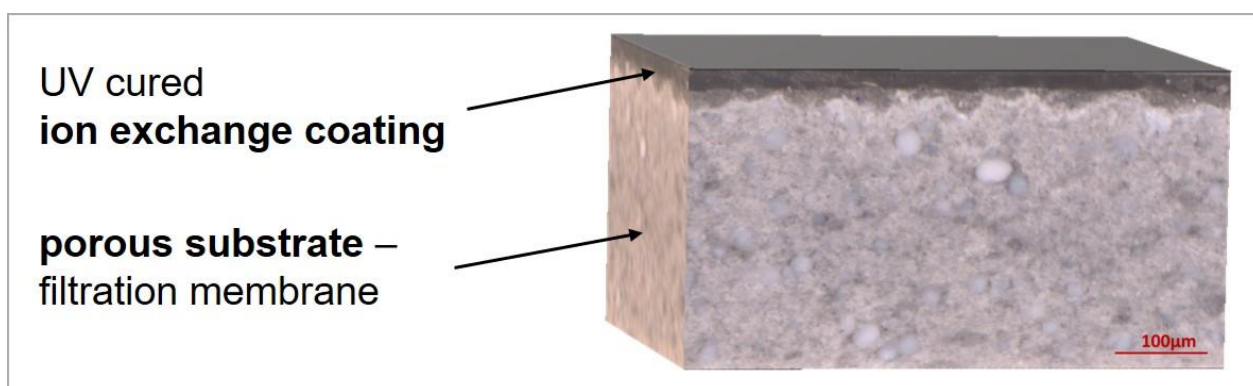
¹Amer-Sil S.A., 61 Rue d'Olm, L-8281, Luxembourg, ²Department of Chemical Engineering, KU Leuven, Celestijnenlaan 200F, B-3001, Leuven, Belgium, ³Amer-Sil S.A.

Main topic: Novel membrane materials

Ion exchange membranes (IEM) are at the core of many electromembrane processes with a key role in tackling today's challenges related to resource scarcity and energy management. IEM applications range from electrodialysis and capacitive deionization—in view of water treatment and resource recovery—over redox flow batteries for energy storage, to fuel cells and artificial photosynthesis cells for energy conversion. The growing number of technologies relying on IEMs creates the need of a wider variety of materials, with targeted and tuneable properties. The next generation of IEMs should be fabricated from largely available precursors, and through sustainable processes with the aim of reducing their end price and thus boost the spread of the related applications.

This poster presents a novel, easily scalable approach to the fabrication of ion exchange membranes, and demonstrates their performance in desalination by electrodialysis. Composite hierarchical ion exchange membranes have been prepared by coating and *in-situ* UV curing a thin layer of radically reactive precursors on top of a porous substrate. In this process a crosslinked functional coating is formed on the substrate surface. The substrate provides mechanical robustness to the membrane, while the ionomer coating controls its ionic selectivity properties. Low thicknesses of the ion exchange coating (currently 30 μm) can be achieved, allowing for a high ionic conductivity and permselectivity without compromising mechanical properties. Both anion and cation exchange membranes can be fabricated by simple adjustments of the ionomer formulation, to include reactive monomers with selected ionic function groups. Area specific resistance values in the range of 4–6 $\Omega\cdot\text{cm}^2$ (through plane, 0.5 M NaCl) have been measured for both cation and anion exchange membranes with permselectivity values exceeding 90%. In electrodialysis desalination experiments the hierarchical membranes allowed to reach desalination rates and current efficiency values in line with commercially available materials.

The presented membrane concept is a flexible platform enabling facile tuning of membrane properties by decoupling mechanical and ion transport properties. The use of industrial grade precursors, in combination with solvent free, low energy processes such as blade coating and UV curing is expected to keep the direct end cost of production of the membranes in the range of 10's $\text{€}/\text{m}^2$.



High flux thin-film composite PIM-1 membranes for butanol recovery

Mohsenpour, Sajjad - Co-Author

Sajjad Mohsenpour, Jorge Contreras-Martínez, Ahmed Ameen, Peter M. Budd, Carmen García-Payo, Mohamed Khaye, Patricia Gorgojo

Main topic: Pervaporation and vapour permeation

High flux thin-film composite PIM-1 membranes for butanol recovery

Department of Chemical Engineering and Analytical Science, School of Engineering, The University of Manchester, Oxford Road, Manchester M13 9PL, UK

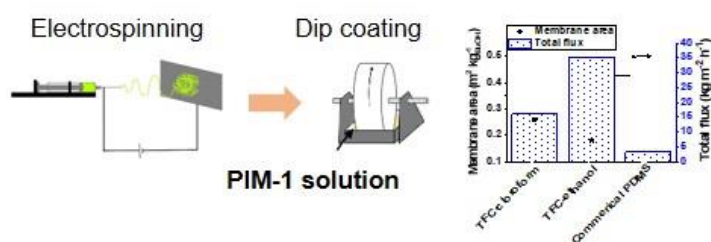
Thin-film composite (TFC) of polymer of intrinsic microporosity (PIM-1) membranes coated on macroporous supports were proposed in pervaporation (PV) process for water/n-butanol separation [1]. It has been claimed that the porosity and effective membrane area of the support can influence the total PV permeate flux. In this study [2], TFC membranes of PIM-1 have been prepared by dip-coating on a highly porous electrospun polyvinylidene fluoride (PVDF) nanofibrous support. The support was impregnated in a non-solvent (methanol, ethanol, and chloroform) before the dip-coating process to prevent the penetration of PIM-1 inside the PVDF nanofibrous (Figure 1). The fabricated membranes indicated very high permeate fluxes with an acceptable n-butanol/water separation factor. Aspen Hysys and Aspen custom modeler were used to model hybrid PV-distillation systems. Different PV membranes including the membranes prepared in this study and commercial PDMS membranes have been used as a PV membrane in the simulation. It was concluded that the butanol recovery cost for the hybrid systems is 10% lower than the recovery cost in a conventional standalone distillation column. In addition, for the membranes prepared in this study, the required membrane is 50% smaller than the commercial PDMS membrane (Figure 1).

Reference 1:

Gao, L.; Alberto, M.; Gorgojo, P.; Szekely, G.; Budd, P. M. High-flux PIM-1/PVDF thin film composite membranes for 1-butanol/water pervaporation. *J. Membr. Sci.* 2017, 529, 207-214.

Reference 2:

<https://doi.org/10.1021/acsami.1c09112>.



Malanca, Alina Anamaria - Co-Author

Main topic: Electro-membrane processes

The production of organic acids from fermentation is a promising approach to obtain building-block chemicals from renewable carbon sources. Production and separation of valuable products from biomass have indeed been successfully achieved and implemented at full scale. However, many are yet not economically competitive with their equivalent oil-based version. In fact, two of the main drawbacks of these type of industries are the costs to counteract the product inhibition in the fermenter and downstream separation costs.

Membranes play a fundamental role in purifying fermentation products and lower the total number of unit operations needed. Membrane electrolysis is a novel electrochemical extraction technique in which electrodes are present in the fermentation broth to drive (bio)electrochemical reactions while utilizing electro-motive forces to transport charged acid anions from a cathode chamber across an anion exchange membrane into an anode site. The main advantages of such setup are the hydroxide ions and the molecular H₂ generated during the cathodic electrolysis: the first could potentially eliminate dosing the fermentation with base, while H₂ can regenerate NADH in many microorganisms, leading to improved conversion yields. Furthermore, protons generated at the anode acidify the products, therefore not requiring further addition of acid. Pateraki et al., (2019) showed that in an integrated fed-batch *Basfia succiniciproducens* succinic acid fermentation with membrane electrolysis the productivity increased of 30% while the NaOH buffer usage was reduced by 33%.

We have implemented the above-mentioned hypothesis with a first simple setup made by an electrochemical cell, anionic exchange membrane and synthetic broth of different organic acids (mainly succinic acid) and we obtained a very promising proof of concept. The work will proceed by integrating the electrolytic cell with a continuous fermentation of *Actinobacillus succinogenes* in which the fermentation broth will recirculate continuously between the fermenter and the cathode of the electrochemical cell.

Subsequently, we will design a new membrane reactor with anionic exchange membrane submerged directly into the fermenter. This solution will increase the membrane area, making the separation potentially more efficient. At the same time the molecular H₂ is going to be closer to the microorganisms and thus improving the product yield.

Reference 1:

C. Pateraki, S. J. Andersen, D. Ladakis, A. Koutinas, K. Rabaey (2019). Direct electrochemical extraction increases microbial succinic acid production from spent sulphite liquor. *Green Chemistry*, 21, 2401-2411, DOI: 10.1039/C9GC00361D

Reference 2:

E. Mancini, S.S. Mansouri, K.V. Gernaey, J. Luo, M. Pinello (20219). From second generation feed-stocks to innovative fermentation and downstream techniques for succinic acid production. *Critical Reviews in Environmental Science and Technology*, 50:18, 1829-1873, DOI: 10.1080/10643389.2019.1670530

High performance thin-film composite membranes as next generation CO2 capture technologies

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¹Leitat Technological Center, ²Orelis, ³SINTEF AS, ⁴University of Twente

Main topic: CO2 capture

Global warming due to greenhouse gases has become a serious worldwide concern. The shifting from fossil fuel to renewable energy has been slow mostly due to technological barriers. Therefore, there is need for an immediate-medium term solution to address CO2 emission of fossil fuel plants in a cost-effective way. CO2 capture technologies are recognized as one of the direct answers to this problem. Currently, CO2 capture technologies have been adopted in different parts of the world but still there is a long way to reach their full potential. Membrane systems offer an attractive alternative to the current available capture technologies.

The development of thin-film composite membranes for CO2 separation has gained increasing attention due to the possibility to optimize the transport properties of each membrane layer independently. In most thin-film composites PDMS or PTFE are used as gutter layer due to their high gas permeability, but their strong hydrophobic character is hampering the uniformly spreading of the hydrophilic selective layer. Atmospheric plasma, due to its simplicity of use and low cost is an interesting technology for modifying the hydrophobic character of the gutter layer. The system is suitable especially for thermally sensitive and geometrically complex surfaces and materials. The treatment is very efficient due to a combination of chemical and physical effects.

In the present work we show an industrial scalable process where atmospheric plasma treatment of the PDMS gutter layer is adopted in fabrication of the thin-film composite membranes. An atmospheric Plasma Jet RD1004 was used, where the effect of the plasma treatment parameters on the performance of the gutter layer and final thin-film composite membrane was studied. The gas selectivity and permeability characteristics of the membranes has been investigated by using of single gas and gas mixtures of CO2 and N2. The findings suggest that atmospheric plasma treatment is a suitable technology to enhance PDMS surface wetting performance for application in thin-film composite membranes. The work has been conducted within the framework of the H2020 GENESIS project that aims to develop and upscale two promising membrane systems for CO2 capture.

Reference 1:

D. Y. C. Leung, G. Caramanna, and M. M. Maroto-Valer, "An overview of current status of carbon dioxide capture and storage technologies," *Renew. Sustain. Energy Rev.*, vol. 39, pp. 426–443, 2014

Reference 2:

O. Selyanchyn, R. Selyanchyn, and S. Fujikawa, "Critical Role of the Molecular Interface in Double-Layered Pebax-1657/PDMS Nanomembranes for Highly Efficient CO2/N2 Gas Separation," *ACS Appl. Mater. Interfaces*, vol. 12, no. 29, pp. 33196–33209, 2020.

High Pressure Reverse Osmosis shows promising perspectives for the Treatment of Electroplating Wastewater and Trivalent Chromium

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¹TH Köln - University of Applied Sciences Cologne, Faculty of Applied Natural Sciences, Leverkusen (Germany), ²BIA Kunststoff- und Galvanotechnik GmbH & Co. KG, Solingen (Germany), ³University of Birmingham, School of Engineering, Birmingham (United Kingdom)

Main topic: Wastewater treatment

Aiming for a closed-loop economy, the European Green Deal does not only ask for substitution strategies and resource-efficient production methods, but also aims towards a zero-waste policy [1]. In this context, the electroplating industry focuses on trivalent chromium (Cr(III)) for plating applications and a process for combined water purification and electrolyte recycling [2]. Due to the high-required electrolyte concentrations, achieving this goal is still regarded as a challenging task. Reverse osmosis has been long recognized as a potential technology for the purification of electroplating wastewater but its application for an appropriate recovery and re-concentration of electrolytes has not been yet extensively investigated.

In this work, we carried out this investigation and attempted to define the limitations of High Pressure Reverse Osmosis (HPRO, up to 80 bar) with regard to the highest achievable Cr(III) concentration. Prior to HPRO trials, a dilution of a real Cr(III) electroplating solution (0.8 g/L Cr(III)) was prepared as a simulated wastewater (pH 4.7), filtrated through a 0.2 µm filter and subsequently used as a feed without further pre-treatment. Permeate fluxes ranging from 10 to 30 L/(m²*h) were set during the crossflow concentration process. A wide range of key compounds was quantified via a combined ICP-OES method, giving insight in the dependency of rejection on the flux. This method was combined with analyses of the total organic carbon (TOC) content as well as the surface tension, showing the accumulation of organic bath components in the concentrate. The rejection of Cr(III), boric acid, sulphate and TOC were then measured for different feed concentrations and permeate fluxes after reaching steady-state condition. For the first time, we successfully demonstrate that a re-concentration of electroplating components from electroplating wastewater (containing Cr(III)) close to the required concentration (7.5 g/L Cr(III)) can be achieved by means of a HPRO process.

The presented work is part of the intelWATT project and receives funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 958454.

Reference 1:

European Commission, The European Green Deal, European Commission. 53 (2019) 24. <https://doi.org/10.1017/CBO9781107415324.004>.

Reference 2:

Commission Regulation (EU) No 348/2013 of 17 April 2013 amending Annex XIV to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), 2013. http://echa.europa.eu/documents/10162/13640/3rd_a_xiv_ (accessed May 11, 2021).

Highly ordered biofunctionalized nanostructured membrane for environmental biomolecular sensing

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¹National Research Council of Italy, Institute on Membrane Technology (CNR-ITM)

Main topic: Biomimetic and bioinspired membranes

The use of nanostructured membranes as support for macrobiomolecules immobilization permits to both impart biological functions to artificial membranes and conformational stability to labile biomacromolecules (such as enzymes, antibodies). In addition to material chemistry and physical properties, engineering of membrane morphology and topography plays a pivotal role in balancing selectivity and stability of heterogenized biomacromolecules. We speculated that immobilization of biomacromolecules onto a support having nanoscale spherical conformation could be beneficial to prevent deactivation due to crowding phenomena (because of the lower steric hindrance guaranteed by the radial spatial orientation of the molecules). Indeed, higher enzymatic efficiency (K_{cat}/K_m) was obtained when immobilizing a phosphotriesterase on nanoparticles loaded to a flat-sheet membrane compared to when immobilizing the enzyme directly on the flat-sheet membrane [1]. The heterogenization of enzymes on nanoparticles loaded on porous membrane matrix permits to tune environment at the nanoscale that may differ from the one at macroscale. For example, using spherical hydrogels loaded into PVDF porous membranes it was possible to guarantee hydrophilic conditions with proper water activity at the level of the hydrogel (where the enzyme was immobilized) while maintaining the macroscopic hydrophobic character of the membrane [2]. These kinds of systems are useful in developing functionalized filters' masks for decontamination of harmful substances present in air. The ordered distribution of nanoparticles within the membrane matrix is also very important, especially for developing biosensing systems based on plasmonic resonance transduction. Smart, clean, and safe environment will more and more rely on these highly selective biofunctionalized materials. The unique properties of membranes in terms of nanostructure, compartmentalization, and mass transport permit to maximize surface so that to capture, increase target analyte concentration and transmit the signal to the transducer. The lecture will illustrate recent results obtained on the biofunctionalization of plasmonic nanoparticles and their ordered distribution in miniaturized polymeric membrane systems.

Acknowledgements

Authors would like to thank POR Calabria FESR-FSE 2014/2020 for the financial support to the SmartMatter project within the M-ERA.NET Call 2019

Reference 1:

Gebreyohannes, A.Y., Mazzei, R., Yahia Marei Abdelrahim, M., Vitola, G., Porzio, E., Manco, G., Barboiu, M., Giorno, L. Phosphotriesterase-magnetic nanoparticles bioconjugates with improved enzyme activity in a biocatalytic membrane reactor (2018) *Bioconjugate Chemistry*, 29 (6), pp 2001–2008, DOI: 10.1021/acs.bioconjchem.8b00214

Reference 2:

Vitola, G., Büning, D., Schumacher, J., Mazzei, R., Giorno, L., Ulbricht, M., Development of a Novel Immobilization Method by Using Microgels to Keep Enzyme in Hydrated Microenvironment in Porous Hydrophobic Membranes, (2017) *Macromolecular Bioscience*, 17 (5), art. no. 1600381, DOI: 10.1002/mabi.201600381

Hollow fibre membrane modules: construction, Computational Fluid Dynamics simulation and optimization

Horvat, Tomislav - Main Author¹; Akkoyunlu, Burcu - Co-Author; Daly, Sorcha - Co-Author; Casey, Eoin - Co-Author
¹University College Dublin

Main topic: Membrane reactors

Converting waste greenhouse gases such as CO₂, CO, and CH₄ into valuable products is an exciting opportunity that is gaining attention in the area of the bioeconomy. Biological gas conversion via fermentation of bacteria as bio-catalysts is increasing in popularity as the reaction does not require extreme operating conditions and expensive catalysts to be performed.¹ One major drawback of gas fermentation is that it is limited by gas to liquid mass transfer which results in low productivity. One way of addressing this problem is the use of membrane modules to increase gas to liquid mass transfer. The relationship between the membrane bioreactor system hydrodynamics and performance be examined in this study. A custom membrane module has been designed, constructed and tested, see figure 1. The key characteristic of this module is its well-defined internal geometry that is straightforward to simulate. This study examines fibre distribution within the bioreactor based on computational fluid dynamics (CFD) simulations of the proposed system. The CFD simulation has been developed, see figure 2, and validated using tracer studies, see figure 3. The validated CFD model will predict the velocity fields within the internal geometry. By altering the internal geometry with the same velocity field, the effect on mass transfer of gases within the system can be measured and observed. This important information can assist further optimisation and scale up of the system.



Figure 1. Constructed membrane module

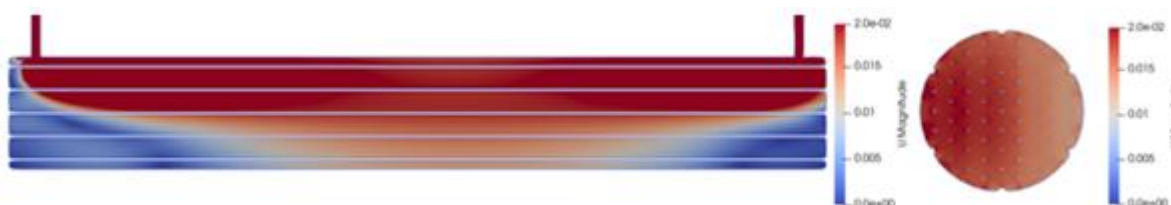


Figure 2. CFD model of the constructed membrane module (cross section area: z-axis – left, y-axis – right)

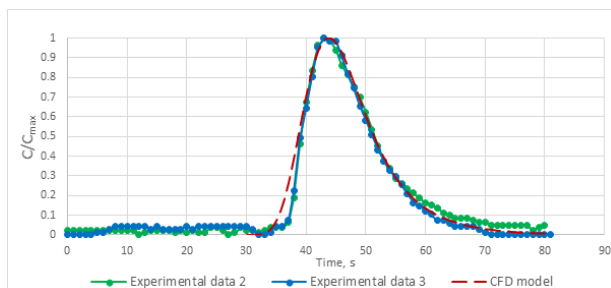


Figure 3. Experimental and modelled RTD experiments

Reference 1:

1. Sun, X., Atiyeh, H., Huhnke, R. and Tanner, R., 2019. Syngas fermentation process development for production of biofuels and chemicals: A review. *Bioresource Technology Reports*, 7, p.100279.

Hot-pressed saloplastic polyelectrolyte complexes as sustainable alkaline stable monovalent-ion selective anion exchange membranes

Krishna B, Ameya - Main Author; Lindhoud, Saskia - Co-Author¹; M. de Vos, Wiebe - Co-Author¹

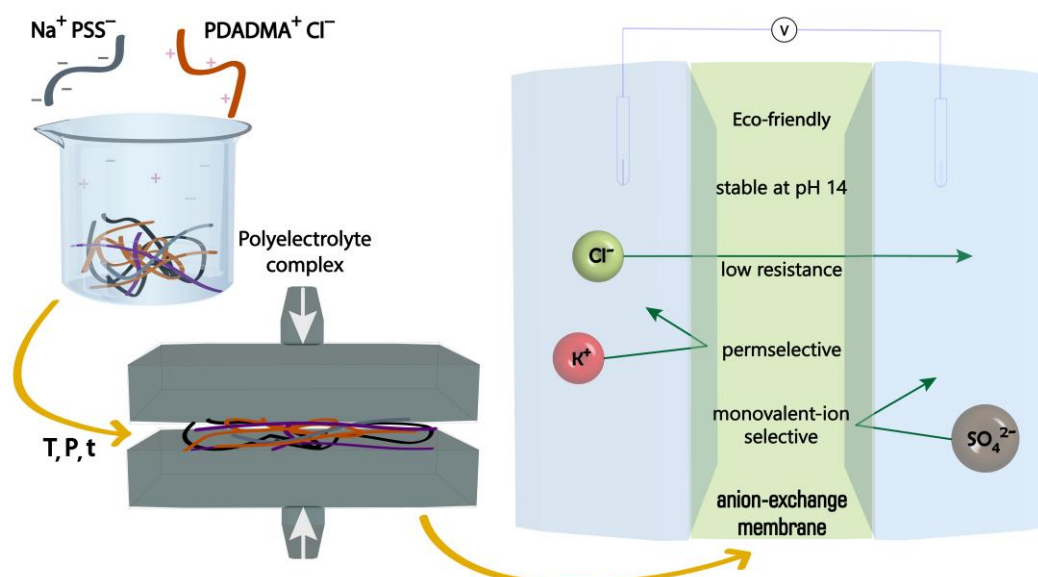
¹University of Twente

Main topic: Novel membrane materials

Polymer-based ion-exchange membranes have benefitted a wide range of processes, ranging from fuel cells to desalination. However, challenges such as alkaline stability, monovalent ion selectivity, cost-effectivity, and process sustainability largely persist. This work uses polyelectrolyte complexes using high molecular weight poly(styrenesulfonate) (PSS) and poly(diallyldimethylammonium) (PDADMA) as the starting point to make anion-exchange membranes by hot-pressing. This completely aqueous production approach leads to dense (non-porous) alkaline stable saloplastics with an excess of cationic groups, demonstrating good stability even at relatively high salinities. Key performance indicators for anion exchange membranes, such as water uptake (~40%), permselectivity (up to 97%), ion exchange capacity (1.01 mmol g^{-1}), and resistance (2.3 ohm.cm^2) are measured and the membranes show comparable values to commercial membranes. What really sets these membranes apart is their natural long term (up to 60 days) stability at extreme acidic (pH 0) and alkaline conditions (pH 14), and a relevant monovalent selectivity of up to 6.3 for Cl^- over SO_4^{2-} . Overall this work showcases PDADMA/PSS based saloplastics as highly promising and stable anion-exchange membranes, that can be produced by a simple, scalable, and sustainable approach.

Reference 1:

Krishna B, A., Lindhoud, S., de Vos, W.M. J. Colloids and Interface Science. 2021, 593, 11-20



How the hell can we model these complex membrane processes?

Crespo, João - Main Author¹; Crespo, João - Main Author¹; Galinha, Cláudia - Co-Author¹

¹FCT - NOVA University of Lisbon

Main topic: Transport models

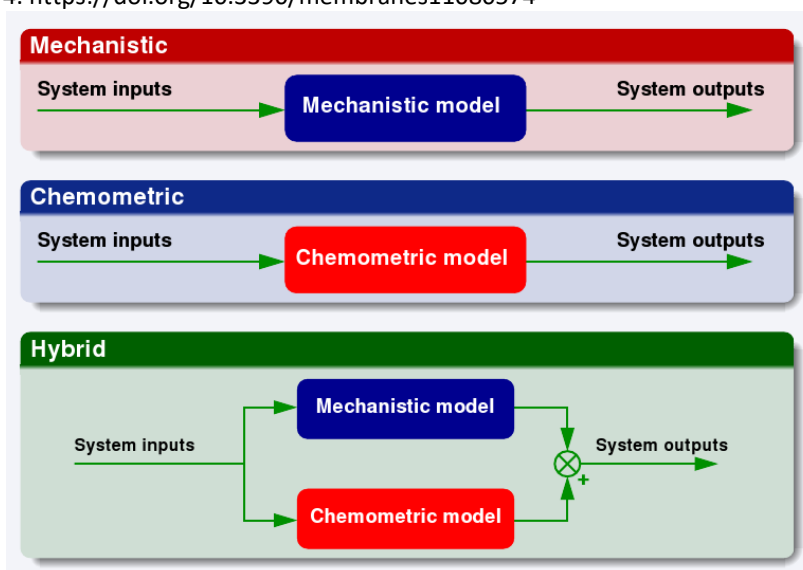
Modelling is a requirement to simulate (and predict) process and membrane performance, to infer about optimal process conditions, to assess fouling development, and ultimately, for process monitoring and control. Despite the actual dissemination of terms such as Machine Learning, the use of such computational tools to model membrane processes was regarded by many in the past as not useful from a scientific point-of-view.

The main goal in this lecture is to illustrate how non-mechanistic modelling techniques (also called chemometrics) can be applied with advantage to such complex membrane processes. These approaches may be applied to situations where other mathematical approaches fail. The first situation deals with cases where the existing mechanistic models are not able to describe correctly the problem under study. This may happen when the phenomena/processes investigated are rather complex in their character and, therefore, mechanistic models supported on the relation between a limited number of variables, are not able to fully capture the variance of the data observed. There are several phenomena which, due to their complexity, are not fully described by mechanistic models. For example, this is the case of the development of reliable models for the processing of solvent mixtures by solvent-resistant nanofiltration (NF) membranes.

The second situation refers to cases where relevant information about the process under study is available in the form of images (i.e., obtained by microscopy techniques) and spectra (from different complementary spectroscopic techniques). Traditionally, the information acquired by these characterization techniques is deconvoluted and interpreted, supported on our knowledge about the material observed and the technique employed. Hybrid modelling aims at reducing this complex information to parameters, which may then be integrated with deterministic models, offering a totally diverse approach for the use of this information: the raw data acquired in an image or in a spectrum are firstly vectorized; once in a numeric form this information may be integrated as input data in a model and related with relevant operating or performance process parameters. This approach will be illustrated in this lecture for modelling of membrane (bio)processes and (bio)fouling using information acquired by two-dimensional (2D) fluorescence.

Reference 1:

Galinha, C.F. and Crespo, J.G., From Black Box to Machine Learning: A Journey through Membrane Process Modelling. *Membranes* 2021, 11, 574. <https://doi.org/10.3390/membranes11080574>



How to: create micron-sized defects in Reverse Osmosis membranes

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¹Ghent University

Main topic: Ageing of polymeric membranes

Background

Dense membranes (e.g. RO), rely on an uninterrupted barrier layer to separate feed from permeate, and safeguard the permeate from contaminants, such as micropollutants or pathogens. However, small defects (<10 μm) are inevitably present, given the large membrane area employed in practice. Studying small defects is difficult, because their detection and quantification is akin to finding a needle in a haystack. Therefore, creating micron-sized defects on purpose is a first step towards systematic study of defects: detection and their impact on membrane transport properties. We explore laser ablation and electrical discharge ablation. Both techniques operate at atmospheric pressure instead of (high) vacuum, and do not require the sample to be coated, so coupons are still usable for filtration tests after defect introduction. This is in contrast to nanofabrication methods such as focused ion beam or plasma etching.

Materials & Methods

Filmtec SW30-HR and FT30 RO membrane coupons were used, membrane performance was evaluated by measuring water and NaCl permeability and Rhodamine WT rejection. Laser ablation is performed by a 3D Micromac microSTRUCT vario ps/fs Laser at 532 nm wavelength. Electrical discharge ablation is performed using an in-house developed machine, which generates 5 kV DC discharges of 10 μs duration. Discharges are directed by micro-needles positioned above a grounded, flat electrode (Fig. 1A,B). Defects are visualized using optical and scanning electron microscopy.

Results

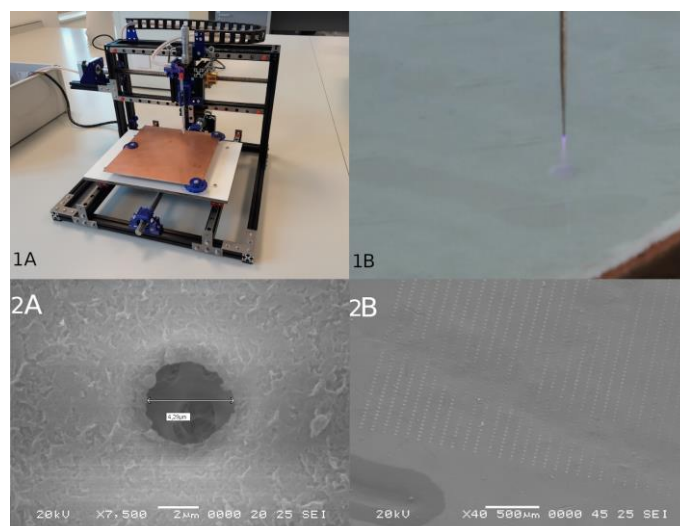
Laser ablation was found to be capable of producing defects down to 4 μm (Fig. 2A), but suffers from having a narrow focal plane ($\sim 2 \mu\text{m}$) in the normal (vertical) direction. This implies that variable membrane thickness causes the laser to be out-of-focus, which inhibits defect formation (Fig. 2B, lower right corner). Work is on-going to automatically refocus the laser at each defect location.

Electrical discharge ablation does not need focusing, significantly simplifying experimental protocols. The defects obtained so far are somewhat larger (a few tens μm) than those obtained by laser ablation. Further refinements include varying spark gap size and discharge current.

Both techniques are capable of introducing micron-sized defects in membranes, without altering the transport properties of the surrounding membrane. This opens up the systematic study of defect-bearing membranes.

Reference 1:

Reverse osmosis integrity monitoring in water reuse: The challenge to verify virus removal - A review. Pype et al., Water Research, 2016



Humidity-enhanced sorption of CO₂ in Polyvinylamine (PVAm) membranes for facilitated transport

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¹University of Edinburgh, ²University of Bologna, ³University of Edinburgh (UK), ⁴INSTM Consorzio Interuniversitario di Scienza e Tecnologia dei Materiali

Main topic: CO₂ capture

Polyvinylamine (PVAm) is used as membrane for CO₂ capture because it contains a high fraction of amine moieties and is highly hydrophilic, thus allowing a facilitated transport mechanism in which CO₂ reacts according to the scheme of Fig. 1, and diffuses as bicarbonate ion (HCO₃⁻) in the membrane

To predict the transport rates and effectively design the membrane-based capture process, one has to quantify the diffusion and sorption coefficients of CO₂ in the membrane. The sorption term requires modelling of the phase equilibrium between the humid gas and the polyelectrolyte solution. To this aim, we used an equation of state model that is based on the Perturbed Chain Statistical Associating Fluid Theory explicitly accounts for ionic interactions and parameters for electrolytes and polyelectrolytes, the pe-PC-SAFT model.

With an appropriate parametrization of the binary systems H₂O-CO₂, CO₂-PVAm and H₂O-PVAm based on binary data, it was possible to predict the absorption of CO₂ in the water-swollen polyelectrolytes at various temperatures and relative humidity. A qualitative experimental analysis of the CO₂ sorption in dry and humid polyvinylamine was also carried out with FTIR-ATR spectroscopy, which confirms the simulated trends.

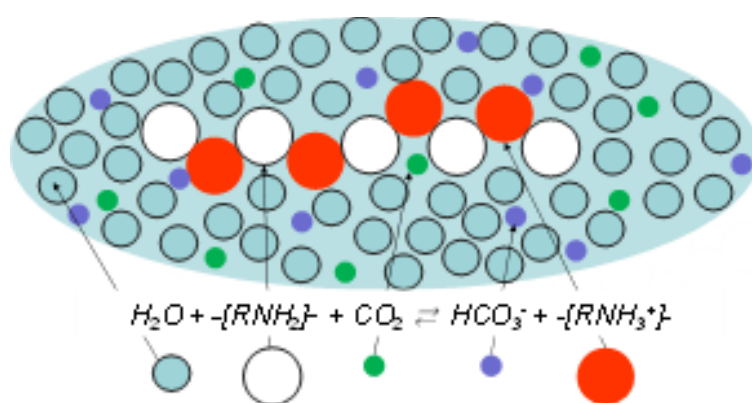
Performed in the framework of the European Project H2020 NANOMEMC2 “NanoMaterials Enhanced Membranes for Carbon Capture”, GA No. 727734

Reference 1:

Held, Cameretti, Sadowski, 2020, Modeling aqueous electrolyte solutions: Part 1. Fully dissociated electrolytes, Fluid Phase Equilib. 270, 87–96.

Reference 2:

Naeem, Sadowski, 2011, pePC-SAFT: Modeling of polyelectrolyte systems 2. Aqueous two-phase systems, Fluid Phase Equilib, 306, 67-75.



Hybrid cascades for post-combustion CO₂ capture using facilitated transport membranes with optional liquefaction train: importance of membrane positioning in the process design

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Main topic: CO₂ capture

The use of membrane module performances obtained in industrially-relevant environment as the basis in process simulation can lead to a more realistic prediction of a membrane-based CO₂ capture system performance. In this work, we report the use of two classes of industrially validated membranes, *i.e.*, hybrid facilitated transport membranes (HFTMs), which are characterized by higher permeances and lower selectivity, and the fixed site carrier (FSC) polyvinylamine (PVAm) membrane, which is characterized by lower permeance and higher selectivity, to study the potential of these membranes in two-stage configurations for post-combustion CO₂ capture applications.

Hybrid membrane cascades developed by using membranes of varying properties in different stages were found to be beneficial in reaching purity and capture rate targets simultaneously. Such cascades showcased reduced membrane area and energy requirements compared to traditional two/three stage membrane processes. Additionally, the positioning of membranes with different properties in different stages was found to influence the performance of the system significantly. Processes with HFTMs in the first stage coupled with a PVAm membrane in the second stage performed best with the lowest total energy/membrane area requirement and recycle ratio for a target of 90% recovery and >90% purity of CO₂. The case of using PVAm membranes in both stages performs best only at a lower purity requirement (<90%). The study reveals the importance of using an optimized combination of membranes with different separation capabilities at different stages.

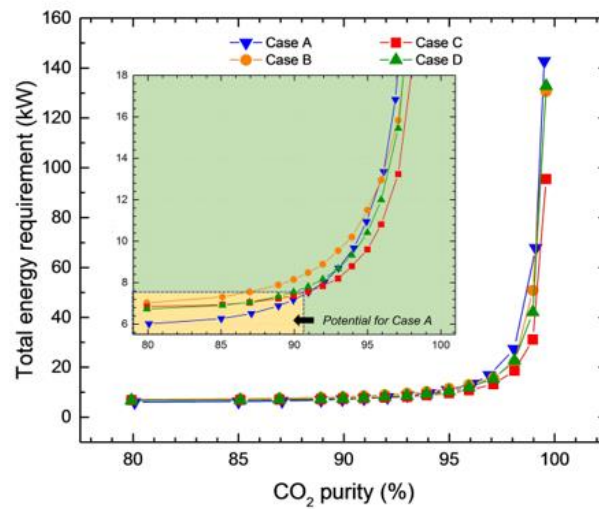
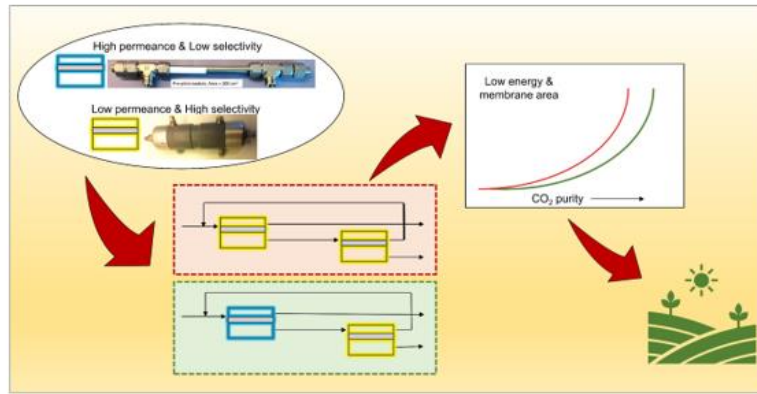
Furthermore, a liquefaction train was implemented downstream of second stage to further increase CO₂ capture targets upto 97% while generating liquified CO₂ stream suitable for transportation and storage. Specific energy demand as low as 0.63 kW/kg_{CO₂} was obtained with a membrane area demand of 7 m²/kg_{CO₂} for the cement flue gas conditions. Additionally, CO₂ concentration in feed was found to significantly influence the specific energy demand. Optimization studies are under investigation to benchmark the performance of the designed membrane-assisted liquefaction process against standard MEA process for post-combustion CO₂ capture.

Reference 1:

Janakiram, S.; Santinelli, F.; Costi, R.; Lindbråthen, A.; Nardelli, G.M.; Milkowski, K.; Ansaloni, L.; Deng, L. Field trial of hollow fiber modules of hybrid facilitated transport membranes for flue gas CO₂ capture in cement industry. *Chem. Eng. J.* 2020, 2020, 127405

Reference 2:

Janakiram, S.; Espejo, J.L.M.; Yu, X.; Ansaloni, L.; Deng, L. Facilitated transport membranes containing graphene oxide-based nanoplatelets for CO₂ separation: Effect of 2D filler properties. *J. Membr. Sci.* 2020, 616, 118626.



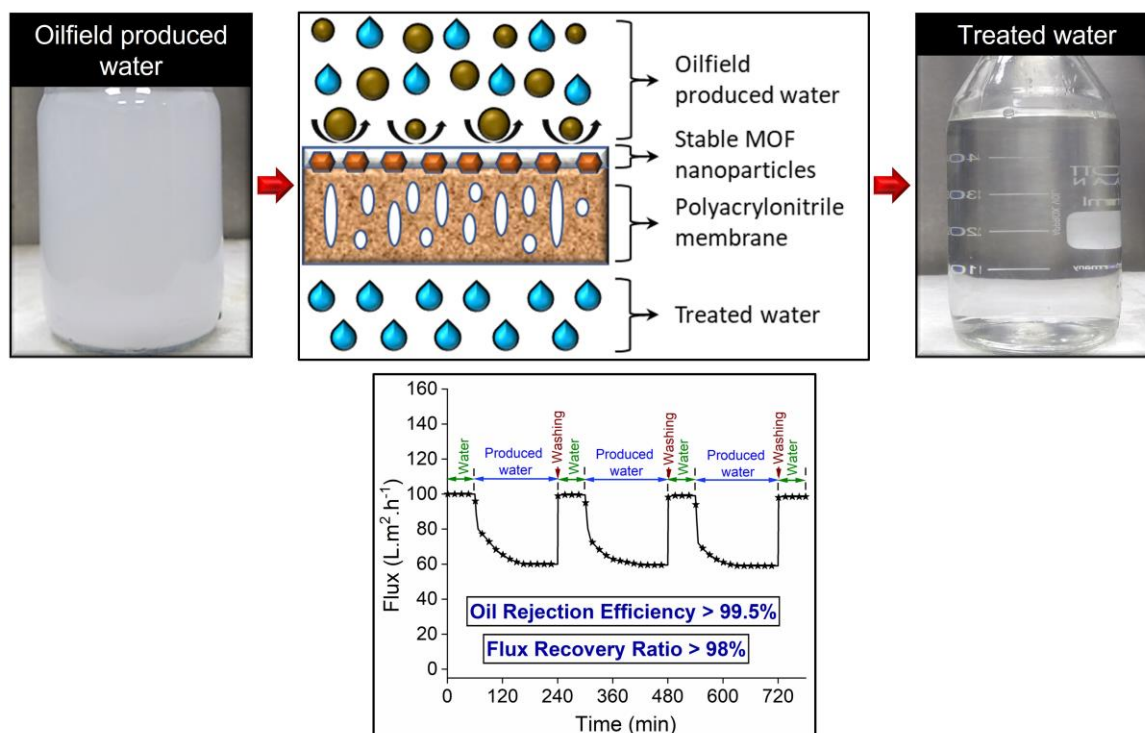
Influence of CO₂ purity on total energy requirement for a fixed CO₂ recovery of 90% for 50 Nm³ h⁻¹ of feed flue gas. Cases A-D vary in membrane positioning between stages. (Feed pressure in stage 1 = 1.7 bar; Interstage pressure = 1.7 bar; Permeate side: 0.1 bar vacuum in both stages; T = 60 °C.)

Hydrogel stabilized MOF nanoparticles on polymeric ultrafiltration membrane shows improved antifouling property and separation performance for oilfield produced water treatment

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¹Ben-Gurion University of the Negev, Israel

Main topic: Membrane fouling and cleaning

Produced water (PW) from the oil and gas industry is generated in an enormous amount to meet the ever-increasing demand of the growing human population in different societal sectors. PW requires treatment before discharge to minimize environmental damage or treatment for freshwater reclamation in water stress regions. Membrane technology is used for PW treatment. However, its performance is limited by membrane fouling. Therefore, to mitigate membrane fouling, surface modification by hydrogel coated nanoparticles interlayer is one of the preferred methods, among several other methods, due to the ease in processing and negligible environmental impact. In this study, an interlayer of metal organic framework (MOF) nanoparticles was in-situ grown on a polyacrylonitrile membrane, followed by coating with a grafted methacrylate hydrogel. The novelty of this study is to hydrostabilize the MOF nanoparticles on the membrane surface during long-term filtration experiments. Compared to the pristine membrane, the prepared membrane showed improved hydrophilic nature, negative surface charge in the operating pH, and minimal surface roughness. The pure water permeance of the functionalized membrane was measured to be $\sim 13\%$ higher ($447.9 \pm 6.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ vs. $396 \pm 6.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) than that of the pristine membrane. Interestingly, the functionalized membrane exhibited exceptionally high antifouling property compared to the pristine membrane (flux recovery was $98.5 \pm 0.6\%$ vs. $8.1 \pm 0.7\%$) when tested with the oilfield produced water for three 3 h long cycles of PW filtration. Moreover, $>99\%$ oil rejection efficiency was also shown by the functional membrane, indicating its outstanding PW separation performance. Overall, the results indicated that the hydrogel coated MOF interlayer on polyacrylonitrile membrane exhibits high flux, excellent fouling-resistance, and oil rejection efficiency for produced water treatment.



Hydrogen sulfide mix gas permeation in Aquivion® perfluorosulfonic acid (PFSA) ionomer membranes for natural gas sweetening

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¹University of Bologna

Main topic: Gas separation

Permeability of binary and ternary mixtures containing H₂S, CO₂ and CH₄ has been tested in short side chain perfluorosulfonic acid ionomer (PFSA), commercialized with the trade name Aquivion® E87-12S, in view of its application in natural gas sweetening. A purposely modified experimental set up was used to allow mixture testing in a fixed volume and variable pressure permeometer.

Permeation tests of CO₂/CH₄ and H₂S/CH₄ binary mixtures and of CO₂/H₂S/CH₄ ternary mixture were carried out at different temperatures, namely 27, 35 and 50°C, and at relative humidity ranging from 20 to 95%.

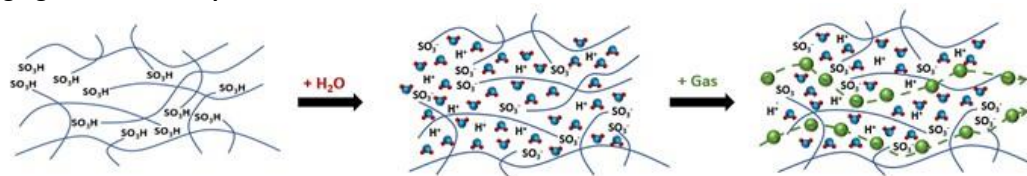
The results confirmed the major influence of water content on the gas permeation behavior in PFSA as permeability strongly increased with RH, thanks to the hydrophilic characteristic of the material which tends to swell in humid condition creating highly permeable water “channels” in the polymeric matrix. In particular, CO₂ and CH₄ results confirmed experimental data already available in the open literature and also H₂S for which no data were available, showed a similar trend with a permeability increase by more than two orders of magnitude in the humidity range investigated. At 95%RH, the permeability values obtained for all CO₂, CH₄ and H₂S are similar to those in pure water, suggesting that the gas transport across the membrane is governed by solution-diffusion mechanism in the water swollen domains of the hydrated PFSA.

H₂S permeability, in particular, reached the value of 500 Barrer at 50°C and 80%RH, and increased with temperature showing an Arrhenius type behavior which is common also to other gases inspected.

In terms of separation behavior Hydrogen sulfide selectivity with respect to methane increased with water activity, but decreased with temperature reaching a maximum value of 32 obtained at 27°C and 95% RH.

The tests performed proved the ability of Aquivion® material to separate acidic compounds from natural gas. The obtained values of permeability and selectivity are not the best observed in open literature but are of potential interest considering also the excellent resistance of the membrane to plasticization and aging in H₂S.

If you wish to upload a photo to support your abstract, please upload it here. File size: maximum 1000 x 1000 pixels. Only .jpg, .jpeg, .png, .gif fiels are accepted.



Mattia, Davide - Co-Author¹

¹University of Bath

Main topic: 1D- and 2D-materials for membranes

Nanofiltration (NF) membranes are widely used in a range of separation processes such as water/wastewater treatment, food processing, chemical transformations, textile manufacturing, pharmaceutical production and others. Most commercial NF membranes are thin film composite (TFC) membranes, which suffer from a number of problems, e.g. low stability to chlorine, ageing and fouling. In contrast, polyvinylidene fluoride (PVDF) possesses excellent chemical resistance, thermal stability, and mechanical strength. Due to these properties, PVDF membranes now has a large market share of commercial microfiltration and ultrafiltration membranes, for a wide range of applications such as drinking water production, pre-treatment for RO systems and wastewater treatment, etc. There is, however, no commercial PVDF NF membrane available in the market which retains its hydrophobicity and chemical stability. Current research on fabrication of PVDF NF membranes can be grouped into two categories, *i.e.*, surface modification and blending modification. In the former, the PVDF support does not contribute to the NF rejection performance, whereas in the latter the resulting membranes are more hydrophilic than the bare PVDF membranes. Here, we report the fabrication of the first poly(vinylidene fluoride) (PVDF) NF membranes retaining their hydrophobicity and surface chemistry. This was achieved by incorporating in the polymer 2D siloxene, which induce a compaction of the PVDF chains, resulting in low free volume and a highly ordered microstructure. Siloxene nanosheets were obtained from deintercalation of Ca from CaSi₂ using HCl, followed by exfoliation and size fractionation, with average lateral dimension of 1 ~ 2 μm and thickness of 3 ~ 4 nm. The resulting membranes, containing 0.075 wt.% of siloxene, have a pure water permeance of $22 \pm 2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and molecular weight cut-off (MWCO) of 530 Da. The same membrane also showed stable hexane permeance of $11 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for 24 h with MWCO of around 535 Da. These results supersede the performance of commercial NF membranes, expanding the potential application of nanofiltration to processes requiring stable, chemically resistant and hydrophobic nanofiltration membranes.

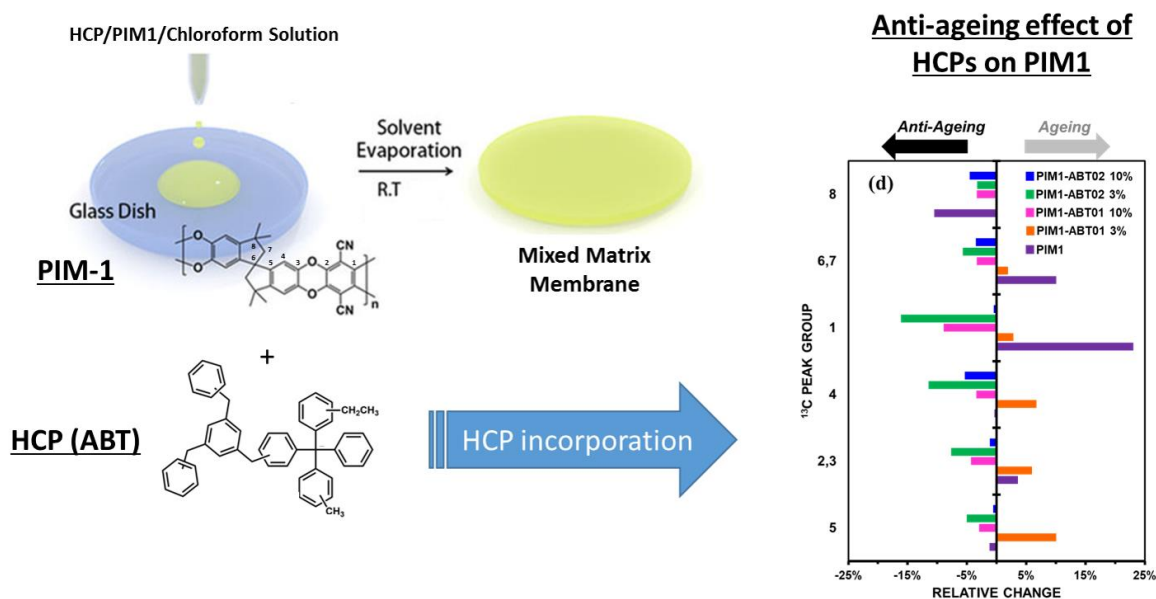
Hyper Cross-Linked Polymers as Additives for Preventing Aging of PIM-1 Membranes

Lasseguette, Elsa - Co-Author¹; Begni, Federico - Co-Author²; Paul, Geo - Co-Author²; Bisio, Chiara - Co-Author²; Marchese, Leonardo - Co-Author; Gatti, Giorgio - Co-Author²; Ferrari, Maria-Chiara - Co-Author¹

¹University of Edinburgh, ²Università degli Studi del Piemonte Orientale

Main topic: Ageing of polymeric membranes

PIM-1 represents one of the most promising polymeric materials for gas separation applications due to its unusually high free volumes (FFV) and high internal surface area, which induces high gas permeabilities and moderate ideal selectivity, especially for O₂/N₂, CO₂/N₂ pairs with values lying above the Robeson's upper bound. However, the high FFV of PIM-1 tends to be shortlived, due to their collapsing which leaves fewer transport pathways and reduces gas permeability. One way to tackle this problem is the addition of fillers within the polymeric matrix. Here we report the use of hyper cross-linked polymers (HCP) to reduce the physical aging of the PIM-1 membrane. Two novel HCP fillers have been developed, based on the Friedel–Crafts reaction between a tetraphenyl methane monomer and a bromomethyl benzene monomer. According to the temperature and the solvent used during the reaction (dichloromethane (DCM) or dichloroethane (DCE)), two different particle sizes have been obtained, 498 nm with DCM and 120 nm with DCE. The change in the reaction process also induces a change in the surface area and pore volumes. Several composite membranes have been developed with PIM-1 as matrix and HCPs as fillers at 3% and 10%wt loading. Their permeation performances have been studied over the course of two years in order to explore physical aging effects over time. Without filler, PIM-1 exhibits the classical aging behavior of polymers of intrinsic microporosity, namely, a progressive decline in gas permeation, up to 90% for CO₂ permeability. On the contrary, with HCPs, the physical aging at longer terms in PIM-1 is moderated with a decrease of 60% for CO₂ permeability. ¹³C spin-lattice relaxation times (T₁) indicates that this slowdown is related to the interactions between HCPs and PIM-1.



Immobilization of carbonic anhydrase on nanoporous ceramic membranes for carbon dioxide capture applications

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Main topic: CO₂ capture

A much promising trend in Carbon Capture Utilization and Storage (CCUS) involves tailored bio-inspired approaches to enhance mass transport and separation processes facilitating CO₂ as a valuable feedstock for sustainable fuels and chemicals production. Metalloenzyme carbonic anhydrase (CA) can accelerate CO₂ capture from post-combustion exhaust gases by catalyzing CO₂ conversion into bicarbonate ion [1]. CA immobilization in the pore walls of ceramic membranes, acting either as Permeators or Gas-liquid membrane contactors, could combine the inherent advantages of membrane technology (e.g. high specific surface area, modular design, no emulsion, etc.) with the benefits of enzymatic CO₂ conversion (e.g. efficient and selective chemical reactions, superior stereo-specificity, etc.) [2].

In this work, CA was immobilized covalently onto nanoporous TiO₂ single tube membranes, pretreated with (3-Aminopropyl)trimethoxysilane (APTMS), (3-Aminopropyl)triethoxysilane (APTES), polyethylenimine (PEI)/gelatin, or chitosan. Two pre-treatment techniques were employed to enhance enzymatic immobilization: i) wetting of the membrane pores in a cross-flow configuration and ii) immersion of single ceramic tubes (1-2hr). Characterization of enzymatically modified membranes by Fourier-transform infrared (FTIR) and Surface enhanced Raman scattering (SERS) spectroscopy were employed. p-NitroPhenyl Acetate (pNPA) and CO₂ assays were exploited to evaluate the activity of the immobilized enzyme towards CO₂ capture.

CA immobilization yield varied from 70%-85% for TiO₂ membranes with different modifications, while enzymes presence was confirmed with FTIR/SERS-RAMAN (Fig. 1), by identifying characteristic Amide I / II bands in all spectra, in both fresh (before use) and aged (after use) samples, while sample exposure to Raman laser temperature provoked a phase change possibly of the silane coating (APTMS-CA before use). Enzyme activity assay (pNPA) (Fig. 2) showed that ceramic membrane coated with PEI/gelatin (by immersion technique) sustained almost 80% of the enzyme initial activity after 10 reaction cycles with CO₂. In addition, CA immobilized on TiO₂-APTMS (by cross-flow technique) exhibited excellent storage stability after 30 days. The CO₂ assay ensured that the immobilized CA was able to convert its substrate (CaCl₂) to bicarbonate (CaCO₃). Next steps involve the evaluation of enzymatically modified membranes in gas separation and gas-liquid contactor experiments in terms of CO₂ capture efficiency.

Financial support: MemCCSea - Innovative membrane systems for CO₂ capture and storage at sea (No 294766).

Reference 1:

[1]. D'Ambrosio, K., De Simone, G., Supuran, C.T., 2015. Chapter 2 - Human Carbonic Anhydrases: Catalytic Properties, Structural Features, and Tissue Distribution, in: Supuran, C.T., De Simone, G. (Eds.), Carbonic Anhydrases as Biocatalysts. Elsevier, Amsterdam, pp. 17–30. <https://doi.org/10.1016/B978-0-444-63258-6.00002-0>.

Reference 2:

[2]. Fu, Y., Jiang, Y.-B., Dunphy, D., Xiong, H., Coker, E., Chou, S., Zhang, H., Vanegas, J.M., Croissant, J.G., Cecchi, J.L., Rempe, S.B., Brinker, C.J., 2018. Ultra-thin enzymatic liquid membrane for CO₂ separation and capture. Nature Communications 9. <https://doi.org/10.1038/s41467-018-03285-x>

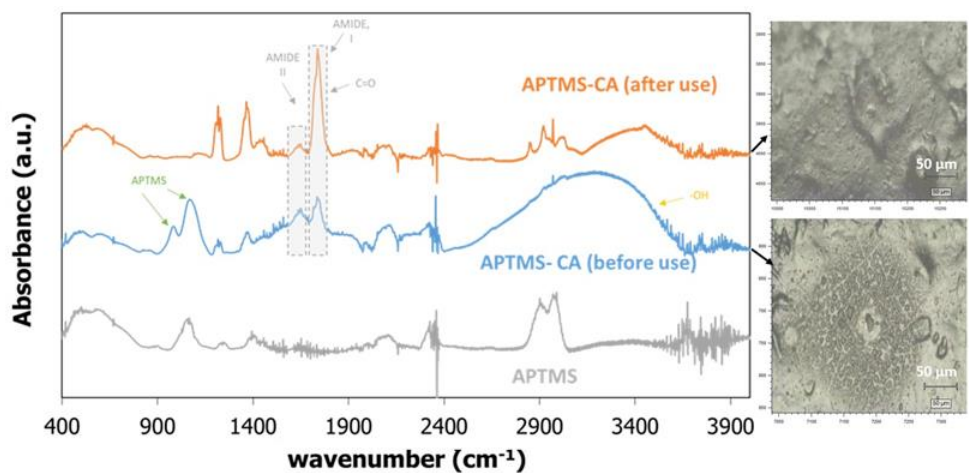


Fig. 1: FTIR analysis on TiO₂-APTMS (cross-flow) membrane and TiO₂-APTMS-CA membrane, before and after use and the respective confocal microscope images from the Raman instrument.

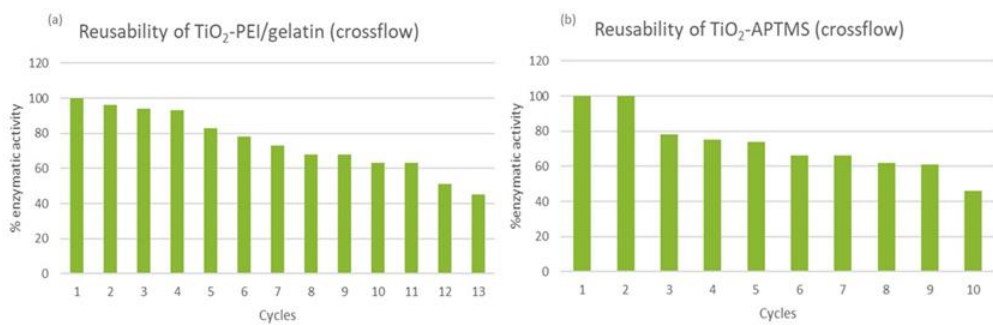


Fig. 2: Enzyme activity evaluated by pNPA assay for (a) TiO₂ membrane coated with PEI/gelatin and (b) TiO₂ membrane coated with APTMS (both by cross-flow technique).

Skuse, Clara - Co-Author; Alberto, Monica - Co-Author¹; Gorgojo, Patricia - Co-Author²; Gallego Schmid, Alejandro - Co-Author¹; Azapagic, Adisa - Co-Author¹

¹University of Manchester, ²Universidad de Zaragoza

Main topic: 1D- and 2D-materials for membranes

2D materials such as molybdenum disulphide and graphene oxide (GO) are being explored as nanofillers to enhance the performance of membranes for water treatment [1].

Commercial membranes can suffer from fouling which leads to flux decline, frequent cleaning and eventually complete deterioration of the membrane. Flux decline in RO also leads to increased pressure demands to compensate, leading to even more energy intensive desalination.

Membrane distillation (MD) is an emerging technology that has the potential to outperform conventional water treatment processes. Low-grade heat sources (such as solar power or waste heat streams) can be used to produce water, enabling sustainable water treatment [2]. However, membrane distillation is currently not widely used in industry due to stability challenges including membrane fouling and pore wetting.

In this work, a range of 2D materials are explored to overcome these issues, with a particular focus on pore-wetting (see Figure 1). Air gap MD (AGMD) and direct contact MD (DCMD) configurations are considered. The feed material is a 35 g/L NaCl solution, surfactants are added as a means of accelerating the wetting phenomena and humic acid is added to monitor fouling behaviour. The 2D material, deposited as a laminate membrane on top of a polymer support (three GO-based membranes in Figure 1), helps reduce foulant attachment while the small pore size reduces pore wetting. Unlike mixed matrix membranes, laminate 2D membranes can have poor adhesion to the substrate. In this work, a successful immobilisation method using anchor molecules was carried out to make sandwich membranes.

Overall this work outlines the current progress in the use of 2D materials for developing anti-fouling and pore-wetting resistant membranes for MD.

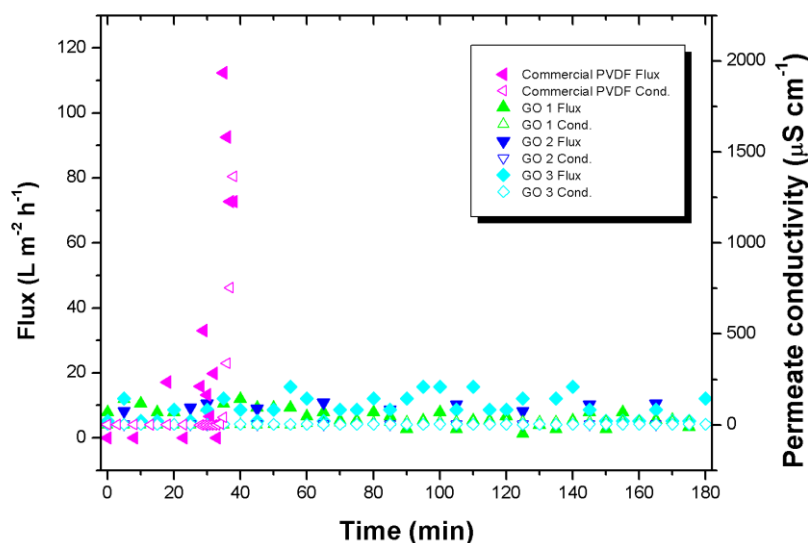
Figure 1 AGMD configuration: rapid pore wetting occurs after 150 mg/L surfactant is added at time 0 for commercial PVDF. GO membranes experience a significant delay before pore wetting.

Reference 1:

[1] S. Leaper et. al, Journal of Membrane Science, 554, 309-323 (2018)

Reference 2:

[2] C. Skuse, A. Gallego-Schmid, A. Azapagic, P. Gorgojo, Desalination. (2020) 114844.



Impact of air backwash on ultrafiltration fouling at semi-industrial scale for seawater and municipal wastewater treatment plant effluent

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Main topic: Membrane fouling and cleaning

Clarification and disinfection of different water matrices / effluents is needed in many industrial applications for water reclamation. Ultrafiltration (UF) can retain all suspended solids and microorganisms whatever the feed water quality with relatively low capital expenditures in comparison with other processes. However, the drawback of UF is fouling that can affect the performance of the process. Thus, many strategies are developed to mitigate fouling, obtain sustainable filtration conditions and also avoid a high frequency of chemical cleanings. The objective is to evaluate the efficiency of air backwash (AB) compared with classical backwash (CB) when treating municipal wastewater or seawater by UF. AB consists of injecting air into the membrane module before a CB. Two pilot-plants ($20 \text{ m}^3 \cdot \text{d}^{-1}$) were installed at a municipal wastewater treatment plant (WWTP) and at an aquaculture industrial partner's site in France with different AB/CB frequencies. The variation of the seawater and secondary effluent qualities were considered by integrating the turbidity variation versus time. This new approach was shown to be adapted to take into account the water quality variation considering suspended solids as the main foulant, and its impact on irreversible fouling increase over time for the two water matrices. Whatever the filtration conditions (i.e. low or high filtration time and low or high flux), the results clearly indicate that AB was more efficient than CB to control membrane fouling over time. For both applications: (i) the average fouling removal efficiency of AB was between 110% and 180% whereas it was between 70% to 100% for CB; (ii) the optimal AB/CB frequency was one AB followed by 3, 4 or 5 CBs leading to reasonable irreversible resistance increase and reduction of chemical cleaning frequency; (iii) the permeate quality was not impacted by AB. In the case of seawater, another advantage of AB arose: biological materials were physically impacted by the air injection leading to their destruction. This study led to the determination of sustainable filtration conditions with an optimization of an innovative membrane cleaning to maintain membrane performance whatever the treated water matrices and their quality.

Impact of backflush conditions on marine scrubber water ultrafiltration

Drouin, maryse - Main Author; Nasser, Samy - Co-Author; Adolphe, Cyril - Co-Author; Moulin, Philippe - Co-Author

Main topic: Membrane fouling and cleaning

Since 2015, the marine atmospheric rejection is more and more restricted. Some ships are retrofitted with hybrid system able to purify the gases and treat the generated liquid waste by membrane process to stay within air and water rejection compliance. The exhaust gas cleaning system installed is a liquid-gas absorption column where the alkaline liquid phase is used to catch pollutants. Due to the liquid circulation on the column, the pollutant concentration as particulate matter, hydrocarbons, salts, and solid alkaline compounds increase. Membrane process offering various advantages for marine usage: high compacity and satisfying water quality, ultrafiltration unit with mineral membrane is chosen to treat scrubber water. The objective of the studies is to determine the impact of backflushing actions on membrane filtration performances in terms of global membrane fouling rates, retention of suspended matter and dissolved salts and permeate water recovery. Experiments are made with multi-tubular silicon carbide (SiC) membrane at constant permeate flowrate and with regular backflush/backwash. The feed suspension is process water directly collected from retrofitted ships. A pilot laboratory unit is designed with automatic backflush modules: frequency, duration and pressure of flushing can be modified.

First filtration results with long backwash actions indicate a good permeability recovery after mechanical cleaning but also an important loss of permeate water. That why, other tests are made, by increasing the delay between two reverse flow or initiating backpulsing to reduce the injected volume. Both conditions involving higher fouling rates during filtration cycle. Considering a constant fouling rate, on average, SiC membranes are able to treat the fluid with a permeate recovery of 85% and permeate flux of $150 \text{ Lh}^{-1}\text{m}^{-2}$ for 8h filtration without chemical wash. The loop solution turbidity increasing over time with a feed value between 30 and 150NTU according to the sampled composition filtrated. Optimizations are in progress and will be tested on board to reduce the volume loss and improve the filtration time of the membrane.

Impact of chlorine addition in physical backwashes for ultrafiltration fouling management

Yang, Jiaqi - Co-Author; Monnot, Mathias - Co-Author; Moulin, Philippe - Co-Author

Main topic: Membrane fouling and cleaning

Membrane fouling is the main cause of permeability decrease during ultrafiltration (UF). Physical backwashes, such as classic backwash (CB) and air backwash (AB), cannot remove irreversible fouling removal by definition during long term filtration, as the residual foulants after backwash would be recompressed with filtration. Previous work showed that the best AB/CB frequency is around 3 CBs followed by 1 AB for different filtrated effluents. Since NaClO can inactivate the microorganisms and oxidize the organic foulants to detach from the membrane surfaces easier, this study aims to use a NaClO-assisted or not backwash and to investigate the influence of chlorine addition on backwash cleaning efficiency and on fouling control for sustainable filtration performance. This study was carried out with a semi-industrial UF pilot plant as tertiary treatment of municipal wastewater treatment for water reuse. The UF process was operated under optimum conditions with a constant flux of $60 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$, filtration time of 60 min and backwash sequence of CB/CB/CB/AB periodically [1]. Here if assuming that Y represents backwash water with 10 ppm NaClO, N represents backwash water without NaClO, four conditions were compared as follows: NNNN, NNNY, YYYN, and YYYY. The chemical cleaning (CEB) occurs when the permeability decreases to $200 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$. As expected, the NNNN condition gave the fastest irreversible fouling increase and more frequent CEBs which were over once a day. Conditions YYYY and NNNY gave both sustainable permeability variation, with a CEB frequency of less than once every 4 days. Condition YYYY showed similar total fouling resistance variation as condition NNNY, but with less and slower irreversible fouling formation. Therefore, NaClO addition in either AB or CB plays a positive role on fouling control thus contributing to more sustainable performance of filtration. The benefit of AB compared to the benefit of chlorine will be fully assessed as well as the impact of chlorine concentration in CB and AB on UF performance. Analyses of backwash water also provide important information to complete this work.

Reference 1:

Y. Jiaqi, M. Monnot, T. Eljaddi, L. Simonian, L. Ercolei, and P. Moulin, Ultrafiltration as tertiary treatment for municipal wastewater reuse, Separation Purification Technology (submitted 2021)

Impact of membrane characteristics on anti-solvent crystallization

Chergaoui, Sara - Co-Author¹; Leyssens, Tom - Co-Author²; P. Debecker, Damien - Co-Author²; Luis, Patricia - Co-Author¹
¹Materials & Process Engineering (iMMC-IMAP), UCLouvain, ²Institute of Condensed Matter and Nanosciences (IMCN), UCLouvain

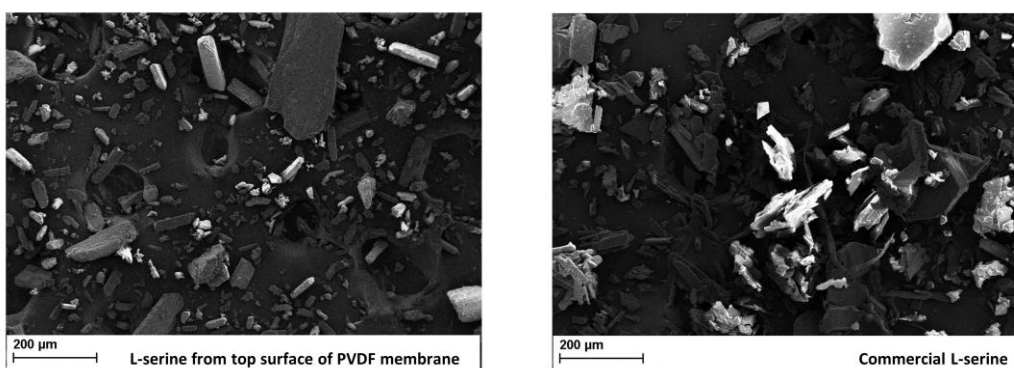
Main topic: Pharmaceuticals and biotechnology

Finer drug production has been an ongoing concern by pharmaceutical industries. The latter has been incorporating advances at different levels; for example, artificial intelligence was used to select compounds for drug formulation, robotics was implemented to reduce the heavy labor loading, etc. Anti-solvent membrane-assisted crystallization can be the next revolutionary intervention within the downstream processing of active pharmaceutical ingredients (APIs) [1]. Amino acids' crystallization is then investigated to verify the potential of this technology.

Membrane-assisted crystallization not only controls the crystal characteristics but also minimizes the amount of anti-solvent used; two important features that are lacking in conventional crystallizers. In this work, aqueous solutions containing dissolved amino-acid reached supersaturation with the controlled addition of the anti-solvent through the membrane pores. The crystallization performance is assessed by determining the resulting crystal shape, size distribution, and growth rate. A series of polyvinylidene fluoride (PVDF) membranes were developed and characterized in terms of hydrophobicity/philicity, roughness, pore size, porosity, and thickness. The impact of PVDF membrane characteristics on crystallization is discussed, which is first in the literature. The findings of this study offer a fundamental understanding that supports the use of this technology in the quest of controlling different API-related aspects such as polymorphism, chirality, and purity.

Reference 1:

J.C.W. Fern, S. Ohsaki, S. Watano, R. Pfeffer, Continuous synthesis of nano-drug particles by antisolvent crystallization using a porous hollow-fiber membrane module, *Int. J. Pharm.* 543 (2018) 139–150. <https://doi.org/10.1016/j.ijpharm.2018.03.025>.



PVDF hydrophobic membrane resulting in the production of uniformly shaped and smaller L-serine crystals, supports the ability of membranes in controlling crystal characteristics, suitable for applications in bio-technological fields.

Impact of membrane fouling on transport and adsorption of organic micropollutants in reverse electrodialysis using impaired water

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Main topic: Electro-membrane processes

Background

Reverse electrodialysis (RED) is a promising technology for energy harvesting from salinity gradients. RED-based hybrid processes (e.g., RED-ED/RO) have been proposed for more energy-efficient desalination in drinking water production. Given the limited supply of freshwater, impaired water (e.g., secondary-treated wastewater) has been proposed as an alternative low-salinity stream in RED [1]. However, impaired water is considered a major source of organic micropollutants (OMPs); thus, raising concerns about the potential contamination of OMPs to the seawater/brine [3]. Also, impaired water can induce membrane fouling, which might impact the fate of OMPs during the RED process [2].

Materials and methods

In the current study, a mixture of 25 OMPs (i.e., pesticides, pharmaceuticals, and personal care products) of different properties (i.e., charge, size, and hydrophobicity) was added to the secondary-treated wastewater at an environmentally-relevant concentration (20 µg·L⁻¹). The influence of membrane fouling on the fate of OMPs (i.e., transport to the seawater, retention in the wastewater, and adsorption onto the membranes and fouling layers) in RED was investigated using different feed solutions (i.e., synthetic and real seawater and secondary-treated wastewater) for 40 days.

Results and conclusions

Real wastewater induced more membrane fouling and channel clogging than its synthetic counterparts and real seawater, as evidenced by pressure drop increase, permselectivity decrease, and ATP levels increase. The OMP transport and adsorption in real seawater conditions were higher than their synthetic counterparts, while OMP transport and adsorption under real wastewater conditions decreased significantly compared to synthetic wastewater conditions, possibly due to: 1) higher OMP-membrane interaction compared to OMP-fouling layer interaction (via steric and electrostatic mechanisms), and 2) OMP adsorption onto the effluent organic matter in real wastewater. In contrast to real wastewater, the influence of real seawater on the fate of OMPs was limited.

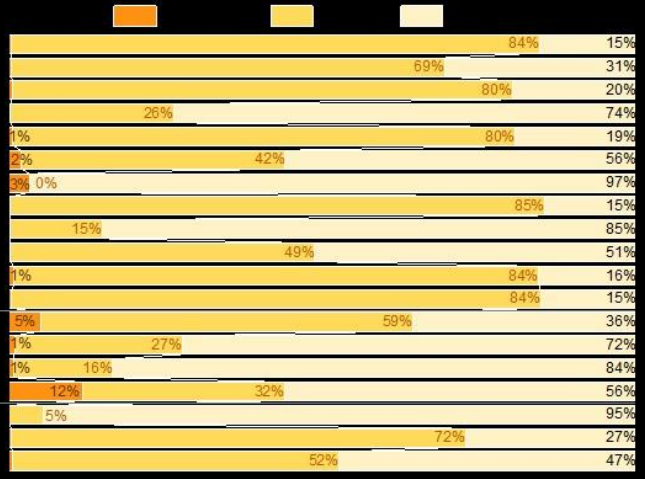
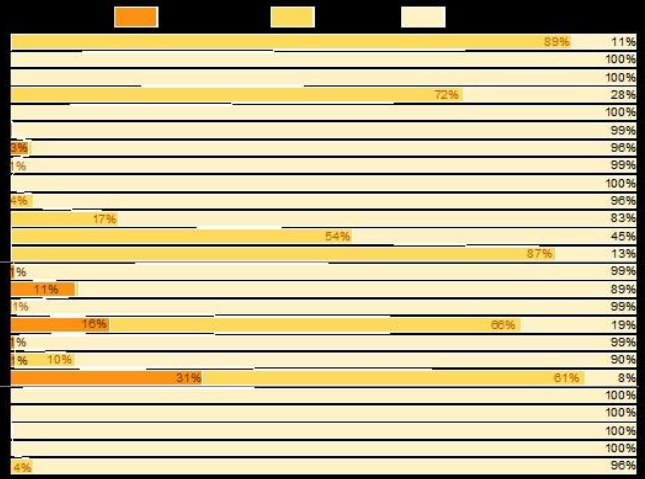
These results provide key implications for real (industrial) scenarios where OMP transport might be overestimated in lab-scale experiments using synthetic streams. Full-scale RED implementation using impaired water sources might result in lower transport of OMPs from impaired water to seawater and, thus, lower contamination of the produced drinking water.

Reference 1:

D.M. Warsinger, S. Chakraborty, E.W. Tow, M.H. Plumlee, C. Bellona, S. Loutatidou, L. Karimi, A.M. Mikelonis, A. Achilli, A. Ghassemi, L.P. Padhye, S.A. Snyder, S. Curcio, C.D. Vecitis, H.A. Arafat, J.H. Lienhard, A review of polymeric membranes and processes for potable water reuse, *Progress in Polymer Science*, 81 (2018) 209-237.

Reference 2:

J. Garcia-Ivars, L. Martella, M. Massella, C. Carbonell-Alcaina, M.-I. Alcaina-Miranda, M.-I. Iborra-Clar, Nanofiltration as tertiary treatment method for removing trace pharmaceutically active compounds in wastewater from wastewater treatment plants, *Water Research*, 125 (2017) 360-373.



Impact of Sulfonated Poly(Ether Ether Ketone) pretreatments on Proton Exchange Membrane Fuel Cells performances

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¹Université de Lorraine, CNRS, LEMTA, 54000 Nancy/France, ²Univ. Claude Bernard Lyon 1, CNRS, CP2M, 69001 Lyon/France, ³Univ. Claude Bernard Lyon 1, CNRS, IMP, 69001 Lyon/France, ⁴Univ. Grenoble Alpes, CEA, CNRS, Grenoble SyMMES, 38000 Grenoble/France

Main topic: Fuel cells

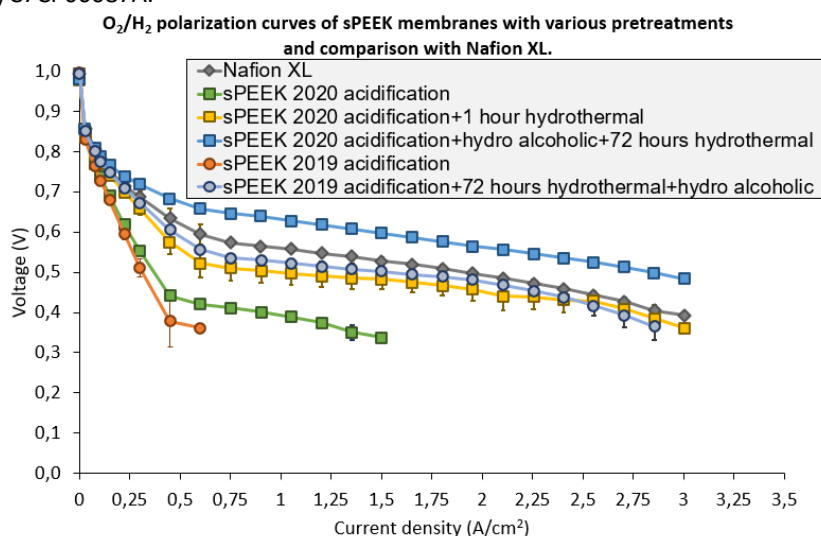
Many works have been devoted to the development of low cost ionomers as alternative to perfluorosulfonic acid membranes for Proton Exchange Membrane Fuel Cells (PEMFC) applications. Among them, sulfonated Poly(Ether Ether Ketone) (sPEEK) membranes. Before use, sPEEK membranes must be pretreated to ensure a complete protonic substitution and removal of residual reagents/solvent. This is generally ensured by soaking the membrane in an acid solution -at room temperature or higher, usually at 80°C [1]- followed by a rinsing step in water at room temperature. In addition to these pretreatment steps, it was reported [2] that an hydrothermal treatment in water at high temperature for a few hours to a few days can improve the membrane nanostructure, water uptake and proton conductivity with expected positive effects on performances. Herein, we studied the impact of sPEEK membrane pretreatment on fuel cell performances using two different batches of Fumapem E730 from Fumatech, acquired in 2019 and in 2020. Five different protocols were tested. The first consists only in membrane acidification and rinsing, while the four others also include a hydrothermal treatment in water at 80°C from 1 hour to 72 hours, and possibly an additional hydro alcoholic treatment. The 2020 batch membranes subjected to a hydro alcoholic pretreatment followed by a 72-hours hydrothermal pretreatment achieved the best performances and the lowest high frequency resistance (R_{hf}) when tested in a fuel cell. Their performances even exceeded those of a Nafion XL membrane. This could be explained by a better ionomer nano-structuration and therefore a better protonic conductivity. These performances will be compared to those of the 2019 batch.

Reference 1:

Jun, M.-S.; Choi, Y.-W.; Kim, J.-D.. J. Membr. Sci. 2012, 396, 32–37. <https://doi.org/10.1016/j.memsci.2011.12.008>.

Reference 2:

Mendil-Jakani, H.; Zamanillo López, I.; Mareau, V. H.; Gonon, L. Phys. Chem. Chem. Phys. 2017, 19 (24), 16013–16022. <https://doi.org/10.1039/C7CP00087A>.



IMPLEMENTATION OF A CONTROL SYSTEM ON LAB SCALE MEMBRANE PLANT

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¹Sapienza University of Rome, ²None

Main topic: Membrane fouling and cleaning

In this work, the implementation of a control system on a lab scale membrane plant will be reported. The implemented control system is of advanced type and developed previously [1], connected to a boundary flux database of the processed stream, that is olive mill wastewater. According to this approach, the control system exhibits several features such as:

- basic PID control of operating pressure and feed flow rate as a function of the setpoint permeate flux with an override in case boundary fluxes are exceeded to avoid severe fouling;
- basic PID control of operating pressure and feed flow rate as a function of the setpoint of operating pressure with an override in case boundary fluxes are exceeded to avoid severe fouling;
- an automatic procedure to measure boundary flux values;

A first problem was the interference existing when both operating pressure and feed flow rate are controlled. A decoupling approach was adopted, and findings are here reported.

Using overrides to avoid severe fouling is the first stage of technical safety in performing the operation, but far away from optimization. For this reason, in the future, the control system will be enhanced by a predictive / adaptive approach to estimate a path of suitable setpoint to reach the separation targets. On the basis of available data, the approach will be presented in theory and practice in this paper.

Additionally, in case of oral presentation only, some preliminary work to port this system on ASPEN HYSYS platform will be reported.

Reference 1:

Stoller, M., Serrão Mendes, R., Advanced control system for membrane processes based on the boundary flux model, (2017) Separation and Purification Technology, 175, pp. 527-535.

Implementation of membrane technology in industrial biorefineries: Potential of membrane bioreactors and membrane modification for improved selectivity

Pinelo, Manuel - Co-Author

Main topic: Bio-separations and bio-refinery

Incorporation of membranes to industrial biorefineries has increased considerably in the last recent years. This is due to several key reasons, amongst others, the possibility of coupling membranes and build hybrid processes, greatly contributing to intensification and to the economy of the process. Secondly, due to the recent advances on the potential of commercial membranes that can be chemically modified to satisfy the separation requirements needed to handle the complex mixtures of compounds normally generated in biomass related processes.

In this work, as an example, we present the potential of coupling reaction and membrane separation in the same device, which enables a better tailoring of the molecular weight and chemical features of the compounds to be recovered. In particular, we focused on the use of membrane bioreactors for production of oligodextrans within a limited range of molecular weight, which are high valued compounds for the pharmaceutical industry. We observed that in process intensification, the coordination of the two “blended” operations is crucial for the economy and efficiency of the process. In our case, the synchronization between kinetics and membrane separation, with concentration polarization and fouling playing a big role, was found to be the key for high performance.

As another example, we have been optimizing the downstream processing for production of biosuccinic acid, in which microfiltration, electrofiltration and nanofiltration show big potential, as demonstrated by the recent incorporation of membrane technology in the main factories producing it in the world nowadays. Nanofiltration was indeed found to be the most important step, as it enables a good separation of succinic acid from the other acids e.g. formic acid, acetic acid, also produced during fermentation.

Lastly, as an another example, we also present the advances in chemical modification of membranes for high performance separation of inhibitors from the liquid of pretreatment, which is currently one of the main challenges in bioethanol production.

Improved asymmetric PEM membranes for OMP removal from wastewater

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¹University of Twente, ²NX Filtration

Main topic: Nanofiltration/Reverse Osmosis

Recently, asymmetric polyelectrolyte multilayer (PEM) membranes were developed with great potential for removing organic micropollutants (OMPs) from wastewater [1]. These membranes consist of a support, made with phase inversion, an open PEM bottom layer and a dense PEM top layer. These nanofiltration membranes have a high permeability ($12.8 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$), high OMP retention (98%) and low monovalent ion retention (10-15% NaCl). Here their low NaCl retention is a real benefit, as it prevents the formation of a difficult to treat saline waste-stream. However, a limit in their practical application is their high divalent ion retention (~90% MgSO_4). Within this current research, an extensive characterization was performed in order to determine whether the majority of the divalent ion retention takes place at the surface (Donnan exclusion) or in the bulk (dielectric exclusion) of these membranes. Salt retentions were measured at different pressures and salt concentrations and the solution diffusion model was applied, highlighting the relevance of carefully selecting operating parameters for these membranes. Subsequently, different polyelectrolyte pairs were applied as a bottom layer for the asymmetric membrane, and their effect on membrane performance was compared. Overall, our work demonstrates a number of clear tuning parameters that allow control over the separation properties, lowering the multivalent ion retention, to optimize these promising asymmetric membranes for removing OMPs from complex wastewaters.

Reference 1:

te Brinke, E., et al., Asymmetric polyelectrolyte multilayer membranes with ultrathin separation layers for highly efficient micropollutant removal. *Applied Materials Today*, 2020. 18: p. 100471.

IMPROVED CO₂ SEPARATION PERFORMANCE OF POLY ETHER BLOCK AMIDE (PEBA)/MOF THIN FILM NANOCOMPOSITE (TFN) MEMBRANES

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¹Instituto de Nanociencia y Materiales de Aragón (INMA), Universidad de Zaragoza-CSIC

Main topic: Gas separation

To achieve the Paris Agreement target of below 1.5 °C in the global average temperature rising, harmful greenhouse gases emissions must be reduced considerably in the coming decades. To accomplish this target, energy-efficient and low-carbon technologies, and CO₂ capture and storage approaches must be developed. Recently, membrane-based processes have emerged as attractive candidates for energy-efficient gas separations. The performance of a membrane can be expressed in terms of (i) permeance, the normalized flux for the pressure gradient (ii) permeability, the permeance multiplied by the membrane thickness, and (iii) selectivity, the ratio of permeances. To achieve an efficient separation, which exceeds the Robeson trade-off relationship between permeability and selectivity, an ideal membrane for gas separation should be as thin as possible, to maximize the flux through it (high CO₂ permeance), highly selective and mechanically robust[1]. To accomplish this target, composite membranes must be prepared with a very thin selective layer. Furthermore, the incorporation of porous nanofillers in ultra-thin dense layers has demonstrated superior gas separation performances compared to that of the bare polymer[2]. In this work, thin-film nanocomposite (TFN) membranes, comprising different porous zeolitic imidazolate frameworks (ZIFs) embedded in a dense polyether-block-amide (PEBA) thin layer have been fabricated. Moreover, the influence of particle loading and functionalization have also been studied.

Acknowledgments

Financial support from the Research Project PID2019-104009RB-I00/AEI/10.13039/501100011033 is gratefully acknowledged.

Reference 1:

J. Benito,, J. Sánchez-Laínez,, B. Zornoza,, S. Martín,, M. Carta,, R. Malpass-Evans,, C. Téllez,, N.B. Mckeown,, Joaquín Coronas,, I. Gascón, *ChemSusChem* 10 (2017) 4014–7. 10.1002/cssc.201701139.

Reference 2:

J. Dechnik,, J. Gascon,, C.J. Doonan,, C. Janiak,, C.J. Sumbly, *Angew. Chemie Int. Ed.* 56(32) (2017) 9292–310. 10.1002/anie.201701109.

In situ modification of microfiltration and ultrafiltration membranes to integrate boron adsorber property

Ke, Qirong - Main Author¹; Ulbricht, Mathias - Co-Author¹

¹Lehrstuhl für Technische Chemie II, Universität Duisburg-Essen, 45117 Essen, Germany

Main topic: Microfiltration/Ultrafiltration

The state-of-the-art reverse osmosis (RO) membranes for desalination have limited competence to remove boron efficiently. One promising approach for boron removal is to integrate membrane-based separation with selective boron adsorption, i.e., membrane adsorber; the porous support layer constituting the largest part of total membrane volume shall be utilized for this function. The membrane adsorber can be designed so that integrating the selective boron binding in the seawater pretreatment stage is feasible. In this context, this project focuses on conducting *in situ* modification of commercial polyethersulfone (PES) microfiltration (MF) and ultrafiltration (UF) membranes and modules toward reactive coating the pore surface with a boron affinity hydrogel. The adapted modification protocols are designed to be ready to upscale. Additionally, the performance of the as-prepared membrane adsorber shall be well controlled to balance the additional boron binding function and filtration throughput. Four different modification schemes are proposed in this work, all of which can be carried out in a closed circulation system (Fig. 1A). Towards the membrane performance, the trade-off between boron uptake and permeance can be well controlled either by tuning modification conditions or adapting different modification schemes

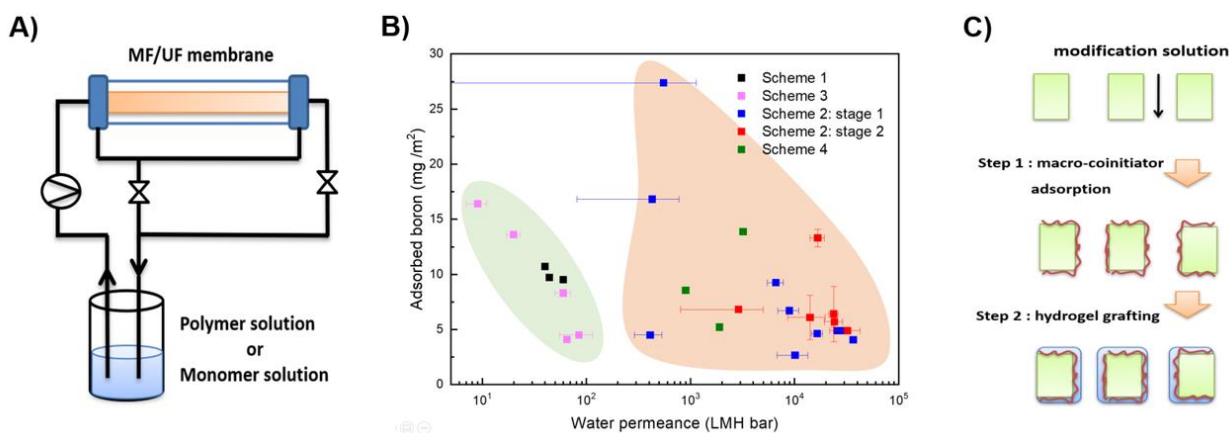
(Fig. 1B).

The most promising modification is carried out via Scheme 2 (Fig. 1C): 1) adsorption of an amphiphilic copolymer which contains tertiary amine groups as co-initiator for a surface-selective free radical generation; 2) grafting of a hydrogel layer by using a monomer solution comprising polyol-containing monomer as boron ligand, a cross-linker monomer, and a redox initiator (cf. [1]). The trade-off between permeance and boron uptake of the modified membrane is systematically studied via Design of Experiment (DOE) and the subsequent parameter fine-tuning. The identified optimal modification condition gives a promising membrane adsorber with competitive performance, i.e., the permeance of $17,000 \pm 3,000$ LMH bar in combination with boron binding capacity of 17.6 ± 0.6 mg/m² in artificial seawater. Furthermore, the as-prepared membrane adsorber shows stable performance in five regeneration cycles.

Figure 1. (A) Illustration of filtration system for *in situ* modification; (B) the trade-off between boron uptake and permeance of modified membranes obtained via different modification schemes (green: UF membranes; orange: MF membranes); (C) the modification flowchart in Scheme 2.

Reference 1:

M. Quilitzsch, R. Osmond, M. Krug, M. Heijnen, M. Ulbricht, J. Membr. Sci. 518 (2016) 328-3337.



In situ investigation of cake fouling using fluid dynamic gauging during cross-flow microfiltration of an organic model material

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¹Doctoral Student at Chalmers University of Technology

Main topic: Fluid dynamics

As a cost- and energy-efficient operation, cross-flow membrane filtration can be expected to be utilized in the future biorefinery. However, membrane fouling is inevitable in membrane operations, so also for complex, heterogeneous mixtures of extracted wood components containing suspended particles and dissolved components [1]. In recent years, various analytical techniques have been developed to characterize fouled membranes (e.g. streaming potential measurements, atomic force microscopy, and scanning electron microscopy). These methods have increased our understanding of fouling, but several fouling aspects are still poorly understood and as a consequence, fouling is still difficult to predict and model. In order to overcome this, a better mechanistic understanding of membrane fouling must be gained. One essential type of knowledge is *in situ* information of the conditions when fouling layers are formed. This study employs fluid dynamic gauging (FDG), an *in situ*, real-time monitoring technique, to estimate the thickness and the cohesive and adhesive strengths of fouling layers.

In this work, we investigated the cake fouling behavior of microcrystalline cellulose (MCC) during cross-flow microfiltration (MF) [2] at 400 mbar transmembrane pressure using 0.45 μm polyethersulfone (PES) membranes in a series of membrane flushing and physical cleaning. Pressure-mode FDG was carried out to estimate the cake thickness and maximum shear stress as the probe approached the PES membrane. Preliminary FDG results, as shown in Fig. 1, revealed that the estimated fouling layer thickness was $616 \pm 5 \mu\text{m}$ for both fouled and refouled membranes at an applied shear stress of $37 \pm 2 \text{ Pa}$ by the probe after 3000 s (50 min) of MF. This suggests that the thickness of the cake layer formed is independent of/only slightly influenced by pore blocking. However, the MCC particles that form the first few cake layers are likely to dictate the membrane's permeability, which is corroborated by the sharp decline in permeate flux. These results highlight how FDG can be used to gain insights into the relationship between surface fouling (i.e. development of a cake fouling layer) and internal fouling due to pore blocking of the membrane.

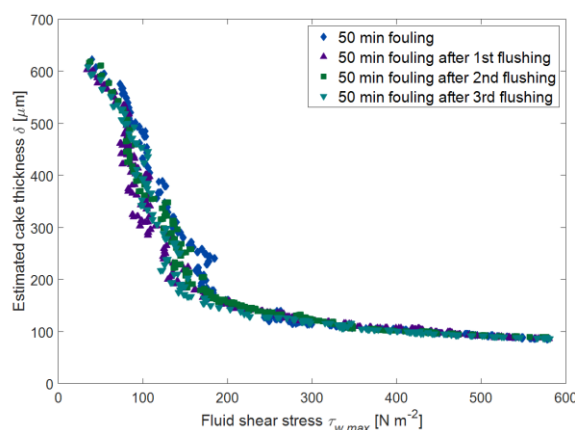
Fig. 1. Estimated cake thickness vs. maximum fluid shear applied to the surface by the FDG probe.

Reference 1:

[1] Arandia, K., Balyan, U., Mattsson, T., 2021. Development of a fluid dynamic gauging method for the characterization of fouling behavior during cross-flow filtration of a wood extraction liquor. *Food and Bioproducts Processing*, 128, 30-40.

Reference 2:

[2] Zhou, M., Sandström, H., Belioka, M. P., Pettersson, T., Mattsson, T., 2019. Investigation of the cohesive strength of membrane fouling layers formed during cross-flow microfiltration: The effects of pH adjustment on the properties and fouling characteristics of microcrystalline cellulose. *Chemical Engineering Research and Design*, 149, 52–64.



In situ production and characterization of bacterial cellulose-based films for biotechnological applications.

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¹Instituto de Biologia Experimental e Tecnológica (iBET), Portugal

Main topic: Pharmaceuticals and biotechnology

In recent years, demand for renewable and sustainable biopolymers has considerably increased because of environmental concerns. Bacterial cellulose (BC) has received a significant interest as a renewable and biodegradable biopolymer. Among BC producers, the strains of the genus *Komagataeibacter* have gained attention because of their unique ability to produce increased levels of crystalline BC films.

This work discusses the use of five strains of genus *Komagataeibacter* as a source for BC production of films. The strains used are *K. uvaceti* FXV3, *K. intermedius* LMG 18909^T, *K. melomenus* LMG 31304^T, and *Komagataeibacter* sp. KOMB2 and KOMB3. These bacterial strains were cultivated in Hestrin and Schramm (HS) medium under static conditions for seven days. To fully exploit the metabolic potential of these cellulose-producing bacteria, the influence of cultivation conditions such as carbon source selection (glucose, glycerol), and ethanol concentrations (0, 1.5%, 3%) has been examined. The obtained cellulose films were washed, dried, and characterized by determining their dry weight, wettability, mechanical properties, and morphology.

After 7 days of incubation, it has been found that an ethanol concentration of 3% (w/v) increased the productivity of BC for all studied bacterial strains in both carbon sources. Among all the strains, *Komagataeibacter* sp. KOMB3 produced 9.58–9.60 g/L BC, the highest yield being observed using both glucose and glycerol substrate. Whereas, in the case of *K. Intermedius*, *K. uvaceti* FXV3, and KOMB2, glycerol was found to be the best substrate for BC production. However, *K. melomenus*, shows no significant difference in BC production when different carbon sources were used.

SEM results from produced BC films show that these bacterial strains produce films with a different woven pattern with different fiber diameters. The most promising KOMB3 strain produced a fiber with an average diameter of 90–100 nm using glucose and glycerol as carbon sources. The chemical character of the films produced and their open network structure make the BC surface very hydrophilic with high surface area, elasticity, and flexibility. Results of this study provide the optimum conditions to produce BC films utilizing these new bacterial strains aiming their use for gas filtration and biomedical applications.

Industrially relevant CHA membranes with high performance for gas separation

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Main topic: Gas separation

Background

Zeolite membranes are attractive for industrial gas separation due to the potentially high selectivity, permeability and stability [1]. However, sufficiently large defect-free zeolite membranes with suitable properties for industrial gas separations has not yet been reported. Chabazite (CHA) zeolite is an ideal candidate for CO₂/CH₄ separation due to the pore diameter of 3.7 Å, in between the molecular size of CO₂ (3.3 Å) and CH₄ (3.8 Å).

Materials and Methods

Single channel tubular zeolite CHA membranes with a length of 500 mm and a membrane area of 100 cm² (see **Fig. 1**) were evaluated by SEM and by single component permeation experiments with CO₂, H₂, CH₄ and SF₆. Industrially relevant mixtures of CO₂/CH₄/H₂O were fed to the membrane with a flowrate of 60 l/min (maximum in the experimental setup) at different feed pressures.

Results

Fig. 1 shows that the film is continuous layer of well inter-grown crystals with a length of < 500 nm and that the thickness is < 500 nm.

The CO₂ permeance was as high as 128×10⁻⁷ mol/(m²·s·Pa) which showed that the zeolite pores were highly permeable. Meanwhile, the SF₆ (5.1 Å [2]) permeance was as low as 4.5×10⁻¹⁰ mol/(m²·s·Pa), which indicated that the membrane was nearly defect free.

The highest observed CO₂/CH₄ separation factor was as high as 169 in combination with a CO₂ flux of 0.23 mol/(m²·s) at 293K and 4 bar feed pressure. The CO₂ flux increased to 0.62 mol/(m²·s) and the separation factor was still as high as 120 when the feed pressure was increased to 10 bar. Estimates indicated a severe effect of concentration polarization on the separation, and that the separation factor and flux would increase significantly at higher feed flow.

Conclusions

Tubular single-channel CHA membranes with a length of 500 mm were evaluated for CO₂/CH₄ separation. The CO₂ flux and separation factor was significantly higher than those reported for other CHA membranes at comparable test conditions. Estimates indicated that even better performance would have been observed at higher feed flow. This work demonstrates the industrial potential of the tubular CHA membranes for CO₂/CH₄ separation.

Reference 1:

[1] R.W. Baker, K. Lokhandwala, Natural gas processing with membranes: An overview, *Ind. Eng. Chem. Res.* 47 (2008) 2109-2121.

Reference 2:

[2] Jian-Rong Li, Ryan J. Kuppler, Hong-Cai Zhou, Selective gas adsorption and separation in metal-organic frameworks, *Chem. Soc. Rev.* 38 (2009) 1477-1504.

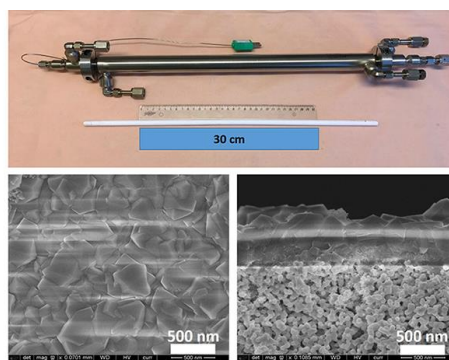


Fig. 1. Photograph of a 500 mm membrane and cell, and SEM images of the membrane top surface and cross-section.

Influence of molecular weight on the performance of polyelectrolyte multilayer nanofiltration membranes

Regensburg, Jurjen - Main Author¹; Martins Costa, Ana - Co-Author¹; Achterhuis, Iske - Co-Author¹; de Vos, Wiebe - Co-Author¹

¹University of Twente

Main topic: Nanofiltration/Reverse Osmosis

Polyelectrolyte multilayers (PEMs) have received a lot of attention over the past years, and have found their application in various fields such as optics and drug delivery. Their versatile use and ease of fabrication by means of layer-by-layer (LbL) deposition has also resulted in their application in the field of membrane science. Recent research, shows that PEMs are able to form excellent selective layers when applied onto the lumen side of hollow fiber membranes.¹ Many studies have by now reported that parameters such as ionic strength, pH and type of polyelectrolyte (PE) influence the layer buildup of PEMs and thereby the separation properties of the resulting membranes. The effect of PE Mw on the layer build-up has been reported for layer growth on model surfaces. Surprisingly, the effect of Mw on the performance of PEMs as selective layers has not been explored yet.

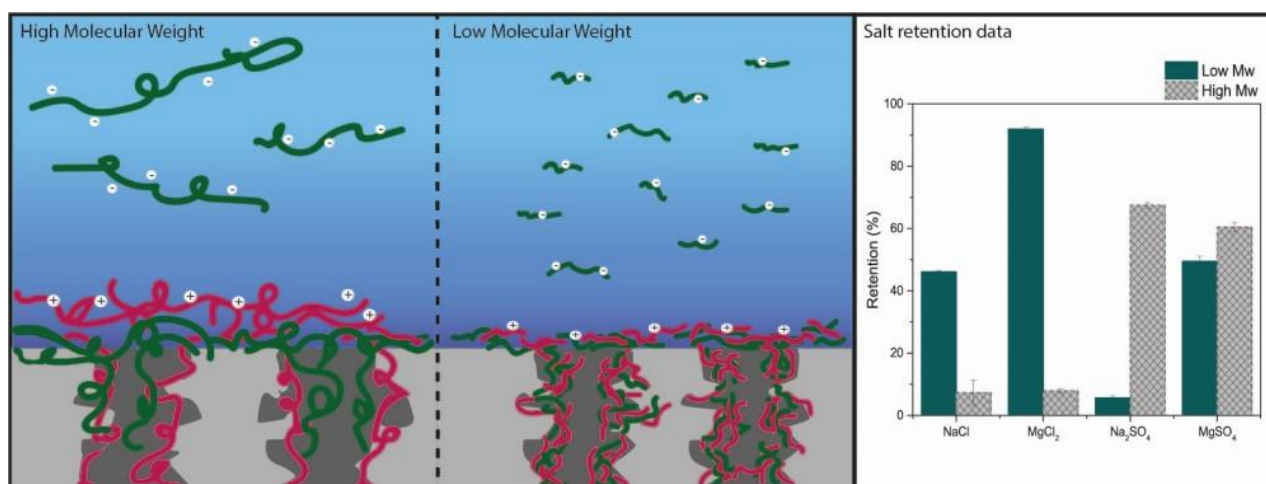
In this work, we apply PEMs of low and high Mw combinations to the lumen side of ultrafiltration support membranes by means of dip coating. Membrane performance is assessed by means of pure water permeability, salt retention and molecular weight cutoff. Furthermore, we investigate layer growth and the stability of low and high Mw PEMs on model surfaces.

The results show that less mobile systems such as poly(allylamine hydrochloric acid) (**PAH**)/poly(4-styrene sulfonate) (**PSS**) appear to be not influenced by a difference in Mw in terms of membrane performance and stability. In contrast, for the more mobile PE combination, **PAH**/poly(acrylic acid) (**PAA**), Mw influences the performance. A combination of low Mw PEs in this system leads to separation properties corresponding to a negatively charged membrane. On the other hand, the high Mw combination of **PAH/PAA** results in a positively charged membrane. Furthermore, we observe that the low Mw **PAH/PAA** membranes are more dense compared to their high Mw counterparts. Here, the higher mobility of low Mw PEs leads to a denser network.

This work showcases the significant influence of Mw in more mobile PEM systems. This means that for these systems, the Mw can be used as an effective tuning parameter to optimize membrane performance

Reference 1:

te Brinke, E.; Reurink, D. M.; Achterhuis, I.; de Grooth, J.; de Vos, W. M. Asymmetric Polyelectrolyte Multilayer Membranes with Ultrathin Separation Layers for Highly Efficient Micropollutant Removal. *Applied Materials Today* 2019, 100471. <https://doi.org/10.1016/j.apmt.2019.100471>.



Influence of porosity ratio on the carbon dioxide absorption capability of supported liquid membranes based on PVdF-based supports

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¹Instituto Tecnológico de la Energía (ITE), Avenida Juan de la Cierva, 24, Paterna (Valencia), ²Instituto Tecnológico de la Energía (ITE), Avenida Juan de la Cierva, 24, Paterna (Valencia) and Instituto de Tecnología Eléctrica, Universitat Politècnica de València, Camino de Vera s/n Edificio 6C 46022 Valencia (Spain)

Main topic: Facilitated transport membranes

Supported liquid membranes (SLMs), based on the idea of the immobilization of a selective liquid phase (facilitating agent) in the pores of a porous support by capillary forces, are a promising technology for CO₂ separation and capture which exhibit high efficiency, small footprint and operational simplicity[1].

Although polymeric support is not the membrane active component in the CO₂ separation process, their structure plays a key role in it. Support wettability and its facilitating agent absorption capability as well as support porosity are essential to ensure final CO₂ absorption.

In this study, the effect of four different surfactants on the porous support structure and final CO₂ absorption are evaluated. Moreover, facilitating agent transport selection based on its CO₂ absorption capability and agent-membrane interaction is also carried out.

Polymer solutions containing same PVdF-HFP: surfactant ratio were prepared and membranes were obtained by solvent casting technology. Resulting membranes were characterized by scanning electron microscopy (SEM), mercury porosimetry and facilitating agent wettability. Once supports were synthesized and characterised, facilitating transport agent was selected and supported liquid membranes were developed. After that, its CO₂ absorption capability was evaluated by means of thermogravimetric analysis (TGA). This technique is a cheap and fast way to measure membrane-CO₂ interaction [2].

Results showed the effect of selected surfactants on the membrane pore size distribution and therefore on facilitating agent absorption capability, as shown in Table 1, which influences the carbon dioxide absorption by SLM.

Table 1. Facilitating agent absorption capability for developed membranes

| Membrane | Facilitating agent absorption (%) |
|----------|-----------------------------------|
| M1 | 104 |
| M2 | 103 |
| M3 | 92 |
| M4 | 75 |

The use of surfactants as non-solvent agent in PVdF-HFP membranes preparation by phase inversion method therefore allows the preparation of tailored polymer membranes with narrow pore size distribution in a single-step and scalable process. Pore distribution design is of paramount importance for this specific application so as to guarantee that facilitating agent penetrates into the membrane pores and its long term stability.

Acknowledgement

This research was funded by the Centro de Desarrollo Tecnológico Industrial-CDTI (ALMAGRID Project-CER-20191006)

Reference 1:

[1] Zi Tong and W. S. Winston Ho (2017). Facilitated transport membranes for CO₂ separation and capture, Separation Science and Technology, 52:2, 156-167

Reference 2:

[2] Yu Chen, Jin Han, Tao Wang and Tiancheng Mu (2011). Determination of Absorption Rate and Capacity of CO₂ in Ionic Liquids at Atmospheric Pressure by Thermogravimetric Analysis Energy & Fuels 2011 25 (12), 5810-5815

Influence of s-NIPS micro-patterned supports and interfacial polymerization conditions on the synthesis and permselective properties of surface patterned thin-film composite membranes

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¹KU Leuven

Main topic: Nanofiltration/Reverse Osmosis

Reduction of **membrane fouling** is one of the most challenging tasks affecting the field and one that offers the prospect of improving the energy efficiency of the separation processes in a substantial way. Recent studies have demonstrated that the presence of periodic surface patterns can **enhance the fluid shear at the membrane surface and promote back-diffusion of foulants to the bulk flow** [1]. Given the generic nature of the pattern-enhanced shear effect, it is expected that surface patterns, once successfully incorporated onto TFC membranes, will also be effective at reducing concentration polarization and enhancing flux. There have been few reports on patterned TFC membranes, however, no significant improvement in membrane permeance was observed due to mere nano-scale pattern heights ranging between 50 - 100 nm. Hence, to fully exploit the potential of patterned TFC membranes, we herein propose using **s-NIPS patterned UF supports** due to their ability to create significantly high pattern heights and subsequently forming a polyamide barrier layer on the patterned surface via interfacial polymerization (IP). s-NIPS patterned supports have been recently reported to show significantly high water permeances due to a notable increase in their effective surface area (up to 400 %) and increased average pore size. In this study, we report systematic experimental studies to **evaluate the effect of s-NIPS patterned supports on the morphological and permselective properties of the corresponding surface-patterned TFC membranes** as a function of the conditions of the IP process and substrate topography. The goal of this work is to **create a micro-patterned TFC membrane with improved permeance, better fouling resistivity, and comparable salt retention**. To the best of our knowledge, IP over **patterned supports with high pattern heights i.e. up to 100 μm** has not been reported yet. Polysulfone patterned supports were successfully prepared via s-NIPs. During the first part, different routes were investigated for successful interfacial polymerization based on exploring adequate removal methods of excess monomer during the reaction. Secondly, the **successful IP protocol was developed** based on the monomers compositions, number of IP reactions, and patterned support characteristics. Lastly, experimental and computational studies were performed to analyze the anti-fouling propensity of the s-NIPS patterned TFC membranes.

Reference 1:

A. Ilyas, A.Y. Gebreyohannes, J. Qian, D. Reynaerts, S. Kuhn, I.F.J. Vankelecom, Micro-patterned membranes prepared via modified phase inversion: Effect of modified interface on water fluxes and organic fouling, *J. Colloid Interface Sci.* (2020).

Insights into the role of water chemistry and organic matter interaction on arsenic(III, V) removal by nanofiltration

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Main topic: Nanofiltration/Reverse Osmosis

Arsenic (As) in drinking water is a major public health concern. Its mobilisation into water sources is associated to organic matter (OM) which is promoted by temperature elevation due to climate change. Arsenic can also co-exist with high salinity in aquifers affected by sea water intrusion. Achieving As removal over such changeable environments requires a robust process that is able to mitigate the impact of OM and salinity (Figure 1). This implies that nanofiltration (NF), which requires lower specific energy consumption compared to reverse osmosis (RO), may be well suited for the treatment of different water types contaminated with As.

Nanofiltration experiments on As(III) and As(V) removal were carried with two membranes (NF270 and NF90) placed in a cross-flow filtration set-up. The operational conditions were at constant flow rates mode. The experiments were conducted at different water chemistries (2 – 12 pH, 0.58 – 20 g/L NaCl, 0 – 100 mgC/L humic acid (HA)). Asymmetric flow field-flow fractionation coupled on-line with inductively coupled plasma – mass spectrometry (FFF-ICP-MS) was used to quantify As-HA complexation. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was performed to evaluate As deposition in the presence of HA.

Figure 1. (A) As(III) retention as a function of humic acid (HA) concentration with (B) the suggested mechanism. (250 µg/L As(III), 1 mM NaHCO₃, 0.58 g/L NaCl, pH 8.1±0.1; Q_F = 0.45 L/min, Q_{P-NF90} = 1 mL/min, Q_{P-NF270} = 9 mL/min, 23 ±0.5 °C). Adapted from Boussouga *et al.* [1]

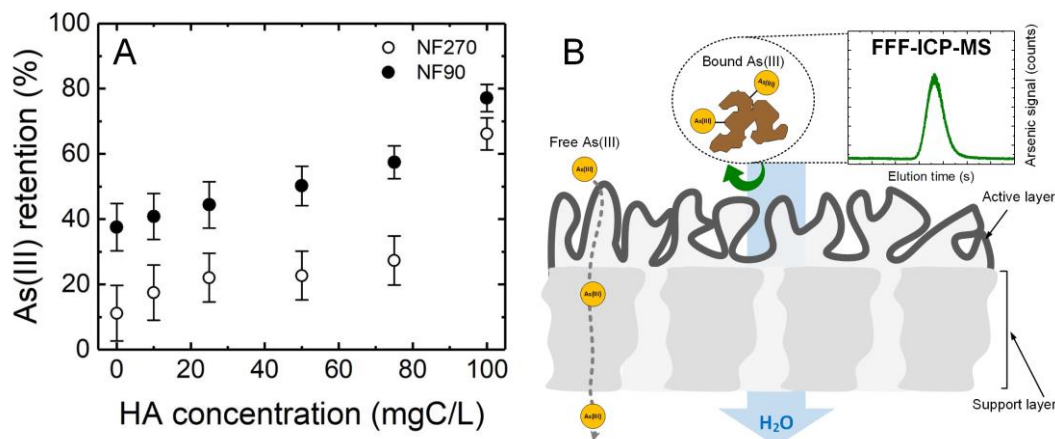
Varying pH from 2 to 12, resulted in a significant increase in As(III) retention at pH>9 (up to 77% for NF90), while As(V) retention remained high (>90% NF90) over the studied pH range [1, 2]. Increasing HA concentration to 100 mgC/L has significantly enhanced As(III) retention by 40% (Figure 1A). FFF-ICP-MS measurements showed that As(III)-HA complexation was the responsible mechanism (Figure 1B). ToF-SIMS analysis revealed that NF90, which had lower fouling potential than NF270, has exhibited lower As(III) deposition in the presence of HA. This finding is of importance for further investigations suggesting a hybrid process complexation enhanced NF using a complex agent with similar binding characteristics as HA.

Reference 1:

Y.A. Boussouga, M. B. Mohankumar, A. Gopalakrishnan, A. Welle, A.I. Schäfer, Removal of arsenic(III) via nanofiltration: contribution of organic matter interactions, *Water Res*, 201 (2021) 117315

Reference 2:

Y.A. Boussouga, H. Frey, A.I. Schäfer, Removal of arsenic(V) by nanofiltration: Impact of water salinity, pH and organic matter, *J Membr Sci*, 618 (2021) 118631



Integrated Innovative Pilot System For Critical Raw Materials Recovery From Mines Wastes In A Circular Economy Context

Morillo Martin, Diego - Co-Author¹; Matencio Lloberas, Sonia - Co-Author

¹Leitat Technological Center

Main topic: Environmental applications

Critical Raw materials (CRMs) are crucial to Europe's economy. They form a strong industrial base, producing a broad range of goods and applications used in everyday life and modern technologies. CRMs are needed for significant economic and strategic sectors, as for example manufacturing batteries, construction tools, sensors and electronic devices, medical devices, metals, automotive, defence or renewable energy sectors. However, limited supply and difficult substitution to CRMs is a growing concern within the EU and across the globe.¹

RAWMINA aims to develop and to demonstrate the RAWMINA pilot system: an industrially scalable and flexible innovative pilot in continuous operation for Mine Waste (MW) valorisation, achieving 95% recovery rate and 95% selectivity for CRMs (Co, Sb, Ge, W), and 80-90% recovery rate and 95% selectivity for Au, Ag and Fe-based high-value products, whilst reutilising 90% of water. RAWMINA will implement and standardize an innovative energy, water- and cost-effective pilot system able to treat up to 100-150 kg MW/day on an industrial demonstration (TRL7) including efficient and robust process control.

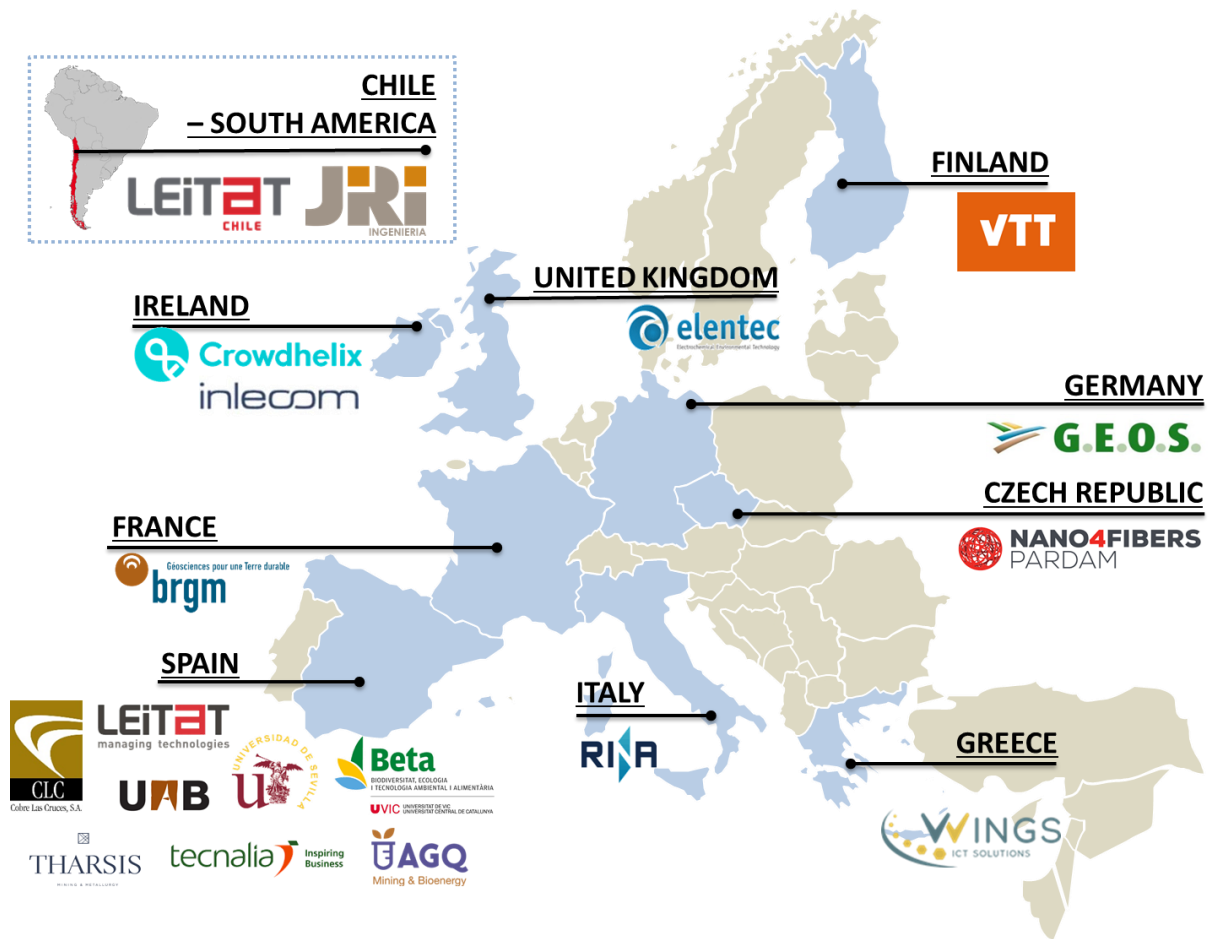
To achieve these aims, RAWMINA activities include MW sampling, MW dressing and characterization, upscaling of innovative technologies such as continuous bioleaching coupled with alkaline leaching of bioleaching residues, iron removal with magnetic separation and CRMs selective recovery through a combination of Nanofibrous Composite Materials and Electrocoagulation processes from "unexploited/underexploited metal containing materials".

Pilot design, integrated system engineering & demonstration with MW of diverse geological compositions from EU and non-EU mine-sites will demonstrate flexibility and adaptability to different mine waste composition and metals grades. RAWMINA will improve EU competitiveness and create added value in RMs processing, refining and equipment manufacturing by developing a new circular business model as an alternative to traditional linear mining economy. The techno-economic and sustainability assessment, social impact and exploitation of the pilot system will be evaluated to ensure market penetration, technology export and Circular Business Plan. Finally, RAWMINA will create a unique community, named "CRM Recovery Helix" to maximise clustering and dissemination to all the relevant stakeholders.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n° 958252.

Reference 1:

EC, 2018. Report on Critical Raw Materials and the Circular Economy. <https://op.europa.eu/es/publication-detail/-/publication/d1be1b43-e18f-11e8-b690-01aa75ed71a1/language-en>



Integrated model for simulation of super-large scale membrane bioreactor process and energy consumption

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Main topic: Membrane bio-reactors

Membrane bioreactor (MBR) involves complex interactions among biology, filtration, and fouling which makes its modeling a challenging task. Integrated models have now been developed and applied to MBRs, mostly ranging from bench-scale to pilot-scale and rarely for full-scale (<100,000m³/day). The applicability of these models for super-large scale MBRs (>100,000 m³/day) has not been studied yet. In this study, a super-large-scale MBR plant with design capacity of 360,000 m³/day is dynamically modeled to simulate its depollution and filtration-fouling processes along with energy consumption. The integrated model combines biochemical (EPS-ASM3-Bio-P, aeration and chemical precipitation) and resistance in series (RIS) filtration models (Rieger et al., 2001; Zarragoitia-González et al., 2008). The biochemical part of the model considers the stoichiometric activity of the biomass for carbon, nitrogen, and phosphorus removal. The filtration part of the model covers the fouling dynamics due to intermittent air scouring synchronized with filtration-backwashing cycles, and also taking into account the influence of temperature, transmembrane pressure (TMP), and biomass characteristics i.e. mixed liquor suspended solids (MLSS) and extrapolymeric substances (EPS) concentrations. After systematic calibration, the model was successful in simulating the biological, chemical, and physical processes. The model was further validated against 92 days of operational data collected from the plant with and without addition of FeCl₃. The simulated effluent COD results fitted reasonably well with the experimental data with a root mean square error (RMSE) value of 0.32, and the model successfully simulated the minimum detection limit for COD measurement. Model accuracy for simulating NH₄-N, NO_x-N (nitrates & nitrites), and PO₄³⁻ in terms of RMSE was found to be 0.80, 0.92 and 0.85, respectively. TMP has also been simulated reasonably consistent with a mean-absolute percentage error (MAPE) of 8.3%. Furthermore, the model successfully simulated the energy consumed in membrane scouring, biological aeration, mixing, and influent pumping, which accounted for approximately 50%, 14%, 17%, and 9%, respectively, while the rest of the energy is being consumed by other allied processes such as recirculation, chemical dosing, foam breaking, permeate suction-backwashing, and sludge extraction. The calibrated model provided an excellent correspondence with the operational data and can be used as a valuable tool for optimizing and developing advanced controls for large-scale MBRs.

Reference 1:

Rieger, L., Koch, G., Kühni, M., Gujer, W., & Siegrist, H. (2001). The EAWAG bio-p module for activated sludge model no. 3. *Water Research*, 35(16), 3887–3903.

Reference 2:

Zarragoitia-González, A., Schetrite, S., Alliet, M., Jáuregui-Haza, U., & Albasi, C. (2008). Modelling of submerged membrane bioreactor: Conceptual study about link between activated sludge bio-kinetics, aeration and fouling process. *Journal of Membrane Science*, 325(2), 612–624.

[Link to image](#)

Galier, Sylvain - Co-Author; Namhaed, Kritsana - Co-Author; Roux-de Balmann, H el ene - Co-Author

Main topic: Bio-separations and bio-refinery

Lignocellulosic biomass is used more and more in production of chemicals and energy to face the decline in reserves of fossil fuel as well as climate change concerns [1], furfural being one of the most promising platform molecules. It is produced from hemicellulose by depolymerization of pentosans into xylose and consecutive acid catalyzed dehydration of xylose. The xylose/acid concentration ratio was found to be a critical factor for the efficiency of the furfural production [2]. Since the biomass composition is generally not in the optimum range, xylose/acid ratio between 2.7 and 4.0, a pretreatment before the dehydration step could be interesting. Since previous studies have reported that it can be used to modify the proportions of organic acids and sugars, nanofiltration can be an option.

An experimental investigation was performed with an NF membrane (desal DK, GE) in dead-end filtration in a concentration mode, with a volume reduction factor (VRF) up to 4.85. Synthetic solutions containing xylose and formic acid were used. The composition was chosen according to that of a hydrolysate obtained from hydrolysis of corn cobs catalyzed by formic acid [1]. Experimental variables such as applied pressure and xylose/formic acid feed concentration were studied. The yield, i.e. the recovery of xylose in the retentate, was also determined.

Figure 1 shows the variation of the xylose yield versus the xylose/formic acid ratio, obtained for two different concentrations during NF. Since the retention of formic acid remains almost constant and close to zero, the concentration of formic acid in the retentate remains constant and equal to that of the initial feed solution. The retention of xylose is about 85% slightly decreasing during the experiment, explaining the decrease in xylose recovery (yield). One can observe that the desired xylose/formic acid concentration ratio can be obtained. For a given xylose/formic acid ratio, the best xylose recovery is obtained with the less concentrated solution. These results show that the membrane based nanofiltration can be used to increase the xylose/formic acid concentration ratio to improve the performances of the furfural production.

Reference 1:

T. Zhu, P. Li, X. Wang, W. Yang, H. Chang, et S. Ma, « Optimization of formic acid hydrolysis of corn cob in xylose production », Korean J. Chem. Eng., vol. 31, no 9, p. 1624-1631, 2014, doi: 10.1007/s11814-014-0073-8.

Reference 2:

W. Yang, P. Li, D. Bo, et H. Chang, « The optimization of formic acid hydrolysis of xylose in furfural production », Carbohydr. Res., vol. 357, p. 53-61, 2012, doi: 10.1016/j.carres.2012.05.020.

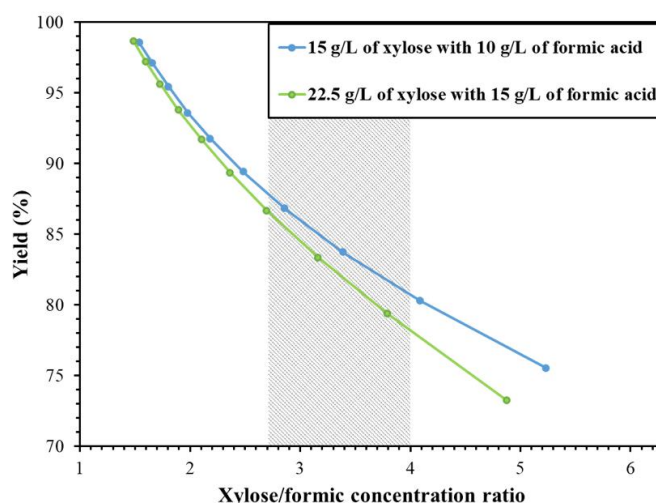


Figure 1: Variation of the xylose yield recovery versus xylose/formic acid concentration ratio (retentate): influence of the feed concentration. *Op. Cond.: initial feed volume $V_f = 500$ mL; transmembrane pressure = 20 bar; VRF up to 4.85. dashed region: optimum composition for furfural production*

Intensification of membrane contactor for gas liquid absorption: the parametric study of CO₂/CH₄ separation

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¹Laboratoire Réaction et Génie des Procédés, UMR 7274, Nancy, France

Main topic: Membrane contactors and membrane distillation

Membrane contactors offer promising performances for the intensification of gas-liquid absorption processes through an impressive volume reduction factor compared to packed columns.[1] However, even if CO₂ capture has been widely investigated for chemical absorption, only a limited number of studies addressed the potentialities of membrane contactors for gas-liquid absorption processes with physical solvents. Many parameters, from the selected solvent to the operating conditions, could have an influence on the volume reduction on the one hand, and energy requirement on the other hand. Figure 1 shows a membrane contactor and the associated parameters related to the membrane, the contactor, the solvent and the operating conditions.

The parametric study has been performed through the investigation of the CO₂/CH₄ gas separation for given inlet and outlet compositions. Focus has been made on the module packing fraction, interstitial velocity ratio, membrane mass transfer coefficient, pressure, temperature, solvents and contactor's configurations. Results have been compared to packed column for the determination of intensification factors (i.e. volume reduction).

Some of the main conclusions obtained from the simulation are summarized as follows:

- Membrane contactors offer promising intensification possibilities compared to a classical packed column with volume reduction ratios
- The maximal intensification factor I is almost independent of the inlet pressure
- Depending on the configuration, an optimal module packing fraction can be chosen
- Membrane mass transfer coefficient and solvent properties are key factors for the intensification performances and specific energy requirement.

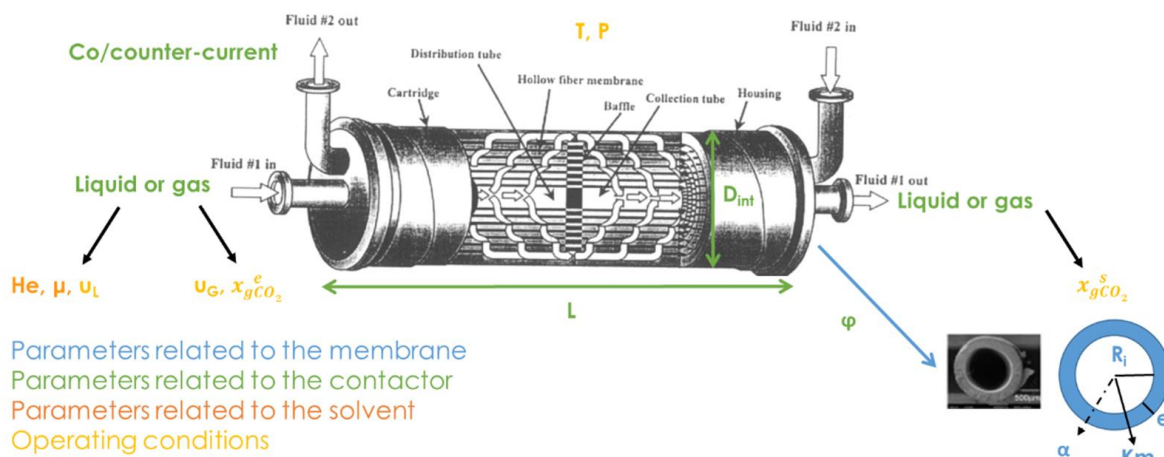
More information are provided in the related published article. [2]

Reference 1:

E. Favre, H.F. Svendsen, Membrane contactors for intensified post-combustion carbon dioxide capture by gas-liquid absorption processes, *Journal of Membrane Science*. 407-408 (2012) 1-7. <https://doi.org/10.1016/j.memsci.2012.03.019>.

Reference 2:

L. Cesari, C. Castel, E. Favre, Membrane contactors for intensified gas-liquid absorption processes with physical solvents: A critical parametric study, *Journal of Membrane Science*. 635 (2021) 119377. <https://doi.org/10.1016/j.memsci.2021.119377>.



Interfacial aspects of whey protein separation using artificial membranes

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¹Soft matter, Fluidics and Interfaces group, Faculty of Science and Technology, University of Twente, Enschede, ²Arla Foods Ingredients Group P/S

Main topic: Microfiltration/Ultrafiltration

Whey and whey derivatives contain a number of different proteins which have a high nutritional value and can be used separately or in mixture as food additives, nutraceuticals, and therapeutics. Therefore, there is considerable interest in recovering, purification, and concentration of individual whey proteins in order to take advantage of their unique physical, chemical, and biological properties.

Pressure-driven membrane processes, such as micro- and ultrafiltration, are regularly used in dairy industry for whey components fractionation. Modern spiral-wound modules (SWM) equipped with polymeric flat sheet membranes separated by net-like spacers quickly became an industrial standard due to their compact size, great performance, and relatively low cost of operation. However, their application is still limited by either reduction of selectivity and filtration efficiency due to membrane fouling or difficulties in separation of proteins with similar size. In addition, protein transport through semipermeable membrane is strongly affected by electrostatic interactions between charged protein and membrane surface. To improve and control already existing industrial practices and facilitate development of more efficient ways of whey treatment, a higher degree of insight into the underlying dominant mechanism governing protein mass transport during ultrafiltration process is required.

In this work, a combination of experimental and theoretical studies was performed in order to investigate the role of feed solution parameters (pH, ionic strength, protein concentration), and operation conditions (TMP, flow rate) on the retention and transport of individual whey proteins during cross-flow filtration process. With the goal of direct and indirect monitoring of membrane fouling and concentration-polarization effects, a special ultrafiltration module equipped with transparent glass window was designed in a way that similar hydrodynamic conditions to the industrially available SWM could be achieved.

Interfacially polymerized hollow fiber membranes by microfluidics for nanofiltration

Paseta, Lorena - Main Author; Malankowska, Magdalena - Co-Author; Téllez, Carlos - Co-Author; Coronas, Joaquín - Co-Author

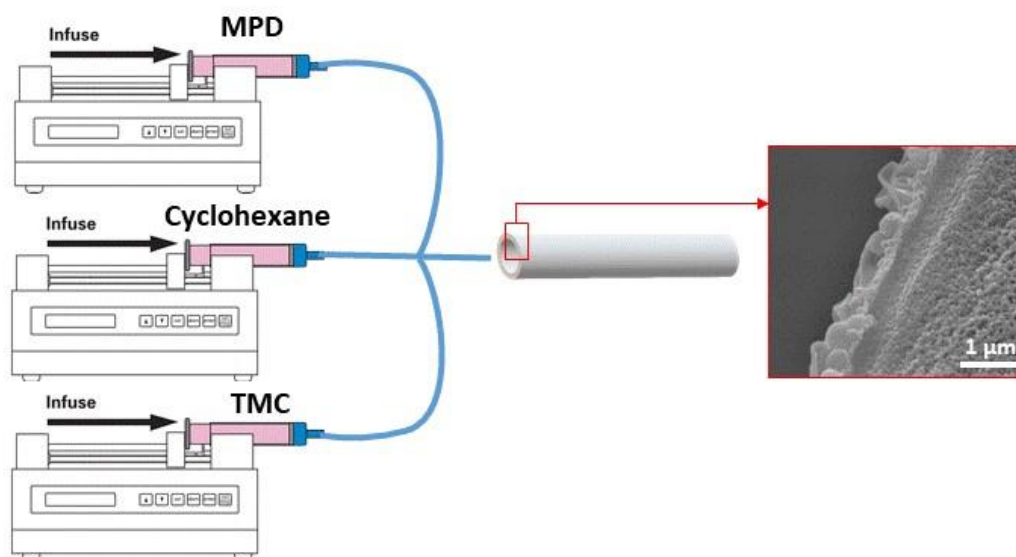
Main topic: Nanofiltration/Reverse Osmosis

Nanofiltration (NF) has attracted attention as an interesting separation process in a wide range of applications (pharmaceuticals, food, water treatment, etc.) becoming a substitute of others separation process like distillation or reverse osmosis thanks to its low energy consumption and low-cost maintenance.

The membranes most used in this application are the so-called thin film composite (TFC), whose structure consist of an asymmetric support with a selective thin layer on top (usually synthesized by interfacial polymerization). This layered structure allows to optimize each layer independently with the aim of maximizing the membrane performance. Most commercial NF modules are made of flat-sheet membranes in spiral-wound configuration. Although, the interest on the fabrication of hollow fiber (HF) NF modules is growing up due to their high m^2/m^3 ratio allowing greater process intensification, ease of handling during module fabrication and operation or that can be self-supported.¹ In this work, the fabrication of TFC HF NF modules was carried out using microfluidics, a synthesis methodology that not only permits the reduction in the amount of reactants used and synthesis optimization, but also allows to increase the number of HF that can be modified at the same time.

Reference 1:

C. Echaide-Górriz, M. Malankowska, C. Téllez and J. Coronas, *AIChE J.*, 2020, 66, e16970



Investigating the influence of process conditions in vacuum membrane distillation using commercial PTFE membranes

Al-Jariry, Nadin - Main Author; Hedlund, Jonas - Co-Author; Yu, Liang - Co-Author

Main topic: Pervaporation and vapour permeation

Desalination of seawater has been the most sought-after solution to meet the growing global demand for potable water. Currently, the largest share of global desalinated water is from the energy demanding process of reverse osmosis [1]. The process of Membrane distillation (MD) has the potential to intensify the desalination process as it is compatible with waste heat and renewable energy resources. The main challenges hindering the commercialization of MD are the low flux and the membrane wetting issues [2]. Significant efforts have been made over the past two decades to counteract these challenges by developing new membrane materials with enhanced characteristics [2]. However, it is crucial to optimize the process operating conditions to harvest these characteristics, yet the process conditions used to evaluate newly developed membranes are not standardized in the literature.

In this study, a commercially available hydrophobic PTFE membrane with a pore size of 0.22 μm was used in a vacuum membrane distillation (VMD) process to evaluate the influence of the process operating conditions on the flux for a feed of pure water. The thickness of the PTFE membrane was about 80 μm and a macroporous support with essentially zero mass transfer resistance was used. The contact angle, liquid entry pressure and helium permeance for the membrane were also evaluated. The observed VMD flux increased with increased feed temperatures and a high flux of up to 287 $\text{kg}/(\text{h} \cdot \text{m}^2)$ was recorded. To the best of our knowledge, this flux is by far the highest reported for PTFE membranes and demonstrates the importance of the support. In addition, the flux was dependent on the feed flow and feed temperature in concert with previous reports. These results will improve the understanding of VMD and may be used to improve the performance of VMD processes.

Reference 1:

[1] F. Virgili, T. Pankratz, and J. Gasson, "IDA Desalination Yearbook 2015-2016," (in English), 2016.

Reference 2:

[2] M. Qasim, I. U. Samad, N. A. Darwish, and N. Hilal, "Comprehensive review of membrane design and synthesis for membrane distillation," *Desalination*, p. 115168, 2021, doi: <https://doi.org/10.1016/j.desal.2021.115168>.

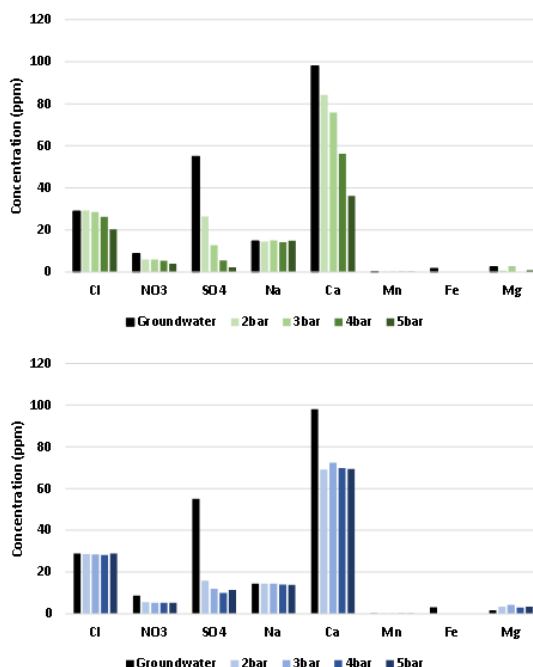
INVESTIGATION OF FOULING ON ION-EXCHANGE MEMBRANES USING FOOD AND BIO-BASED INDUSTRIAL STREAMS

Vincent, Evert - Co-Author^{1,2}

¹Particle and Interfacial Technologies, ²University of Ghent

Main topic: Drinking water

WPC Klein-Sinaai is currently used for the production of drinking water abstracted from the region Moerbeke-Waas. Groundwater abstraction in Klein-Sinaai has been arrested since 1991 due to high organic matter concentrations found in the water. Due to increased water demands, De Watergroep is now looking to expand drinking water production from the Moerbeke-Waas abstraction region. For this expansion, a new or improved treatment chain will be required, as the current treatment chain (aeration coupled with coagulation and rapid filtration) is not capable of producing drinking water of high enough quality to satisfy customers. Breakthrough of organic matter also causes the formation of disinfection byproducts in the downstream sterilization. The goal of this project is to assess multiple viable treatment plans for WPC Klein-Sinaai, comparing traditional and recent water treatment technologies in order to devise a system capable of treating water with high iron and organic matter content. Recent trends suggest that capacity to remove the OMP bentazon will also be crucial in the future. Through literature research, multiple technologies were reviewed for possible lab-scale testing. Currently tests are being performed towards assessment of optimized coagulation/flocculation, as well as assessment of capillary nanofiltration. Tests indicate that the current coagulation process step can be improved upon through the adjustment of pH as well as applying synergistic coagulants such as for improved iron and NOM removal. Experimental results from batch and continuous filtration runs with capillary nanofiltration indicate that high quality drinking water can be produced at high recovery, with limited flux reduction due to fouling being observed. As such plans are being made for increasing the scale of capillary nanofiltration experiments to pilot scale, as well as looking into the pretreatment of groundwater with optimized coagulation to further increase recovery rates.



Investigation of Hydrodynamic Conditions and Wetting Patterns in Polymeric Multi-channel Membranes via MRI and CFD

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¹DWI - Leibniz Institute for Interactive Materials e.V., ²RWTH Aachen University, AVT.CVT - Chemical Process Engineering

Main topic: Fluid dynamics

Membranes with several lumen channels in their support structure, so-called multi-channel membranes, convince with robustness, high packing density, and beneficial fouling behavior. Due to these advantages, they are used in many applications, such as drinking water production and seawater desalination. Several studies have focused on optimizing the geometry and material properties of multi-channel membranes. However, these studies mainly investigate the overall stationary performance of the whole membrane module only and do not provide detailed information on flow distribution inside the individual channels and the module as a whole during filtration.

In this study, we analyze multi-channel membranes in a membrane module to unravel flow field distribution in the whole module during filtration and backwashing using flow-MRI measurements and CFD simulations ^[1]. We focus on the impact of membrane position inside the module on the hydrodynamic conditions as well as silica particle deposition. A systematic simulation study identifies flow patterns based on simplified geometrical features, e.g., an eccentric membrane position, and is experimentally validated by flow-MRI and permeation measurements. An eccentric membrane position, for example, introduces a secondary flow field on the shell side that generates drag forces in the lumen channels leading to regions of agglomerated fouling. These investigations reveal that minor geometric deviations from the idealistic arrangement result in unexpected fluid flow and fouling dynamics in membrane modules.

Furthermore, we experimentally investigate unsteady wetting-pattern evolution inside multi-channel membrane modules during the initial membrane wetting phase via MRI ^[2]. The spatio-temporal evolution of an aqueous solution wetting the membrane fibers was investigated as a function of the applied flux, packing density, and position along the module length. This in-situ investigation reveals a slow wetting progression of more than six hours to obtain complete wetting and a non-uniform wetting progression along the module length. This wetting analysis helps to understand complex wetting phenomena inside multibore membranes during dead-end filtration.

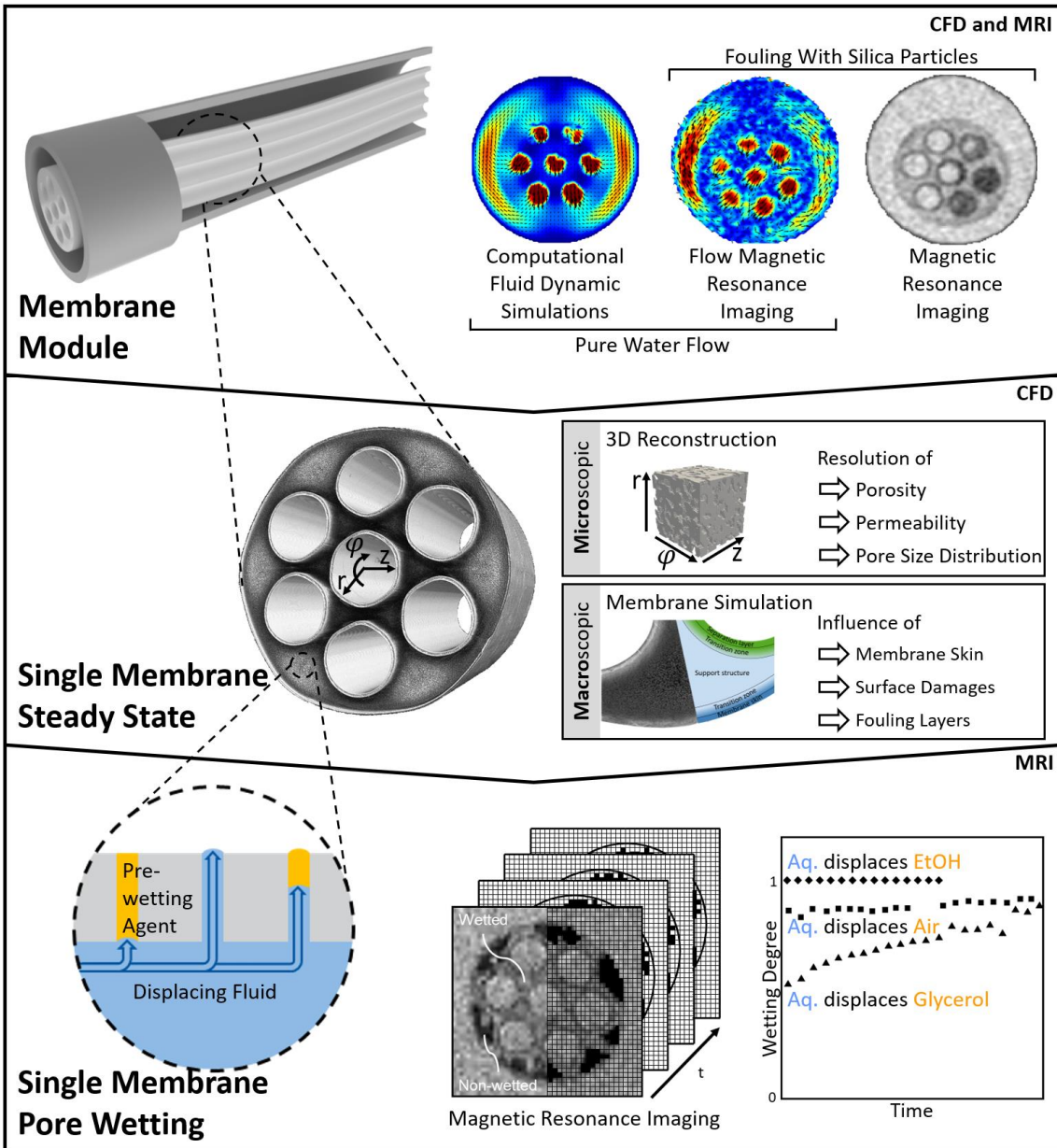
These studies show that the combination of MRI, flow-MRI, and CFD is a promising tool to unravel fluid dynamic conditions in multi-channel membrane modules to a full extend. Especially non-invasive, online in-situ MRI measurements characterize membrane modules close to operating conditions.

Reference 1:

[1] D. Wypysek, D. Rall, M. Wiese, T. Neef, G.-H. Koops, M. Wessling, Shell and lumen side flow and pressure communication during permeation and filtration in a multibore polymer membrane module, *Journal of Membrane Science* 584 (2019) 254-267. doi: 10.1016/j.memsci.2019.04.070

Reference 2:

[2] D. Wypysek, A.M. Kalde, F. Pradellok, M. Wessling, In-situ investigation of wetting patterns in polymeric multibore membranes via magnetic resonance imaging, *Journal of Membrane Science* 622 (2021) 119026. doi: 10.1016/j.memsci.2020.119026



Investigation of the side chain effect on gas and water vapor transport properties of the anthracene-maleimide based PIM polymers

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¹Dr., ²Prof. Dr.

Main topic: Gas separation

Since the discovery, PIM-1 has become attractive due to high free volume elements, good solubility in low boiling point solvents (THF, CHCl₃) and accessibility to chemical modifications [1]. Owing to its splendid features, PIM-1 has been drawn the attention especially for gas separation. An effective way to improve gas separation performance is to insert rigid/bulky side groups which create high free volume and provide better size discrimination ability, thus, greater selectivity [2]. In addition to abundant studies of PIM on gas separation, there is lack of studies on water transport properties since it is intricate using hydrophobic nature of PIM-1.

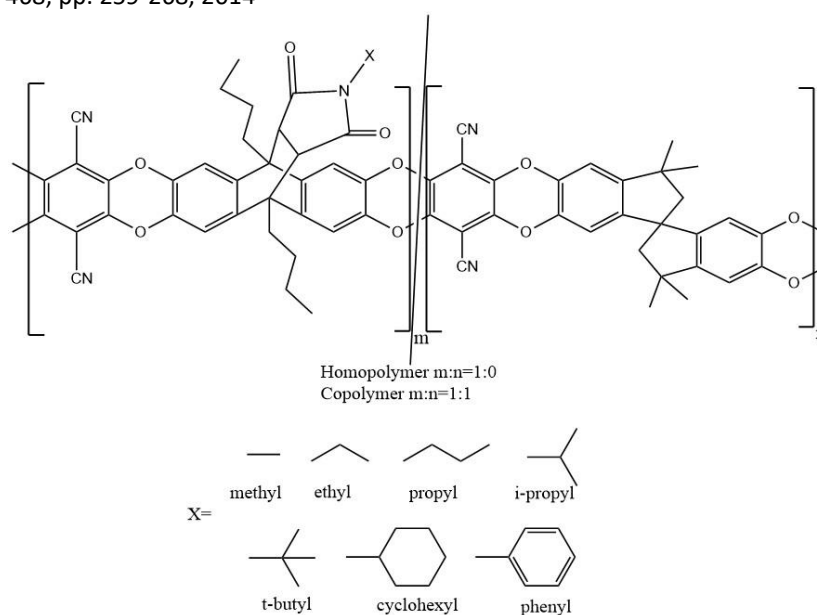
Taking all into consideration, a set of anthracene maleimide monomers with different aliphatic side groups, which are further used as precursors for the series of polymers of intrinsic microporosity (PIM) based homopolymers and copolymers were successfully synthesized and characterized in this study. The polymers with different size and shape of aliphatic side groups were characterized by GPC, ¹H-NMR, TG-FTIR and density measurements. Gas and water vapor transport properties of homopolymers and copolymers were investigated by time-lag measurements. Homopolymers with bulky side groups (i-propyl-100 and t-butyl-100) has a strong impact on fractional free volume (FFV) and on penetrant permeability compared to the homopolymers with linear alkyl side chains. The effect of anthracene maleimide derivatives with variety of aliphatic side groups on water vapor transport was discussed. Maleimide moiety increased the water affinity of the homopolymers. Phenyl-100 homopolymer exhibited high water solubility which is corresponded to higher aromatic rings presence. Copolymers (methyl-50 and t-butyl-50) showed higher CO₂ and CH₄ permeability compared to PIM-1. In summary, introduction of bulky substituents improved free volume and permeability whilst maleimide moiety enhanced the water vapor affinity of the polymer.

Reference 1:

P. M. Budd, N. B. McKeown, and D. Fritsch, "Free volume and intrinsic microporosity in polymers," *Journal of Materials Chemistry*, vol. 15, no. 20, 2005

Reference 2:

K. E. Hart and C. M. Colina, "Estimating gas permeability and permselectivity of microporous polymers," *Journal of Membrane Science*, vol. 468, pp. 259-268, 2014



Investigation on self-assembly of amphiphilic polystyrene-block-poly(vinyl alcohol) diblock copolymers for preparation of pervaporation membranes

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Main topic: Novel membrane materials

Amphiphilic block copolymers are a fascinating and versatile class of polymers. Due to their ability to self-assemble into well-defined nanostructures, along with the combination of different properties arising from distinct structural and functional moieties, block copolymers open up a new approach for the development of promising membrane materials. Thanks to the advances in polymer synthesis, a plethora of block copolymers can now be synthesized to broaden their application range. However, studies on synthesis and self-assembly of tailor-made amphiphilic block copolymers with potential applications in a specific industrial domain are still scarce.

In this work, we will present the synthesis of amphiphilic diblock copolymers with high molecular weights based on poly(vinyl alcohol) (PVA) and polystyrene (PS). The synthesis involves three consecutive steps: (i) atom transfer radical polymerisation (ATRP), (ii) copper catalysed azide-alkyne cycloaddition reaction, and (iii) reversible addition-fragmentation chain transfer polymerisation (RAFT). This versatile strategy of synthesis allows us to obtain a series of amphiphilic block copolymers that can self-assemble into nanostructures in aqueous solutions (*e.g.* Figure 1). Hence, we will show new insights on how to engineer the nanostructure of block copolymer materials for obtaining membranes with enhanced separation performance.

Figure 1. TEM micrograph of PS-*b*-PVA micellar nanostructures obtained by self-assembly in aqueous solution.

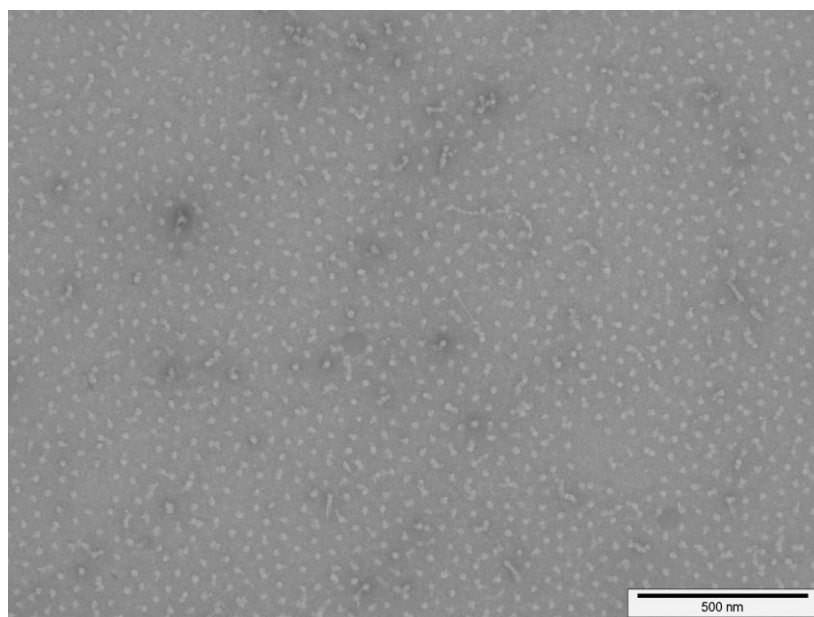
This innovative approach offers thus the possibility to significantly improve the overall separation performance of polymer membranes (Zuo, 2014).

The self-assembly studies are performed in solution followed by casting. The resulting nanostructures are correlated with the membrane structure and its separation performance.

In addition, a new route of solution preparation for producing block copolymer membranes with controlled nanostructure will be presented.

Reference 1:

J. Zuo, G. M. Shi, S. Wei and T.-S. Chung, The Development of Novel Nexar Block Copolymer/Ultem Composite Membranes for C2–C4 Alcohols Dehydration via Pervaporation, *ACS Appl. Mater. Interfaces*, 2014, 6, 13874-13883



Investigations on Donnan Dialysis using Different Membranes and Subsequent Scaleup for Nitrate Removal from Water/Wastewater

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¹Zuckerberg Institute of Water Research, Blaustein Institute for Desert Research, Ben Gurion University of the Negev, Sede Boqer Campus, Midreshet Ben Gurion, Israel

Main topic: Wastewater treatment

Nitrogen rich fertilizers contribute world-wide nitrate to the environment, as a result the contamination of water (surface, ground and wastewater) with nitrate has been a global potential source of concern. Most of the conventional processes have several associated limitations for effective nitrate removal from water environment. Therefore, Donnan dialysis using an appropriate anion exchange membrane may be thought as one of the viable and sustainable options for the purpose. In the present study, three different types of membranes FAB, FAD and FAS by FuMA-Tech GmbH and a membrane from PC-Cell were screened in batch Donnan dialysis experiments and characterized on the basis of nitrate transport from feed (0.005 M NaCl + 100 mg/L NO₃⁻) to receiver (0.05 M NaCl) compartment. The FuMA-Tech membranes produced substantial nitrate flux which was largely linearly dependent on nitrate concentration to a great extent ($R^2 > 0.97$). Highest nitrate flux of 119 meq/h/m² was shown by FAD based on initial flux. To scale up the system for nitrate removal and to take up higher nitrate loadings, an FAD based spiral membrane module (Spiraltec, GmbH) (with 2.75 m² membrane area and 6 m of path length) was adapted for the purpose as a co-current contactor. Since the system will have a bioreactor operating on the receiving side (IEMB – ion exchange membrane bioreactor mode), the spiral module contactor has higher spacer thickness on the receiver side (to prevent an excessive increase in differential pressure). Donnan dialysis with this upscaled module was performed under co-current mode with bioside of 100 meq/L chloride at 100 L/h and feed side with 150 mg/L of nitrate at different flow rates of 40 L/h to 100 L/h. The nitrate flux across the membrane steadily increased with increased feed flow rate and nitrate removal rates ranged from 96% to 88%. The average mass transfer coefficient and nitrate flux was found to steadily increase with the feed flow rate. On the basis of these findings, the present study demonstrates the feasibility of applying an FAD based spiral membrane contactor for selective nitrate transport from water/wastewater with rich nitrate concentration and its subsequent biological denitrification from the receiving solution under IEMB mode.

Ion permeation in narrow carbon nanotubes: putting the puzzle together via combined ab initio and mean-field modeling

Freger, Viatcheslav - Main Author; Neklyudov, Vadim - Co-Author

Main topic: 1D- and 2D-materials for membranes

Narrow carbon nanotubes (CNTs) are unique mimics of water channels in biological membranes, yet the physics behind their selectivity, especially, relative roles of water and ion interactions within CNT and with surrounding matrix, is still unclear. Here we report ab initio investigation of water and ion transfer from solution into CNTs of diameters 0.68 nm and wider 0.8 nm tubes, common in experimental studies.

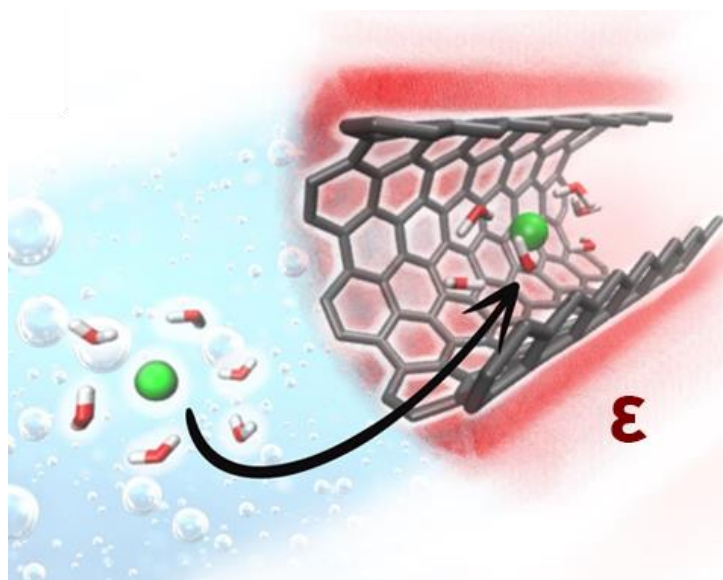
We first focus on the effect of the medium surrounding CNT, defined by its dielectric constant ϵ . The transfer energies computed for $1 < \epsilon < \infty$ permit a transparent breakdown of transfer energy to three main contributions: binding to CNT, intra-CNT hydration, and dielectric energy. The dielectric energy is small for water but very significant for ions and scales linearly with $1/\epsilon$, reminiscent of the Born equation, with the slope of the order 100 kJ/mol for all ions and CNTs. It may easily turn ion transfer from preferential to strong exclusion, as observed for potassium. In contrast, chloride appear to be strongly excluded for all ϵ . Curiously, simulations demonstrate that, while water arranges in a single file in (5,5) tubes, it is strongly distorted in (6,6) tubes, both for water without and with some (but not all) ions. Subsequently, we incorporate thermodynamic quantities computed ab initio in a mean-field model, adding to the picture proton and hydroxide inherently present in water. We first considers transfer of free ions, to which ions pair formation is subsequently added as a proxy of ion-ion interactions. Experimentally observed affinity of CNTs to hydroxide does not show up in computed quantities for single ions, yet it is revealed as an exceptionally favorable transfer of KOH pairs. Nevertheless, we conclude that free ions, coexisting with more abundant, but less mobile ions pairs control the ion transport. The model successfully explains most observed effects of salt concentration and pH on conductivity, ion transport numbers, ion permeation, activation energies, and current rectification. The proposed modeling approach may be extended to other sub-nanometer nanochannels, which may advance our understanding and help design novel desalination and osmotic materials and devices.

Reference 1:

V Neklyudov, V Freger, Water and Ion Transfer to Narrow Carbon Nanotubes: Roles of Exterior and Interior, J Phys Chem Lett 12 (2020) 185-190

Reference 2:

V Neklyudov, V Freger, Putting Together the Puzzle of Ion Transfer in Single-Digit Carbon Nanotubes: Ab Initio Meets Mean-Field, submitted



Ion transport of monovalent ions in electrodialysis: An experimental and theoretical study

Mubita, Tania - Main Author¹; Porada, Slawomir - Co-Author²; Biesheuvel, Maarten - Co-Author²; van der Wal, Albert - Co-Author^{3,4}; Dykstra, Jouke - Co-Author³

¹Wageningen Food & Biobased Research, ²Wetsus, European Centre of Excellence for Sustainable Water Technology,

³Environmental Technology, Wageningen University & Research, ⁴Evides Water Company

Main topic: Electro-membrane processes

Selective ion removal is of interest in water technology applications, especially for water purification and resource recovery. Electrodialysis (ED) is mainly used for water desalination, i.e., removing salt ions from water, but has the potential to achieve desalination with preferential ion removal. In ED, an electrical potential difference is used as a driving force to transport ions across ion-exchange membranes (IEMs). In general, state-of-the-art IEMs only allow the transport of counterions and hinder the transport of co-ions. However, achieving selective ion removal with ED requires that IEMs show selectivity to the transport of a specific counterion while hindering the transport of the other counterions present in the water stream. In the present work, we study the performance of a newly fabricated anion-exchange membrane (AEM) for the selective removal of nitrate over chloride. The home-made membrane shows higher selectivity towards nitrate compared with that of two commercial AEMs, **Figure 1**. To describe the transport of ions across the AEMs, we developed a numerical model based on the Nernst-Planck equation. The model includes the chemical affinity, to account for the preference of membrane materials towards specific ionic species. Our model can closely describe ion selectivity between counterions that not only have the same valence but also the same hydrated size. Interestingly, we also use our model to develop strategies to increase ion selectivity in the AEMs. Results show that possible strategies are to increase the thickness of the AEMs or to decrease their charge density.

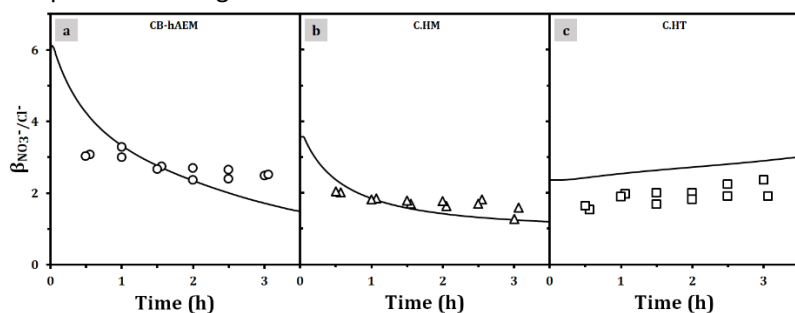


Figure 1. Separation factor ($\beta_{\text{NO}_3^-/\text{Cl}^-}$), experimental data (symbols) and numerical model (lines), as a function of time for a) home-made heterogenous anion-exchange membrane (CB-hAEM); b) commercial homogeneous membrane (C.HM); and c) commercial heterogeneous membrane (C.HT). $\beta_{\text{NO}_3^-/\text{Cl}^-}$ is the $\text{NO}_3^-:\text{Cl}^-$ concentration ratio in the concentrate stream over the $\text{Cl}^-:\text{NO}_3^-$ concentration ratio in the diluate stream. Duplicate symbols represent two independent sets of experiments.

Ion-solvating membranes for high-rate alkaline water electrolysis

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¹Technical University of Denmark, Energy department

Main topic: Electro-membrane processes

Ion-solvating membranes, as conceptually illustrated in Figure 1, are recently applied in water electrolysis, and allow for remarkably high rate capability and non-noble catalyst. A polybenzimidazole membrane based electrolyzer system could display an impressive rate capability of 2.8 A/cm^2 at less than 2.0 V .¹ However, the long-term stability of PBI membranes remains to be a problem currently, which leaves significant space for the development of alternative novel stable membrane materials applied in harsh alkaline environment.²

Among classes of polymers, non-polarized all-carbon backbone based polymers should be promising candidates. For example, plenty of polyphenylene derivatives could be fabricated from bottom-up synthesis through Friedel-Crafts reaction, Suzuki coupling or Yamamoto coupling. However, due to the limitation of polymerization mechanism, the molecular weight of polyphenylene is generally limited, which easily causes brittleness of the membrane. Herein, we chose commercial polyalkylene based polymer as the membrane material, and randomly modify the backbones with functional groups, for instance, benzene ring, carboxyl and sulfonate to tune the balance between electrolytes uptake and mechanical strength. Moreover, by systematically research on the introduction of different groups into the polymers, we could explore the fundamental relationship between the chemistry architecture and comprehensive properties of the membranes.

Reference 1:

1 M.R. Kraglund, M. Carmo, G. Schiller, S. A. Ansar, D. Aili, E. Christensen, J.O. Jensen, 2019, Energy Environ. Sci., 2019, 12, 3313-3318.

Reference 2:

2 D. Aili, A.G. Wright, M.R. Kraglund, K. Jankova, S. Holdcroft, J.O. Jensen, J. Mater. Chem. A 2017, 5, 5055-5066.

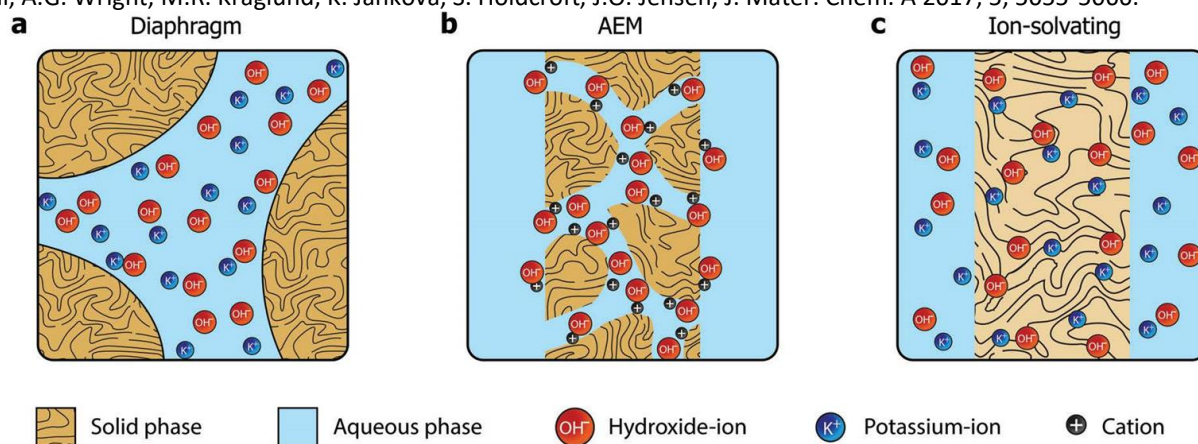


Figure 1 Schematic illustration of the ion-solvating membrane concept in comparison to porous separators and anion exchange membranes.¹

Isolation of extracellular vesicles from citrus limon through membrane-based techniques

Giancaterino, Sara - Co-Author¹; Boi, Cristiana - Main Author¹

¹University of Bologna

Main topic: Bio-separations and bio-refinery

Extracellular Vesicles (EVs) and exosomes have significant physiological properties that make their use particularly interesting in the diagnosis of different diseases, including cancer, in drug delivery and for the regeneration of tissues or wound healing, as specific therapeutic agents. EVs can transport different biomolecules, such as lipids, proteins, nucleic acids and polysaccharides, thus playing a clear key role in intercellular communication.

The recent discovery of plant based EVs made possible the application of edible plant vesicles as carriers of many different molecules in the fields of diagnostics and advanced therapy¹. The purification of EVs from biological and vegetal complex fluids has so far been based on the use of ultracentrifugation, sucrose gradient centrifugation and immunoaffinity chromatography: despite the high yield of product recovery achieved with these techniques, their application on large industrial scale is not feasible.

Aim of this work is to present a simple, less expensive and much faster integrated membrane process for the purification of EVs. Nanosized vesicles from *Citrus Limon* were chosen as a simple and economic system to develop the purification process. Indeed, *Citrus Limon* juice extracts, represent an innovative and still poorly studied source of EVs that have very promising therapeutic use as they inhibit cancer cell proliferation on different cell lines. In the chosen strategy the focus is placed upon the development of a protocol potentially suitable for large-scale operations, conversely to differential ultracentrifugation method, the benchmark in extracellular vesicles production, whose applicability is limited to lab-scale operations. In this context dead-end and crossflow MF/UF units are compared, both as concentration and purification steps. Followingly, the isolated vesicles were analysed and characterized with SEC liquid chromatography and both physical and biochemical methods. Finally, passive cargo loading techniques are applied to the isolated vesicles to test their encapsulation capability with bioactive phytochemicals, as curcumin.

Reference 1:

G. Pocsfalvi, L. Turiák, A. Ambrosone, P. del Gaudio, G. Puska, I. Fiume, T. Silvestre, K. Vékey, Protein biocargo of citrus fruit-derived vesicles reveals heterogeneous transport and extracellular vesicle populations, *J. Plant Physiol.* 229 (2018) 111-121, <https://doi.org/10.1016/j.jplph.2018.07.006>.

Reference 2:

S. Gandham, X. Su, J. Wood, A.L. Nocera, S.C. Alli, L. Milane, A. Zimmerman, M. Amiji, A.R. Ivanov, Technologies and Standardization in Research on Extracellular Vesicles, *Trends Biotechnol.* 38 (2020) 1066-1098, <https://doi.org/10.1016/j.tibtech.2020.05.012>.

Isothermal membrane distillation demonstrated in pilot scale at a communal waste water treatment plant for energy and resource efficiency

Muster-Slawitsch, Bettina - Co-Author; Moritz, Eva - Co-Author; Guillen-Buriezza, Elena - Co-Author

Main topic: Membrane contactors and membrane distillation

Waste water treatment plants (WWTP) have a large potential to become a future hub on energy supply and resource efficiency. While communal WWTP are currently often energy consumers, intelligent novel concepts can render the plants to deliver regional energy supply. One of the most energy intensive processes in WWTP is the aerobic denitrification process resulting to a specific energy demand of 5-15 kWh/kg TN for nitrification/denitrification based systems [1]. To enhance energy and resource efficiency of WWTP, this study presents the selective removal of ammonia from the waste water via low temperature membrane distillation with the aim to reduce the energy demand of the WWTP and deliver ammonia sulfate as byproduct for the regional market.

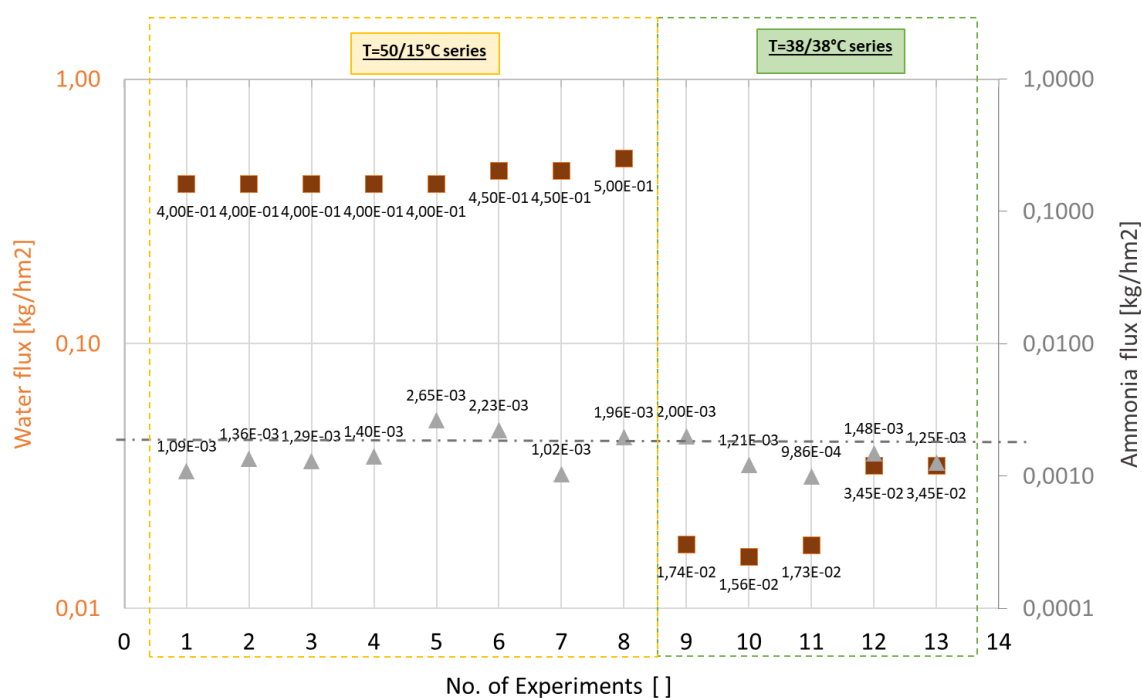
For the first time, a pilot plant for selective ammonia removal from the centrate water of a WWTP was studied for long-term operation. Based on a detailed DoE work of membrane distillation optimization – presented in a separate paper to this conference – optimized process and operating parameters were applied to study the operation of membrane distillation under real environment over several weeks. A commercial plate MD module was used with 14 m² membrane surface area. Temperature conditions of 50°C feed temperature and 15°C permeate temperature were applied for reference and compared to optimized operating conditions of isothermal operation at 38°C. Feed water was treated batch-wise in 100l batches, while permeate concentration was increased over the experiments. Ammonia removal and recovery were monitored over the experimental days.

The results show that the isothermal operation of membrane distillation can reach highly selective ammonia removal with remaining ammonia concentrations of less than 20 mg/l. Energy demand is reduced with isothermal operation down to 12 kWh/kg NH₄, enabling full supply with waste heat at 38°C. The study presents high potential for deploying the concepts in communal waste water treatment plants, with future efforts laying in reduced chemical needs and increasing permeate concentrations for product usages.

Reference 1:

[1] ACS EST Water 2021, 1, 4, 796–807 Publication Date: January 6, 2021 <https://doi.org/10.1021/acsestwater.0c00154>

Ammonia and Water Fluxes



Lava Rock Facilitated Gravity-driven Membrane Filtration of Municipal Wastewater in Cold Climate

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¹Faculty of Civil and Environmental Engineering, University of Iceland

Main topic: Membrane fouling and cleaning

Gravity-driven membrane filtration (GDM) processes are especially suitable for decentralized wastewater treatment because of their low energy consumption and simple maintenance (Pronk et al., 2019). To achieve enhanced water productivity, the GDM operation is commonly operated with periodical physical/ chemical cleaning. This research studied the effects of cleaning protocols on the performance of lava stone facilitated-GDM systems in treating primary wastewater under Icelandic conditions.

In detail, primarily treated wastewater was collected from the wastewater treatment plant and fed into two parallel lab-scale lava rock biofilm reactors (8°C and 22°C) respectively. The effluents were then led into GDM systems with microfiltration membranes (PVDF, 0.08 µm), which were periodically cleaned by high temperature (50°C) geothermal water-based cleaning protocols, including (1) physical flushing, (2) flushing with air sparging, (3) chemical (PMS)-enhanced physical flushing, (4) flushing with ultrasonication. The membrane performance, water quality and microbial community composition were examined.

The results showed that (1) biofilm reactor could achieve ~47-64% removal of organics, regardless of temperature and cleaning protocols; (2) cake layer resistance was dominant in all filtration scenarios. The GDM at low temperature had lower total resistances; (3) Constant pressure filtration model fitting revealed that GDM fouling followed a combined pore constriction and cake filtration mechanism; (4) Combined ultrasonication and geothermal flushing resulted in the highest flux recovery and stabilized flux. Specifically cleaning protocols were more efficient for the GDM operated at 8°C, indicating more loosely attached foulants compared to that operated at 22°C.

Overall, the results showed the feasibility of GDM in treating municipal wastewater under the Icelandic scenario. The technology could be used for small communities and seasonal touristic places to improve wastewater treatment and protect the sensible Icelandic environment.

Reference 1:

1) Wouter Pronk, An Ding, Eberhard Morgenroth, Nicolas Derlon, Peter Desmond, Michael Burkhardt, Bing Wu, Anthony G. Fane, 2019, Gravity-driven membrane filtration for water and wastewater treatment: A review. *Water Research*, Volume 149, Pages 553-565, ISSN 0043-1354, <https://doi.org/10.1016/j.watres.2018.11.062>.

Life-like pulsatile membranes designed from self-oscillating polymer interfaces

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¹European Membrane Institute, Montpellier University

Main topic: Novel membrane materials

Background

Soft matter materials research has considerably evolved the last decades mainly by promoting responsive polymer systems. Up to now, the dynamic behavior, although bringing new functions, was always reached by the action of an outside trigger (pH, light, T...). In this work, it is envisioned to prepare autonomous oscillatory polymer interfaces synchronized by chemical reaction networks (pH-oscillators). The self-regulating pH waves will be read in time by synthesized polymer interfaces to undergo autonomous macroscopic motions. The objectives are the preparation of autonomous dynamic soft interfaces characterized by their constantly evolving surface properties, and the design of new integrated filtration membranes showing a chemically-powered autonomous pulsatile flow.

Results

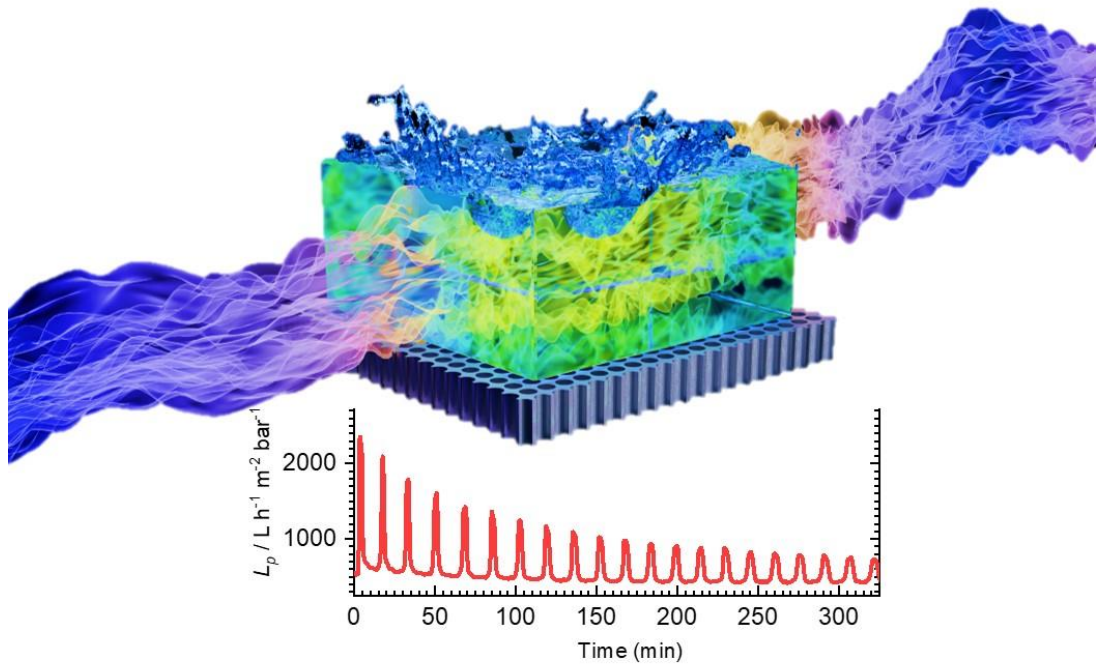
The self-oscillatory system is obtained from the combination of a pH-responsive polymer and an oscillating chemical reaction. In this work, functionalized poly(methacrylic acid) (PMAA) was prepared by RAFT polymerization and grafted at the interface of commercial membranes (PES and alumina ultrafiltration membranes). While alumina membranes could be directly modified via a grafting of PMAA chains end-functionalized with a dopamine unit, PES membranes were first covered by a thin layer of polydopamine and grafted via an aza-Michael reaction with the pH-sensitive polymer. The grafting of PMAA was characterized and confirmed by XPS, SEM-EDX and contact angle investigations. Then mounted in a filtration setup, the PMAA-functionalized membrane was synchronized to a pH oscillator (Bromate-Sulfite-Ferrocyanide: BSF). When the flow through the membrane reaches the pH oscillation domain, a pulsatile flow with impressive permeability cycles was observed. BSF pH-oscillator leads to a cyclic change of the pH between 3.5 and 6.5 in the filtration cell. Since PMAA has a pKa around 4.8, a cyclic extension-contraction of the polymer chains is obtained which leads to a synchronized change in the pore size. Therefore, a direct consequence is an oscillatory modulation of the membrane permeability.

Conclusion

In conclusion, chemically-powered autonomous pulsatile flow has turned a commercial filtration membranes into a lifelike materials characterized by an effective chemomechanical feedback loop. A higher degree of autonomy could be reached by integrating the oscillator components into the membrane structure and it will constitute the perspectives of this work.

Reference 1:

Benoit, M.; Bouyer, D.; Sostat, P.; Ayrat, A.; Cot, D.; Rebiere, B.; Fournier, D.; Lyskawa, J.; Woisel, P.; Antonelli, C.; Quemener, D. Self-Oscillating Membranes with Polymer Interface Synchronized with Chemical Oscillator to Reproduce Lifelike Pulsatile Flow. *Chem. Mater.* 2021. 33, 3, 998–1005. Supplementary journal cover. <https://doi.org/10.1021/acs.chemmater.0c04009>.



Lignin as a renewable resource for polyelectrolyte multilayer based nanofiltration membranes

Watt, Tjerk - Main Author¹; de Vos, Wiebe - Co-Author¹; Regenspurg, Jurjen - Co-Author¹; Jonkers, Wendy - Co-Author¹; Wurm, Frederik - Co-Author²; Peil, Stefan - Co-Author²

¹University of Twente, Membrane Surface science group, ²University of Twente, Sustainable polymer chemistry group

Main topic: Novel membrane materials

Polyelectrolytic multilayer membranes (PEMM) have recently shown great promise as nanofiltration type membranes. Thereby they have found applications in the cleaning of surface and drinking water through their ability to selectively remove ions, micropollutants and small solutes.¹ Unfortunately, these membranes are currently being fabricated using fossil-based polyelectrolytes. With the inevitable depletion of fossil-based materials, it is important to investigate renewable resources as a sustainable alternative. One such alternative is lignin, an abundant biopolymer originating from vascular plants that is currently being obtained as a waste product from the pulping process in the paper industry. Negatively charged lignosulfonates originating from the sulfite pulping process (Figure 1a) can be combined with chemically modified Lignin, obtained from the Kraft pulping process, as a polycation (Figure 1b) to generate stable multilayers by a layer-by-layer approach.²

Here, we aim to study the properties of (modified) lignin as a sustainable alternative to the conventional fossil-based polyelectrolytes used for PEMMs. Using a so-called Layer-by-Layer assembly, polycations and polyanions are adsorbed alternately onto a porous support membrane to form a polyelectrolyte multilayer. Using lignosulfonates as polyanions and modified cationic Kraft lignin as polycation we were able to form an all-lignin PEMM with nanofiltration properties. The membranes had a pure water permeability of 28 L/(bar*h*m²) with a low divalent salt retention of 19%. The membranes had a molecular weight cut-off (MWCO) of 1 kDa. The results thus clearly indicate that PEMMs with promising separation properties can be produced using renewable resources such as lignin.

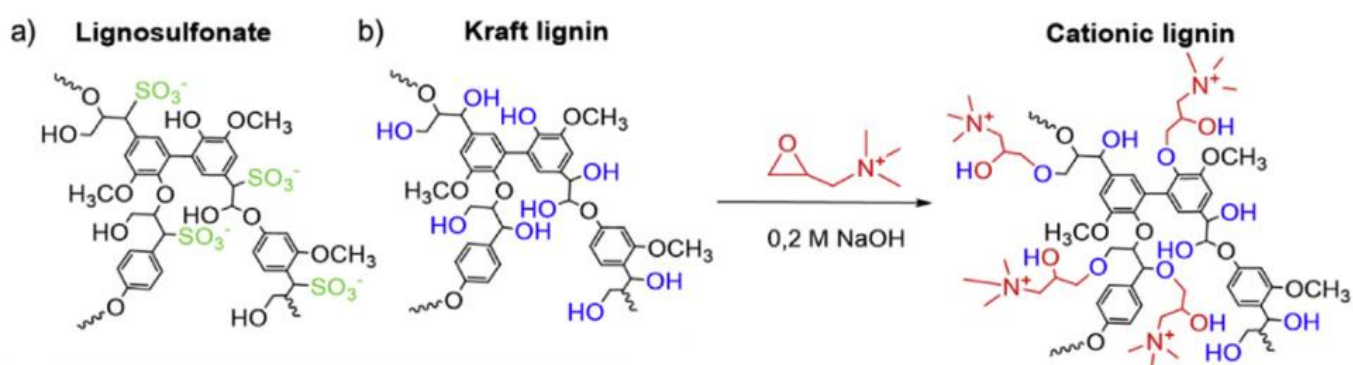
Figure 1: a) Structure of lignosulfonate molecule; b) Reaction for attaching cationic groups to kraft lignin.²

Reference 1:

te Brinke, E., Reurink, D. M., Achterhuis, I., de Grooth, J. & de Vos, W. M. Asymmetric polyelectrolyte multilayer membranes with ultrathin separation layers for highly efficient micropollutant removal. *Applied Materials Today* 18, 100471, doi:https://doi.org/10.1016/j.apmt.2019.100471 (2020).

Reference 2:

Peil, S., Beckers, S. J., Fischer, J. & Wurm, F. R. Biodegradable, lignin-based encapsulation enables delivery of *Trichoderma reesei* with programmed enzymatic release against grapevine trunk diseases. *Materials Today Bio* 7, 100061, doi:https://doi.org/10.1016/j.mtbio.2020.100061 (2020).



Limited swelling of deposit layer obtained in crossflow ultrafiltration of casein micelles dispersion

Loginov, Maksym - Co-Author¹; Doudies, Floriane - Co-Author¹; Hengl, Nicolas - Co-Author²; Karrouch, Mohamed - Co-Author²; Leconte, Nadine - Co-Author¹; Garnier-Lambrouin, Fabienne - Co-Author¹; Perez, Javier - Co-Author³; Pignon, Frederic - Co-Author²; Gesan-Guiziou, Genevieve - Co-Author¹

¹STLO, INRAE, ²LRP, Université Grenoble Alpes, ³SWING, Synchrotron SOLEIL

Main topic: Microfiltration/Ultrafiltration

In the crossflow filtration, analysis of deposit swelling after the transmembrane pressure decrease can shed light on deposit properties and removal mechanism.

Recently [1], we proposed a method for the deposit analysis, which is based on a comparison between modeled and experimentally observed deposit swelling curves. The method was applied for the analysis of membrane fouling deposits obtained during the crossflow ultrafiltration of casein micelles dispersions.

Special cell was used for the simultaneous measurement of the average filtrate flux and the local deposit structure (i.e. dependency of local casein micelles concentration on the distance to the membrane, $c(z)$). The deposit structure was measured with the help of a small-angle X-ray scattering (SAXS) method. Fouling deposits with a thickness of about 100 μm and 150 μm were obtained under transmembrane pressures of 0.5 bar and 1.1 bar, respectively, and the crossflow velocity of 3.1 cm/s. For both studied transmembrane pressures (both deposits), SAXS data were combined with the average filtrate flux data in order to calculate the local compressibility-permeability of deposit: $k \cdot dP/dc$ vs c , where k is the local hydraulic permeability and P is the local osmotic (or compressive solid) pressure. Despite of the difference in $c(z)$ curves observed for two studied pressures (two studied deposits), two $k \cdot dP/dc$ vs. c curves merged, as it is expected for a function describing a material property.

Further, the transmembrane pressure was removed and the $c(z)$ curves were measured via SAXS during the pressure relaxation stage of experiment. The deposit swelling (i.e. decrease of the local micelles concentration) was observed for both studied deposits. Also, the swelling kinetics was modelled numerically using the conventional filtration-consolidation equation with the $k \cdot dP/dc$ -function obtained as described above.

For both studied deposits, the model predicted significantly slower swelling, as compared to that measured in experiments. It was concluded that the deposit compression resulted in micelles interaction (attraction), which was partially reversible, since the deposit swelled and re-dispersed in course of time.

Reference 1:

[1] M. Loginov, F. Doudiès, N. Hengl, M. Karrouch, N. Leconte, F. Garnier-Lambrouin, J. Pérez, F. Pignon, G. Gesan-Guiziou, *Journal of Membrane Science*, 630 (2021) 119289.

Limiting current phenomena in electro-membrane processes: local occurrence or stack-dependent one?

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¹Università degli Studi di Palermo

Main topic: Electro-membrane processes

Background

Electro-membrane processes are gaining great interest in the field of desalination and brine valorisation. However, limiting current phenomena can be a bottleneck for their techno-economic performances. In the present work, the in-out distribution of current density is measured to elucidate the achievement of limiting conditions in real stacks.

Materials and Methods

A 10-cell pairs Electrodialysis stack (10×40 cm² active area), equipped with four-segmented electrodes, was tested. NaCl solutions at an inlet concentration ranging from 0.5 to 60 g/l were fed at velocities of either 2 or 4 cm/s in parallel flow. Current density-voltage curves were built by applying equal increasing steps of voltage to each electrode. Outlet concentrations and current efficiency were investigated [1].

Results

Figure 1 shows the current density-voltage curves for two couples of inlet concentration. Between the final tract of the ohmic region and the plateau region of the overall stack curve, the current density distribution at the four segments changes markedly. In fact, while at the first electrode the current density continues to increase, at the other three it reaches a maximum and decreases. Thus, as the voltage increases, the current concentrates in a shorter tract of the channel, while it reduces in the remaining part, becoming ineffective for desalination, due to its high resistance. This is caused by the high desalination rate in the first few centimetres, making the dilute conductivity much lower. Moreover, the longer tract of channels at high salinity gradient in the final part of the stack promotes larger diffusion, lowering the current efficiency [2].

Figure 1. Current density-voltage curves for tests at a) $C_{dil,IN}=0.5$ g/l and $C_{conc,IN}=30$ g/l and b) $C_{dil,IN}=C_{conc,IN}=1$ g/l.

Conclusions

The attainment of limiting conditions in electrodialysis stacks is strongly related to ohmic phenomena and to the distribution of current density, highlighting its importance in the design of efficient electro-membrane systems.

Acknowledgments

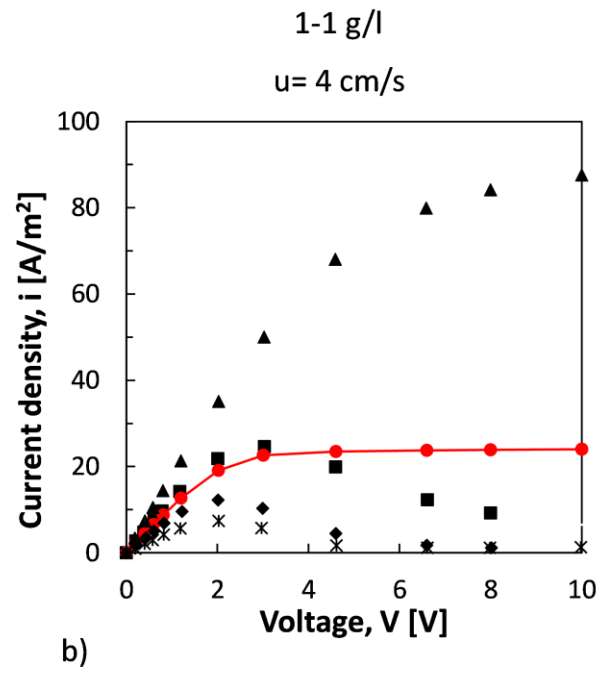
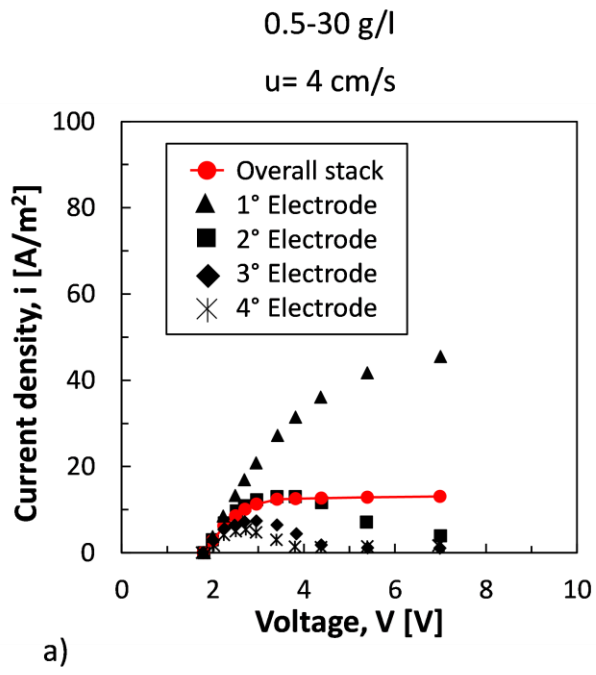
This work was supported by the SEARcularMINE (Circular Processing of Seawater Brines from Saltworks for Recovery of Valuable Raw Materials) project – Horizon 2020 programme, Grant Agreement no. 869467. The authors are grateful to REDstack B.V. and Fujifilm Manufacturing Europe B.V. for supplying stack and membranes, respectively.

Reference 1:

Gurreri L., Filingeri A., Ciofalo M., Cipollina A., Tedesco M., Tamburini A., Micale G., Electrodialysis with asymmetrically profiled membranes: Influence of profiles geometry on desalination performance and limiting current phenomena, *Desalination*. 506 (2021) 115001. <https://doi.org/10.1016/j.desal.2021.115001>.

Reference 2:

M. La Cerva, L. Gurreri, M. Tedesco, A. Cipollina, M. Ciofalo, A. Tamburini, G. Micale, Determination of limiting current density and current efficiency in electrodialysis units, *Desalination*. 445 (2018) 138–148. <https://doi.org/10.1016/j.desal.2018.07.028>.



Liquid crystalline membranes for the valorization of aqueous streams

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Main topic: Novel membrane materials

Efficient and effective separation technologies are crucial to make the transition from the present “linear” economy to a “circular” economy. Currently, many waste streams in e.g. the dairy industry are discarded and valuable resources, such as lactose, minerals and proteins, are lost. This is because molecular separation, i.e. the separation between similarly charged ions or selective recovery of small valuable molecules, is not yet possible. Unfortunately, conventional membrane materials and their fabrication methods mostly lack design and control over pore size and selectivity at a true molecular level. On the contrary, using the self-assembly properties of polymerizable liquid crystal (LC) molecules ensures control at the molecular level and gives rise to narrow pore size distributions and control of pore size and functionality [1].

Here we report the fabrication and characterization of an isoporous pyridyl-functional LC membrane, building on the LC network of Mulder et al. [2]. LC polymer films were obtained by photo-polymerization of LC monomers. Subsequently, pores were obtained by selective removal of the template LC molecule (Fig 1a). X-ray diffraction measurements show an ordered LC network with a layer spacing of 4.19 nm and an intermolecular stacking of 0.44 nm. The pore size is calculated by subtracting the length of the remaining monomer (2.3 nm) from the layer-spacing, which results in a maximum pore size of 1.9 nm (Fig 1b). The membrane retained at least 99% of several dyes and ions tested in a diffusion cell. Lastly, the pore interior was modified from a neutral to a fixed positive charge by methylation of the pyridyl nitrogen. The modified membrane retained 99% of the dyes (methylene blue, methyl orange and riboflavin) in a diffusion cell. Future work will focus on the membrane performance of the modified membrane.

Reference 1:

J. Kloos, N. Joosten et al., J. Membr. Sci. 620 (2020) 118849

Reference 2:

D.J. Mulder et al., J. Mater. Chem. C 18 (2018) 5018-5024

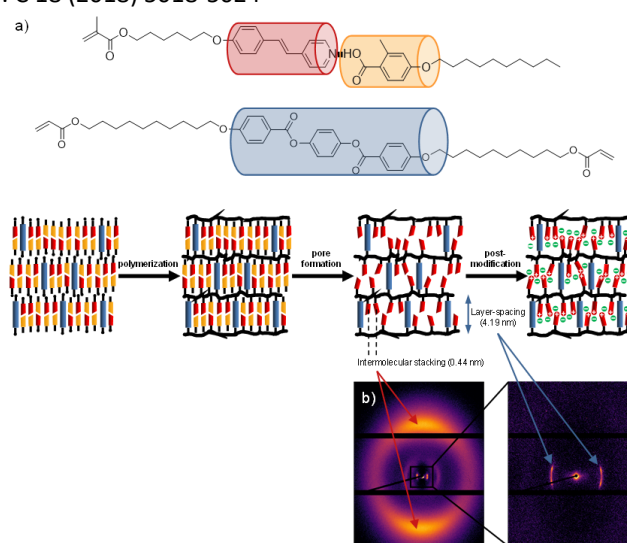


Figure 1 a) Molecular structure of the LC monomers and schematic overview of the fabrication steps for nanoporous self-aligned LC networks. b) 2D x-ray diffractograms (WAXS and MAXS) with a schematic drawing of the LC network which explains the designations.

Liquid fertilizer production from domestic wastewaters using different types of hydrophobic liquid-liquid membrane contactors

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Main topic: Membrane contactors and membrane distillation

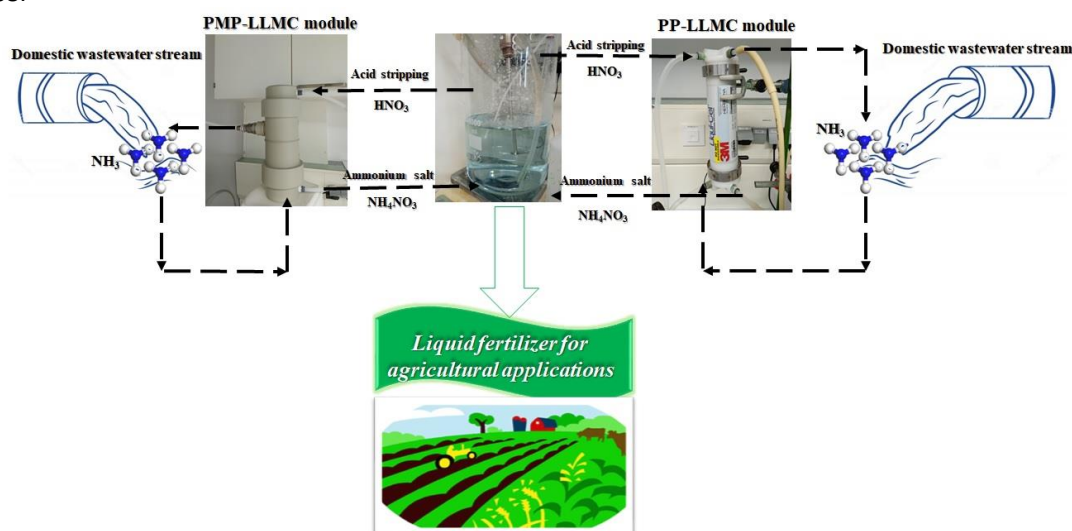
Nitrogen (N) compounds, in the form of ammonia (NH_3) and ammonium (NH_4^+), present in domestic wastewater discharges are recoverable and beneficial resources. To promote global environmental sustainability, more efficient N recovery technology is necessary. Various green technologies are currently emerging toward providing environmentally friendly and cost-effective fertilizers [1,2]. In this study, poly(4-methyl-1-pentene) liquid-liquid membrane contactor (PMP-LLMC) was proposed to produce N liquid fertilizers. Additionally, PMP-LLMC performance was compared with previously studied polypropylene (PP) LLMC under the same operating conditions, such as acid stripping solution (0.4 M HNO_3), feed (450 mL/min) and acid (770 mL/min) solution flow rates and initial feed concentration (around 5 g NH_3/L). The PMP-LLMC used was EF-010-Q-A60 (Separel (Japan)); whereas the PP-LLMC used was 2.5x8 Liqui-Cel[®] Membrane Contactor X-50 PP fibre (3 M Co. (USA)). By using a high concentrated feed stream, more than 93.0 NH_3 recovery was obtained for both PMP-LLMC and PP-LLMC in a closed-loop configuration after 26 and 16 h of treatment, respectively. On the other side, PMP-LLMC showed a better performance in the production of liquid fertilizers, 7.4% N (based on NH_4^+), in comparison with PP-LLMC (4.9% N). Herein, the N content acquired in the liquid fertilizers could allow their direct application in agricultural activities and fertigation services.

Reference 1:

[1] X. Vecino, M. Reig, B. Bhushan, O. Gibert, C. Valderrama, J.L. Cortina. Liquid fertilizer production by ammonia recovery from treated ammonia-rich regenerated streams using liquid-liquid membrane contactors. Chemical Engineering Journal 360 (2019) 890-899.

Reference 2:

[2] M. Reig, X. Vecino, O. Gibert, C. Valderrama, J.L. Cortina. Study of the operational parameters in the hollow fiber liquid-liquid membrane contactors process for ammonia valorization as liquid fertilizer. Separation and Purification Technology 255 (2021) 117768.



Local fouling characteristics in a hollow fiber membrane modules used in pilot-scale hybrid process designed for drinking water production

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¹Research work was carried out in Department of Separation Science, LUT University. Current affiliation: FCG Finnish Consulting Group Oy, ²LUT University, ³Helsinki Region Environmental Services Authority HSY, ⁴Department of Separation Science, LUT University

Main topic: Membrane fouling and cleaning

Due to the globally increasing need for clean water, new processes for drinking water production are constantly being investigated. In this case study, in-line coagulation with different dosages of ferric sulfate (PIX) and polyaluminium chloride (PAX) was combined with hollow-fiber UF and applied in pilot scale to produce drinking water from surface water of Lake Päijänne. The 6 month pilot run was interestingly shaped by emergence of severe membrane fouling issues and unexpected technical complications, despite the application of recommended operating parameters throughout the experiment. Therefore, improvement of the hybrid process performance required insight into filtration data and nature of developed fouling layer, and the pilot run was followed by autopsy investigations of fouled and chemically cleaned membrane modules. It has been reported in several previous studies that in filtrations of surface waters, the fouling is typically caused by natural organic matter but there are only few studies concerning dynamic formation of fouling or local differences in fouling. Thus, our autopsy investigations aimed to show what kind of impact dosage and nature of the used coagulants and cleaning protocols had on the development of reversible and irreversible fouling, to identify compositions of both organic and inorganic foulants, and to reveal differences in local fouling across the fouled and chemically cleaned modules. Moreover, effectiveness of ultrasound cleaning, and acidic and alkaline cleaning chemicals in the removal of the fouling was studied by sequential desorption experiment. The results showed considerable differences in the local fouling, which was heavier near the open ends of the membrane. The visible cake layer contained 30-50 % of natural organic matter which consisted mainly of humic substances and polysaccharides, while inorganic fraction contained Al and Fe flocs and minor amounts of Ca, K and Mg. Regions which were not covered by cake were fouled more by organics and less by Fe. The high amounts of iron remaining after 8 cleaning cycles was surprising. Moreover, it appeared that the chemical cleaning procedure was ineffective at removing cake layer from the modules because it had rather pushed foulants towards the center of the modules, both horizontally and vertically.

Low-Cost Mixed Matrix Nanofiltration PVC/Mn₂O₃ Membranes for Wastewater Treatment

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¹National Research Centre, ²National Research centre, ³National Research Centre, ⁴Zhejiang University

Main topic: Nanofiltration/Reverse Osmosis

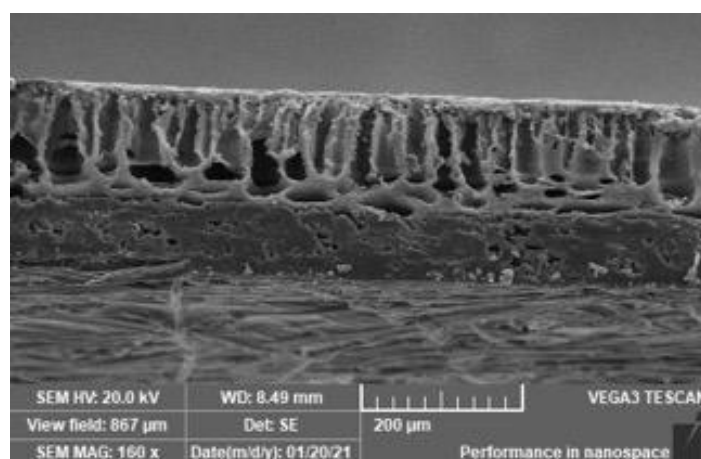
Nanofiltration membranes were prepared using Mn₂O₃ powder as nanoparticles to be used in polymeric blend solution. PVC was used as the main polymer, where four membranes were prepared using polymer content 14% and different percentage of Mn₂O₃ from 0.1 to 0.5 wt%. The prepared membranes were tested using a cross-flow membrane filtration cell to separate different salt concentrations: Na₂SO₄ of 1000 ppm, MgSO₄ of 500 ppm, MgCl₂ of 2000 ppm and NaCl of 5000 ppm. The aforementioned mixed salts are used as model synthetic wastewater stream having di- and monovalent salts. The founded results in this work indicated that the prepared nanofiltration membrane exhibited good separation for divalent salts, showing a separation percentage of 92.2% for MgSO₄, 86.8% for MgCl₂, 75.8% for Na₂SO₄ and 71.3% for NaCl and the permeate fluxes were 11.3, 16.2, 13.4 and 17.2 LMH respectively at using nanofiltration membrane (NF2). Application of Mn₂O₃ in PVC-polymer blend enhances membrane performance due to the improvement of hydrophilicity. The prepared membranes will be subjected to full chemical characterization. Fig (1) indicates the separation percentage for different prepared membranes. Fig (2) illustrates the scan electron microscope for NF2 which indicates wide finger like structure and dense top layer accordingly the membrane is considered asymmetric membrane, and provides good performance in terms of rejection % and permeate flux.

Reference 1:

Mehrjo, F., Pourkhabbaz, A., & Shahbazi, A. (2021). PMO synthesized and functionalized by p-phenylenediamine as new nanofiller in PES-nanofiltration membrane matrix for efficient treatment of organic dye, heavy metal, and salts from wastewater. *Chemosphere*, 263. <https://doi.org/10.1016/j.chemosphere.2020.128088>

Reference 2:

Wei, S., Chen, Y., Hu, X., Wang, C., Huang, X., & Liu, D. (2020). Journal of the Taiwan Institute of Chemical Engineers Monovalent / Divalent salts separation via thin film nanocomposite nanofiltration membrane containing aminated TiO₂ nanoparticles. 112, 169–179.



Mass transfer of Volatile Fatty Acids through Nanofiltration membranes: Relationship between feed and permeate proportions

Galier, Sylvain - Co-Author; Zhu, Yin - Co-Author; Roux-de Balmann, H el ene - Co-Author

Main topic: Bio-separations and bio-refinery

Volatile Fatty Acids (VFAs), fatty acids having up to six carbon atoms, are recognized as promising chemical building blocks in the biorefinery concept [1]. There is a great interest in producing VFAs by fermentation of various biomass like household solid waste or waste streams such as waste water or waste activated sludge, with a double purpose of waste valorization and production of valuable compounds. Amongst VFAs, acetic, propionic, and butyric acids are the main components obtained in the fermentation broth.

Nanofiltration is considered to have a great potential for purification of valuable products such as VFAs. However, it was also pointed out that the process performances vary significantly according to the environmental parameters, like the pH or the broth composition [2].

In this work, nanofiltration experiments were carried with synthetic solutions of different synthetic solutions with increasing complexities, from single, binary and ternary solutions of VFAs, i.e., acetic (Ac), propionic (Pr), and butyric acid (Bu), to mixed solutions containing VFAs and inorganic salts at different compositions. Two NF membranes (NF 45 and XLE, Filmtec) were used in dead-end filtration. The influence of ionic composition on the transfer of the solutes are discussed.

Although the retention of charged solutes can be significantly modified according to the composition of the solution, it is observed that for any condition the retention sequence follows the solutes molecular weight,

Reference 1:

M. Atasoy, I. Owusu-agyeman, E. Plaza, Z. Cetecioglu, Bio-based volatile fatty acid production and recovery from waste streams : Current status and future challenges, *Bioresour. Technol.* 268 (2018) 773–786. doi:10.1016/j.biortech.2018.07.042

Reference 2:

C. Umpuch, S. Galier, S. Kanchanatawee, H. Roux-de Balmann, Nanofiltration as a purification step in production process of organic acids: Selectivity improvement by addition of an inorganic salt, *Process Biochem.* 45 (2010) 1763–1768. doi:10.1016/j.procbio.2010.01.015

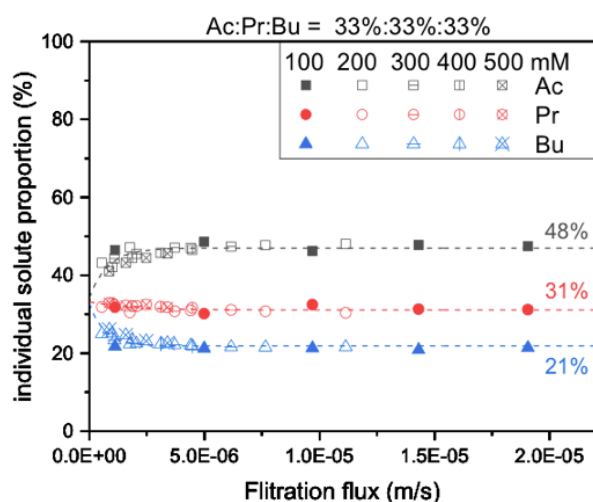


Figure 1: Individual VFAs proportions in the permeate for ternary (Ac/Pr/Bu) solutions at different concentrations with equal VFAs proportion in the feed using NF 45 membrane at pH 8.

Mathematical model for fouling in membrane bioreactor systems

Christensen, Morten - Co-Author

Main topic: Membrane bio-reactors

Membrane bioreactors is an established method for treating wastewater, but fouling remains the Achilles heel as it reduces permeability and membrane lifetime, and elevates operating costs. Dissolved extracellular polymeric substances (EPS) are often considered to be the main foulant that reduce the membrane performance due to a hydraulic resistance, an osmotic pressure or a combination of these¹. The performance loss has been monitored by measuring the transmembrane pressure (TMP) at constant permeate flux. Salt concentration has been varied to change the concentrations of sludge flocs and free EPS. Three different mathematical model has been set-up: 1) Osmotic pressure model, 2) Gel filtration model, and 3) Cake-enhanced osmotic pressure model. Osmotic pressure was calculated as the sum of the EPS polymers (Flory-Huggins Lattice model) and counter-ions at the membrane surface including the effect of concentration polarization. The osmotic pressure model cannot explain the increasing TMP with time. The gel filtration model was used assuming that EPS polymers are immobilized at the membrane surface. The permeability through a polymer network was calculated using the Jackson and James model developed for randomly distributed fibers. The model describes well the TMP increase and the TMP jump if it is assumed that the gel layer is compressible. EPS are negatively charged and both concentration polarization and gel layer compression increase the counter ion concentration. It also increases the relative concentration of divalent ions, which may induce gel formation. The Donnan equilibrium model was used to calculate counterion concentration. The cake enhanced osmotic pressure model was suggested where a cake layer of larger particles was build up. EPS pass the cake but back-diffusion was continuously reduced due to the increasing cake thickness and cake compression. The gel layer model and the cake-enhanced osmotic pressure model describes well the TMP development. Both models highlight the importance of the counterions and the divalent ions for the osmotic pressure and the gel formation. The monovalent-to-divalent ion ratio is reduced at the membrane surface, which reduces the osmotic pressure, but increases the risk for gel formation.

Reference 1:

Christensen ML, Jørgensen MK, Van De Staey G, De Cock L, Smets I. (2021) Hydraulic resistance and osmotic pressure effects in fouling layers during MBR operations. *Journal of Membrane Science*. 627, 119213.

MBR Digital Twin enabling data-driven water reclamation solutions

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¹Norwegian University of Life Sciences (NMBU)

Main topic: Membrane bio-reactors

The world is in the midst of the Fourth Industrial Revolution. This transition to Industry 4.0 will enhance processes with intelligent and autonomous systems fuelled by data and machine learning.

Digital transformation will lead the water industry to a world where all people, “things” and processes are connected through the “Internet of Everything”, leading to capillary networks and sensors, meters, and water system monitoring for innovative decision support and governance systems.

MBR Digital Twin is a replica of a physical membrane bioreactor system that can tackle the fundamental challenges of MBR plant operation: minimisation of OPEX, stable operation preventing membrane fouling and discharges of uncompliant effluent, process operation with as little human interaction as possible.

Virtual representation of MBR can help to react immediately to changes in the environment and automate process like pre-treatment, aeration, mixed liquor recycling, dosing of chemical flux enhancers, chemically enhanced backwash, and cleaning-in-place. The idea is to shift from a reactive management strategy based on sensor data to a proactive strategy with focus on optimal process control with the help of simulation and data-driven models.

Our research group on Process Analytics and Water Treatment has been working on creating a Digital Twin of a Biofilm-MBR (Bf-MBR) pilot plant with silica carbide ceramic membranes since 2015. In the first part of the study, we have determined the fouling propensity of filtered biomass in a pilot-scale Bf-MBR enabling the prediction of fouling intensity. Three dynamic models were derived depending on the operating conditions applying partial least squares regression analysis of the data from one-year operation of the pilot plant.

Using advanced multivariate statistics, we connected the dynamic models of Bf-MBR with results of chemical enhancement applying coagulants in membrane separation experiments. The final virtual representation of Bf-MBR was used to develop and control chemical enhancement for retrofitting MBBR and IFAS systems into more efficient Bf-MBR.

Reference 1:

Kulesha, O.; Maletskyi, Z.; Ratnaweera, H. Multivariate Chemometric Analysis of Membrane Fouling Patterns in Biofilm Ceramic Membrane Bioreactor. *Water* 2018, 10, 982. <https://doi.org/10.3390/w10080982>

Reference 2:

Maletskyi, Z.; Zigta, D.K.; Kulesha, O.; Ratnaweera, H. Chemical Enhancement for Retrofitting Moving Bed Biofilm and Integrated Fixed Film Activated Sludge Systems into Membrane Bioreactors. *Membranes* 2019, 9, 135. <https://doi.org/10.3390/membranes9100135>

Measuring Methanol Vapor Sorption and Transport Properties on Model Fuel Cell Membranes

Guo, Meishan - Main Author¹; Dowd, John - Co-Author

¹Surface Measurement Systems

Main topic: Fuel cells

Direct Methanol Fuel Cells (DMFC) has continued to be an active area of research due to the potential for improved electrocatalysis for methanol oxidation and advantages for using liquid fuels in comparison to hydrogen [1]. A potential downfall of DMFC's is methanol crossover from anode to cathode due to high methanol permeability through the membranes [2]. This leads to lower overall fuel cell efficiency. As a result, the membranes used in DMFC applications should have improved methanol barrier properties. Therefore, understanding the methanol sorption and transport properties in DMFC membranes is vital in the development of these materials.

The Dynamic Vapour Sorption (DVS) system provides a well-established method for the determination of water and organic vapour sorption and desorption properties. DVS could also be applied to study the adsorption kinetics and vapour diffusion at different temperatures. In this study, the methanol sorption capacity and diffusion kinetics were studied on three different Nafion® based membranes over a range of temperatures and methanol vapor concentrations.

Reference 1:

[1] Dillon, R., Srinivasan, S., Arico, A. S., & Antonucci, V. (2004). International activities in DMFC R&D: status of technologies and potential applications. *Journal of Power Sources*, 127(1-2), 112-126.

Reference 2:

[2] Lu, G. Q., Liu, F. Q., & Wang, C. Y. (2004). Water transport through Nafion 112 membrane in DMFCs. *Electrochemical and Solid State Letters*, 8(1), A1.

Mechanistic modeling of membrane contactor type crystallization reactor: prediction of crystal size distribution using multidimensional population balance-based modeling

Tanmoy K, DEB - Co-Author

Main topic: Membrane reactors

Mechanistic modeling of membrane contactor type crystallization reactor: prediction of crystal size distribution using multidimensional population balance-based modeling

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² Last position hold: Marie Skłodowska-Curie ESR, Membrane Engineering in the framework of EM3E-4SW (2013-2015).
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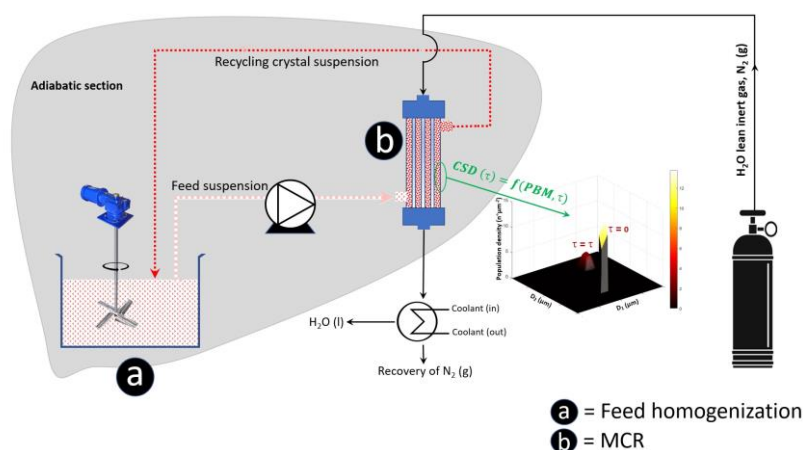
Given that molecular organization in drug formulation (particulate solid) is central to drug efficacy, the evaporative membrane crystallization reactor (MCR) has charming potentiality over any other crystallization technique, with guaranteed microscale mixing induced strict control of molecular integrity in produced crystal, executability at almost any temperature, and minimized need of additional chemicals.

In order to explore the role of different anatomical and operational aspect of an MCR, seeded (and non-seeded) crystallization of four molecules with pharmaceutical and cosmetic interest is simulated in a virtual hollow fiber MCR system.

The crystallization suspension was charged (with recycling) to the MCR from a feed tank, and the moisture lean N₂ gas charged in the lumen side of the hollow fiber constantly supersaturated the membrane surface by distillative extraction (of water). The simulation was adiabatic and an incompressible flow of suspension parallel (an ideal configuration) to the membrane surface was considered. Once the distillation is initiated, the nucleation, growth and aggregation induced time evaluation of (one-, two- or three-dimensional depending on the molecule) crystal size and shape distribution (CSD) was simulated using a developed local reaction rate (tailored from CFD simulation-based concentration profiling) impregnated multidimensional extension of population balance (PBM) based modeling framework. To reduce computational cost, the original MCR anatomy specifications were rationally scaled down.

The impact of different operational configurations of varied lean gas (flow rate, temperature, and humidity), crystallization suspension (flow rate, temperature, seed size distribution and concentration), and non-reactive membrane-material (thickness, thermal and physical) properties on CSD is simulated using this modeling framework.

The excellent controllability of the crystallization reaction rate, CSD, processing fluid temperature, and approaches for scaling up to large scale is mathematically demonstrated. Towards the end of the study, a convincing impact/potential of local concentration gradient and flow property to stress the aspect ratio of the crystal is demonstrated.



MEMBRANE ASSISTED CRYSTALLIZATION: A THEORETICAL EVALUATION

Tocci, Elena - Co-Author¹; Perrotta, Maria Luisa - Co-Author; Macedonio, Francesca - Co-Author; Bruno, Antonio G. - Co-Author²; Muzzi, Chiara - Co-Author; Cui, Zhaoliang - Co-Author³; Drioli, Enrico - Co-Author

¹Institute on Membrane Technology (CNR-ITM), ²University of Leicester, ³Nanjing Tech University

Main topic: Membrane contactors and membrane distillation

Membrane assisted crystallization (MCr) is a well-known technology where microporous hydrophobic membranes are used to promote the water vapor transfer between phases inducing supersaturation in solution¹. Membrane crystallization is an efficient process for the production, purification, and/or recovery of solid materials with interesting advantages in comparison to traditional crystallization techniques, such as well-controlled nucleation and growth kinetics and fast crystallization rates, and reduced induction time². It is generally difficult to monitor the growth mechanisms of crystals formation however; molecular modelling helps to investigate the mechanism of nucleation and crystals growth².

Our contribution was aimed at analyzing the crystal nucleation and growth of sodium salts in contact with hydrophobic polyvinylidene fluoride (PVDF) surfaces at a supersaturated concentration of salt.

The salt nucleation is faster with the amorphous PVDF model than α and β PVDF and can be attributed to differences in the ability of the amorphous membrane to induce supersaturation in less time.

Acknowledgement The authors extend their appreciation to the Deputyship for Research and Innovation, Ministry of Education in Saudi Arabia for funding this research work through the project number (632)

Reference 1:

Macedonio F., Drioli E., *Desalination and Water Treatment*, 18 (1-3): 224–234, 2010.

Reference 2:

M.L. Perrotta, A.G. Bruno, F. Macedonio, Z. Cui, E. Drioli and E. Tocci* Influence of PVDF polymorphs in Membrane-assisted Crystallization: NaCl crystals nucleation and growth, *General Chemistry*, 7, 200015 (1-10), 2021

Membrane condenser for particulate abatement from gaseous streams

Frappa, Mirko - Main Author; Macedonio, Francesca - Co-Author; Cui, Zhaoliang - Co-Author; Bamaga, Omar A. - Co-Author; Drioli, Enrico - Co-Author

Main topic: Membrane contactors and membrane distillation

The demographic growth and the related activities caused an increasing water demand for several applications. The pioneering Membrane Condenser (MCo) might support the treatment of gaseous waste streams (plume of cooling tower, biogas, flue gas, etc.) for the production of pure water. Moreover, Membrane condensers can be utilized for the removal of contaminants and the abatement of the particulates contained in waste gaseous streams. The process utilizes hydrophobic porous membranes to retain water molecules thus providing a new unconventional source of water. If condensables or particles are present in the feed streams, they are retained in recovered water thus minimizing the impact of waste gaseous streams on the environment. This leads to a certain versatility of the system and translates into a further advantage with respect to other operations, since the retained contaminants can, in principle (when properly handled) be purified and reused.

Preliminary tests of MCo were performed for studying the performance of the process in the removal of polystyrene particles of different size. It was found how the morphology, structure and mass transport properties of the membranes, together with the characteristics of the gaseous stream and of the particles contained, determine the capability of the condenser in retaining particles. For having an efficient abatement of particles is thus fundamental having membranes with a pore size lower than the nominal particles size and a narrow pore distribution, as also experimentally confirmed.

Acknowledgement

The authors extend their appreciation to the Deputyship for Research and Innovation, Ministry of Education in Saudi Arabia for funding this research work through the project number (421).

Reference 1:

Brunetti, Adele, Francesca Macedonio, Zhaoliang Cui, and Enrico Drioli. 2020. "Membrane Condenser as Efficient Pre-Treatment Unit for the Abatement of Particulate Contained in Waste Gaseous Streams." *Journal of Environmental Chemical Engineering*.

Reference 2:

Frappa, Mirko, Adele Brunetti, Enrico Drioli, Zhaoliang Cui, Jun Pan, and Francesca Macedonio. 2020. "Membrane Condenser for Particulate Abatement from Waste-Gaseous Streams." *Journal of Membrane Science and Research*.

Membrane crystallization with anion-exchange hollow fibres

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Main topic: Membrane reactors

Due to climate change and population growth, fresh water is becoming the important commodity. Many states, especially those situated near ocean or sea, are using big RO osmosis plants to produce fresh water from sea water. However, produced RO brine is becoming environmental threat when disposed and economic burden since fees for waste disposals are increasing. On the other hand, brines can be convenient source of minerals. For example, seawater brine can contain over 30 g/L of dissolved magnesium. [1] Membrane crystallization can represent one method how to extract magnesium from RO brine. In this work, membrane crystallization with anion-exchange hollow fibres is presented. The process is based on coupling Donnan dialysis with reactive crystallization. For this, we designed module in annular shape with anion-exchange hollow fibres. This model was immersed in tank with solutions 0.5M MgCl₂ or model solutions of RO brines[1, 2]. Solutions were mixed. In the lumen side of membranes NaOH solution was flowing. In the process, OH⁻ and Cl⁻ anions are exchanged through the anion-exchange hollow fibres and MgOH₂ precipitate. We discussed influence of NaOH concentration on mass transfer through fibres, conversion, and particle size. In experiments with model RO brines, we focused on purity of the MgOH₂ since its price is proportional to its purity. Membrane crystallization can help produce product with high purity over 90% even when the RO brine is mixture of various cations and anions in different concentrations

Reference 1:

Kieffer, R., Mangin, D., Puel, F., Charcosset, C. 2009 Precipitation of barium sulphate in a hollow fiber membrane contactor, Part I: Investigation of particulate fouling, Chemical Engineering Science 64, p. 1759-1767

Reference 2:

Curcio, E., Simone, S., Di Profio, G., Drioli, E., Cassetta, A., Lamba, D. 2005 Membrane crystallization of lysosome under forced solution flow, Journal of Membrane Science 257 p. 134-143

Membrane emulsification for preparation of tailored crude oil-in-water emulsions

Ali, Amer - Main Author; Quist_Jensen, Cejna - Co-Author

Main topic: Membrane emulsification

Oil-in-water emulsions have gained interest for enhanced oil recovery applications; these emulsions, however, must possess well controlled pore size and pore size distribution according to the microstructure of the oil reservoir. In current study, emulsions with the controllable droplet size and size distribution have been prepared by applying membrane emulsification (ME) on produced water. The emulsions were prepared by applying a commercial hollow fiber membrane and by using a synthetic produced water (1% oil from North Sea along with a tween 80 and lecithin based dispersant) as to-be-dispersed phase and distilled water as well as synthetic seawater as continuous phase. It has been demonstrated that the average droplet size of the emulsions could be tuned from 0.24 to 0.65 μm by varying the pressure on to-be-dispersed phase from 0.25 to 1 bar, respectively. The emulsions demonstrated excellent stability under high pressure, temperature and during storage over more than 24 hours. It was noted that the effect of fouling on flux was more detrimental at low pressures however; the flux could be fully recovered by cleaning the membrane with distilled water. The calculations demonstrate that an ME unit with weight and spatial dimensions of < 100 kg and <1 m^3 is sufficient to convert the entire volume of produced water in the Danish part of the North Sea into the emulsions. The study offers an innovative route, compatible with requirements (low-weight and small spatial footprints) of the offshore rigs, to prepare tailored size emulsion from produced water.

Acknowledgement: This work was partly funded by the Danish Hydrocarbon Research and Technology Centre (DHRTC), Denmark.

Reference 1:

C.A. Quist-Jensen, A. Ali, Minerals, Membrane Emulsification for preparation of a tailored emulsion to be used as smart injection fluid, Project Book of Radical Innovation Sprint, 2019, Danish Hydrocarbon Research and technology Centered, Copenhagen, Denmark

MEMBRANE EXTRACTION WITH DENSE MEMBRANES: PROMISING TOOL FOR CHALLENGING AFFINITY-BASED SEPARATIONS

Buekenhoudt, Anita - Co-Author¹; De Sitter, Kris - Co-Author¹; Salvador Cob, Sara - Co-Author¹; Vandezande, Pieter - Co-Author¹

¹VITO

Main topic: Membrane contactors and membrane distillation

Nowadays, many chemical companies are confronted with very challenging liquid separations, aiming at separating molecules with very similar physical properties. The current trend towards more bio-based and/or highly-tailored chemicals, will only increase the number of these demanding separations. These challenges would benefit from efficient affinity-based separations. The most traditional affinity-separation technology is liquid-liquid extraction, where the extracting solvent acts as the separation agent. It is well-known that in many cases the use of open-porous membrane contactors can boost the extraction process, can possibly combine extraction and stripping, while minimizing solvent use. However, leakage of extraction solvent from the membrane pores might jeopardize the advantages of membrane extraction (ME).

A few years ago, VITO showed that the use of dry fine-porous or dense hydrophobic membranes can avoid the stability issues encountered in open-porous ME (supported liquid membrane configuration) used for in-situ product recovery of chiral amines in a transaminase bio-process, and this without serious decrease of the membrane transport. The hydrophobic membranes take over the role of the apolar solvent, and except for the solutes, no solvent transport is observed during the process [1].

In a running Flemish SBR project EASiCHEM, the parameters governing this innovative, dense ME process are being extensively studied in a variety of model streams and ME configurations. Moreover, it is investigated how solute-membrane affinity can add extra selectivity to the process. To this end, the performance of multiple polymeric membranes as well as (functionalised/grafted) ceramic membranes have been compared. For proper benchmarking, ME results are also contrasted with results of traditional liquid-liquid extraction and/or nanofiltration for the same feed streams. In this contribution results will be shown for different, challenging, industrially relevant separation cases.

Acknowledgement

EASiCHEM has received funding from the Flemish Strategic Basic Research Program of the Catalisti cluster and Flanders Innovation & Entrepreneurship, under the contract HBC.2018.0484

Reference 1:

Satyawali, Vanbroekhoven, Ormerod, Buekenhoudt, patent application WO 2017/103163 "Process for the separation of chiral amines", applicant VITO, priority date December 2015.

Membrane fouling by lysozyme: Effect of local interaction

Ma, Yunqiao - Co-Author; Zydney, Andrew - Co-Author; Chew, Jia Wei - Co-Author

Main topic: Membrane fouling and cleaning

Molecular dynamics simulations were performed to understand the adsorption of positive-charged lysozyme onto negative-charged polyvinylidene fluoride membrane at three pH and two ionic strengths. The lysozyme was initialized at six orientations at 10 Å from the membrane and adsorption was deemed to occur when the lysozyme is less than 4 Å from the membrane. Local interactions are clearly important: (i) despite opposite net charges, no adsorption occurs in some cases throughout; (ii) lysozyme-membrane separation distances differ among the initial orientations of lysozyme; and (iii) the correlation between lysozyme-membrane interaction energy and adsorption probability is poor. Correspondingly, seven key local adsorption sites on lysozyme were identified. Of the two most common sites, one anchors due to electrostatics, while the other is not electrostatics-based. Also, different sites are dominant in different feed conditions and have different interaction energies. These results reveal the importance of local interactions in membrane fouling by proteins in different feed conditions.

Reference 1:

<https://doi.org/10.1002/aic.17212>

Membrane fractionation of hydrothermally solubilized waste activated sludge for the recovery of valuable biocompounds: assessment of membrane material and size

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Main topic: Wastewater treatment

The recovery of carbohydrates, proteins and humic acids from waste activated sludge (WAS) is a promising way to valorize this residue in the context of circular economy [1]. However, its valorization required a previous solubilisation, which results in a highly complex matrix, thus making it difficult to recover these added-value biocompounds. Membrane filtration is a suitable technology for this purpose due to its high selectivity and low cost, but it has not yet been studied in WAS. The performance of the membrane filtration depends on several factors, especially the molecular weight cut-off (MWCO) and material [2].

Therefore, the aim of this work was to study the influence of the membrane MWCO and material on the fractionation of hydrothermally solubilised WAS, towards the recovery and purification of carbohydrates, proteins, and humic acids.

For the membrane material screening, flat-sheet polyethersulfone (PES50), permanently hydrophilic polyethersulfone (PESH50), and polyacrylonitrile (PAN50) membranes of 50 kDa were used. For the size fractionation experiments, PES membranes of 10 and 3 kDa (PES3) were also used. In addition, the nature of the fouling of the different materials was studied considering the Hermia's and the resistance-in-series fouling models.

PESH and PAN membranes permeabilities were higher ($\sim 100 \text{ L/m}^2\text{h}$) than in PES membrane ($30\text{--}40 \text{ L/m}^2\text{h}$). Nevertheless, the PES membrane showed both the highest retention values and difference between proteins (68%) and HA (47%) retentions, thus being selected for the size fractionation analysis.

The resistance-in-series model showed that the main fouling in the membranes of PAN and, to a lesser extent, of PES, is reversible. On the contrary, the fouling of the PESH membrane had a strong irreversible character. These results were in accordance with their best fitting to Hermia's fouling model: cake formation (reversible) for PAN and PES, and complete pore blocking (irreversible) for PESH.

The best size fractionation results were obtained filtering the PES50 membrane permeate with the PES3 membrane, retaining 83% of carbohydrates, 87% of proteins and 69% of humic acids. These results open the possibility of purifying carbohydrates and proteins by diafiltration of the PES50 permeate, and humic acids by nanofiltration or reverse osmosis of the PES3 permeate (Fig 1).

Reference 1:

A. Raheem, V.S. Sikarwar, J. He, W. Dastyar, D.D. Dionysiou, W. Wang, M. Zhao, Opportunities and challenges in sustainable treatment and resource reuse of sewage sludge: A review, *Chem. Eng. J.* 337 (2018) 616–641. doi:10.1016/j.cej.2017.12.149.

Reference 2:

D.M. Kanani, W.H. Fissell, S. Roy, A. Dubnisheva, A. Fleischman, A.L. Zydney, Permeability-selectivity analysis for ultrafiltration: Effect of pore geometry, *J. Memb. Sci.* 349 (2010) 405–410. doi:10.1016/j.memsci.2009.12.003.

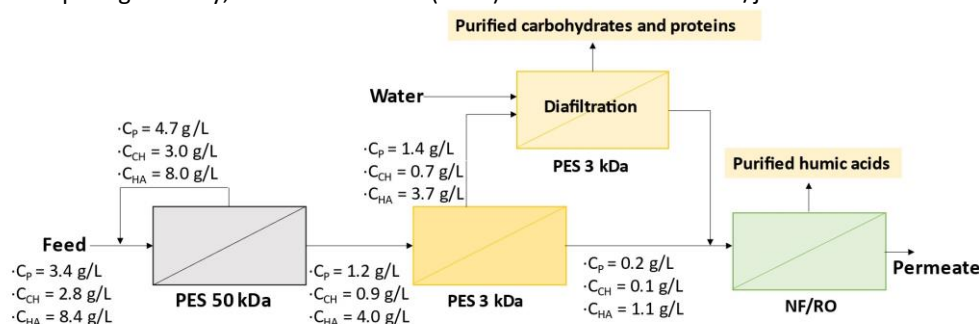


Figure 1. Size fractionation results and proposal for carbohydrates (CH) and proteins (P), and humic acids (HA) purification.

Membranes functionalization for biorecognition and biosensing

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Main topic: Environmental applications

Biosensors are attracting increasing attention for environmental monitoring. A biosensor consists of various associated elements, among which the bioreceptor (a biological element such as enzyme, antibody, cell, etc.) that recognizes the analyte and the transducer, which converts the (bio)chemical signal into a physical signal are core elements. The bioreceptor immobilization is a crucial step to develop biosensors with appropriate performances in terms of sensitivity, selectivity, stability, reproducibility and response time. Membranes represent a suitable category of 3D porous matrix components to host bioreceptors and assist biosensing. There are many advantages leading to use membrane as component of biosensor, for example i) the membrane can allow selective access (e.g. of the analyte only) to the receptor, ii) if the transducer is a separate chemical species, the membrane either used as support for the receptor immobilization or tool for bringing it close to the detector, can allow to integrate the sensing system, iii) the membrane can provide a large surface for bioreceptor immobilization.

In this work, the immobilization of enzymes on various membranes is reported. Two enzymes, phosphotriesterase and lipase, were selected as model bioreceptors and were immobilized on four porous membranes made of regenerated-cellulose, polyvinylidene-fluoride, nylon and polyethersulfone coated with polyethyleneimine. The bioreceptors immobilization was carried out covalently by exploiting reactive amino groups created on-purpose on the different membranes. Surface modification of regenerated-cellulose membrane was carried out by oxidizing the hydroxyl groups of the glucose units into aldehydes, which were subsequently derivatized with ethylenediamine [1]. Amino groups were introduced on the polyvinylidene-fluoride membrane by using 1,5-diamino-2-methylpentane, under basic conditions. Nylon membrane was activated by a hydrolytic treatment using hydrochloric acid, whereas the polyethersulfone membrane was used as received since the polyethyleneimine coating provided free amino groups. Afterward, all the amino-groups exposing membranes were reacted with glutaraldehyde which has been used as crosslinker for the enzyme amino groups. The obtained biofunctionalized membranes were characterized by FT-IR, SEM and water contact angle. Both activity and stability of immobilized enzymes were evaluated. Furthermore, their selectivity towards recalcitrant microcontaminant (such as pesticides) was investigated.

Acknowledgments

The authors acknowledge Project SmartMatter, M-ERA.NET–Joint Call 2019-Project co-financed within the “Azione 1.1.4.-POR Calabria FESR 2014/2020”.

Reference 1:

G. Vitola, R. Mazzei, T. Poerio, E. Porzio, G. Manco, I. Perrotta, F. Militano, L. Giorno, Biocatalytic membrane reactor development for organophosphates degradation, *J. Hazard. Mater.* 365 (2019) 789-795.

Membrane Gas Absorption (MGA) for acid gas treatment

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¹Chemical Process & Energy Resources Institute (CPERI), Centre for Research and Technology Hellas (CERTH)

Main topic: Membrane contactors and membrane distillation

Gas-liquid membrane contactors are devices where gas and liquid flow on the opposite sides of a porous membrane, which forms the interface for their contact. Using a hydrophobic membrane, the pores of the membrane are gas-filled and as long as the pressure of the liquid is kept slightly above that of the gas, an immobilized gas-liquid interface is formed at the pores' mouth in the liquid side. Gas-liquid membrane contactors offer several advantages over conventional contacting devices. The most prominent one is the very high specific surface area. Moreover, there are no weeping, foaming, emulsion or entrainment problems, since there is no fluid/fluid dispersion. Finally, their inherent modular design allows a membrane plant to operate over a wide range of capacities.

In this work the efficiency of a MGA process for acid gas treatment is studied, using commercial *3M Liqui-Cel* polypropylene membrane modules as contact devices. Post-combustion CO₂ capture in the maritime sector and biogas upgrade have been selected as two representative case studies. Different solvents (e.g. DEA, MDEA, NaOH, etc.), process operating parameters, (e.g. gas and liquid flow rates, gas composition, etc.) and modes of operation (once-through or liquid recycle) were assessed. The experimental results revealed the high potential of the proposed MGA process, allowing different extents of acid gases removal to be achieved by properly selecting the process parameters. Fig. 1 shows indicative saturation curves of combined CO₂ and H₂S removal from a representative biogas stream, using lean (0.25 M) DEA aqueous solution in recycle mode and demonstrates the ability to control CO₂ capture while achieving an initially deep H₂S removal.

Fig. 1: CO₂ and H₂S saturation curves in biogas upgrade through MGA using lean DEA solvent in recycle mode.

Acknowledgements

The work has received financial support through the projects:

- MemCCSea - Innovative membrane systems for CO₂ capture and storage at sea, funded through the ACT programme (Project No 294766).
- CERESIS - ContaminatEd land remediation through energy crops for soil improvement to liquid biofuel strategies, funded through HORIZON2020 (Project No 101006717).

Membrane integrity in lab-scale systems: we need better cells

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Main topic: Ageing of polymeric membranes

Introduction

Ideally, the active layer of dense membranes (e.g., RO) provides a perfect barrier between feed and permeate. It protects the permeate from chemical contaminants and pathogens in water treatment processes, and determines fundamental transport properties of the membrane. In reality, barrier imperfections are inevitably present. Since full-scale installations and bench-top lab systems differ dramatically both in membrane surface area and sealing methods, this raises the question whether lab systems can accurately predict full-scale system performance.

In lab systems, small membrane coupons are typically mounted inside cells sealed by O-rings, as opposed to glue seams used in spiral-wound modules. O-rings and/or cell edges pressed against coupons can adversely impact membrane integrity. This in turn reduces the predictive power of lab-scale selectivity tests. We therefore aim to evaluate membrane integrity breaches originating from bench-scale systems, and compare selectivity with spiral-wound systems.

Materials and Methods

Two flat sheet cell designs were used, a dead-end HP4750 cell (Sterlitech) and a crossflow cell. Filmtec SW30-HR and FT30 RO membrane coupons were used. Membranes were challenged by NaCl and 3 fluorophores (Rhodamine WT, Quinine, and Pyranine). Several remedial options to preserve membrane integrity were explored, including different O-ring materials, cell tightening torques, coating the membrane area in contact with the O-ring with lacquer before cell assembly, and using 3D-printed permeate spacers (Fig.1).

Results

We found unexpectedly low rejection of fluorophores (96-99%; LRV 1.4-2), which, interestingly was independent of fluorophore molecular weight. Breakthrough of fluorophores into the membrane was observed at the edge of the flow channel (Fig.1) for both cell designs, demonstrating that cell sealing causes breaches. Varying the closing torque upon cell assembly did not influence selectivity. The lacquer coating and 3D-printed permeate spacers somewhat improved membrane selectivity, but NaCl permeability remained 1.5 times higher compared to the manufacturer's specifications. Notably, NaCl rejection was still >99% in the latter case, given that the membranes used in this study are high-selectivity SWRO membranes.

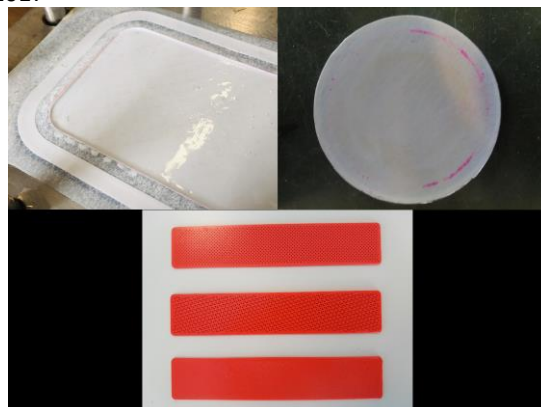
This study demonstrates that common bench-top cell designs damage membrane coupons, leading to reduced selectivity, and aims to raise awareness among scientists studying high selectivity membranes. Optimized cell and sealing designs are needed to alleviate this shortcoming.

Reference 1:

Microbial removal and integrity monitoring of RO and NF membranes, Kitis et al., American Water Works Association. Journal, 2003

Reference 2:

Realizing Reverse Osmosis Potential for Potable Reuse: Demonstrating Enhanced Pathogen Removal, Trussel et al., Bureau of Reclamation DWPR Report No. 196, 2017



Membrane preparation via non-solvent-induced phase separation based on recycled poly(ethylene terephthalate)

Breite, Daniel - Main Author; Krause, Maria - Co-Author; Knoch, Kurt - Co-Author; Went, Marco - Co-Author; Prager, Andrea - Co-Author; Kühnert, Mathias - Co-Author; Schulze, Agnes - Co-Author

Main topic: Microfiltration/Ultrafiltration

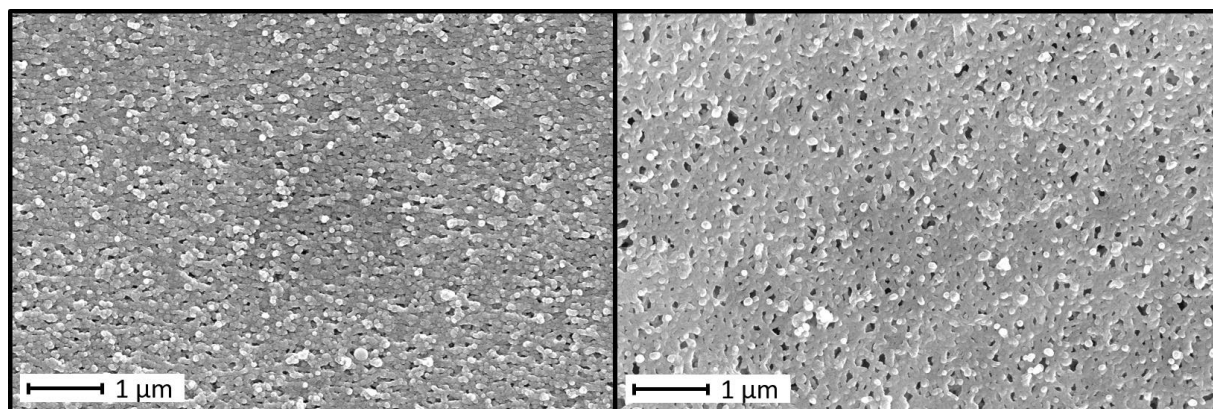
Membranes can be prepared from a variety of polymers, and membrane characteristics highly depend on the choice of polymer. Poly(ethylene terephthalate) (PET) is a promising material for membranes as it is highly inert and possess good mechanical and chemical stability, especially considering its stability against organic solvents. Furthermore, PET can be obtained from plastic waste, which has good availability and a lower price compared to other membrane polymers (e.g. PES, PVDF). Unfortunately, it is not possible to prepare PET membranes via non-solvent induced phase separation (NIPS) using process parameters and solvents conventionally used in membrane production. Alternative NIPS approaches described in literature uses harmful and expensive solvents like trifluoroacetic acid, dichloromethane, or hexafluoroisopropanol [1] to prepare PET membranes. However, it is questionable whether this can be applied to large-scale membrane production.

In this study, recycling PET (from beverage bottles) was used as source material to demonstrate the development of sustainable membrane filters. An alternative approach for the preparation of PET membranes via NIPS using unconventional process parameters is introduced. The new approach takes advantage of the fact that PET is soluble at higher temperature in less harmful organic solvents. These organic solvents can also be used in membrane preparation but are not capable to solve a sufficient amount of PET at room temperature to be applicable for membrane preparation via NIPS. However, when PET is solved at higher temperature, membrane casting solutions with polymer concentrations up to 20 wt.-% can be prepared. The casting solution needs to be processed in hot state and the coagulation can be carried out as usual in the NIPS process. Conventional pore forming agents like e.g. poly(ethylene glycol) or poly(vinylpyrrolidone) can be applied to support uniform pore formation.

Different PET membranes (figure 1) were prepared according to a design of experiments approach and a thorough characterization was carried out. The best membranes were characterized in detail and compared to a commercially available PVDF membrane, demonstrating a similar membrane performance. This new NIPS procedure enables the preparation of sustainable, cheap, and robust self-standing porous PET membrane filters.

Reference 1:

[1] B. A. Pulido, et al., ACS Appl. Polym. Mater., 2019, 1, 2379–2387



Membrane reactor to enhance a methanol production from CO₂ and H₂ in biomass to biodiesel route

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Main topic: Membrane reactors

Liquid biofuels have a significant role to play in meeting the climate change targets. Presently approximately 0.1 percent of all biomass is used to produce biodiesel, owing to an inefficient and complex production process. The EU CONVERGE project demonstrates a new innovative process, that will make biodiesel competitive with fossil fuels in terms of both effectiveness and price.

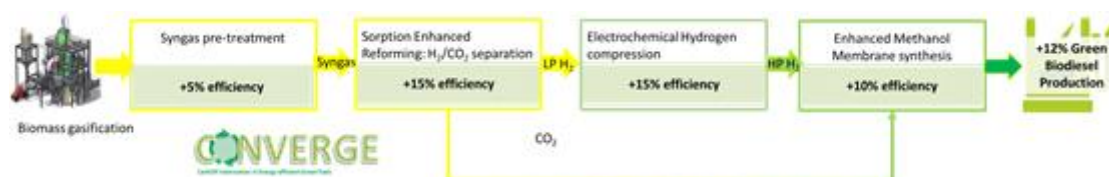


Figure 1: Simplified Converge process flowsheet

One of the technologies developed in this project, is an enhanced methanol membrane reactor. In-situ methanol and/or water separation greatly enhances per pass production of methanol, thereby reducing equipment size significantly. Additionally, selective removal of reaction products will decrease the energy demand in downstream processing. This project aims to increase the CO₂ and H₂ conversion per pass to 33% and to reduce CAPEX by 10%. The main challenge is to develop highly stable and selective membranes at high temperatures and pressures. Seven membranes (5 polymeric and 2 hybrid silica), were prepared on tubular ceramic support and tested in relevant separation conditions. Figure 2 summarizes the experimental results. Tested membranes showed good stability at these specific temperature range required for the methanol production. All measured permeances are in accordance with the values reported in the literature [1]. Polyimide (PI) membrane is selected, as the most promising membrane to integrate in the multi-tubular membrane reactor system.

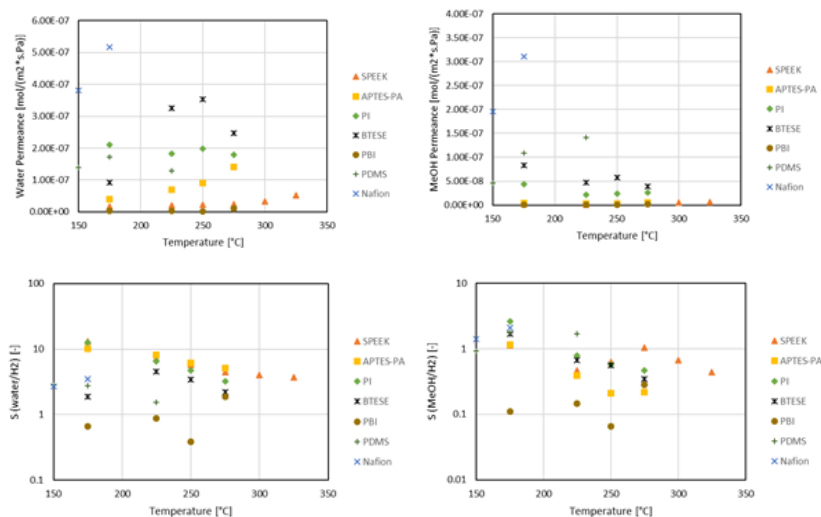


Figure 2: Measured water, methanol permeances and selectivities of MeOH, water over H₂ at $p_{\text{feed}}=35$ bar, $p_{\text{perm}}=1.5$ without sweep. Feed gas mixture: 60% H₂, 10% (50/50)methanol/steam, 20% CO₂, 1% CO, 19% N₂

This multi tubular system that consists of: packed bed reactor and, cooler and multi-tubular membrane reactor in series. The membrane reactor has 7 membrane tubes with total effective area of 0.25 m². An isothermal conditions are maintained by circulating of the thermal oil. This system will be further investigated to confirm the overall and the long-term performances.

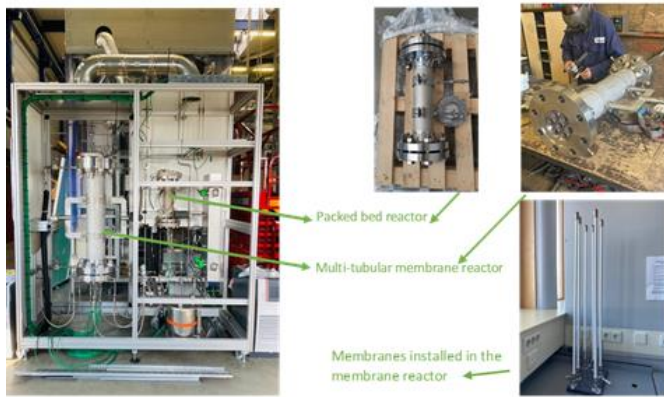


Figure 3: Constructed multi-tubular membrane system

Acknowledgment:

This work has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 818135

Reference 1:

J. Van Kampen et al, Chemical engineering Journal 374, 2019,1286-1303

Membrane selection for drinking water fractionation related to biological stability

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Main topic: Drinking water

Dissolved organic carbon (DOC) present in drinking water can negatively influence taste, color, odor and can result in bacterial regrowth. Chlorine use in many countries can also lead to disinfection by-products (DBP).

The importance and reactivity of different DOC fractions in drinking water in relation to microbial regrowth potential and DBP-formation is largely unknown. Separating and isolating these DOC fractions to study them individually is necessary to better understand their relation to (1) the biological stability of drinking water and (2) the individual treatment processes.

Drinking water is fractionated by a sequence of membrane steps (MF, NF and UF) to obtain three distinct DOC fractions enriched in either biopolymers (> 20 kDa), humics (500 – 1000 Da) or low molecular weight compounds (< 350 Da). An important factor is the isolated fraction purity, which is determined by the operational conditions of the membrane processes (concentration and diafiltration steps) and the membrane selection. As a first step, we have screened various commercial UF and NF membranes using LC-OCD as an evaluation tool.

Flat sheet crossflow testing showed that for NF, *TS40* (Microdyn Nadir) proved capable of separating both biopolymers and humics (retention >98%) from LMW compounds (retention <50%). A diafiltration step will have to be applied to wash out the remaining LMW compounds. *NF270* (DowDuPont) was less suited.

For UF, the three membranes that were tested: *XT*, *MT*, *ST* (Synder) proved capable of separating biopolymers (retention > 98%) from humics (retention 50%). Preference goes to the membrane with the largest pore size (*ST*, 10 kDa), since it allows for a higher flux and hence faster fractionation process.

Furthermore, a mass balance was constructed using the analytical results from liquid-chromatography organic carbon detection (LC-OCD) and ion chromatography (IC) to verify the validity of the experiment by analyzing the feed, retentate and permeate.

Using LC-OCD, one NF and one UF membrane have been selected capable of separating DOC fractions in drinking water.

Next, we will investigate spiral wound elements to determine concentration and diafiltration factors to increase the purity of the DOC fractions. Later, these fractions will be investigated for their contribution to biological stability and DBP-formation.

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Favere, J., Barbosa, R. G., Sleutels, T., Verstraete, W., De Gussemme, B., & Boon, N. (2021). Safeguarding the microbial water quality from source to tap. *npj Clean Water*, 4(1), 1-6.

Reference 2:

Yin, W., Li, X., Suwarno, S. R., Cornelissen, E. R., & Chong, T. H. (2019). Fouling behavior of isolated dissolved organic fractions from seawater in reverse osmosis (RO) desalination process. *Water research*, 159, 385-396.

Membrane separation of mixtures of fluorinated hydrofluorocarbons employed in refrigeration and air conditioning applications

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¹Chemical and Biomolecular Engineering Department, Universidad de Cantabria

Main topic: Gas separation

Background

The refrigerant gases employed in refrigeration and air-conditioning (RAC) are formed by mixtures of fluorinated hydrofluorocarbons and hydrofluoroolefins that most often exhibit near-azeotropic or azeotropic behavior. This feature hinders the separation and recycling of value-added refrigerants sought by the current legislative framework in Europe and international agreements such as the Kigali Amendment. Herein, we present the progress achieved in the application of membrane technology to the separation of hydrofluorocarbon refrigerants within the framework of project KET4F-Gas (www.ket4f-gas.eu).

Materials and Methods

The permeability of the most common fluorinated hydrocarbons employed as refrigerants (R32, R134a, R125, R1234yf, and R1234ze) has been determined for the first time through thick dense films of rubbery copolymer poly(ether-block-amide), and polymer membranes functionalized with ionic liquids (ILs) to enhance the separation properties of the pristine polymer. The best-performing membrane materials were also casted in the form of free IL-containing thin-film composite membranes (IL-TFCs) using a spray-coating technique. The membranes were tested in a wide range of pressures using a continuous permeation setup working in steady-state conditions. In addition, the mixed-gas separation performance was also determined for some common mixtures such as R410A, R454B, R513A.

Results

Among the different block copolymer tested, Pebax[®]1657 can be employed as membrane material for the separation of azeotropic refrigerant mixtures.¹ In addition, all composite polymer and ionic liquid membranes (CPILMs) outperformed the performance of the neat polymer membrane in terms of permeability; however, only the CPILMs based on small molar volume ILs were able to improve the separation selectivity of the neat Pebax[®]1657 films. The CPILMs prepared with 40 wt % IL content proved stable up to 12 bar feed pressure and during long-term runs (25 days).² Moreover, IL-TFCs were successfully prepared with selective layer thickness below 10 μm while keeping the permselectivity of the dense thick membranes.

Conclusions

Our recent work shows that membrane technology can provide an efficient solution to the separation of azeotropic and close boiling mixtures of fluorinated hydrocarbons. This will enable the recovery of value-added refrigerants and their reuse in more environmentally-friendly refrigerant blends, thus increasing the sustainability of the RAC market. Support of projects KET4F-Gas-SOE2/P1/P0823 (Interreg-SUDOE) and PID2019-105827RB-I00 (AEI-Spain) is acknowledged.

Reference 1:

Pardo, F.; Zarca, G.; Urriaga, A., Separation of Refrigerant Gas Mixtures Containing R32, R134a, and R1234yf through Poly(ether-block-amide) Membranes. *ACS Sustain. Chem. Eng.* 2020, 8, (6), 2548-2556. DOI: 10.1021/acssuschemeng.9b07195

Reference 2:

Pardo, F.; Zarca, G.; Urriaga, A., Effect of feed pressure and long-term separation performance of Pebax-ionic liquid membranes for the recovery of difluoromethane (R32) from refrigerant mixture R410A. *J. Membr. Sci.* 2021, 618, 118744. DOI: 10.1016/j.memsci.2020.118744

Membrane technologies for polyphenols recovery from winery and olive mill wastes

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Main topic: Bio-separations and bio-refinery

Winery and olive mill industries, two major industries of southern Europe, generate large amounts of wastes, causing important environmental problems, such as soil and water contamination. Olive oil production generates about 10 million tons of wastes per year, which includes olive pomace and olive mill wastewater. Regarding wine production, almost 20 million tons of winery by-products are discarded each year, such as wine lees, grape pomace and steams [1,2]. On the other hand, only a small part of olive and grape phytochemicals is extracted into the final products. In particular, these wastes are an abundant and inexpensive source of polyphenols compounds, with high nutraceutical and antioxidant power, and potential applications in the food, cosmetic, pharmaceutical industries. In this work, membrane separation processes (microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO)) were evaluated for the recovery of polyphenols from aqueous extracts of lees filters and olive pomace. Membrane processes were tested separately in a batch system, and by an integration in an open sequential design. For the experiments, the feed flow rate was varied from 1 to 10 mL min⁻¹ (one by one), and a permeate sample was taken after each increase in feed flow rate, in order to measure the polyphenols concentration. The separation and concentration efficiency, was evaluated in terms of total polyphenol content, and by polyphenols families (hydroxybenzoic acids, hydroxycinnamic acids, and flavonoids), using high performance liquid chromatography (HPLC-UV). Trans-membrane flux was dependent of the feed flow rate for MF and UF membranes, and independent of the feed flow rate for NF and RO membranes. MF membranes removed impurities from the extracts; whereas UF, NF and RO membranes were able to separate and concentrate polyphenols streams. The most selective membrane train for polyphenols separation and concentration for lees filters extracts was: 30 kDa (UF), DURACID (NF) and BW30LE (RO) and for olive pomace extracts was almost the same but changing the type of NF membrane (NF270). Membranes sequential designs for lees filters and olive pomace extracts, were able to obtain polyphenol rich streams (19 and 82 mg L⁻¹, respectively), and high-quality water streams for reuse purposes.

Reference 1:

De Bruno, A.; Romeo, R.; Fedele, F.L.; Sicari, A.; Piscopo, A.; Poiana, M. Antioxidant activity shown by olive pomace extracts. *J. Environ. Sci. Heal. - Part B Pestic. Food Contam. Agric. Wastes* 2018, 53, 526–533, doi:10.1080/03601234.2018.1462928.

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Melo, P.S.; Massarioli, A.P.; Denny, C.; Dos Santos, L.F.; Franchin, M.; Pereira, G.E.; Vieira, T.M.F.D.S.; Rosalen, P.L.; De Alencar, S.M. Winery by-products: Extraction optimization, phenolic composition and cytotoxic evaluation to act as a new source of scavenging of reactive oxygen species. *Food Chem.* 2015, 181, 160–169, doi:10.1016/j.foodchem.2015.02.087.

Metal ions-doped ultrahigh flux composite graphene oxide/carbon nanotubes (GO-SWCNT) membranes for targeted gas separations

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Main topic: 1D- and 2D-materials for membranes

We report on the preparation, modification and gas separation performance of high flux composite GO-SWCNT membranes. Thin selective GO layers[1] were deposited on the top of ultrapermeable SWCNT supports [2]. Combining these two materials led to similar or higher H₂/CO₂ selectivity compared to previously reported self-standing GO membranes [1] but with substantially higher fluxes and dramatically better mechanical and time-stability. Fabricated GO-SWCNT membranes exhibited remarkable gas separation performance towards H₂/CO₂, H₂/CH₄, H₂/N₂ and N₂/CH₄ gas pairs that far exceed the corresponding 2008 Robeson upper bound, especially after the doping by selected metal ions. Such doping caused specific structure/properties modification of GO-SWCNT and improved substantially gas permeability and selectivity. Presented composite GO-SWCNT membranes demonstrate a promising route towards large-scale fabrication of high flux hydrogen-selective gas membranes intended for H₂/CO₂, H₂/CH₄ or H₂/higher alkanes separations.

This work was supported by the Czech Science Foundation (grant No. 19-14547S) and by specific university research (MŠMT No. 20-SVV/2020 and 2021).

Reference 1:

D. Bouša et al., Chemistry-A European Journal, 23 (47) 11416-11422, 2017.

Reference 2:

M. Boháčová et al., Applied Materials Today 15, 335-342, 2019.

Metal removal from hydrothermally treated secondary sewage sludge by ultrafiltration with polymeric membranes

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Main topic: Wastewater treatment

The content of hazardous components in secondary sewage sludge (SS), such as pathogens and metals, greatly challenge its reuse, essential due to its steadily increasing generation. Hydrothermal solubilization of SS deals with the pathogen issue, as it sterilizes the SS, but it does not remove metals [1]. Ultrafiltration can be an effective treatment to this end, but its performance regarding the removal of metals from a complex matrix like hydrothermally treated SS has not been studied yet. Furthermore, this efficiency can be affected by the membrane material, as its composition affects the fouling nature [2].

Therefore, the aim of this work was to study the behaviour of different polymeric membranes to remove the main metals present in solubilised SS.

Hydrothermally treated SS was ultrafiltered with flat-sheet polyethersulfone (PES), permanently hydrophilic polyethersulfone (PESH), polyvinylidene fluoride (PVDF) and polyacrylonitrile (PAN) membranes of 50 kDa of molecular weight cut-off (MWCO). Metal content on ultrafiltration retentates and permeates was measured by inductively coupled plasma mass spectrometry (ICP-MS) to calculate metal retentions. Besides, a semi-quantitative elemental analysis by scanning electron microscopy (SEM) was performed on the water-rinsed fouled membranes to assess membrane-metals interactions.

Metals were mainly found forming part of mineral particles on the surface of the membranes, with minimum adsorption within the membrane.

A semi-quantitative ICP-MS analysis showed that the main metals present in solubilised SS were Fe, Zn, Mn, Al, Ni, Cu, Cr and Pb, in that order.

PES membrane showed higher retentions, except for Pb, where the highest ones were achieved with the PAN membrane (Fig. 1). Excellent retentions of up to 96% were obtained, and even the least retained metal, Mn, showed acceptable mean retentions (41% with PES membrane).

The high metal retentions with membranes of such MWCO can be explained by the complexation of these metals with proteins or humic acids. Further works in this topic will include the study of the interaction between each metal and each of the main macromolecular components present in SS (proteins, humic acids and carbohydrates), alone or combined.

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M. Park, N. Kim, S. Lee, S. Yeon, J.H. Seo, D. Park, A study of solubilization of sewage sludge by hydrothermal treatment, *J. Environ. Manage.* 250 (2019) 109490. doi:10.1016/J.JENVMAN.2019.109490.

Reference 2:

P. Pal, Introduction to membrane materials, processes, and modules, *Membr. Technol. Environ. Pollut. Control.* (2020) 3–69. doi:10.1016/B978-0-12-819455-3.00001-7.

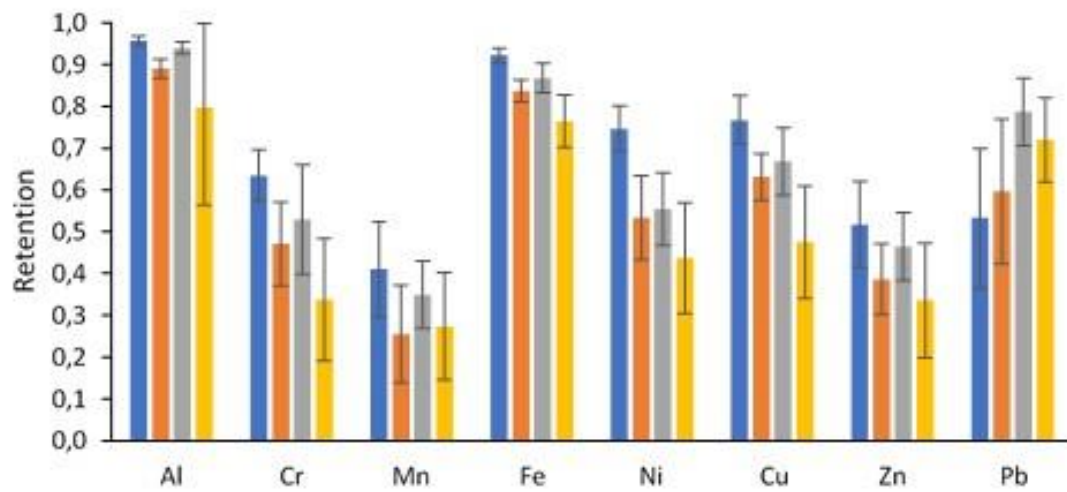


Figure 1. Mean metal retentions with PES (■), PESH (■), PAN (■) and PVDF (■) membranes.

Methacrylate hydrogel-MOF as a separating layer on functional polymeric membrane to efficiently remove nitrate from groundwater of Israel coastal aquifers

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¹Ben-Gurion University of the Negev, Israel

Main topic: Novel membrane materials

The contamination of water bodies by nitrates is a serious global problem. The main reasons include the excessive use of fertilizers in agriculture. Nitrate poses a significant health risk, causing blue-bay syndrome and mental retardation in children and forming a carcinogenic product in adults. Beyond a specific limit, it is harmful to aquatic lives. Thus, nitrate removal has attracted the attention of the scientific community [1]. Among the various methods available, micellar-enhanced ultrafiltration is a promising treatment method because it has several advantages: high removal efficiency, low energy requirement, and simple operation. Further, the membrane should be designed to exhibit an excellent fouling mitigation property to ensure its longevity. In this study, the surface of a polymeric membrane was modified with a layer of in-situ grown ZIF-L nanoflakes, which were then stabilized by a methacrylate hydrogel. The prepared HyZifLG membrane exhibited a hydrophilic surface with lower roughness than the pristine membrane. The efficacy of the membrane towards the nitrate removal was tested using a feed solution that simulated the composition of heavily nitrate-polluted groundwater of the coastal aquifers in Israel. The results showed that the HyZifLG membrane removed $94.1 \pm 1.7\%$ nitrate from the contaminated water. Further, the membrane was tested with actual samples of groundwater collected from the coastal aquifers of Israel. Interestingly, the removal efficiency varied between 85–57%, depending on the samples' composition, making the nitrate level well below the maximum permissible limit in the permeate. The membrane's performance remained consistent for multiple filtration cycles, with permeate flux ranging between $32\text{--}60 \text{ L}\cdot\text{m}^2\cdot\text{h}^{-1}$. The membrane also completely removed the surfactant from the permeate. The flux recovery ratio was $>96\%$ for all the groundwater samples. These results indicated that the membrane prepared in this study holds a promise for the efficient removal of nitrate from the water bodies.

Reference 1:

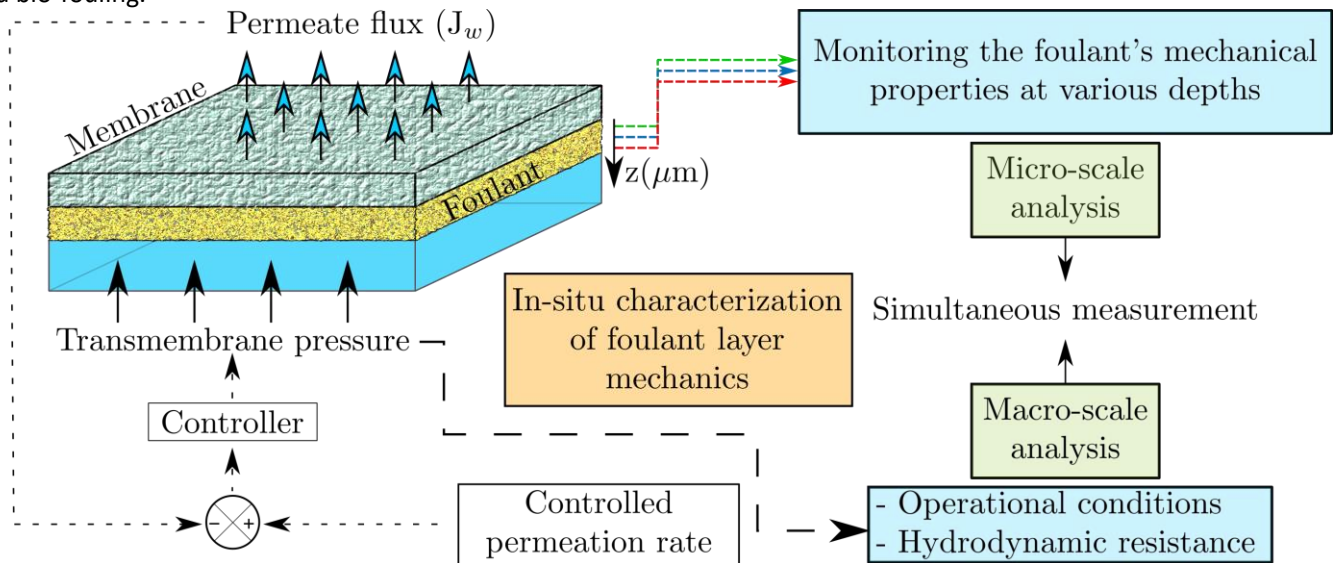
Epsztein et al. Selective nitrate removal from groundwater using a hybrid nanofiltration–reverse osmosis filtration scheme. *Chemical Engineering Journal* 279 (2015) 372-378.

Micro to macro: Connecting foulant structure and mechanics with hydraulic resistance

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Main topic: Membrane fouling and cleaning

Fouling remains a major operational concern in membrane-based water purification and desalination. Understanding how the pressure-driven permeate flux affects the mechanical and hydraulic properties of a foulant layer can provide important insight leading, for example, to more efficient mechanical cleaning methods. Here, we present a new approach that enables in-situ analysis of a foulant layer at the membrane surface. Specifically, we aim to connect the foulant's mechanical properties on the microscale with their macroscopic effect - the observed hydrodynamic resistance - all under pressure and with the ability to control and vary the permeate flux. A video microscopy-based particle-tracking technique is employed to visualize a foulant layer located on a membrane surface, within a custom-made filtration cell, enabling high-resolution imaging with a confocal microscope. Specifically, the motion of fluorescent tracers embedded in the foulant layer is monitored. Through the analysis of particle trajectory statistics, the mechanical properties of the foulant layer are characterized in terms of the frequency-dependent elastic and viscous components. The method was employed to study an alginate layer deposited on a Nanofiltration membrane, under a step-wise increase of the permeate flux. In each experiment, the foulant layer was visualized at different distances from the membrane surface. Our results reveal a positive correlation between the foulant's complex viscosity and its hydrodynamic resistance, in response to changes in the induced permeate flux, indicative of possible structural changes due to compaction. Further, the foulant layer exhibited depth-heterogeneity, with clear variations observed at different distances from the membrane surface, becoming more 'stiff' in adjacent to the membrane surface. The presented approach opens new possibilities for studying fouling, particularly soft, gel-like deposits typical of organic and bio-fouling.



Micro-CT analysis of swelling and shrinkage in a heterogeneous cation-exchange membrane during ion exchange

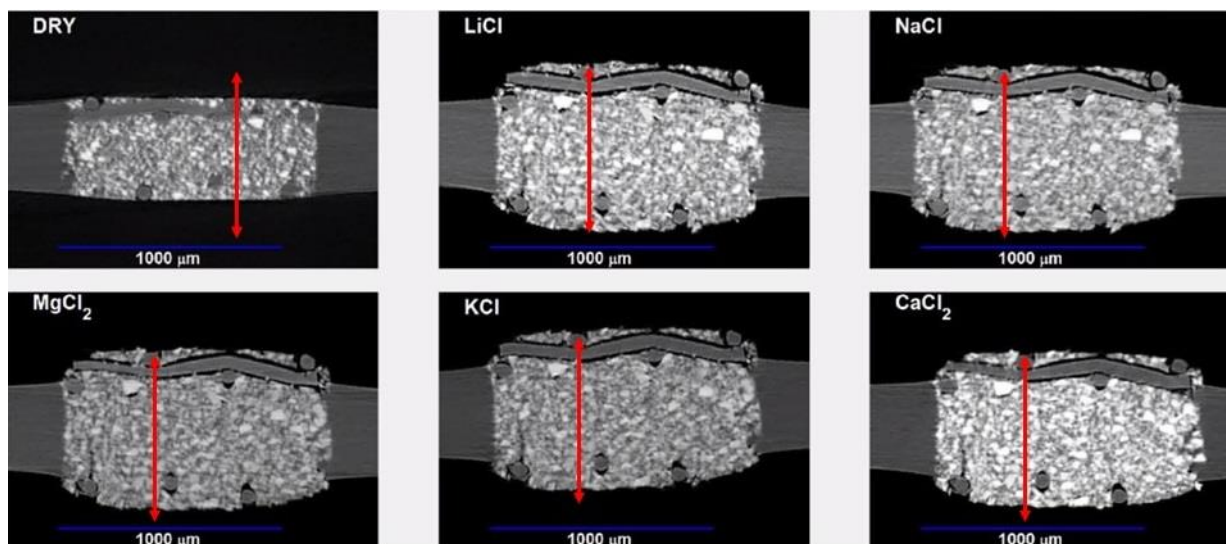
Svoboda, Miloš - Main Author¹; Beneš, Jan - Co-Author¹; Vobecká, Lucie - Co-Author²; Slouka, Zdenek - Co-Author¹
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Main topic: Electro-membrane processes

Ion selectivity of ion exchange membranes originates from the electric field generated by membrane fixed charges and the internal membrane structure, providing efficient interaction between the fixed charged and mobile ions. The electric forces determine what type of ions can pass through such membranes. However, the electric forces are also responsible for membrane swelling and deswelling when immersed in water solutions of various electrolytes. The degree of swelling is influenced by many factors such as ionic strength, pH, type of counterions, and many others. To understand the effect type of counterion on a heterogeneous cation-exchange membrane swelling and shrinkage, we employed micro-computed tomography to reconstruct a membrane's spatial composition sequentially soaked in solutions of LiCl, NaCl, KCl, MgCl₂, CaCl₂. Our analysis showed the ion exchange is accompanied by profound changes in the spatial membrane composition. The results can be summarized in the following points: (i) the membrane reaches the largest volume in LiCl solution and decreases in the following order of solutions: NaCl, MgCl₂, KCl, and CaCl₂, (ii) the swelling and shrinkage is reflected on the membrane surface at which the resin occupies the largest surface area for CaCl₂ solution, (iii) the swelling and shrinkage is history-dependent and to a large degree irreversible. Our study indicates that the change in the type of the counterions in the membranes may lead to the creation of large pores displaying poor ion selectivity. This effect may, in turn, result in the worsened performance of the membrane in processes such as electrodialysis or electrodeionization.

Reference 1:

Swelling induced structural changes of a heterogeneous cation-exchange membrane analyzed by micro-computed tomography M Svoboda, J Beneš, L Vobecká, Z Slouka, Journal of membrane science 525, 195-201



Micropollutant removal from water using mixed-matrix membrane adsorbers

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Main topic: Wastewater treatment

The increasing contamination of water by various chemical substances is a serious challenge of the world. These chemicals are a heterogeneous group of substances originating from different industrial processes, agriculture, cosmetics or pharmaceuticals. Thereby these molecules are released into the sewage system where they occur in trace concentrations; thus they are called micropollutants. However, conventional sewage treatment plants can't completely remove these micropollutants, hence they start to accumulate in surface, ground and even in drinking water as well as in the environment. Here, their long-term effects cannot be estimated, but their potential toxicological impact on the biological environment is known. Therefore the separation of such micropollutants is of crucial importance and new separation processes beyond conventional treatment plants are required.

The incorporation of functional groups into membranes combines filtration and adsorption capabilities that enable the separation of complex material streams. Such mixed-matrix membrane adsorbers are promising candidates for the removal of micropollutants and furthermore they enable the simple adaption to various contaminants.

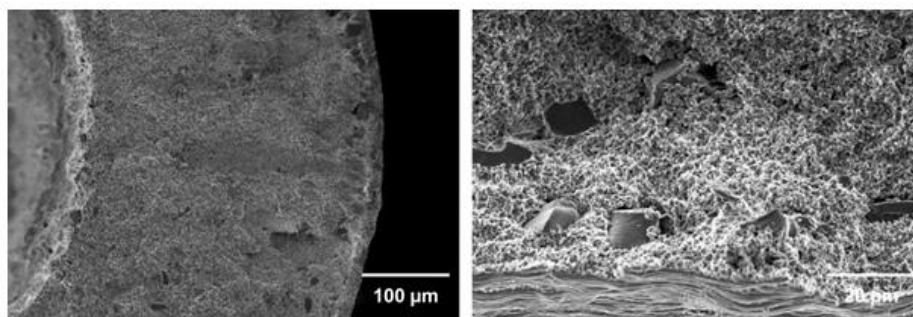
For this purpose, mixed-matrix membrane adsorbers containing different functional groups were developed for water purification.

Porous poly(vinylidene fluoride) (PVDF) hollow fiber membranes were manufactured by the non-solvent-induced phase separation (NIPS). Different polystyrene particles with several functional groups were directly incorporated into the membrane structure during NIPS process. The adsorption performance of the membrane adsorbers to simultaneously separate micropollutants like diclofenac, carbamazepine, metoprolol and sulfamethoxazole was determined via dynamic adsorption experiments.

Figure 1 shows the cross-section of a mixed-matrix membrane adsorber. The porous, sponge-like structure is favored to homogeneously distribute the particles over the cross-sectional area, which ensures the contact between adsorber particles and micropollutants. For membrane adsorbers with anion exchange functionality adsorption capacities up to 13 g m⁻² of diclofenac were achieved while also the micropollutants sulfamethoxazole or carbamazepine were separated simultaneously. Additionally diclofenac in a trace concentration of 2 µg L⁻¹ was separated successfully from tap water using a membrane adsorber with anion exchange functionality, enabling the treatment of 10 m³ water at a removal of > 99 % [1]. Furthermore, the membrane adsorbers can be regenerated, therefore used several times, without loss in adsorption capacity.

Reference 1:

[1] I. Gehrke et al., Neue Materialien und Verfahren zur Spurenstoffelimination. KA Korrespondenz Abwasser, Abfall 2021 68 (4), 273.



Microscopic insight into the separation properties of organic solvents through the P84 Polyimide membrane

Ouinten, Mohammed Lamine - Co-Author; Szymczyk, Anthony - Co-Author; Ghoufi, Aziz - Co-Author

Main topic: Organic solvent nanofiltration

Separation is among the most energy-intensive processes in the chemical and pharmaceutical industry. It costs between 40 and 70% of energy consumption [1]. Membrane separation seems to be among the most promising solutions to reduce this energy cost. However, their use for organic fluids is relatively less studied compared to the purification of water and gas separation because of the difficulty of developing membrane materials that are both stable and scalable in organic media [2]. Organic Solvent Nanofiltration (OSN) is a separation process that started in the 2000s with the development of polymer membranes that had improved resistance to organic solvents. This technique has recently shown great potential, particularly in the petrochemical and pharmaceutical industries.

Among several OSN membranes the polyimide P84 membrane is a nanoporous material with very interesting properties in terms of separation. To optimize thus the transport and the separation properties it is then necessary to understand them at the nanoscale.

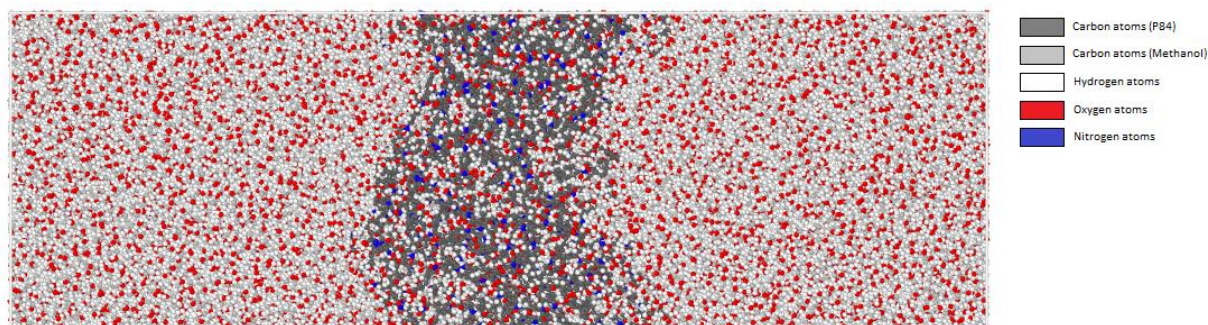
To do so molecular dynamics simulations seem particularly well suited to investigate solvent-membrane interactions and to elucidate the separation mechanisms involved in OSN. In this work, equilibrium molecular dynamics and pressure driven simulations have been carried out to investigate Methanol, Ethanol, Acetone and Toluene liquids and their mixtures through the P84, paying special attention structural and dynamic properties of the confined fluids.

Reference 1:

P. Marchetti, M.F. Jimenez Solomon, G. Szekely, A. Livingston, Chem. Rev. 114 (2014) 10735.

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R.P. Lively, D.S Sholl, Nat. Mater. 16 (2017) 276.



Mitigating water crossover by crosslinked coating of cation-exchange membranes for brine concentration

Roth, Hannah - Main Author^{1,2}; Rommerskirchen, Alexandra - Co-Author^{1,2}; Linnartz, Christian - Co-Author^{1,2}; Roghmans, Florian - Co-Author¹; Wessling, Matthias - Co-Author^{1,2}

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Main topic: Electro-membrane processes

Undesired water crossover through ion-exchange membranes limits electrically driven desalination processes significantly. The effect of mitigating the water crossover is two-fold: The desalination degree increases due to reduced water removal, and the dilution of the brine is reduced due preventing unwanted crossover of water molecules. Hence, water crossover limits the desalination and concentration efficiency of the processes, while the energy demand to achieve a certain level of desalination or concentration increases. This effect is especially pronounced when treating high salinity solutions [1], which goes hand in hand with the crossover of many ions through the ion-exchange membranes.

We present a crosslinked coating for cation-exchange membranes, reducing the water crossover in electrically driven desalination and concentration processes applying ion-exchange membranes. Inspired by thin film composite nanofiltration membranes, we apply a polyamide layer onto a cation-exchange membrane via the interfacial polymerization of piperazine with trimesoyl chloride. The operation of a flow-electrode capacitive deionization (FCDI) process applied for the desalination and concentration of saline brines at feed concentrations of 60 and 120 g/L NaCl showcases the efficacy of the coated membrane. With the application of just a single coated cation-exchange membrane (CEM) as a central membrane in the single-module FCDI cell, the water crossover was reduced by up to 54% [2].

We conclude that the resulting thin crosslinked layer mitigates water crossover successfully. The strongly crosslinked membrane surface retains parts of the ions hydration shells. Additionally, the drag of water molecules in connection with the ion transfer and purely osmotic water passage might be reduced as well. By choosing a layer chemistry related to nanofiltration, the additional resistance for ion transport is kept low.

The presented coated cation-exchange membrane improves the performance of desalination and concentration processes significantly. By further tuning the coating chemistry's, we envision to decrease the water crossover further in the future. Additionally, the development of a comparable coating for an anion-exchange membrane is of high interest to also study its impact on the water crossover.

Reference 1:

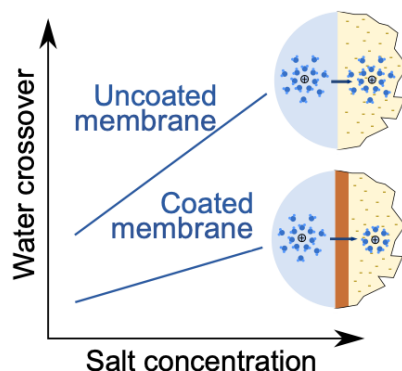
Rommerskirchen, A., Linnartz, C. J., Egidi, F., Kendir, S., & Wessling, M. (2020). Flow-electrode capacitive deionization enables continuous and energy-efficient brine concentration. *Desalination*, 490, 114453.

<https://doi.org/10.1016/j.desal.2020.114453>

Reference 2:

Rommerskirchen, A., Roth, H., Linnartz, C. J., Egidi, F., Knepeck, C., Roghmans, F., & Wessling, M. (2021). Mitigating Water Crossover by Crosslinked Coating of Cation-Exchange Membranes for Brine Concentration. *Advanced Materials Technologies*, 2100202.

<https://doi.org/10.1002/admt.202100202>



Mixed matrix adsorbers for regenerative hemodialysis

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Main topic: Novel membrane materials

In 2018, more than 80.000 individuals in Europe started renal replacement therapy for end-stage renal disease (ESRD), also known as chronic kidney failure, almost the 84% of them were receiving blood dialysis [1]. Hemodialysis is in charge of replacing kidney functionality, that is comprehensive of toxins clearance from blood circulation, restorage of electrolytic balance and excess fluid removal. Hemodialysis is an extracorporeal treatment based on the exchange of a broad class of toxins and ions through a semipermeable membrane with a buffered solution, known as dialysate.

The process suffers some technological issues such as the ultrapure water consumption and the efficiency in uremic toxins (UT) removal. These limitations are crucial in sustainability, accessibility, delivery and safety of the therapeutic treatment that requires more than one hundred litres of water per cycle. Nonetheless, patients usually need three or four cycles per week requiring hospitalization for some hours.

The encapsulation or the dispersion of micro/nanoparticles of adsorbing material, known as fillers, in a polymeric membrane matrix allows the production of the so called mixed matrix membranes (MMMs). This typology of membranes clear toxins through both a diffusive and adsorptive strategy. [2]

These adsorbing membranes own a potential application in the development of a more efficient dialyzer, in terms of water consumption and clearance efficiency, or in the implementation of a wearable artificial kidney or in the design of a regeneration unit of spent dialysate.

This work focus on the technological issues and the requirements for the development of MMMs or other composite systems for hemodialysis applications, with special focus on dialysate regeneration. Activated carbon and mesoporous silica are traditionally the most employed materials for adsorption of UT. A new class of material such as zeolites, metal organic frameworks or other highly porous structures gained interest as potential absorbers. Different materials have been proposed and various manufacturing and casting techniques were experimented to obtain improved adsorbing systems.

Innovative candidates, relative encapsulation methods, the impact on performances and technological employment are reviewed and critically discussed to address promising strategies for MMMs. Nonetheless, attention is paid to dynamic adsorption performance of this novel materials.

Reference 1:

[1] A. Kramer, R. Boenink, V. S. Stel, C. Santiuste de Pablos, F. Tomović, E. Golan, J. Kerschbaum, N. Seyahi, K. Ioanou, P. Beltrán, O. Zurriaga, Á. Magaz, M. F. Slon Roblero, "The ERA-EDTA Registry Annual Report 2018: a summary," *Clinical Kidney Journal*, vol. 14, pp. 107-123, 12 2020.

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Modeling of layer-by-layer coated capillaries used in nanofiltration process

Evdochenko, Elizaveta - Main Author¹; Kalde, Anna - Co-Author^{1,2}; Kamp, Johannes - Co-Author¹; Wessling, Matthias - Co-Author^{1,2}

¹RWTH Aachen University, AVT.CVT - Aachener Verfahrenstechnik, Chemical Process Engineering, ²DWI - Leibniz Institute for Interactive Materials

Main topic: Transport models

Polyelectrolyte (PE) multilayer membranes are widely used in water purification processes. One promising technique to fabricate PE membranes is the layer-by-layer (LbL) method. In this method, polycation and polyanion layers are stepwise deposited onto a porous support structure. The resulting complex of charged PEs shows high salt rejections. However, during the fabrication process, the exact location of the selective PE layer formation is still unclear. It is hypothesized to form on top or inside of the support pore structure. Recently, it was observed experimentally that the same set of PEs on different support membranes showed different retention data. Therefore, the porous support has an important influence on membrane performance. So far, in transport models presented in literature, this influence has not been considered.

In our previous work, we focused on modeling one-dimensional ion transport through a selective layer formed on top of the support membrane [1,2]. In this work, we present a new two-dimensional model able to account for the selective layer formed on top as well as on walls of the support capillary.

COMSOL Multiphysics software was utilized to solve a set of two-dimensional nonlinear equations: the Extended Nernst-Planck-Poisson (ENPP) and Navier-Stokes (NS). The model allows for the resolution of the ionic movement resulting from sharp gradients of the electric potential on a nanometer scale. We also account for the deviation from electroneutrality in the double layers, which adds high complexity to the problem. The model can differentiate between ionic rejections of the top- and wall-coatings.

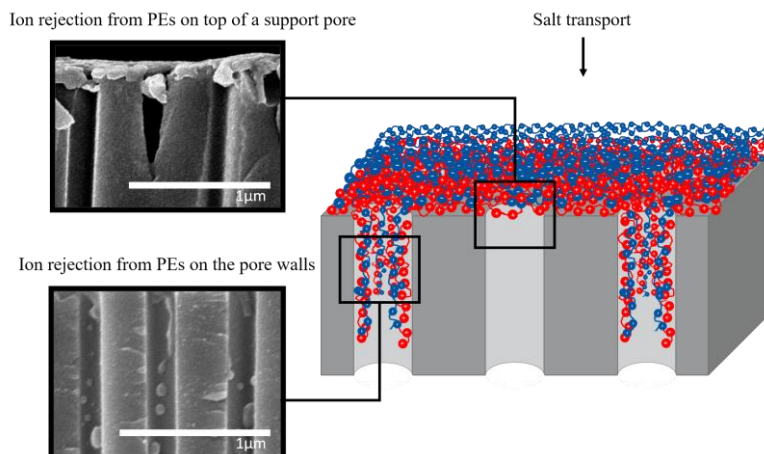
All in all, we reveal the influence of the pore coating and address the challenge of enhancing rejection rates. The results indicate that high salt rejection can result from PE coating on the support pore walls alone. With the use of our model, we can further explain the influence of the support pore radius, PE charge density, operating pressure. We show that the support material does have an impact on the membrane properties. The modeling results are in good agreement with experimental data reported in the literature.

Reference 1:

E. Evdochenko, J. Kamp, R. Femmer, Y. Xu, V. V. Nikonenko, M. Wessling, Unraveling the effect of charge distribution in a polyelectrolyte multilayer nanofiltration membrane on its ion transport properties, *J. Membr. Sci.* 611 (October 2020). URL <https://doi.org/10.1016/j.memsci.2020.118045>

Reference 2:

E. Evdochenko, J. Kamp, R. Dunkel, V.V. Nikonenko, M. Wessling, Charge distribution in polyelectrolyte multilayer nanofiltration membranes affects ion separation and scaling propensity, *J. Membr. Sci.* (July 2021). URL <https://doi.org/10.1016/j.memsci.2021.119533>



Modelling of an innovative membrane crystallizer for the production of magnesium hydroxide from waste brine

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Main topic: Membrane reactors

Background

The discharge of industrial waste brines into natural water bodies has gained large interest in recent years, both for its possible environmental impact, but also for the high potential of raw materials recovery contained in brines, pushing towards a circular economy approach. Among such raw materials, magnesium is often abundant and has been defined as a Critical Raw Material by EU [1]. Within this framework, a Crystallizer with Ion Exchange Membrane (CriEM) has been proposed as an innovative process to recover magnesium from waste brines exploiting low-cost alkaline reactants. In the present work, a novel mathematical model of the CriEM process is proposed providing a useful tool for its design in different working conditions (Batch and feed & bleed configurations).

Materials and Methods

The CriEM (Figure 1) consists of an Anion Exchange Membrane interposed between a brine and an alkaline compartment, which allows the selective passage of OH⁻ into the brine compartment, promoting the precipitation of Mg(OH)₂.

Figure 1. The CriEM's pilot set-up in a feed and bleed configuration.

The basics of the modelling tool developed lay on the Donnan Dialysis theory. One dimensional (1D) differential mass balance equations were solved adopting a numerical method. An original algorithm was also developed to describe the time-dependent phenomena occurring in the CriEM and in two feed tanks. Batch and feed & bleed configurations were investigated considering: (i) the variation of the alkaline and brine concentration in their tanks over time and (ii) the spatial 1D variation of the main parameters inside the CriEM. Original experimental data and literature information [2] were used for model validation.

Results and Conclusions

Good agreements between model predictions and experimental data were found for both configurations, proving the reliability of the proposed model for the design of the CriEM. Magnesium conversion was well predicted exhibiting discrepancies < 5%. Moreover, ions concentrations in the brine channel, hydroxyl transmembrane fluxes and pH trends were well predicted (max discrepancies of 4%, 17% and 5%, respectively).

Acknowledgements

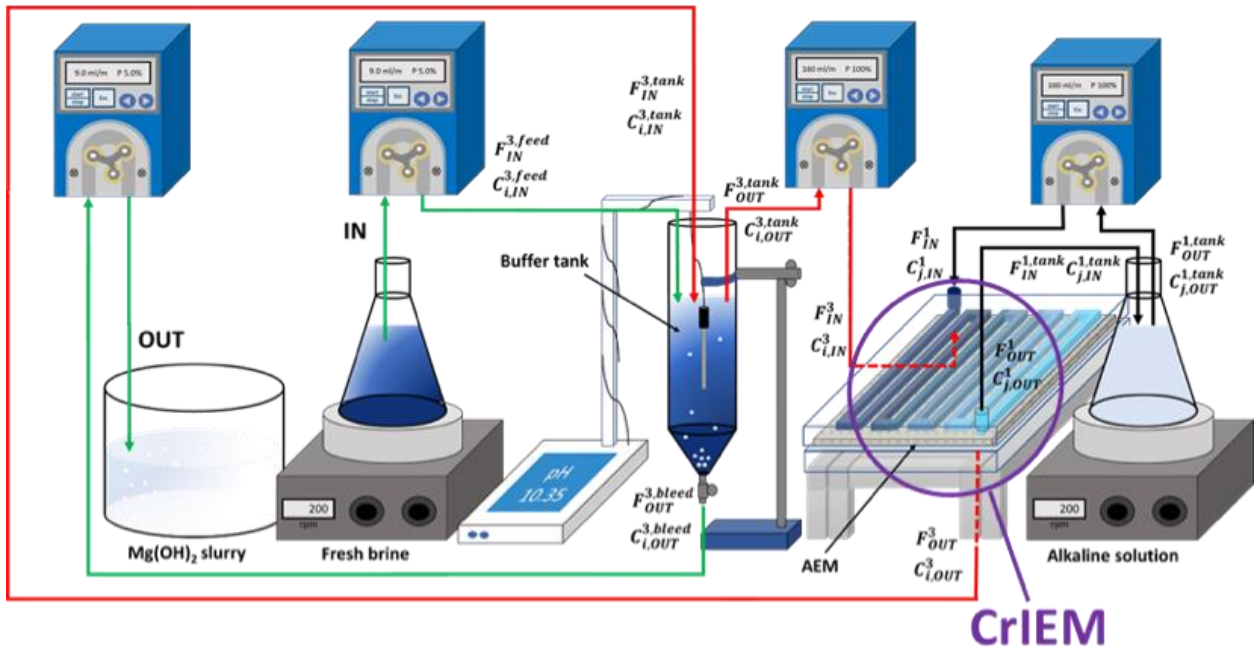
This work was funded by the ZERO BRINE project (ZERO BRINE – Industrial Desalination – Resource Recovery – Circular Economy) - Horizon 2020 programme, Project Number: 730390: www.zerobrines.eu.

Reference 1:

A. Cipollina, M. Bevacqua, P. Dolcimascolo, A. Tamburini, A. Brucato, H. Glade, L. Buether, G. Micale, Reactive crystallisation process for magnesium recovery from concentrated brines, *Desalin. Water Treat.* 55 (2015) 2377–2388. doi:10.1080/19443994.2014.947771.

Reference 2:

D. La Corte, F. Vassallo, A. Cipollina, M. Turek, A. Tamburini, G. Micale, A novel ionic exchange membrane crystallizer to recover magnesium hydroxide from seawater and industrial brines, *Membranes (Basel)*. 10 (2020) 1–14. doi:10.3390/membranes10110303.



Modelling of single-phase fluid flow in membrane boundary layer at top porous membrane

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Main topic: Fluid dynamics

Porous membranes in water treatment application are characterized by the ability for physical separation between solid and liquid components. Considering how complex is to predict numerically such behavior due to interaction between the free and porous flow regime a combination of Darcy and Navier-Stokes (Eq. 1) is proposed to predict a two-dimensional model under laminar flow condition in a rectangular channel with a permeable region in the geometry center. The modelling efforts are devoted to membrane boundary layer for investigating the single-phase fluid flow during Dead-End filtration. The method applied starts with the modifying of the original Navier-Stokes for formulation which end up in reducing the classical form in the fluid region while a resistance term S_m is included.

While S_m represents the membrane permeable region modelled by Darcy law, the velocity field is calculated considering an average fluid velocity on sample volumes of the porous medium sufficiently large with respect to the pore size. For this, boundary conditions have been set for a 2D problem (Fig. 1), but with the possibility of extension to 3D or other membrane application.

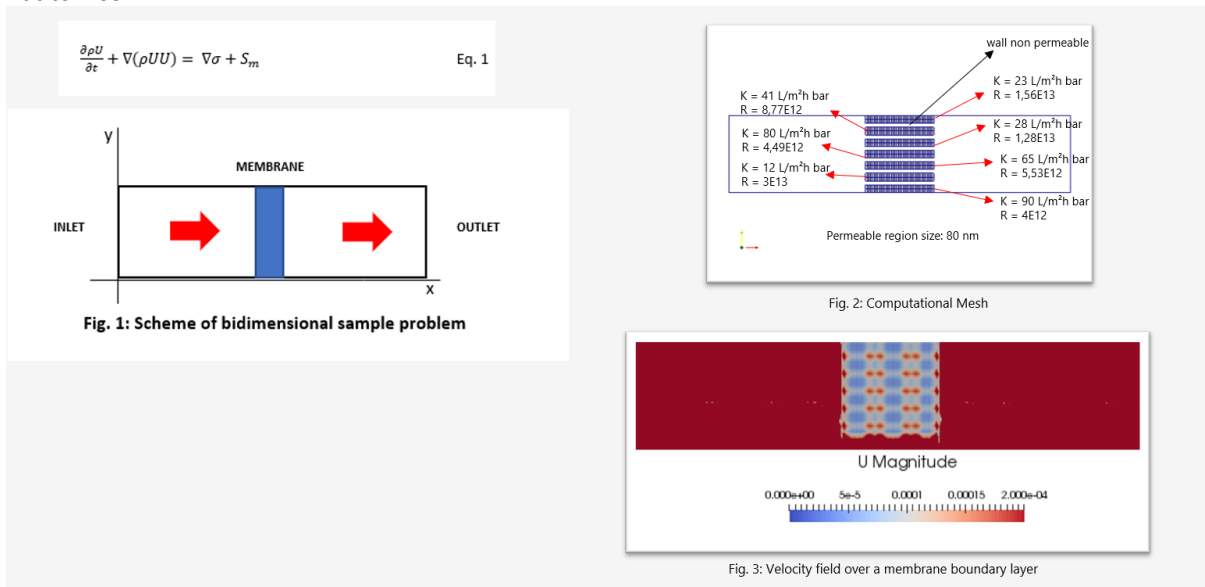
The 2D computational mesh was considered to represent a system with 13 regions, among only seven regions are permeable with different Darcy factor values. The domain has a length of 50 mm in the x-direction, 4mm in the fluid domain and porous regions. Figure 2 shows the axial and radial velocity profiles at laminar condition. Considering the flow rate balance, the axial velocity is higher in the regions where the Darcy Factor is lower, increasing from zero at the inlet towards the porous membrane where the maximum value is reached. This confirms that the numerical method proposed considerably predicts the velocity profile difference when different resistances in the permeable regions are applied. Also, the distance over a membrane boundary layer can be seen once the maximum velocity is obtained.

Reference 1:

Mansour. H, Kowalczyk. W (2015). Investigation of inlet boundary conditions on capillary membrane with porous wall during Dead-End backwash. Journal of Membrane Science Technology. 5: 138.

Reference 2:

F.Cimolina, M.Discacciati (2013). Navier–Stokes/Forchheimer models for filtration through porous media. Applied Numerical Mathematics. 205 - 224.



Modelling the accumulation of salts and organic micro-pollutants in hollow fiber nanofiltration of wastewater treatment effluent with concentrate recirculation

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Main topic: Nanofiltration/Reverse Osmosis

The presence of organic micro-pollutants (OMPs) in surface water leads to growing concern. This work proposes to extend a wastewater treatment plant (WWTP) with a nanofiltration (NF) step to prevent OMPs from entering surface waters through WWTPs, as depicted in Figure 1. The aim is to concentrate the OMPs from the effluent and treat them further in the WWTP by recycling the concentrate. OMP recycling is enabled by recent improvements in polyelectrolyte multilayer based hollow fiber NF membranes with a relatively low salt retention but high OMP retention [1]. The goal of this research is to understand the separation and degradation performance of the hybrid process. Specific membrane characteristics need to be included within the process scheme to accurately predict the accumulation of OMPs and salinity, which necessitates understanding and describing OMP and ion transport through these membranes.

Realistic scenarios are mapped using a simple mass balance model. A systematic experimental study representing typical wastewater salt matrices and commercial operating conditions is used to validate state of the art literature models, based on the Donnan steric partitioning pore & dielectric exclusion (DSPM&DE) and Solution-diffusion-electromigration (SDEM) models.

Differences in accumulation of compounds predicted by the state of the art and the simple mass balance model are compared for the full process. The state of the art models can predict negative retentions for monovalent ions, which is validated by the experimental results for ion mixtures. The simple mass balance model does however not show this. Furthermore, all models show that salts with low solubility (e.g. CaSO_4) might exceed the solubility limit, creating the potential issue of scaling. Sensitivity analyses show that adding a purge or fabricating membranes with a higher dielectric constant are promising solutions to mitigate the risk of scaling. Changing overall recovery, flux or crossflow velocity only results in minor differences in accumulation. Finally, if a first-order rate is assumed for OMP degradation in the bioreactor, the process is able to increase the overall removal of OMPs from 30 to 80-90%.

Reference 1:

E. te Brinke, D. M. Reurink, I. Achterhuis, J. de Grooth, and W. M. de Vos, "Asymmetric polyelectrolyte multilayer membranes with ultrathin separation layers for highly efficient micropollutant removal," *Appl. Mater. Today*, vol. 18, p. 100471, 2020, doi: 10.1016/j.apmt.2019.100471.

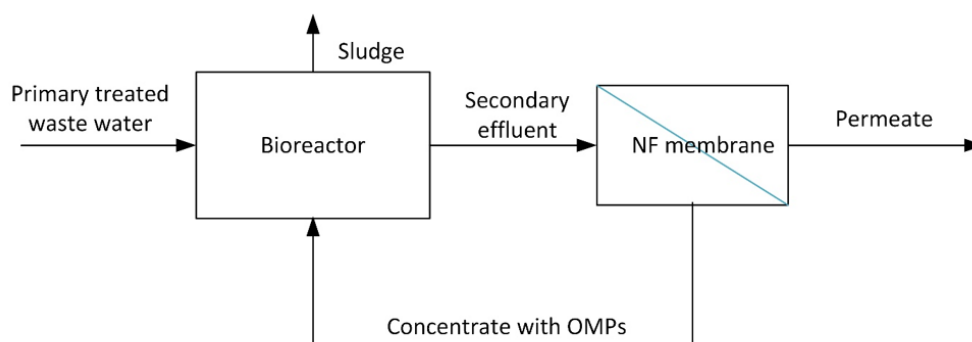


Figure 1: Process flow diagram of organic micro-pollutant (OMP) removal from wastewater by combining a municipal waste water treatment plant with a nanofiltration membrane and concentrate recirculation

MODIFICATION OF POLYMERIC HOLLOW FIBERS BY MICROFLUIDICS FOR GAS SEPARATION

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Main topic: Gas separation

The majority of the current energy is produced from burning fossil fuels, being it electricity, fuel or gas. Without a doubt these processes result in the emission of carbon dioxide to the atmosphere. CO₂ holds a major share in causing dramatic climate changes and its impact can now be seen on the world panorama. Gas streams focused on the separation of CO₂ from CH₄ is one of the possible remediation technologies, especially important for the gas industry.

Membranes can provide an eco-friendly and low energy consumption alternative to traditional separation techniques. Various membranes with different structures have been studied for this purpose and thin film composite (TFC) membranes being especially attractive due to their high performance thanks to their small thicknesses (ca. 50 nm) and possibility of modification with porous nanoparticles (e.g. metal-organic frameworks (MOF)). In general, the structure of these membranes, usually prepared by interfacial polymerization, enables that the chemistry and porosity of both layers are changed separately. In this work, we focused on synthesizing a continuous MOF layer on the lumen side of the hollow fibre instead of MOF being dispersed in the polymeric matrix. Gas separation with MOF based thin-film nanocomposite membranes represent a unique opportunity to produce a technology breakthrough able to address the environmental tasks just mentioned. Until now the fabrication of these membranes has been mainly demonstrated with a single hollow fiber (HF) [1,2]. Thus, another goal of this work is the implementation of the microfluidic synthesis methodology at larger scale and to increase the number of HF membranes that can be modified simultaneously of up to 10.

Briefly, the synthesis procedure involves using three syringe pumps and pumping of first: metal salt, second: ligand, and third: methanol to the inner side of the polysulfone hollow fiber. The fabricated containing a thin selective MOF layer mini-modules are tested in a gas separation set-up provided of gas chromatograph for the estimation of the membrane performance.

Acknowledgment

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 862330 (INNOMEM project). Also, financial support from the research project PID2019-104009RB-I00/AEI/10.13039/501100011033 from the AEI is gratefully acknowledged.

Reference 1:

[1] F. Cacho-Bailo, I. Matito-Martos, J. Perez-Carbajo, M. Etxeberria-Benavides, O. Karvan, V. Sebastian, S. Calero, C. Tellez, J. Coronas, Chem. Sci., 2017, 8, 325-333.

Reference 2:

[2] C. Echaide-Górriz, M. Malankowska, C. Téllez, J. Coronas, AIChE, 2020, 66, 16970.

Ma, Yunqiao - Co-Author

Main topic: Membrane fouling and cleaning

Membrane fouling, which is a key obstacle in implementing membrane technology, has been studied extensively for aqueous feeds. With increasing interests in organic solvent applications, a corresponding effort on understanding membrane fouling is warranted. This study employs molecular dynamics simulations to unveil the mechanisms underlying the different adsorption behaviors of dextran onto a polyacrylonitrile (PAN) membrane in three polar and protic solvents, namely, water, formamide and ethanol. The dextran-membrane separation distance is the lowest for water, followed by ethanol then formamide, which agrees with the worse flux decline for water relative to formamide. The greatest adsorption tendency in water is tied to the most attractive dextran-membrane interaction. On the other hand, the lower adsorption tendency in formamide and ethanol is linked to enhanced solvation of the dextran molecule and membrane, which deters dextran adsorption onto the membrane. Specifically, formamide, which leads to the least adsorption, exhibits the most attractive solvent-dextran and solvent-membrane interaction energies, the highest solvent-accessible surface area (SASA) for dextran, and also the highest density of solvent molecules in the solvation shell closest to the membrane. As for ethanol, it gives the highest density of solvent molecules in the solvation shell closest to a part of the dextran. The solvation of foulant and membrane by water deviates from that by other similarly polar and protic solvents, which has important implications in membrane fouling and highlights the need for enhancing the understanding of membrane fouling behaviors in organic solvents.

Reference 1:

<https://doi.org/10.1016/j.memsci.2021.119329>

Molecular Mobility and Physical Aging of Polymers with Intrinsic Microporosity (PIM-1) Revisited: A Big Glassy World

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¹Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany

Main topic: Ageing of polymeric membranes

Polymeric membranes represent a cost- and energy-efficient solution for gas separation. Recently Polymers of Intrinsic Microporosity (PIMs) have been in a great interest because of their outstanding BET surface area larger than 700m²/g and pore size smaller than 2 nm [1]. PIMs are a promising candidate in gas separation with high permeability and appealing selectivity due to their inefficient packing derived from a combination of ladder-like rigid segments with sites of contortion. However, it is recognized this class of polymers suffer from decrease in performance with time due to physical aging. The initial microporous structures approach a denser state via local chain rearrangements, leading to a dramatic reduction in permeability. As chain packing during film casting and physical aging are the key factors determine the performance in separation applications, characterization of the molecular mobility in these materials has been proved to provide valuable information. In recent researches on PIM-1 the archetypal PIM, a molecular relaxation process with high activation energy together with a significant conductivity in the glassy state has been found and explained with the formation of local intermolecular agglomerates due to interaction of π -electrons in aromatic moieties of the polymer backbone [2]. In this work, the dielectric behavior of the polymeric films and their response upon heating (aging) were measured by isothermal frequency scans during different heating/cooling cycles in a broad temperature range down to 133K for the first time. Multiple dielectric processes following Arrhenius behavior were observed. Local fluctuations, Maxwell-Wagner-Sillars (MWS) polarization and structural relaxations were discussed correlating to structural-properties of PIM-1. Up to now, no other work has studied the role of porosity and thermal history of PIM-1 film in dielectric processes. The goal is by eliminating thermal history and considering storing conditions provide better understanding on aging and plasticizing in high free volume glassy polymer PIM-1.

Reference 1:

Budd, Peter M., et al. "Solution-processed, organophilic membrane derived from a polymer of intrinsic microporosity." *Advanced Materials* 16.5 (2004): 456-459.

Reference 2:

Konnertz, Nora, et al. "Molecular mobility of the high performance membrane polymer PIM-1 as investigated by dielectric spectroscopy." *ACS Macro Letters* 5.4 (2016): 528-532.

Molecular Simulations Study for CO₂-selective mixed matrix membranes with ionic liquids and metal-organic frameworks composites

Ortiz Albo, Paloma - Co-Author¹; Cunha-Silva, Luís - Co-Author; Takaba, Hiromitsu - Co-Author; Kumakiri, Izumi - Co-Author; Crespo, João - Co-Author; Neves, Luísa - Co-Author

¹Universidade Nova de Lisboa

Main topic: Gas separation

Mixed matrix membranes (MMMs) have been studied as an attractive alternative in CO₂ capture processes. MMMs are a combination of inorganic/hybrid fillers with a polymeric matrix to ideally integrate their benefits into an advanced membrane material. Among the multiple filler options, metal-organic frameworks (MOFs) present several advantages mainly due to their hybrid organic-inorganic nature and high CO₂ adsorption capacity.

Dispersing ionic liquids (ILs) in MOF-MMMs is reported to enhance the separation performance and the mechanical properties. Incorporated ILs inside the MOFs cavities (IL@MOF composites) is one possible composite structure, which improved CO₂ sorption selectivity. Dispersion of these IL@MOF composites in polymeric matrix (IL@MOF-MMMs) is also reported. However, recent studies have approached IL@MOF-MMMs differently, using IL as an external binding agent in the MOF-polymer interphase (Li et al., 2016; Vu et al., 2019). The extensive experimental characterization required for the IL-MOF arrangement, and the constantly evolving potential materials make unfeasible to evaluate the possible MMMs by purely experimental studies.

Therefore, this work aims to perform a comprehensive analysis of the key factors in IL-MOF-MMM preparation for CO₂ separation enhancement. Experimental data of gas permeation with observations from Grand-Canonical Monte Carlo and molecular dynamics simulations were compared, being key analyzed variables the IL/ZIF-8 loading, and potential MMM configurations (Figure 1).

As well-known model materials, bis(trifluoromethanesulfonyl)imide [EMIM][Tf₂N] (Io-li-tec GmbH) IL, Basolite®Z1200 (ZIF-8) (Sigma-Aldrich) MOF, and Ultrason S6010 (polysulfone-PSf) (BASF) as polymeric matrix were selected.

Simulation results successfully modeled experimental data, inferring through several potential scenarios about the IL location in the experimentally prepared membranes. The optimal arrangements for CO₂ separation from gases such as N₂ and CH₄ were strongly dependent on the ZIF-8 loading. Low loading ZIF-8-MMMs will benefit from using IL as external binding agent, that is, the interphase MOF-polymer results as a key factor to obtain higher selectivity. Instead, higher loading ZIF-8-MMMs will be most enhanced by dispersing the IL in the polymer.

Hence, the use of Molecular Simulations proved to be a useful tool to model IL-MOF-MMMs and to provide a methodology to design membrane preparation guidelines, potentially to be extended to other novel materials.

Reference 1:

Li, H., Tuo, L., Yang, K., Jeong, H.-K., Dai, Y., He, G., & Zhao, W. (2016). Simultaneous enhancement of mechanical properties and CO₂ selectivity of ZIF-8 mixed matrix membranes: Interfacial toughening effect of ionic liquid. *Journal of Membrane Science*, 511, 130–142. <https://doi.org/10.1016/j.memsci.2016.03.050>

Reference 2:

Vu, M.-T., Lin, R., Diao, H., Zhu, Z., Bhatia, S. K., & Smart, S. (2019). Effect of ionic liquids (ILs) on MOFs/polymer interfacial enhancement in mixed matrix membranes. *Journal of Membrane Science*, 587, 117157. <https://doi.org/10.1016/j.memsci.2019.05.081>

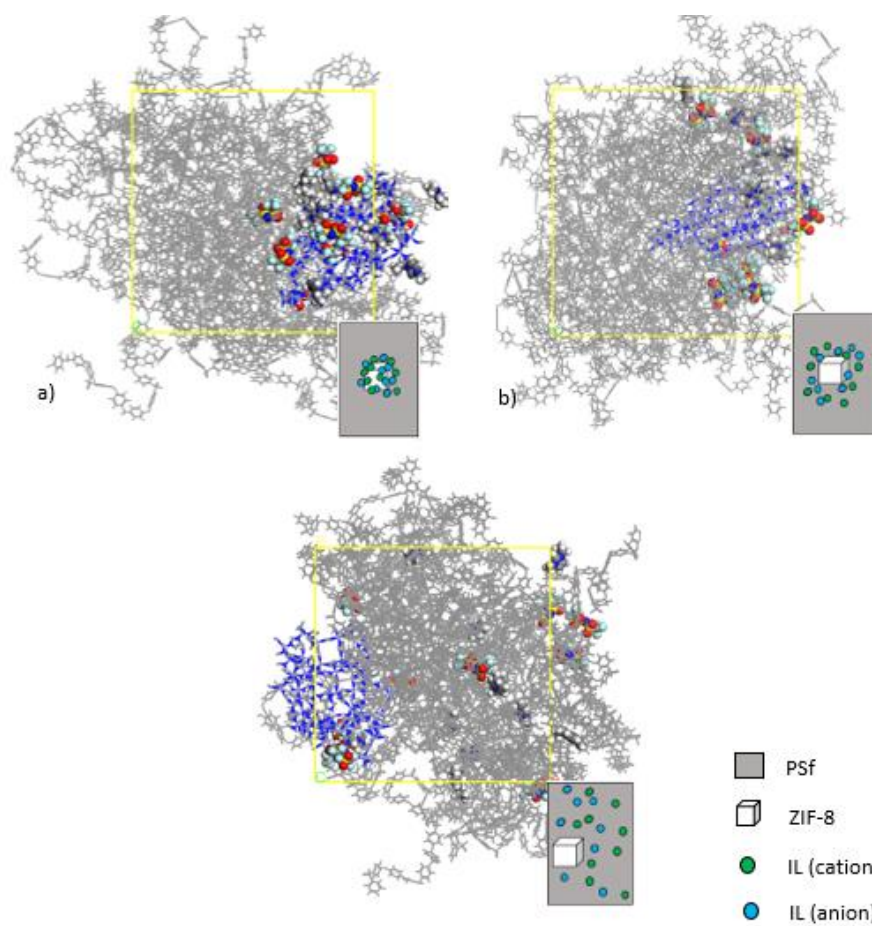


Figure 1. MMMs configurations with schematic description considered for 10wt.%ZIF-8/9wt.%IL in PSf: a) incorporation of IL inside ZIF-8; b) external coverage of ZIF-8 with IL; and c) free dispersion of both ZIF-8 and IL.

Molecularly organized liquid crystalline polymer membranes for gas separation

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Main topic: Novel membrane materials

Liquid crystals (LCs) are promising materials to fabricate nanostructured polymer membranes with a high degree of molecular order. Using the self-assembly of polymerizable LCs to prepare membranes ensures control over the supramolecular organization and alignment of the building blocks at a molecular level and gives rise to potentially overcome the tradeoff between permeability and selectivity that is limiting the performance of current polymeric membranes for gas separation. In this work, we demonstrate the importance of molecular order and orientation in free-standing thermotropic LC polymer membranes for gas permeation. Robust free-standing LC membranes were fabricated that have various, distinct morphologies (isotropic, nematic cybotactic and smectic C) that differ in type and degree of molecular order, while using the same chemical composition (Figure 1a and b). Single gas permeation data shows that the permeability decreases with increasing molecular order due to a decrease in free volume (Figure 1c). Selectivities towards He and CO₂ though increase tremendously (34-fold for He/N₂ and 21-fold for CO₂/N₂) when going from the randomly ordered (isotropic) to the highly ordered smectic C morphology (Figure 1d). Gas sorption of CO₂ showed that the gas solubility coefficient is similar for all morphologies, elucidating that the decrease in permeability with increasing order is attributed to a lower diffusion coefficient. The calculated diffusion coefficients showed a tenfold decrease when going from the randomly ordered membranes to the highly ordered smectic C membranes. For the smectic C membranes it is proposed that a decrease in free volume hinders the diffusion of gasses with a relatively larger kinetic diameter (N₂ and Ar) more compared to gasses with a smaller kinetic diameter (He and CO₂) thus inducing the selectivity. Comparison of gas sorption and permeation performances of planar and homeotropic aligned smectic C membranes shows the effect of molecular orientation by a threefold decrease of the diffusion coefficient of homeotropic aligned smectic C membranes resulting in a decrease of gas permeation. These results strongly highlight the importance of molecular order and orientation in polymeric membranes for gas separation and more specifically stress the value of liquid crystalline polymers in membrane applications.

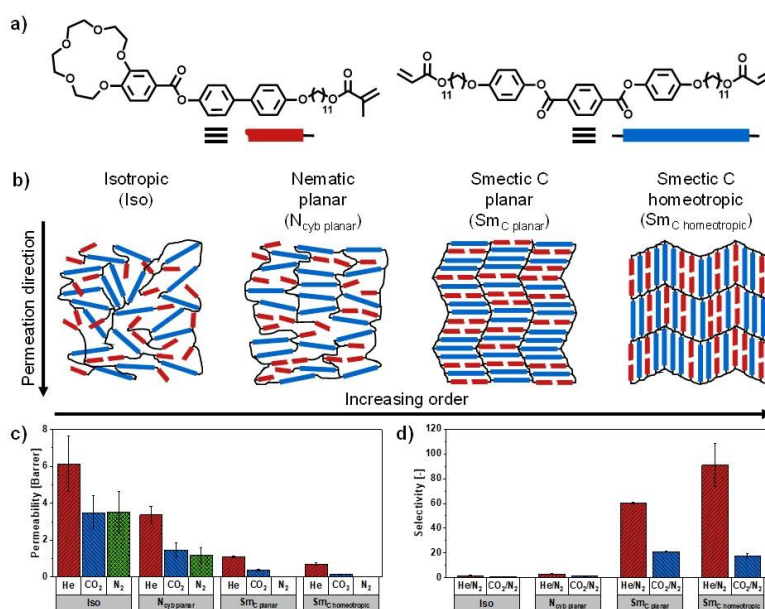


Figure 1: (a) Molecular structures of a monoacrylate LC (red rods) and diacrylate LC crosslinker (blue rods) which are used in a 1:1 (wt%) ratio for all membranes. (b) Schematic representation of free-standing LC membranes with various morphologies that differ in degree of molecular order. (c) Single gas permeability (He, CO₂ and N₂) of LC membranes with different molecular morphologies and orientation measured at 20 °C with a feed pressure of 6 bar. (d) Ideal selectivity of He/N₂ and CO₂/N₂ of LC membranes with different molecular morphologies and orientation.

Monitoring of membrane fouling by the zeta potential

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¹Anton Paar GmbH, ²University of Maribor, Faculty of Chemistry and Chemical Engineering, ³Aquaporin A/S

Main topic Membrane fouling and cleaning

The tendency of a membrane towards fouling is influenced by the properties of the membrane, the composition of the feed solution, and the filtration conditions. Among the properties of a membrane, parameters which describe the interaction of membranes with their environment are of major importance for studies of membrane fouling. The membrane zeta potential gives direct information on electrostatic interactions between the membrane surface and compounds in the feed solution, which contribute to membrane fouling. The surface charge of a membrane can also be tuned to favor or suppress certain interactions with components in the feed solution. Surface charge analysis can also be used to optimize membrane cleaning by evaluating the effects of different cleaning agents on the membrane surface.

We report on the zeta potential analysis of the inner surface of Aquaporin Inside® hollow fiber forward osmosis (HFFO) membranes, which were employed for the up-concentration of fermentation broths from vaccine production processes. Aquaporin Inside® HFFO fibers assembled in a lab-scale filtration module offers ideal conditions for the surface zeta potential analysis by the streaming potential method. The isoelectric points (IEPs) of pristine and fouled HFFO membranes were assessed by a pH scan of the zeta potential and compared with the IEP of fouled HFFO membranes after rinsing with deionized (DI) water. The preliminary zeta potential results suggest a temporary deposition of a fouling layer by organics in the fermentation broth that is successfully removed after rinsing. The efficient removal of HFFO membrane fouling is confirmed by the same flux of DI water determined before and after filtration and rinsing. The streaming potential technique is a unique method for the non-destructive analysis of the inner surface of hollow fiber membranes. It allows monitoring of fouling layer deposition on the membrane surface and supports quantification of the cleaning efficiency.

Morphology and performance of Polyvinylidene fluoride (PVDF) membrane prepared by the CCD method: thermodynamic considerations

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¹Imperial college london

Main topic: Microfiltration/Ultrafiltration

The recently developed technique of Combined Crystallisation and Diffusion (CCD) is a promising new technique to prepare high-performance ultrafiltration (UF) membranes with excellent process controllability and batch reproducibility [1, 2]. This study explores the thermodynamic implications of changing the cooling temperature during the CCD process and the effect it has on the PVDF membrane morphology and performance. PVDF with two different molecular weights was studied and different batches of membranes were prepared by progressively changing the cooling temperature from -30 °C to 0 °C. The results showed that for both the PVDF grades, with an increase in cooling temperature, the separation surface pore sizes increased but more so for the one prepared using the larger molecular weight PVDF. The membrane permeation characteristics revealed high water permeation rates for all these membranes due to the unidirectional freezing used by CCD method, from which high surface porosity and aligned supporting pore structure were generated. Pure water permeation of 1170 and 4900 LMH bar⁻¹ were obtained for membrane with 37 and 160 nm pore size, respectively. The cooling temperature also affected the crystallisation kinetics of PVDF during membrane formation, wherein a high cooling temperature facilitated the expansion of the polymer crystal domain. The binary phase diagram which describes the thermodynamics behind the CCD process was used to explain the observed results. In addition to characterising the membranes for their morphology and pore sizes, they were also characterised for their permeation performance, mechanical strengths and crystallization behaviour to help further understand the role of cooling temperature in affecting CCD membrane properties.

Reference 1:

Wang, B., J. Ji, and K. Li, Crystal nuclei templated nanostructured membranes prepared by solvent crystallisation and polymer migration. *Nature communications*, 2016. 7(1): p. 1-8.

Reference 2:

Shah, V., B. Wang, and K. Li, Blending modification to porous polyvinylidene fluoride (PVDF) membranes prepared via combined crystallisation and diffusion (CCD) technique. *Journal of Membrane Science*. 618: p. 118708.

Multi-cation crosslinked poly(arylene piperidinium) membranes for high-performance water electrolysis.

Wang, Xiuqin - Co-Author

Main topic: Novel membrane materials

As a kind of clean energy, hydrogen energy has attracted great attention in recent years since hydrogen can be stored and converted into other forms of energy without polluting the environment. However, the current steam reforming method that is used for producing hydrogen from fossil fuels could release carbon dioxide and cause air pollutants [1]. In this case, anion exchange membrane water electrolyzers (AEMWEs) are developed to produce hydrogen due to their advantages environmentally friendly, high hydrogen production rate, usage of less expensive Pt-free catalyst. However, it is still at an early stage of development, and its performance, especially conductivity and alkali resistance, is far lower than that of systems based on proton exchange membranes. The crosslinking process is widely employed to improve the physicochemical stability of anion exchange membranes. However, in the general situation, the polymer cross-linking through a cross-linking agent improves the dimensional stability by sacrificing ion exchange capacity which indirectly loses the ionic conductivity. In order to solve this "trade-off" problem, multi-cation crosslinked poly(arylene piperidinium)-based anion exchange membranes were developed in this work. The introduction of a multi-cation crosslinker facilitates the construction of a highly efficient ion-conducting pathway, resulting in a high conductivity of 95 mS cm^{-1} for the membranes and a good water electrolysis performance reached 0.88 A cm^{-2} . The ether-bond-free structure combined together with multi-cationic crosslinker endows good durability of the AEMWE. The voltage of crosslinked AEMs based water electrolysis cell had hardly changed after operating at a current density of 100 mA cm^{-2} for more than 600 mins.

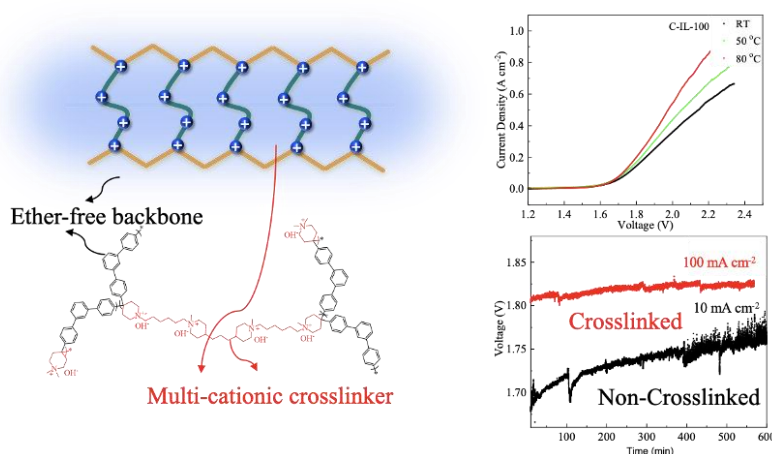


Fig. 1 The configurations and schematic diagram of the membranes and their performance in water electrolysis.

Reference 1:

[1] D. Li, A.R. Motz, C. Bae, et al. Energy Environm. Sci., 14 (2021) 3393-3419.

Multi-level assessment of ozonation as feed pre-treatment strategy in pressure retarded osmosis

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Main topic: Forward osmosis/Pressure retarded osmosis

Feed water pre-treatment represents a significant issue hindering the potential of salinity gradient energy production via pressure retarded osmosis (PRO). Conventional pre-treatment is reported to require similar specific energy input (0.1-0.45 kWh/m³) as the energy that can be extracted by PRO (Kim and Kim, 2018).

In this work, continuous low ozone dosage on the feed stream is assessed as potentially energy-convenient alternative to conventional strategies for fouling control. The assessment was carried out on two levels: (i) bench scale experiments were performed to study the effectiveness of ozone in the reduction of membrane fouling and (ii) a system-level analysis of PRO was performed to estimate the energy consumption of such pre-treatment strategy.

The experiments were carried out using cellulose triacetate membranes, ozone concentrations between 0.05 to 0.2 mg/L and two model foulants (humic and alginate acid). The water flux is described using the resistance-in-series model (Figure 1a) (Nagy et al., 2018). The main focus of the experiments was to estimate the membrane structural parameter S , which was assumed to be the only parameter affected by feed-side fouling. The results show that O₃ concentration of 0.1 mg/L can reduce the fouling by humic acid but not completely avoid it (Figure 1b and Figure 1c). Mechanistically, this behaviour was related to the breakage of the larger humic acid aggregate achieved with low O₃ dosage.

The system-level analysis was then performed considering the energy requirement to achieve 0.05-0.2 mgO₃/L in the feed stream. The following steps were considered: (i) oxygen generation; (ii) ozone generation from oxygen (iii) gaseous oxygen dissolution in water. From this analysis, it was estimated that ozone pre-treatment energy requirement is in the range 3-9 Wh/m³ of feed stream, consistently lower compared to net specific energy extractable for a sea water-river water PRO process.

In conclusion, continuous dosage of low concentration ozone is an interesting option to implement in a PRO process due to its potential in fouling reduction at a convenient energy expense.

Reference 1:

Minseok Kim and Suhan Kim. "Practical limit of energy production from seawater by full-scale pressure retarded osmosis". In: Energy 158 (2018), pp. 373–382. doi:<https://doi.org/10.1016/j.energy.2018.06.042>.

Reference 2:

Endre Nagy et al. "Effect of fouling on performance of pressure retarded osmosis (PRO) and forward osmosis (FO)". In: Journal of Membrane Science 565 (2018), pp. 450–462. doi: <https://doi.org/10.1016/j.memsci.2018.08.039>.

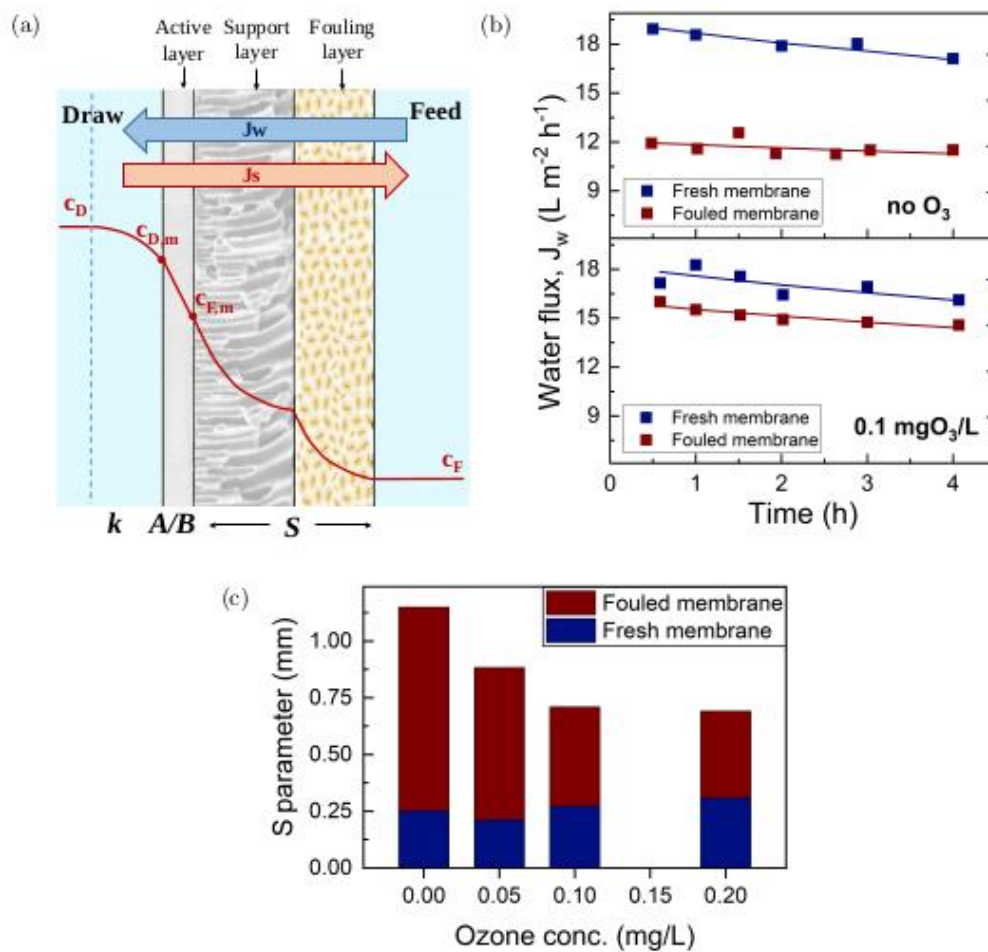


Figure 1: (a) Schematic representation of the concentration profile in a PRO membrane; (b) Experimental (scatter) and simulated (line) water flux for a fresh membrane and fouled membrane (subjected to humic acid fouling for 24 h); (c) effect of ozone concentration on the membrane structural parameter for a fouled membrane

Multiobjective optimization of skimmed milk microfiltration based on expert knowledge

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Main topic: Food processing

Optimizing food filtration processes is complex due to the lack of knowledge about process performances mechanisms, the complexity of the food product itself and the heterogeneity of the variables involved in prediction models. This is the case for skimmed milk crossflow microfiltration with 0.1 μm pore size (MF). This operation is commonly used to separate the two major milk proteins and produce fractions with high interest in cheese making and ingredient preparation. In this process, the choices of membrane configurations (Uniform transmembrane Pressure system, membranes with gradient of permeability or spiral wound membranes), processing designs and operating conditions are mainly based on the know-how of equipment manufacturers and the available expert knowledge. However, despite its high interest, this process has never been optimized regarding stakeholder's conflicting objectives (high quality, low costs). This work aims to optimize skimmed milk MF 0.1 μm by considering conflicting objectives defined by stakeholders and integrating expert knowledge into the formulation of a multiobjective problem. The methodology used was based on "Knowledge integration" and composed of four steps: 1) the acquisition of scientific and expert knowledge about the objectives to optimize; 2) the modeling of objectives as computable functions; 3) the solving of the multiobjective problem by using an adapted metaheuristic multiobjective optimization algorithm; 4) the decision support. The multiobjective MF problem was formulated by considering the product, operating variables, design and economic costs. 1000 pareto-optimal solutions were found, including solutions close to those used in industry and at lower cost. The multiobjective optimization of the MF has opened up new thinking about installation designs and combinations of operating conditions by improving product characteristics while keeping investment and production costs constant. The result of the optimization is a proof of concept whose feasibility and viability at an industrial scale must be validated. This work opens new perspectives for multiobjective optimization of food membrane processes and generally to food processes.

Mw resolution and temperature effect of Crosslinked PVDF membrane in non-polar solvents

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Main topic: Organic solvent nanofiltration

Recently developed one-pot crosslinked poly(vinylidene difluoride) (PVDF) nanofiltration membranes were prepared and tested for solvent resistance nanofiltration (SRNF) applications. Experiments with seven different dyes, namely Rose Bengal (1036Da), Acid fuchsin (585Da), Richard dye(551 Da) and Rhodamin B (479 Da) in water and ethanol and Sudan Black B(456 Da), Zinc tetraphenylporphyrin (ZTPP) (678 Da) and 5,10,15,20-Tetrakis(3,5-di-tert-butyl phenyl)porphyrin (TBPP) (1036 Da) in isopropanol, butyl acetate, chloroform, xylene, and toluene were performed. Depending on the solvent and the solute, the MWCO of crosslinked PVDF membrane can change. Butyl acetate filtration releases the sharpest MWCO for more hydrophobic dyes. High-temperature solvent resistant nanofiltration of SS4 in butyl acetate, chloroform, xylene, and toluene using crosslinked-PVDF membranes illustrated permeance increase with temperature for all four solvents. TBPP Retention decreases slightly in xylene, butyl acetate, and chloroform and increased marginally in toluene. The results of consecutive room temperature show that the performance of crosslinked PVDF is the same for xylene, butyl acetate and toluene, but 50% decrease in chloroform after the high temperature filtration.

Reference 1:

M. Mertens, C. Van Goethema,¹ M. Thijs, G Koeckelberghs, I. F.J. Vankelecom, Crosslinked PVDF-membranes for solvent resistant nanofiltration, *Journal of Membrane Science* 566 (2018) 223–230.

Reference 2:

C. Van Goethem, M. Merwin Magboo, M. Mertens, M. Thijs, G. Koeckelberghs, I. F.J. Vankelecom, A scalable crosslinking method for PVDF-based nanofiltration membranes for use under extreme pH conditions, *Journal of Membrane Science* 611 (2020) 118274.

NaCl and alkaline cleaning of PVDF based MF membrane fouled by skim milk: real efficiency and misleading interpretation associated to flux recovery

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Main topic: Membrane fouling and cleaning

MF of skim milk to separate casein micelles and soluble proteins is generally achieved with ceramic 0.1 μm membranes. However, recently PVDF membranes (for which pH limitation close to 11 during cleaning are given by the provider) were introduced at industrial scale aiming at a cheaper operation cost compared to ceramic MF, but leading to retentate and permeate fractions of different compositions than those reached with ceramics. Nevertheless, the membrane fouling and cleaning remains a bottleneck. Recent literature evidenced that NaCl cleaning of protein fouled polymer membranes could be an alternative to recover a significant part of the membrane flux and conclude to the NaCl cleaning efficiency.

In the present study, a PVDF based MF membrane (FR800 kDa, Synder) was fouled by skim milk at 0.5 bar and room temperature, then carefully rinsed with deionised water at increasing temperature up to 46°C and finally cleaned at 0.5 bar, 46°C either with (2.5 and 5.0 $\text{g}\cdot\text{L}^{-1}$) NaCl solutions at natural pH or with 2 commercial formulated alkaline solutions at different pH (Ultrasil 10, Ecolab ; Deptal 117L, Kersia) and an alkaline prototype solution. Finally, cascades of NaCl + one alkaline formulated detergent were tested.

Besides the classical hydraulic characterisation of the membrane cleanliness obtained from the water flux recovery (J/J_0), the chemical cleanliness was measured from the residual protein quantification achieved by ATR-FTIR. Figure 1 depicts (1) that the flux recovery has to be decoupled to the chemical cleanliness as already proved for skim milk UF by PES/PVP membrane [1, 2] and (2) that NaCl cleaning seemed to have no real efficiency (with respect to the residual proteins present in/on the membrane) and can even decreased the alkaline detergent efficiency when used in cascade after NaCl, as evidenced with two different alkaline detergents.

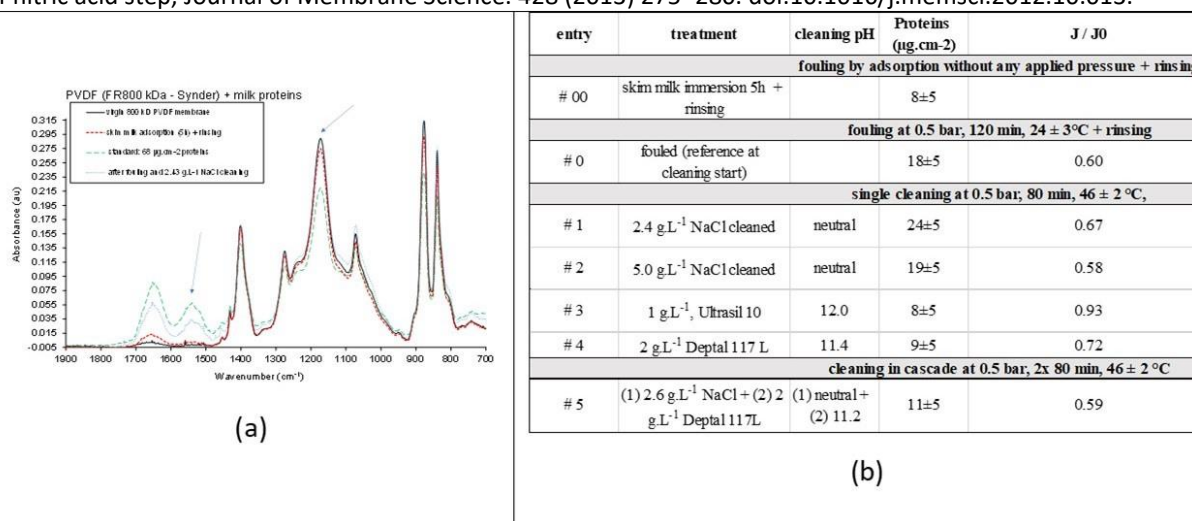
Figure 1: ATR-FTIR spectra of the PVDF membrane, either virgin, or fouled by proteins in different conditions (a) and cleaning results (b)

Reference 1:

[1] N. Wemsy Diagne, M. Rabiller-Baudry, L. Paugam, On the actual cleanability of polyethersulfone membrane fouled by proteins at critical or limiting flux, *Journal of Membrane Science*. 425–426 (2013) 40–47. doi:10.1016/j.memsci.2012.09.001.

Reference 2:

L. Paugam, D. Delaunay, N.W. Diagne, M. Rabiller-Baudry, Cleaning of skim milk PES ultrafiltration membrane: On the real effect of nitric acid step, *Journal of Membrane Science*. 428 (2013) 275–280. doi:10.1016/j.memsci.2012.10.013.



Nafion membranes modified by cationic cyclodextrin derivatives for enantioselective separation

Izak, Pavel - Co-Author

Main topic: Novel membrane materials

Nafion117[®] membranes modified by three cationic cyclodextrin (CD) derivatives have been prepared by strong ionic bonding. All CD derivatives contained bis(methylimidazolium) (MIM2) cationic anchor covalently bound to the CD unit, either using no spacer or using diethylene glycol (DEG) or tetraethylene glycol (TEEG) spacers. The modified membranes were tested in chiral separation of a model racemic mixture (d/l-tryptophan) from water. Different experimental set-ups for characterising membranes in enantioselective separation – pertraction, two kinds of sorption, and pressure-driven membrane separation – have been described and rigorously compared. The membranes CD-MIM2, CD-DEG-MIM2 have reached the highest enantiomeric excess, 14 and 44 % respectively, in 280 days. The lowest performance of the CD-TEEG-MIM2 membrane, with the long spacer, has been visibly ameliorated by applying pertraction; enantiomeric excess rose from 2 to 27% in 80 days. Even though sorption played the main role in pertraction, this process substantially enhanced the separation of racemic mixtures. The pressure-driven approach has allowed the operation to be continuous and faster, which has the potential for continuous large-scale production of enantiopure compounds and could pave the way for many more commercial applications, satisfying the considerable demand for large-scale chiral separation techniques.

Nafion-Based Mixed-Charged Nanofiltration Membrane for Wastewater Treatment: Preparation and Performance

Zelner, Michael - Main Author; Jahn, Philipp - Co-Author; Ulbricht, Mathias - Co-Author; Freger, Viatcheslav - Co-Author

Main topic: Wastewater treatment

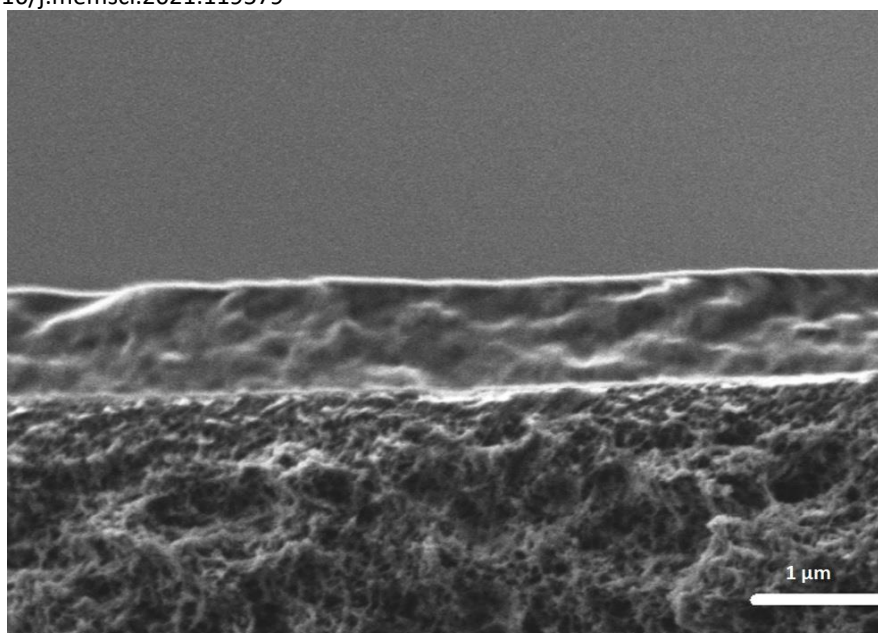
Nanofiltration (NF) is an attractive solution for tertiary wastewater treatment when mild desalination is required, yet the process severely suffers from scaling due to the high rejection of multivalent ions. We investigate the preparation and performance of a new stable binary charged complex NF membrane prepared by a new two-step coating of an ultrafiltration support membrane with oppositely charged polyelectrolytes, Nafion, and polyvinylamine (PVAm). In our approach, the first Nafion layer determines the final membrane thickness, while PVAm coating seals the defects in Nafion layer and neutralizes its charge.

We found that the first Nafion layer contains defects and showed poor rejection, which suggested that their “caulking” with PVAm could form a mosaic-like structure, attractive in terms of ion selectivity. However, ultimately, we concluded that the final structure of the new mixed-charge membrane was that of a uniform polyelectrolyte complex (see Figure). After optimization of the second coating with PVAm, a membrane with a symmetrical rejection of MgCl_2 and Na_2SO_4 was obtained, indicative of a neutral membrane and different from rejection by commercial polyamide NF membranes such as NF270. Varying Nafion thickness resulted in the same symmetrical pattern but a higher rejection, consistent with ζ -potential measurements and morphology. The membrane also showed excellent stability in 10% NaCl water solution and examined pH range 3 to 10.

Closer inspection of the variation of ion rejection of the new membrane with salt concentration shows a similar monotonic increase of the permeabilities of all salts, mono- and divalent, which is distinctly different from NF270. Similar experiments in acidic (pH 4) and basic (pH 10) conditions indicate that, depending on pH, the membrane may behave both as neutral and charged. This difference points to distinctly different ion rejection mechanisms in the two membranes, especially in the case of salt of divalent cations. We consider this feature attractive in applications where the more uniform rejection of different ions is preferred, such as wastewater treatment. Our current research is focusing on the investigation of other performance characteristics of the new membranes, such as pollutant rejection and fouling, to fully assess the benefits for such applications.

Reference 1:

Michael Zelner, Philipp Jahn, Mathias Ulbricht, Viatcheslav Freger, A mixed-charge polyelectrolyte complex nanofiltration membrane: Preparation, performance and stability, *Journal of Membrane Science*, Volume 636, 2021. <https://doi.org/10.1016/j.memsci.2021.119579>



Nanobubbles' effect on Desalination via Direct Contact Membrane Distillation

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Main topic: Membrane contactors and membrane distillation

A rapid growth of bulk nanobubbles on the research and extraordinary applications, including membrane technology, is recorded during the last decade. Nanobubbles (NBs) are generated by the injection of a gas through a ceramic membrane while at the same time nanobubbles, due to high mass transfer efficiency, could potentially prevent fouling of ceramic membrane filtration processes [1]. Recent papers report the use of NBs as a novel, energetically and environmentally friendly approach in membrane technology.

An additional potential use of nanobubble technology is proposed in this work, this of water treatment via direct contact membrane distillation process. Here the advantages of the nanobubbles in the presence of higher vapor pressure, compared to the pristine water, provide a gradient force in the permeation flux of the water through the membrane structure.

In our work air and oxygen bulk nanobubbles with an average size of approximately of 200 nm (see Fig. 1) were produced in a custom generator which takes advantage of hydrodynamic cavitation method [2]. For the DCMD experiments, a commercial hydrophobic macroporous flat sheet PTFE on PP support membrane (Fironi Filters), was used having 0.2 μm pore size diameter. Performance evaluation was conducted by using a feed solution containing 0.5M NaCl at feed and distillate side temperature 60 and 15°C respectively. The best performance was achieved by using air NBs increasing the water flux by 85% while retaining 99.99% salt rejection efficiency.

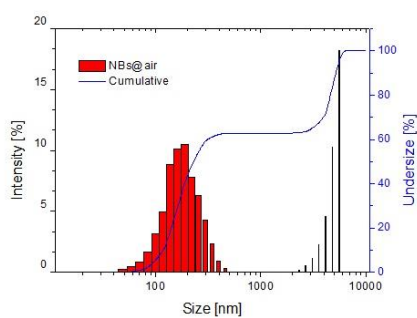
Acknowledgement: The project IntelWATT (GA ID: 958454) is acknowledgement for partial funding this work.

Reference 1:

[1] A. Ghadimkhani, W. Zhang, T. Marhaba, Ceramic membrane defouling (cleaning) by air Nano Bubbles, Chemosphere 146 (2016) 379–384.

Reference 2:

[2] E.D. Michailidi, G. Bomis, A. Varoutoglou, G.Z. Kyzas, G.Mitrikas, E.K. Efthimiadou, A.Ch. Mitropoulos, E.P. Favvas, Bulk nanobubbles: Production and investigation of their formation/stability mechanism, J. Colloid Interface Sci. 564 (2020) 371–380.



| Experiment | LEP (bar) | Permeance LMH | Salt Rejection % |
|---------------------|-----------|---------------|------------------|
| H ₂ O | 2.01 | 17.1 | > 99.95 |
| air-NBs | 3.87 | 26.3 | > 99.95 |
| O ₂ -NBs | 4.15 | 31.7 | > 99.95 |

Fig. 1. Air-NBs size distribution by DSL measurement (A), and membrane distillation performance–water flux vs. salt rejection for the system of PTFE membrane and the cases of pure and enhanced with air-NBs and O₂-NBs feed saline water (B).

Nanocellulose based Facilitated transport membranes for CO₂ separation

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¹University of Bologna

Main topic: Facilitated transport membranes

Facilitated transport membranes (FTMs), have recently considered with high interest for its ability to separate CO₂ with high flux and selectivity thanks to reversible reaction of this gas with functional groups, embedded within the polymeric matrix [1]. FTMs for CO₂ separation are often based on aminated polymers which unfortunately shows low mechanical stability if not mixed and crosslinked with a supporting polymer.

Recently another option to stabilize such materials was found in the mixing with nanocellulose fibers, a 1-D nanomaterial with ever growing applications, due to its large availability, renewability and stable mechanical properties.[2]. Following this approach, in this work, novel nanocomposite materials obtained by coupling carboxymethylated nanocellulose (CMC-NFC) with polyvinylamine (PVAm) and L-Arginine as mobile carrier, were studied.

Membranes were fabricated via solvent casting protocol and permeation tests were conducted with nitrogen, CO₂ and Methane at different temperatures (35 and 96°C, 1 bar) and high humidity. The results showed a strong improvement of both selectivity and permeability once high loadings of the carrier were reached. As an example, CMC-NFC/L arginine membranes with 45 wt% of the amino acid, showed a 7-fold carbon dioxide permeability increase with respect to pure nanocellulose films, reaching 225 Barrer with CO₂/N₂ selectivity of 186.

Interestingly the addition of PVAm, increased the membrane stability, but did not improved the separation performances. Indeed, at 35°C, self-standing films, containing both PVAm and L-Arginine, exhibited a maximum permeability of 130 Barrer and a CO₂/N₂ selectivity of 58.

At high temperature, the tests revealed a significant increase of membrane properties, which resulted particularly elevated for the ternary system. The latter indeed showed CO₂ permeability up to 600 Barrer at 96 °C, while in similar conditions films made exclusively by fixed carriers could not exceed 200 Barrer. Also the selectivity with respect to N₂ was substantially increased with value always higher than 80.

The new materials therefore showed interesting properties that, coupled with the good stability, the tunable performances, and last but not least the intrinsic sustainability, makes it an interesting candidate for carbon capture as well as for other applications involving CO₂ separation.

Reference 1:

R. Rea, M.G. De Angelis, M.G. Baschetti, Models for facilitated transport membranes: A review, *Membranes* 9 (2019). doi:10.3390/membranes9020026.

Reference 2:

D. Venturi, D. Grupkovic, L. Sisti, M.G. Baschetti, Effect of humidity and nanocellulose content on Polyvinylamine-nanocellulose hybrid membranes for CO₂ capture, *J. Memb. Sci.* 548 (2018) 263–274. doi:10.1016/j.memsci.2017.11.021.

Nanofibers for water purification

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Main topic: Wastewater treatment

Water scarcity is a global issue that demonstrates the importance for water reuse. Water purification is needed to fulfil the requirements for water reuse and includes several processes being membrane filtration among them. Nanofiber membranes are promising mediums that possess high filtration efficiencies and better performance than conventional membranes due to its high surface area and porosity. Nanofibers are produced by electrospinning technique which uses an electrostatic field to generate ultrafine fibres from polymeric solutions. The nanofiber structure and morphology can be tuned by varying the polymeric solution composition (molecular weight, concentration, solvent, additives) and electrospinning parameters (voltage, flow rate, needle-substrate distance, needle gauge, ambient parameters etc..). The nanofiber properties can be further engineered with embedding of nanomaterial either by addition of nanomaterial to the polymeric solution or by nanofiber post-treatment.

Innovative filters made of electrospun nanofibers have been produced to remove target contaminants from wastewater such as bacteria and emergent pollutants. Polymeric nanofibers with biocide particles have been developed for the inactivation and removal of bacteria and polymeric nanofibers with photocatalytic nanoparticles have been developed for degradation of pharmaceutical contaminants. The morphology and filtration efficiencies have been investigated and a prototype will be designed and implemented in a pilot study.

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Nanofiltration for the treatment of black liquor in the paper and pulp industry

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¹Suez Water Technologies and Solutions, ²Universidade NOVA de Lisboa

Main topic: Paper and pulp industries

In the paper and pulp industry, pure cellulose fibers from the wood chips are obtained when a caustic solution is used for chemical pulping, thus, highly alkaline wastewater rich in lignin is generated. This wastewater is called black liquor and studies have shown that nanofiltration could be used to recover the caustic solution [1]. In this study, the filtration performance of two in-house made NF membranes (Membranes A and B) is evaluated and compared with that of a commercial NF membrane (Membrane C) to determine the feasibility of their use for the treatment of black liquor. For this purpose, experiments with simulated black liquor were performed.

Using simulated black liquor at pH 12 and pH 14, the membranes proved to be stable under alkaline conditions during both static and dynamic (filtration) tests. The filtration experiments demonstrated that Membrane A has a higher potential for this application, because it presented the best trade-off between permeate flux and solutes rejection. It offered a flux of $24 \text{ l m}^{-2} \text{ h}^{-1}$ (in average) at 35 bar of operating pressure, and high rejection of organic compounds and salts that may affect the composition of the recycled cooking liquor. In average, the rejections were 92.5% for the TOC, 84.1% for the CO_3^{2-} , 88.7% for the sulphates, 73.2% for the Na^+ and 99.9% for the Mg^{2+} . For OH^- , a negative rejection of -317.9% (in average) was observed. Therefore, a high recovery and concentration of NaOH in the permeate was achieved. It can be concluded that Membrane A seems suitable for the treatment of black liquor. The NF permeate may still require causticization, but a critical part of the chemical recovery process would be already optimized.

Reference 1:

Kevlich N. et al. Membranes for Kraft black liquor concentration and chemical recovery: Current progress, challenges, and opportunities. *Separation Science and Technology* 2017. Vol. 52. No. 6. 1070–1094.

Nanofiltration in non-polar solvents using fluorinated thin film composite membranes

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Main topic: Organic solvent nanofiltration

Polyamide (PA) thin film composite membranes are highly effective for nanofiltration (NF), mainly for filtering water and other polar solvents. However, being rather hydrophilic, they are less successful in the case of nonpolar solvents. We propose the incorporation of fluorinated monomers in a polyamide network is a strategy to increase the hydrophobicity and obtaining membranes with enhanced permeance of nonpolar solvents. PA thin-film composite membranes were prepared by interfacially reacting trimesoyl chloride (TMC) and lab-made fluorinated monomer (HFBC) in the organic phase mixed with 5-trifluoromethyl-1, 3-phenylenediamine (TFMPD) in an aqueous phase, all of which was conducted in a single step. The resulting membrane obtained using (HFBC) exhibited a considerably increased nonpolar solvent flux and selectivity in the nanofiltration range. The fluorinated composite membrane demonstrated excellent stability in organic solvents, thermal stability, and it maintained excellent performance over an extended time. This novel strategy makes it possible to obtain high-performance membranes for nonpolar solvent separation in petroleum refineries, as well as purification in the pharmaceutical industry.

Nanofiltration of seawater desalination brines as pretreatment for metals and minerals recovery

Figueira Alves, Mariana - Main Author; López, Julio - Co-Author; Reig, Mònica - Co-Author; Cortina, José Luis - Co-Author; Valderrama, César - Co-Author

Main topic: Nanofiltration/Reverse Osmosis

Seawater desalination is one of the most efficient technologies to reduce potable water scarcity. However, seawater desalination plants (SWDP) still face economic and environmental issues, one of them is the management of the brine produced during the process (about twice the salt concentration of seawater). Nowadays, most of the plants directly discharge the brine back to the sea, which consumes energy and affects local ecosystems (e.g., decreasing the amount of flora and creating salinity gradients). Nevertheless, this waste stream contains significant amounts of valuable metals and minerals that can be recovered following the circular economy principle.

As part of the H2020 SEA4value project, this work aims to recover magnesium, boron, lithium, scandium, gallium, vanadium, indium, rubidium and molybdenum from SWDP brines, making desalination plants the third source of valuable raw materials in the European Union. To optimize the recovery of these raw materials, the project proposes two pretreatment stages based on calcium removal, followed by nanofiltration to separate monovalent from multivalent ions. This study focuses on the nanofiltration of SWDP brines using commercial membranes: FilmTec NF270, FilmTec Fortilife XC-N (DuPont), and Hydranautics PRO-XS2 (Nitto Denko Corporation). Tests were carried out using flat-sheet membranes (0.014 m²) to investigate the effect of trans-membrane pressure (from 6 to 30 bar) on rejections and permeate flux using two different synthetic brines (one using SWDP brine and the other considering a previous calcium removal stage, up to 90%). The brines contain as major elements calcium, magnesium, sulfate, carbonate, sodium, potassium and chloride. As minor elements boron, lithium, scandium, vanadium, gallium, rubidium, molybdenum and indium.

Initial results using SWDP brine showed that Fortilife XC-N has a better rejection for multivalent major ions (>80% for calcium and >90% for magnesium), while Hydranautics PRO XS2 separates better the minor elements. Hydranautics PRO XS2 presents a high rejection of multivalent minor elements, >95% for indium, molybdenum, gallium e scandium and around 80% for vanadium through the complete pressure range, and very low rejection for the monovalent, < 5% for lithium and boron (B(OH)₃ neutral) and around 15% for rubidium.

Nanoscale mapping of renewable polyether-block-polyamide copolymer membranes using Infra-Red Nanospectroscopy

David, Oana - Main Author¹; Amenabar Altuna, Iban - Co-Author; Fernandez Carretero, Francisco Jose - Co-Author; Diaz De Guereñu Zabarte, Maria del Mar - Co-Author; Goikoetxea Larruskain, Monika - Co-Author; Pineau, Quentin - Co-Author; Etxeberria Benavides, Miren - Co-Author; Hillenbrand, Rainer - Co-Author

¹Tecnalia

Main topic: New characterisation methods

Unmatched CO₂ separation performance has been found for a new polyether block polyamide copolymer grade (Pebax® Rnew® 30R51 SA 01) partially based on renewable resources. Different gas separation properties have been found for thin film membranes when using different membrane fabrication techniques as shown in Table 1. In order to understand these differences, the two films were analyzed by differential scanning calorimetry (DSC) and ATR-FTIR and nano-FTIR spectroscopy.

DSC results show two melting temperatures (within 130-140 °C and 150-160 °C) for the PA block of the solvent cast films while only the second melting temperature (150-160 °C) for the PA block in the melt extruded film and in the bulk polymer.

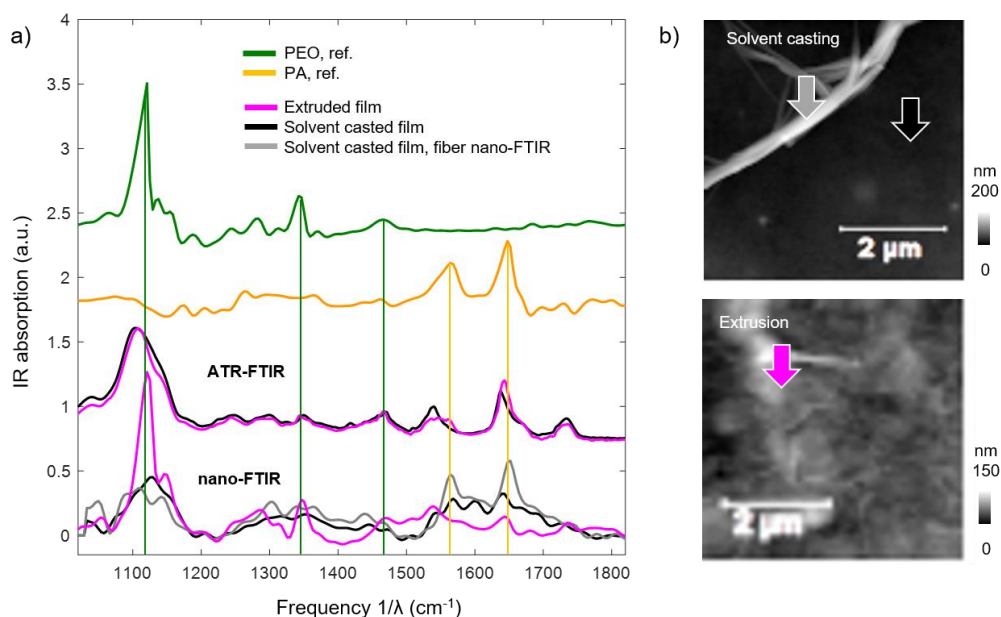
ATR-FTIR absorption spectra (Figure 1a) of both samples were very similar, which only showed subtle differences in the PA related Amide I and II absorption bands. However, nano-FTIR spectra were rather different evidencing the existence of clear nanoscale chemical differences between the two samples. In the extruded film the PEO block seems to be more crystalline compared to the solvent casted film (i.e. the characteristic band at 1120 cm⁻¹ is sharper and significantly higher at the extruded film). On the other hand, only at the solvent cast film we observed many nanoscale fibers (see Figure 1b top panel). Such fibers yielded nano-FTIR spectra with high, sharp and shifted Amide I and Amide II bands compared to the nano-FTIR spectra recorded at the matrix at the same sample. This observation, together with the DSC results, suggests the coexistence of two crystalline populations for the PA block in the solvent cast films, which denotes a much slower crystal formation rate than for the extruded film. A lower crystal growth rate leads to a larger decoupling of the crystals from the amorphous structure and a higher mobility of the polymer chains within the amorphous phase [1], therefore, a more available PEO network for gas permeation.

Figure 1: a) ATR- FTIR and nano-FTIR absorption spectra of the films and nano-FTIR reference spectra and b) exemplary AFM topography images of the films.

This work has been carried out within **BIOCOMEM** project.

Reference 1:

A. Arun, R.J. Gaymans / European Polymer Journal 45 (2009) 2858–2866



Nanotechnology methods to fabricate isoporous membranes with high density of micro/nanopores for broad range of applications

Sabirova, Ainur - Main Author¹; Nunes, Suzana - Co-Author¹

¹King Abdullah University of Science and Technology

Main topic: Advanced fabrication methods

Isoporous membranes with high pore density, and, sharp pore size distribution in the micro- and nanoscale providing effective separation are necessary for different biomedical and diagnostic applications, such as cancer cell separation, biosensing, controlled drug delivery, microfluidic devices for organ-in-a-chip, as well as investigations in plant and bioscience.

Hereby, we propose two nanotechnology methods, both combined with lithography and dry reactive ion etching processes, to fabricate a series of polyester membranes with isopores of size in microscale (0.7 to 50 μm) and in nanoscale (300 nm), which demonstrated high pore density and surface area of 38.5 cm^2 . The membranes fabrication methodologies are environmentally friendly as they do not require solvents, and, without water waste characteristics. The membranes are flexible, easy to handle and have excellent chemical and thermal resistance as well as biocompatibility characteristic. All membranes have pore density 10-fold higher than track-etched analogues and exhibit permeance of 220,000 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ and 108,000 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ for microporous and nanoporous membranes respectively.

The isoporous system in micron and submicron scales was successfully tested for the organelles mild fractionation of Arabidopsis homogenates and could be potentially extended to other biological fractionations in substitution of more tedious centrifugation steps. While the nano- isoporous membrane was successfully demonstrated for nanoparticles sieving. Moreover, by presenting the successful fabrication of polyimide isoporous membrane, we have proved that the developed fabrication protocol can be easily adapted to other homopolymeric materials.

(images are not available)

Figure. SEM images of polyester isoporous membrane: (a) cross-section, (b) microporous membrane via photolithography (c) nanoporous membranes via nanoimprint lithography.

Reference 1:

Sabirova, A., Pisig, F., Rayapuram, N., Hirt, H. & Nunes, S. P. Nanofabrication of isoporous membranes for cell fractionation. Scientific reports 10, 1-9 (2020)

NaOCl ageing of Graphene Oxide/Polyethersulfone (GO/PES) Mixed Matrix Membranes

Rabiller-Baudry, Murielle - Co-Author¹; Samhari, Omar - Co-Author^{2,3}; Lesdesma Molinero, Mariel - Co-Author⁴; Alami younsi, Saad - Co-Author⁵

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Main topic: Ageing of polymeric membranes

PES/PVP ultrafiltration membranes are widely used at industrial scale to filter dairy fluids. As the membranes are severely fouled by proteins, chemical cleaning followed by NaOCl disinfection are achieved twice daily at industrial scale to recover the membrane performances. Literature proved that PVP (minor component of the PES + PVP blend) is the Achille's heel of such membranes commonly guaranteed up to 5,000 ppm.d Total Free Chlorine (TFC) dose. However, PES hydrophilisation is required to limit the fouling. The development of low fouling PES membranes without PVP could be a significant improvement if it is associated to a longer membrane lifespan.

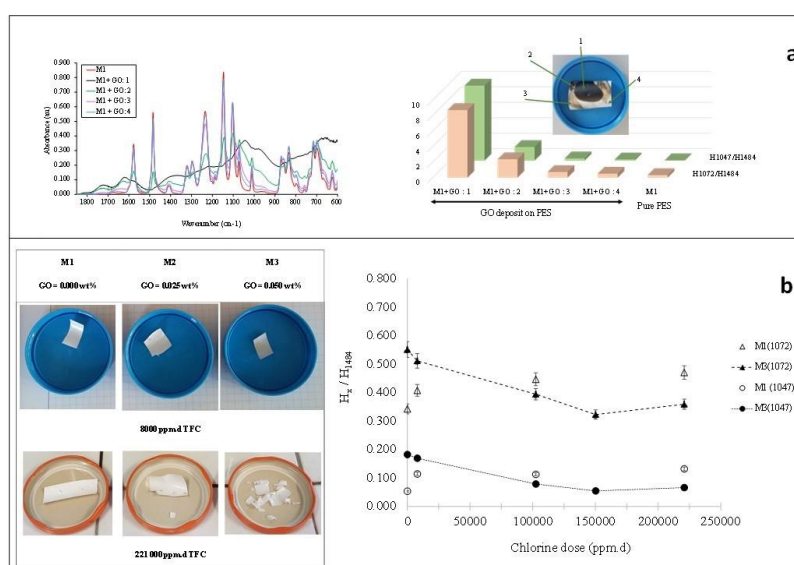
Self-supported Mixed Matrix Membranes (MMM) with graphene oxide (GO) embedded in PES ($M_w = 53\,000\text{ g}\cdot\text{mol}^{-1}$, dispersity = 2.8) were elaborated by the dry/wet phase inversion method using NMP as solvent and water as non-solvent. Different GO concentrations in the dope suspension (0, 0.025 and 0.050 wt%) were tested. First the cloud curves of the ternary phase diagram PES/NMP/water were determined and presence of GO was evidenced to have no significant impact compared to pure PES. All elaborated membranes were proved to be UF membranes with (i) estimated pore radius close to $2.0 \pm 0.2\text{ nm}$. The expected anti-fouling properties due to the GO presence were evidenced by filtering 1/20 diluted skim milk used as a model dairy up to 30 bar.

Elaboration of a supported MMM was successfully achieved on a PP+PE support.

ATR-FTIR was proved to be able to evidence the variation of the GO amount in/on the MMM membranes (Figure 1).

Then self-supported membranes were aged at room temperature in a 8,000 ppm NaOCl solution at pH 12 up to a 221,000 ppm.d TFC dose. ATR-FTIR allowed to evidence the GO protection of PES up to 8,000 ppm.d, then the simultaneous PES degradation and GO departure were progressively evidenced, accompanied by mechanical degradation at the higher TFC doses.

Figure 1: ATR-FTIR evidencing of graphene oxide (GO) on/in self-supported PES based membranes (a) and impact of NaOCl ageing (b)



Natural concentration of Food and Beverage solutions using the Aquaporin Inside® technology

Friis Andersen, Mads - Co-Author

Main topic: Forward osmosis/Pressure retarded osmosis

Natural concentration of Food and Beverage solutions using the Aquaporin Inside® technology

Head of Forward Osmosis Product Development, Mads Friis Andersen¹

Aquaporin A/S, Kgs. Lyngby, Denmark

The concentration of Food and Beverage (F&B) solutions is an established technique in food processing to create concentrates that can be used in further processing or reduce costs of storage and shipping. The concentration step is often performed by Reverse osmosis (20°-30°Brix), freeze-concentration (~50°Brix) and thermal evaporation (>60°Brix). However, common for these technologies is that they require heat or pressure that change the flavor and aroma profile of the original solution and thereby lower the final product quality. The potential of producing higher quality concentrates drives manufacturers to look for alternative technologies ensure full preservation of the unique aromas and flavors in the concentrates.

Natural concentration via Forward Osmosis is a low-energy, low-pressure process for dewatering aqueous solutions. It allows water removal without heat, preserving all nutritional and aromatic compounds, while reaching higher Brix than RO processes which are limited by operational pressure. Due to the high level of valuable retention provided by the Aquaporin Inside® technology concentrates of extreme high the result is high quality can be produced.

This talk will provide further insights into natural concentration using examples of various F&B applications ranging from low brix applications such as coffee using hollow fibers to high brix applications like coconut water using tubular membranes.

Dejaeger, Karlien - Co-Author^{1,2}

¹Ghent University, ²University of Lille

Main topic: Drinking water

Introduction

Natural organic matter (NOM), contained in drinking water resources, negatively affects drinking water quality by acting as nutrients for bacterial regrowth in the distribution system. Chlorine is a common disinfectant to inactivate pathogens, but it also reacts with NOM during disinfection to form disinfection by-products, which are correlated with health issues such as cancer. To identify the precursors that are responsible for the formation of these by-products from the complex NOM mixture, the latter is split into smaller fractions with similar chemical or physical properties. Dead-end ultrafiltration membrane fractionation is the most commonly used technique to split NOM by size, but is unable to produce sharply separated fractions. Therefore, this research will seek for a new membrane fractionation method that separate NOM into biopolymers, humic substances and low, molecular weight compounds. Subsequently, their reactivity towards chlorine and the formation of disinfection by-products will be determined.

Material and Methods

During fractionation, both a normal filtration step and a diafiltration step is executed. A model was constructed that predicts the concentration change for a certain compound during these two steps and was validated with a nanofiltration (Dow NF270). The model will be used to determine the time needed to have a good separation of the organic compounds for a certain water source.

$$\ln \frac{C_{f,t}}{C_{f,0}} = -R * \ln \left(1 - \frac{Q_p}{V_0} * t \right) \quad (\text{normal filtration})$$

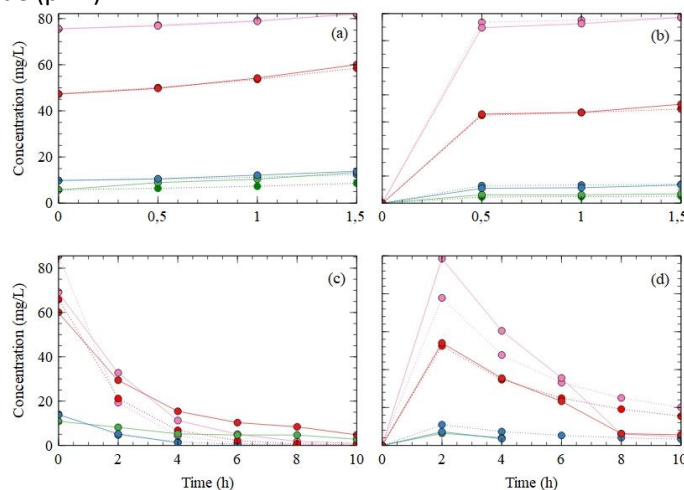
$$\ln \frac{C_{f,t}}{C_{f,0}} = (R - 1) \frac{Q_p}{V_0} * t \quad (\text{diafiltration})$$

With C_f the concentration of the compound in the feed tank, R the retention, Q_p the flowrate and V_0 the initial feed volume.

Results and Conclusion

Figure 1 clearly shows that the model fits the experimental data very well during normal filtration mode (a,b). The fit during diafiltration is less accurate, but is rather explained by experimental variation (discontinuous adjustment of feed volume). The model will be equally validated with NOM concentrations and used to optimize membrane fractionation conditions.

Figure 1: Ion concentrations in (a),(c) retentate and (b),(d) permeate during normal filtration ((a),(b)) and diafiltration ((c),(d)). Full lines represent experimental data, dotted lines predicted data of sodium (red), potassium (blue), magnesium (green) and chloride (pink).



Falca, Gheorghe - Co-Author

Main topic: Organic solvent nanofiltration

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King Abdullah University of Science and Technology, Biological and Environmental Science Engineering Division (BESE), 23955-6900 Thuwal, Saudi Arabia

Interfacial polymerization (IP) is the most widely used method to produce thin-film composite membranes for nanofiltration and reverse osmosis. While water constitutes the polar phase in which amino-functionalized monomers are dissolved, organic solvents like hexane and toluene are frequently used as apolar phase for the acid chloride monomers. The goal of this work is their substitution by greener and renewable solvents making the membrane fabrication more environmentally friendly. We report the production of an interfacially polymerized film using oleic acid (Figure 1) as IP organic phase. Oleic acid has nearly zero vapor pressure and high temperature stability. Monomer concentrations from 0.02 to 2 wt%, temperature from 25 to 60 °C were investigated as preparation conditions. The polyamide crosslinked formation was confirmed by spectroscopic methods (e. g. XPS and FTIR). Scanning electron microscopy (SEM) images revealed the difference between the various polymerization conditions, going from a smooth layer for low trimesoyl chloride (TMC) concentration (0.02 wt%, 1 minute reaction) to a thicker self-assembled structure as the concentration and reaction time increased up to 0.8 wt% and 60 minutes reaction time. Figure 1 shows morphologies observed for 2 selected conditions. Transmission electron microscopy images indicated that the thickness of the thin polyamide films obtained with 0.02 wt% TMC was 20 nm or lower. The thickness increased with the reaction time. No pronounced effect was seen by varying the temperature or monomer concentration. The thinner membranes had a high permeance of 38 and 13 L m⁻² h⁻¹ with a molecular weight cut-off of 420 and 580 g mol⁻¹ for water and methanol respectively, confirming an attractive performance for nanofiltration.

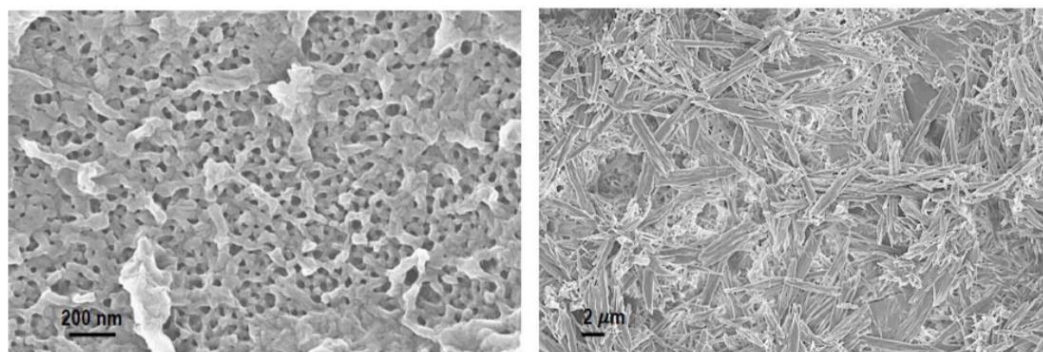


Figure 1. SEM images of polyamide films obtained with oleic acid as non-polar solvent for interfacial polymerization with (a) 0.2 wt% TMC, reaction time 10 min, and (b) 0.8 wt% TMC, 3h reaction time.

Navigating the balance between combined nanofiltration and UV/H₂O₂ oxidation for organic micro-pollutant removal

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¹Membrane Science & Technology, Faculty of Science & Technology, University of Twente, the Netherlands, ²NX Filtration, Enschede, the Netherlands

Main topic: Wastewater treatment

To prevent organic micro-pollutants (OMPs) from entering the environment through wastewater effluent, wastewater treatment plants (WWTPs) need to be extended with a tertiary treatment step. Currently available methods such as oxidation or adsorption can be expensive or unsustainable. For instance, UV peroxide oxidation typically suffers from high energy costs at the relatively low transmittance of WWTP effluent. Therefore, this work proposes to combine an open nanofiltration membrane with UV peroxide oxidation of the permeate, as shown in Figure 1. The membrane is used as a pretreatment step, removing large organics and thus increasing transmittance. When the large organics are removed by the membrane and recirculated to the WWTP, the oxidation step can focus on the removal of OMPs from the permeate. This work aims to find the optimal point of openness of the membrane in terms of costs, while increasing OMP removal compared to only a dense membrane or only advanced oxidation.

Two commercially available and four new membranes are investigated, all based on polyelectrolyte multilayer coatings on hollow fiber supports. Firstly, the membranes are characterized for permeability, MgSO₄ retention and 90% molecular weight cut-off (MWCO), all at different fluxes. The membranes have a pure water permeability between 6 and 117 Lm⁻²h⁻¹bar⁻¹ and a MgSO₄ retention ranging from 0 to 90%. The MWCO varies from 300 Da to 10 kDa and is shown to depend strongly on the applied flux, additionally described using transport models.

The performance of the membranes is also investigated with effluent from a WWTP. The transmittance of the permeate varies from 70 to 98% with feed transmittances of 20 to 45%, showing that especially the denser membranes can increase the transmittance to more than 80%, which is desired for UV peroxide oxidation. Increasing the recovery in batch experiments leads to lower transmittance values. However, the denser membranes can keep the transmittance above 80% even at recoveries of 90%. Finally, an economic analysis is performed, proving that the hybrid process can be affordable with a total cost of ownership of 0.09 €/m³ while meeting an OMP removal rate of 80-90%.

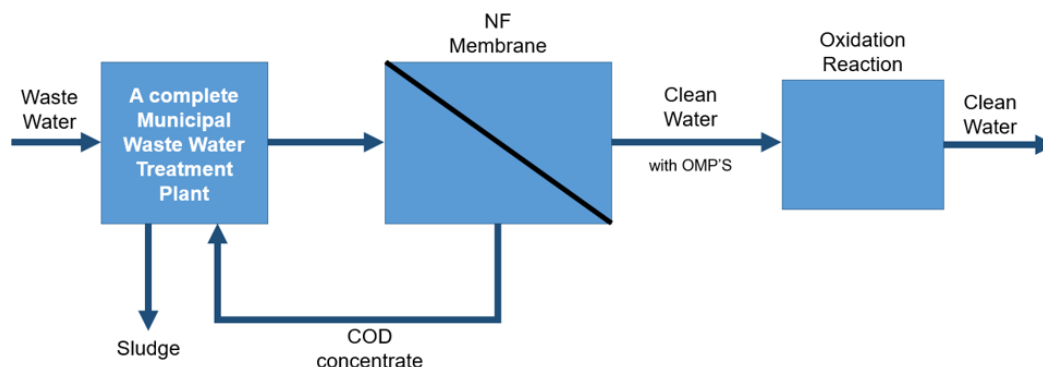


Figure 1: Process flow diagram of OMP removal from wastewater by combining a municipal waste water treatment plant with a nanofiltration membrane and an oxidation reaction

Nernst-Planck transport theory for bipolar electro dialysis: effect of salt leakage in bipolar membranes

Tedesco, Michele - Co-Author¹

¹Wetsus, European Centre of Excellence for Sustainable Water Technology

Main topic: Electro-membrane processes

Background

Bipolar membranes (BPMs) are mainly used nowadays for acid/base production via bipolar electro dialysis (BMED) [1]. Ideally, a BPM should promote only the transport of water molecules inside the membrane, where the production of protons and hydroxyls takes place due to water dissociation. However, other ions in solution will transfer through the BPM to some extent, thus affecting the pH evolution inside the membrane, and therefore the process performance. The aim of this work is to investigate theoretically and experimentally the ion transport in BPMs, taking into account the transport of four ions (Na^+ , Cl^- , H^+ , OH^-) inside the membrane.

Materials and Methods

We theoretically investigate the membrane behaviour by adopting a model based on the Nernst-Planck theory [2], where the BPM is modelled as two ion-exchange layers with constant fixed charge density. The model uses only the membrane thickness and charge density as input parameters, and predicts the concentration profiles of all the ions inside the membrane. We compared the model results with original experimental data collected using commercial BPMs under different feed conditions.

Results

The model shows a good agreement with experimental data. In particular, it shows that the electrolyte bulk concentration significantly affects the pH evolution, due to the competing ion transport inside the bipolar membrane.

Conclusions

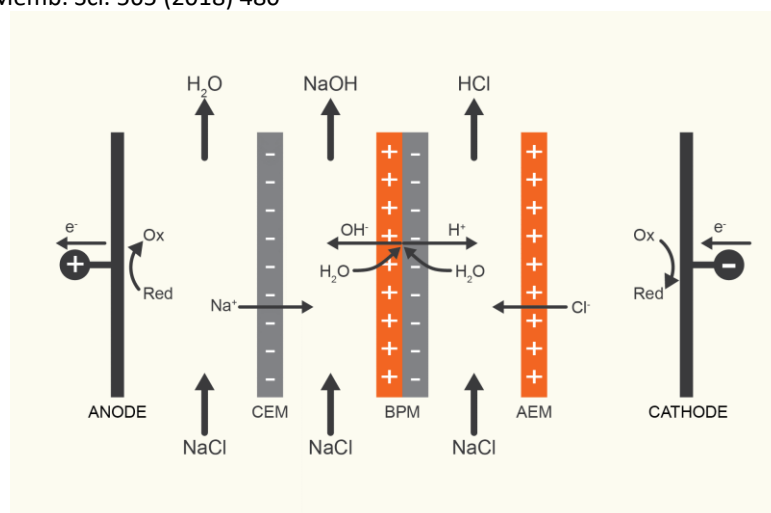
This work aims to understand the effect of salt concentration in the BMED process, to identify the optimal range of operating conditions (i.e., current density, bulk concentration) for enhancing current efficiency and water dissociation in bipolar membranes. A fundamental understanding of ion transport in BPMs is of high importance, especially nowadays that BPMs are used for different novel applications.

Reference 1:

R. Parnamae, ..., Tedesco, "Bipolar membranes: A review on principles, latest developments, and applications", J. Memb. Sci. 617 (2021) 118538

Reference 2:

M. Tedesco et al, "Nernst-Planck transport theory for (reverse) electro dialysis: III. Optimal membrane thickness for enhanced process performance", J. Memb. Sci. 565 (2018) 480



New membrane characterisation from the support to the skin layer applied to SiC membranes

trevisan, mathilda - Main Author; vicente, jerome - Co-Author; ghidossi, remy - Co-Author; moulin, philippe - Co-Author¹

¹aix marseille university

Main topic: New characterisation methods

The use of mineral membranes is becoming more and more important compared to organic membranes thanks to the advantages such as better thermal and chemical stabilities, superior mechanical resistance and longer lifetime. SiC (silicon carbide) membranes (Saint Gobain, France) are used in many industrial fields as wastewater, oil or wine filtration with very high performances and good retention efficiency. This study proposes the combination of results obtained by the usual techniques of porous materials analysis and by 3D characterization by X-ray tomography to obtain a morphological description of both solid and porous phase on the total thickness of the membrane from 25 to 0.25 μm as pore size. Combination of results on all layers is relevant for the study of SiC membranes, showing not only the surface properties of SiC but also the 3D description of the porous material i.e. support, intermediate layers and separating layer. Hydrophobicity, porosity and tortuosity allows to justify the use and superior performance of SiC membranes for the filtration of loaded liquids. More specifically, the three layers of the membrane analysed by micro and nano tomography and then reconstructed in 3D enabled numerous structural properties to be extracted: average pore diameter, morphology of the constrictions, which are essential information for understanding the passage of particles within the pores during filtration. For the mechanical support and the intermediate layer, the mean pore diameter obtained by analysis of the pore space grain size correlated perfectly with the mean pore size diameters obtained by mercury intrusion porosimetry. The calculated particle accessible volume also provides new and relevant information for the use of SiC membranes: what proportion of the pore space is accessible for a given particle size. For the separation layer, the size of the constrictions, linked to an accessible pore volume is more representative and found to be around 250 nm, consistently with mercury intrusion porosimetry. The calculation of the tortuosity over the whole membrane shows a very low tortuosity of the SiC membranes (~ 1.2) compared to other ceramic membranes which coupled with the other properties highlighted in this study may explain their significantly higher fluxes.

New Mixed Matrix Membranes Made from Polyimides and Porous Organic Polymers Containing Bipyridine Groups for Gas Separation Applications

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¹IU CINQUIMA / Inorganic Chemistry, Science Faculty, University of Valladolid, 47011 Valladolid (Spain)., ²Department of Applied Macromolecular Chemistry, Institute of Polymer Science and Technology, ICTP-CSIC, 28006 Madrid (Spain).,

³Surfaces and porous materials (SMAP), Associated Research Unit to CSIC, University of Valladolid, 47011 Valladolid (Spain).

Main topic: Gas separation

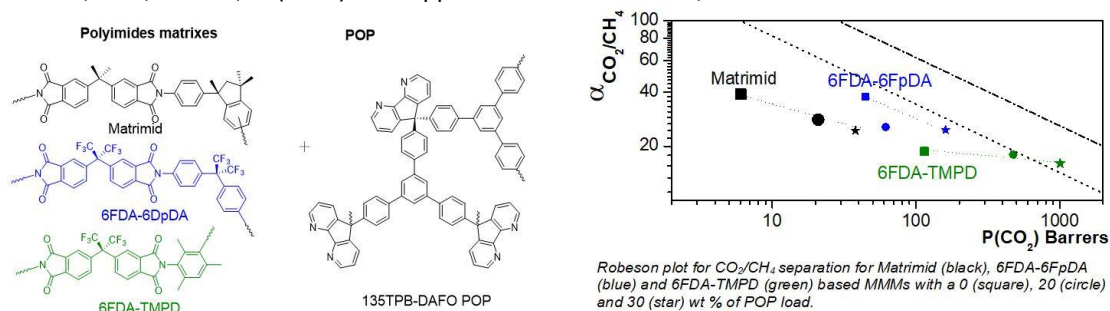
The urgent need to reduce pollution has led to research into new materials for CO₂ capture processes, notably CO₂/N₂ separation of combustion gases and CO₂/CH₄ separation in the natural gas purification process. Membrane-based technology is emerging as a promising alternative to conventional gas separation processes due to its high energy efficiency, low cost and carbon footprint. The addition of a porous polymer (Metal Organic Framework, MOF, or Porous Organic Polymer, POP) to a conventional polymeric membrane has caused great interest because the resulting mixed matrix membrane (MMM) presents the potential to overcome the problematic relationship between permeability and selectivity. [1] In this work new MMMs consisting of variable loads (20-30% w/w) of a porous organic polymer (POP), 1,3,5-triphenylbenzene-4,5-diazafluoren-9-one (135TPB-DAFO), added to different polyimides (Matrimid, 6FDA-6FpDA and 6FDA-TMPD) had been successfully prepared. The POP was synthesized by an electrophilic aromatic substitution reaction between 135TPB and DAFO ketone in a superacid media, trifluoromethanesulphonic acid, resulting in a highly microporous network having a high CO₂ uptake [2], and high chemical and thermal stability, which caused an increase in the degradation temperature and glass transition temperature of MMMs relative to the pure polyimide membranes. SEM images showed morphologies without forming aggregates, which implied a good compatibility between both components, polyimides, and POP. The addition of the POP to polyimide matrix improved the permeability of all gases tested (N₂, O₂, CH₄, CO₂). For instance, gas permeability with a 30% w/w load increased 8-fold as compared with 6FDA-TMPD membrane, whereas CO₂/CH₄ ideal selectivity decreased only by a mere 10%. Therefore, we conclude that this highly microporous material, having good compatibility with polyimides, superior chemical and thermal resistance, and high gas permeability could be a good candidate for the separation of CO₂ over N₂ and CH₄.

Reference 1:

Aguilar-Lugo, C., Suárez-García, F., Hernández, A.; Miguel, J.A., Lozano, A.E., de la Campa, J.G. (2019). *Ind. Eng. Chem. Res.* 58, 9585–9595.

Reference 2:

López-Iglesias, B., Suárez-García, F., Aguilar-Lugo, C., González Ortega, A., Bartolomé, C., Martínez-Illarduya, J.M., de la Campa, J.G., Lozano, A. E., Álvarez, C. (2018). *ACS Appl. Mater. Interfaces.* 10, 26195–26205.



Robeson plot for CO₂/CH₄ separation for Matrimid (black), 6FDA-6FpDA (blue) and 6FDA-TMPD (green) based MMMs with a 0 (square), 20 (circle) and 30 (star) wt % of POP load.

New possibilities for the valorisation of waste aqueous fractions from the essential oil industry using nanofiltration.

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¹University of Chemical Technology and Metallurgy

Main topic: Nanofiltration/Reverse Osmosis

The possibility to fractionate hydrosols and extracts (residual waters) from the steam and hydrodistillation of essential oil plants using nanofiltration was investigated. The separation performance of five commercial nanofiltration membranes with respect to key biologically active components of the studied waste aqueous fractions was predicted based on regression models [1,2]. Membranes of different MWCO, structure and composition were analysed. Descriptors in the models for the membrane rejection were the membrane MWCO and zeta potential as well as solute's molecular weight, octanol-water partition coefficient ($\log P$) and charge at pH of the solution (or pKa). For consistency of the results, $\log P$ and pKa of all studied components were calculated according to the COSMO-RS method, which has the quantum-chemical basis of the Conductor-like Screening Model (COSMO). The calculations were performed using the BIOVIA COSMOsuite software package (Dassault Systèmes SE). The theoretical assessment was subjected to experimental verification by nanofiltration of hydrosols and extracts collected from industrial facilities using commercial polyethersulfone and composite polyamide membranes. The results showed that independently of the membrane material, the polymeric membranes exhibit high retention capability against charged solutes such as the contained in the residual waters phenolic acids. Since the pKa of the phenolic compounds, representatives of the flavonoid family is within the range of pH of the aqueous extracts, their retention or permeation could be controlled by slight variations of the pH. The dissolved in the aqueous fractions essential oil components would be easily permeating through the membranes. These results clearly demonstrated the viability of nanofiltration for isolation of refined polyphenolic fractions from the extracts effluents and for recovery of phenethyl alcohol and eugenol from hydrosols of *Rosa damascena* and cloves respectively.

Reference 1:

K. Boussu, C. Vandecasteele, B. Van der Bruggen, J. Mem. Sci., 310, 51 (2008)

Reference 2:

D. Peshev, Bul. Chem. Commun., 52, 4, 532 (2020)

NF and RO treatment of H₂S scavenging wastewater from offshore oil and gas production

Nikbakht Fini, Mahdi - Co-Author¹; Montesantos, Nikolaos - Co-Author¹; Maschietti, Marco - Co-Author¹; Muff, Jens - Main Author¹

¹Section of Chemical Science and Engineering, Department of Chemistry and Bioscience, Aalborg University

Main topic: Environmental applications

After removing H₂S from natural gas in offshore oil and gas installations, triazine-based spent scavenger solution remains as a wastewater stream, which in some cases is discharged untreated into the sea.

Three nanofiltration (NF) membranes (NF270, NF99HF, and DL), as well as a reverse osmosis (RO) membrane (XLE), were used for TOC reduction from spent and unspent scavenger (SUS) wastewater. The NF270 membrane reduced the TOC of SUS wastewater (61.5 g/L) by 65% while having a superior permeate flux compared to the other studied membranes and thus was subjected to elaborated study. In particular, this membrane showed a separation between the unreacted/unspent scavenger triazine (1,3,5-tris(2-hydroxy-ethyl)hexahydro-*s*-triazine, HET) and the main spent scavenger reaction product (5-(2-hydroxyethyl)hexahydro-1,3,5-dithiazine, DTZ) as it removed HET by 71% versus zero removal of DTZ. DTZ is a polar and hydrophobic molecule and consequently passes readily through the membrane despite an expected removal value of 50% based on a simple size exclusion pore flow model. The NF270 permeate was then used as a feed for RO filtration by the XLE membrane to further reduce the TOC of effluent stream by 98% (1.1 g/L). Lastly, both membranes were resistant towards fouling when they were tested in 24 h experiments with a constant-concentration feed. An overview of the combined processes is illustrated in Figure 1. A promising aspect of treating the SUS wastewater by membrane separation is the potential for recovery and recycling of scavenger chemicals (HET and monoethanol amine, MEA) from the spent scavenger compound (DTZ). As seen from the composition of the NF retentate, the fraction of DTZ declined from 25% in the SUS feed to 17%, whereas the fraction of HET in this stream increased to 59%, from 50% in the initial feed.

This paper is the first published study on SUS wastewater treatment using membrane technology proving its applicability. The study was funded by the Danish Hydrocarbon Research and Technology Center (DHRTC).

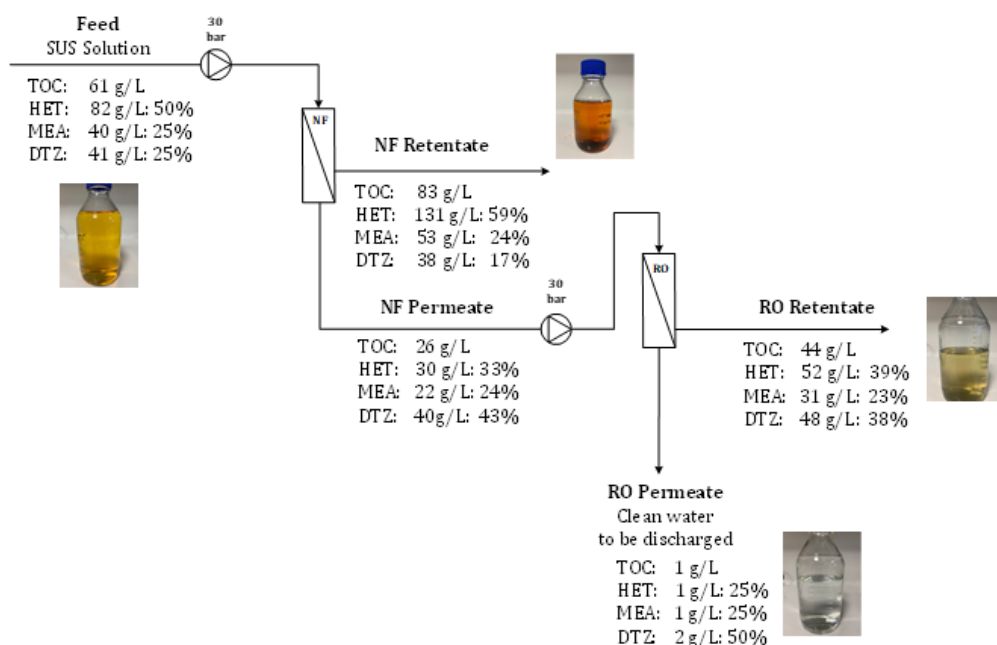


Figure 1. Schematic illustration of a combined NF and RO process, with concentration and mass fraction (water-free basis) of the specific compound indicated.

Nitrogen recovery from sludge centrate by means of membrane contactor

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¹University Research Institute for Industrial, Radiophysical and Environmental Safety (ISIRYM), Universitat Politècnica de València, Spain., ²Department of Chemical and Nuclear Engineering, Universitat Politècnica de València, Spain, ³University Research Institute for Industrial, Radiophysical and Environmental Safety (ISIRYM), Universitat Politècnica de València, Spain

Main topic: Membrane contactors and membrane distillation

The sludge generated in an urban wastewater treatment plant must be treated before disposal in order to decrease its volume and reduce the impact on the environment. Anaerobic digestion is an extensively sludge treatment method that achieves an organic matter reduction and bioenergy generation. After anaerobic digestion, the sludge is dehydrated by centrifugation. The liquid stream after centrifugation process is commonly called sludge centrate. This waste has a high content in nitrogen and phosphorous and must be returned to the head of work for treatment or manage separately [1]. However, the recovery of nutrients from this stream could be an excellent opportunity for fertilizer production and is getting increased attention. Membrane contactor is a promising technology what includes a membrane module with a porous hydrophobic membrane that acts as a selective barrier between the wastewater and the receiving agent. The hydrophobic character of the membrane allows ammonia permeation in vapour phase across the membrane. The receiving agent reacts with the ammonia at the interface and it can be recovered the ammonia as an ammonium salt and it can be used it as fertilizer product [2].

The main idea of this study was to treat sludge centrate and recovery the ammonia nitrogen by means of membrane contactor, using sulfuric acid. In this way, a laboratory membrane contactor model "X50 2.5×8 Liqui-Cel®" (3M, USA) was used for the experiments. The sludge centrate was previously filtered with a 5 µm cartridge filter and then was ultrafiltered with a 5 kDa ultrafiltration membrane. The influence of the concentration of the acid solution, pH of the wastewater and flow rate of the feed and acid stream were varied in order to study the influence on the ammonium nitrogen removal efficiency. In this way, a total of 8 experiments with a duration of 2 hours were carried out in this study (Table 1).

The ammonium nitrogen concentration was measured in the wastewater at the beginning and at the end of the experiment using kits from Merck. In addition, at the end of the experiments was also measured the ammonium nitrogen content in the acid solution in order to control the total mass balance of the process. Results demonstrated that test number 1, 3, 5 and 6 achieved an ammonium nitrogen removal efficiency higher than 99%. These results showed that the best acid concentration was 0.1 M and the optimal pH was 10. The flow rate had not influence on the results. In general terms, it can be concluded that the membrane contactor technology was an effective technique to recover ammonium nitrogen since all the experiments obtained ammonium nitrogen removal efficiencies higher than 60-70%.

Reference 1:

R.W. Holloway, A.E. Childress, K.E. Dennett, T.Y. Cath, Forward osmosis for concentration of anaerobic digester centrate, *Water Res.* 41 (2007) 4005–4014. doi:10.1016/j.watres.2007.05.054

Reference 2:

S. Yu, Y. Qin, Q. Zhao, M. Li, H. Yu, G. Kang, Y. Cao, Nafion-PTFE hollow fiber composite membranes for ammonia removal and recovery using an aqueous-organic membrane contactor, *Sep. Purif. Technol.* 271 (2021) 118856. doi:10.1016/j.seppur.2021.118856.

Table 1: Experimental conditions for the experiments.

| Test | Wastewater pH | Wastewater flow rate (L/h) | Acid flow rate (L/h) | Acid concentration (M) |
|------|---------------|----------------------------|----------------------|------------------------|
| 1 | 10 | 25 | 25 | 0.10 |
| 2 | 10 | 25 | 25 | 0.05 |
| 3 | 9 | 25 | 25 | 0.10 |
| 4 | 9 | 25 | 25 | 0.05 |
| 5 | 10 | 30 | 15 | 0.10 |
| 6 | 10 | 30 | 15 | 0.05 |
| 7 | 9 | 30 | 15 | 0.10 |
| 8 | 9 | 30 | 15 | 0.05 |

NOVEL ANION EXCHANGE MEMBRANES FOR USE IN ALKALINE ELECTROLYSERS

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Main topic: Novel membrane materials

There were prepared anion exchange membranes based on polymer backbone of block copolymer PSEBS (polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene), that was chloromethylated by „indirect method“, cast on Teflon plate and subsequently reacted with 1,4-diazabicyclo[2.2.2]octane (DABCO). Obtained membranes show high hydroxide conductivity 6.0; 7.2 and 7.5 S m⁻¹ at 30, 50 a 70 °C. Membranes show high stability in concentrated KOH. Same polymer was used for binder of catalyst, where it showed higher current densities than PFTE.

Hydroxide conductivity of PSEBS CM DABCO membrane compared to commercial FuMA Tech FAA-3-50 membrane

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 875118. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme, Hydrogen Europe and Hydrogen Europe Research

Reference 1:

J. Electrochem. En. Conv. Stor. May 2021, 18(2): 024001

Novel aroma-based hydrophobic deep eutectic solvents for sustainable production of nanoemulsions by membrane emulsification for enhanced antifungal and antibacterial activities

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¹LAQV/Requimte, Department of Chemistry, NOVA School of Science and Technology, FCT NOVA, NOVA University of Lisbon, ²Department of Chemical Engineering and Environmental Technology, University of Zaragoza, ³Faculty of Pharmacy, University of Porto, Porto, ⁴Instituto de Biologia Experimental e Tecnológica [iBET], Oeiras, ⁵Instituto de Tecnologia Química e Biológica, NOVA University of Lisbon, ⁶iBET - Instituto de Biologia Experimental e Tecnológica, Oeiras, ⁷Department of Organic Chemistry, University of Zaragoza

Main topic: Membrane emulsification

Hydrophobic deep eutectic solvents (DESs) are a recent class of green solvents that offer 100% atom economy, low cost, potential biodegradability and negligible toxicity [1]. In this work, novel aroma-based therapeutic hydrophobic DESs were synthesised and dispersed in aqueous media by a membrane emulsification technique to potentiate biomedical applications, where polar media is encountered.

A microengineered stainless-steel isoporous membrane (9 µm pores; 100 µm pitch) was fabricated by a low energy-intensive laser drilling technique. This robust membrane was reused numerous times unlike other membrane materials [2]. Three novel hydrophobic DES systems were successfully synthesized; DES A comprising of menthol and vanillin, DES B comprising of menthol and raspberry ketone, and DES C comprising of thymol and raspberry ketone. Based on Karl-Fischer titration (water content: <0.5%) and viscosity measurements, 9:1 molar ratio of all the DESs were screened as dispersed phase for further emulsification studies. A 2% (w/w) Tween 80 solution was recirculated as continuous phase with cross-flow velocity of 150 ml.min⁻¹. Among the 2%, 4% and 6% (v/v) dispersed phase concentrations tested, 4% (v/v) DES C operated at a dispersed phase flowrate of 0.05 ml.min⁻¹ was established as the optimised nanoemulsion, exhibiting a monomodal distribution of emulsion droplets of 146.8 ± 0.5 nm size and polydispersity index of 0.22 (see Fig. 1). Interestingly, although a 9 µm pore-sized membrane was used, we were able to formulate uniform emulsion droplets of ~147 nm. This effect might be attributed to the self-assembly traits of DES in an emulsion system [2].

From the application perspective, these DES-in-water nanoemulsions were evaluated for their antifungal and antibacterial properties. Four fungi strains, namely, *Aspergillus fumigatus*, *Candida albicans*, *Candida krusei* and *Trichophyton mentagrophytes*, and two bacterial strains, gram-positive *S. aureus* and gram-negative *E. coli* were tested against the individual compounds, synthesised DES and optimised nanoemulsion to determine the MIC (minimum inhibitory concentration) and MFC/MBC (minimum fungicidal/bactericidal concentration) values (see Table 1). The therapeutic effect of raspberry ketone was enhanced ~100x when present with thymol in DES or in the nanoemulsions. Furthermore, these nanoemulsions were effective against all the tested microorganisms. Lastly, a synergetic effect of the components of nanoemulsion led to enhanced antimicrobial activities.

Reference 1:

Cao, Jun, and Erzheng Su. "Hydrophobic deep eutectic solvents: The new generation of green solvents for diversified and colorful applications in green chemistry." *Journal of Cleaner Production* (2021): 127965.

Reference 2:

Syed, Usman T., et al. "Microengineered Membranes for Sustainable Production of Hydrophobic Deep Eutectic Solvent-Based Nanoemulsions by Membrane Emulsification for Enhanced Antimicrobial Activity." *ACS Sustainable Chemistry & Engineering* 8.44 (2020): 16526-16536.

Characterisation of the optimised DES-in-water nanoemulsion

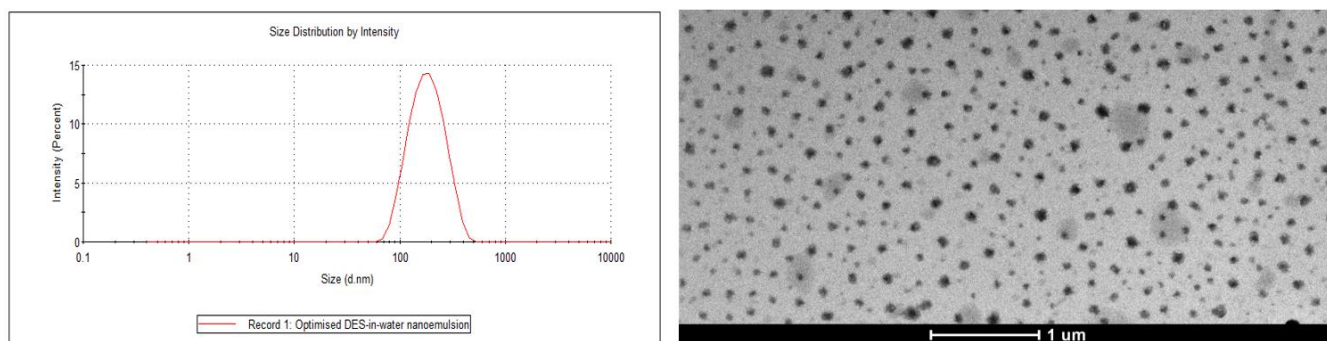


Fig. 1: DLS and TEM images of the optimised nanoemulsion

Novel CO₂ gas separation membranes prepared by chemical modification of highly permeable polymers

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Main topic: CO₂ capture

Background

Despite the development of new polymeric materials for CO₂ capture membranes such as thermal rearranged polymers, polymers with intrinsic micro porosity, only three membranes have arrived at the stage of testing at pilot scale with real flue gas: the FSC from NTNU, Polyactive from HZG and the Polaris from MTR. The approaches of current gas separation membranes are based on increasing either the CO₂ solubility or CO₂ diffusivity over N₂ by using different methods to increase the free volume of polymers and their sieving capacity.

Materials and methods

Our approach is based on modifying in precise and controlled manner polymers and their membrane surfaces with CO₂ reactive groups. This will lead to ultrathin CO₂ selective regions (nanometer scale) which will further decrease the mass transfer resistance of CO₂ through membranes. This represents a new approach in gas separation membranes that mitigates the risks associated with use of polymer blends, addition of various CO₂ enhancement materials (nanoparticles, etc): incompatibility between materials, and difficulty in upscaling membranes.

We will report membrane preparation by using surface grafting of Teflon AF 2400, polydimethylsiloxane (PDMS) membranes with CO₂-philic groups and will discuss the influence of various parameters on membranes structure and their separation performances. A variety of new functionalities can be integrated on surfaces, for instance amino groups, by applying various grafting techniques and procedures. The density of the grafting can be varied by varying the initiator concentration, and the length of the polymer chains grafted on the surface can be varied by varying both the monomer concentration and the UV exposure time.

Results

The uniformity of grafting plays a major role on separation properties and is dependent on grafting conditions, contact angle, type of solvents used etc. Excessive crosslinking due to some grafting conditions and certain monomers reduced the expected CO₂ flux and needed to be further investigate.

The membranes structure is characterized by SEM pictures and FT-IR, XPS. The structural characterization is correlated with the results from mixed gas permeation testing using a synthetic flue gas: 10 % CO₂ in N₂, fully humidified.

Conclusions

Excellent gas permeation results were obtained with CO₂ permeabilities in excess of 1000 Barrer and CO₂/N₂ selectivity greater than 100.

Reference 1:

Acknowledgements: This study was supported by the Research Council of Norway through the POLYMEM project (Grant No. 254791) in the CLIMIT program and UEFSCDI Romania through the CO₂Hybrid project (Grant No. 13/2020)

Numerical methods and 3D tomography boost the prediction of fluid transport in novel diagnostic membranes

Bohr, Sven Johann - Co-Author; Kneer, S. Barbe – Co-Author

Main topic: Fluid dynamics

ABSTRACT:

The relevance of diagnostic membranes increased dramatically due to the COVID-19 pandemic. They are essential in point-of-care testing with lateral flow antibody tests. Improving their reliability while lowering the use of antibody conjugates requires the understanding and prediction of fluid transport within diagnostic membranes.

The Lucas-Washburn differential equation gives an accurate mathematical description of capillary fluid transport through porous structures, such as macroporous membranes. The prediction of the fluid transport is based on the physical properties of the transported fluid and the membrane parameters like porosity, permeability and effective pore radius. In this regard, a solver based on the Lucas-Washburn differential equation was implemented, to determine the influence of the different membrane parameters on the wicking speed performance and to find the optimum set of parameters for a fast sample transport along a porous structure.

In this work, we explore the potential of strong asymmetric membranes to enhance fluid transport within diagnostic membranes. For this purpose, a novel polymer solvent system was developed that allows a very fast surface fluid transport.

The description of the fluid transport inside an asymmetric membrane becomes more complex and this research demonstrates how the Lucas-Washburn solver assisted by 3D tomographs can help membrane scientists to predict and better understand the fluid transport within diagnostic membranes.

Olive leaves biorefinery for production and formulation of phytotherapeutic compounds by integrated membrane processes

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Main topic: Bio-separations and bio-refinery

The olive leaves are considered a rich source of biophenols with various pharmacological properties. Oleuropein is the major phenolic compound found in the olive leaves extract, which can be converted to oleuropein aglycone (OA) by enzymatic hydrolysis. The OA is not yet commercially available, and it is gaining interest due to anti-Alzheimer's disease, anti-breast cancer, anti-inflammatory, anti-hyperglycemic and antioxidant properties [1].

The development of eco-friendly strategies for the valorization of this renewable waste through the production of phytotherapeutic compounds is an important challenge in the perspective of the circular economy. The purpose of this work was to promote the development of integrated membrane processes for the bioproduction of oleuropein aglycone and its encapsulation in microparticles based on a hydrophilic or hydrophobic matrix. The OA rearranges in different isomers in the aqueous phase after the production and lost preferred properties, therefore an extraction and stabilization of phenolic compound in a green organic solvent were carried out by membrane emulsification (ME). Olive leaves valorization was accomplished via bioconversion of oleuropein (contained in olive leaves) to the OA using a lab-scale prototype biocatalytic membrane reactor. Subsequently, OA was encapsulated in solid lipid or polymeric microparticles by ME. In the case of OA encapsulation in the hydrophobic matrix, it was initially extracted in the organic phase (ethyl acetate) and then encapsulated in solid lipid microparticles by ME. The biocatalytic membrane reactor with immobilized β -glucosidase promoted continuous production of oleuropein aglycone with a conversion of 40% at each passage of the oleuropein through the catalytic membrane, while the membrane emulsification process allowed obtaining oleuropein aglycone extraction (90%) in ethyl acetate and the production of solid lipid or polymeric microparticles with tuned size, high encapsulation efficiency of OA and low energy consumption compared to traditional device.

Acknowledgements

The work was carried out within the RAVEL project funded within the POR CALABRIA FESR-FSE 2014-2020.

Reference 1:

Mazzei R., Piacentini E., Nardi M., Poerio T., Bazzarelli F., Procopio A., Di Gioia M. L., Rizza P., Ceraldi R., Morelli C., Giorno L., Pellegrino M., *Frontiers in bioengineering and biotechnology*, 8 (2020) 908.

On-board high purity hydrogen production by low temperature ammonia decomposition using a Hollow Fibre Membrane Converter

Mazzone, Simona - Co-Author; Zhang, Guangru - Co-Author; Li, Kang - Co-Author; Garcia-Garcia, Francisco R. - Co-Author

Main topic: Membrane reactors

Green ammonia, liquid at room temperature and low pressure conditions, has been proposed as a promising hydrogen carrier candidate for on-board hydrogen production at low temperature. Unlike steam reforming of fossil fuels, ammonia decomposition allows for hydrogen production avoiding CO₂ emissions, without requiring a water tank and steam generation¹. However, thermodynamic limitations of ammonia decomposition reaction at low temperature (*i.e.* $x_{\text{NH}_3} = 100\%$ at $T \geq 450^\circ\text{C}$) and the ammonia poisoning effect on the fuel cell's anode, still present challenges in the adoption of green ammonia as a future fuel carrier for vehicular applications.

The use of a hollow fiber membrane converter (HFMC) offers the opportunity for addressing these challenges, opening the door for a new line of catalytic converters for on-board applications. In this respect, the HFMC would combine both the reaction and separation units integrating a palladium membrane with a 100% selectivity to hydrogen and high permeability. By Le Chatelier's principle, the membrane allows to increase the ammonia conversion beyond thermodynamic equilibrium limits by continuously removing one of the reaction products, enabling the membrane reactor to produce high-purity hydrogen at lower temperatures than conventional catalytic reactors. Furthermore, the use of a highly selective membrane avoids traces of ammonia poisoning fuel cell's anode feed stream. For the development of the HFMC for the ammonia decomposition reaction, asymmetric $\alpha\text{-Al}_2\text{O}_3$ hollow fibers have been used as a support of a palladium membrane, due to their narrow pore size distribution of their outer surface (*i.e.* 0.1 μm) and high surface area/volume ratio². Furthermore, a ruthenium-based catalyst has been packed in contact with the membrane in the shell side of the reactor (see Figure 1).

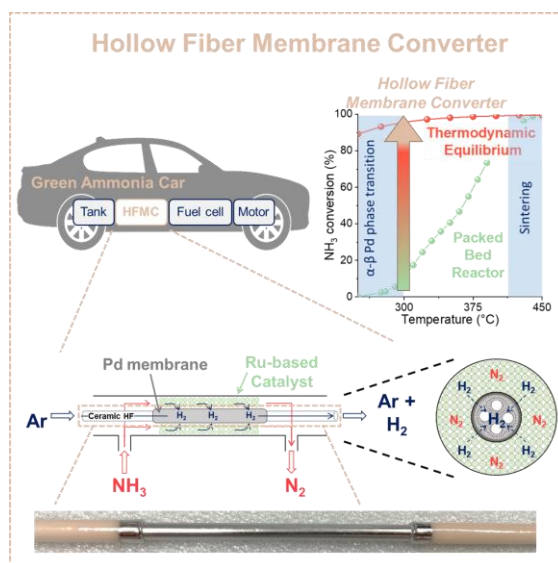
The main scope of this work is to study the feasibility of a HFMC for on-board hydrogen production at low temperature. To avoid damaging the membrane, compromising its selectivity and mechanical strength, the performance of the HFMC will be assessed between 300°C and 450°C and successively compared with the performance of a traditional packed bed reactor.

Reference 1:

Chiuta, S.; Everson, R. C.; Neomagus, H. W. J. P.; van der Gryp, P.; Bessarabov, D. G. Reactor Technology Options for Distributed Hydrogen Generation via Ammonia Decomposition: A Review. *Int. J. Hydrogen Energy* 2013, 38 (35), 14968–14991.

Reference 2:

García-García, F. R.; Li, K. New Catalytic Reactors Prepared from Symmetric and Asymmetric Ceramic Hollow Fibres. *Appl. Catal. A Gen.* 2013, 456, 1–10.



One-Step Grafting of Bovine Serum Albumin Protein on Polymer Membranes

Schmidt, Martin - Main Author¹; Abdul Latif, Amira - Co-Author¹; Prager, Andrea - Co-Author¹; Gläser, Roger - Co-Author²; Schulze, Agnes - Co-Author¹

¹Leibniz Institute of Surface Engineering (IOM), ²Leipzig University, Institute of Chemical Technology

Main topic: Biomimetic and bioinspired membranes

Immobilization of proteins on polymer membranes offers several benefits for industrial applications, such as prevention of contamination or improved long-term stability. Covalent binding is the most promising way of immobilization, as it allows very strong binding and thus prevents delamination. However, the prevailing chemical coupling methods have significant drawbacks such as multistep reactions, expensive or toxic chemicals, long reaction times, or harsh conditions. Therefore, protein-modified polymer membranes still fall short of their true potential, despite their many advantages in medicine or water treatment. For instance, bovine serum albumin (BSA) has been used to improve blood compatibility by reducing hemolysis or to adsorb bilirubin in treatment of liver diseases[1]. In this study, BSA was covalently coupled to polyvinylidene fluoride (PVDF) flat sheet membranes using a one-step, clean and fast electron beam process. The membrane was impregnated with an aqueous solution of the protein and simultaneously irradiated. According to the principle of radiation-induced graft immobilization (RIGI), activation of the polymer substrate and protein molecules, enhanced by water radiolysis, lead to reactive species rapidly forming covalent bonds[2]. By using the response surface methodology (RSM) as a statistical tool, the BSA grafting yield could be optimized to achieve protein coverage up to 1300 mg/m² (130 µg/cm²), which is one of the highest values reported so far. Furthermore, since no coupling chemicals are required, the impregnation solution could be reused at least five times without any decrease in yield. Due to the high graft yield and the short reaction times, an efficiency 230-times higher than best literature values was calculated for this promising electron beam processing technology. This method eventually enables the development of innovative materials applying a variety of exciting biomolecules such as antimicrobial peptides, medical proteins or biocatalytically active enzymes.

Reference 1:

K. Wu, et al.: Immobilization of bovine serum albumin via mussel-inspired polydopamine coating on electrospun polyethersulfone (PES) fiber mat for effective bilirubin adsorption, *Applied Surface Science* 451 (2018) 45-55.

Reference 2:

M. Schmidt, et al.: Radiation-Induced Graft Immobilization (RIGI): Covalent Binding of Non-Vinyl Compounds on Polymer Membranes, *Polymers* 13 (2021).

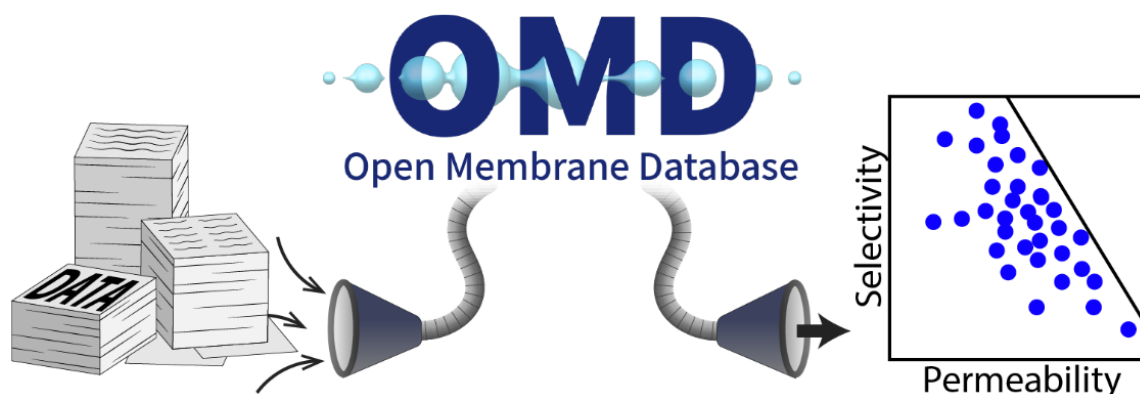
Open-access synthesis–structure–performance database for reverse osmosis membranes: The OMD

Nulens, Ines - Co-Author¹; Ritt, Cody - Main Author²; Stassin, Timothée - Co-Author¹; Davenport, Douglas - Co-Author¹; DuChanois, Ryan - Co-Author²; Yang, Zhe - Co-Author³; Ben-Zvi, Adi - Co-Author⁴; Segev-Mark, Naama - Co-Author⁴; Ramon, Guy - Co-Author⁴; Vankelecom, Ivo - Co-Author¹; Verbeke, Rhea - Co-Author¹

¹KU Leuven, ²Yale University, ³University of Hong Kong, ⁴Technion-Israel Institute of Technology

Main topic: Nanofiltration/Reverse Osmosis

Since the advent of thin film composite polyamide membranes over 50 years ago, the permselectivity of water purification and desalination membranes has improved only marginally. The slow progression is partly attributable to limited understanding of membrane synthesis–structure–performance relationships. A centralized archive of membrane characterization data may lead to a shared understanding of features that maximize performance and unify research efforts. The Open Membrane Database, which launches online in late 2021, is a database of over 600 water purification and desalination membranes that are sourced from peer-reviewed journals, patents, and commercial product data. Here, we outline the detailed functionality of the database and the transport theory underlying the performance calculations. The open-access database may be used to benchmark novel membranes against the state of the art, conduct meta-analyses, and develop synthesis–structure–performance relationships, each of which will be critical to advancing membrane development.



Optimization of flow electrode channel geometry to boost the desalination performance in membrane flow capacitive deionization

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¹LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, Universidade NOVA de Lisboa

Main topic: Fluid dynamics

Abstract: Membrane flow capacitive deionization (MFCDI) is a new and promising desalination technology at which flow electrodes (flowable carbon slurries) are used to remove ions from saline water based on the electro-sorption principle. MFCDI performance depends on operation conditions, cell architecture and physical properties of its components. The geometry of flow electrode channels, which provide the path and ensure distribution and mixing of the flow electrodes, is considered as one of the most important aspects to be optimised. Herein, flow electrode channel gaskets were 3D printed, instead of carving them on current collector's surfaces, and three different geometries were investigated: open, horizontal serpentine and vertical serpentine. Electrochemical and rheological studies were carried out to understand and select the best flow electrode channel geometry in terms of mass (salt) transport and the flowability of the electrodes in a MFCDI cell. Desalination tests performed with flow electrodes containing 10 wt.% of commercial activated carbon (AC) revealed that salt adsorption capacity in a FCDI cell with horizontal serpentine flow electrode channels was the highest one (16.44 mg/g), while during the operation of FCDI cell with vertical serpentine flow electrode gaskets, the flow electrode channels clogged. To elucidate these results, a computational fluid dynamics (CFD) study showed that the geometry of flow electrode channels has strong impact on the internal pressure drop and the rheology of flow electrodes, thus on their flowability (Figure 1). However, CFD simulations also revealed that none of the studied geometries provide an efficient mixing of flow electrodes, which behave as pseudoplastic fluids, thus it is imperative to develop alternative designs. Currently, we are developing such new designs of flow electrodes channels by exploring the concept of fluidic oscillators with the aim of promoting formation of the Coanda effect.

Acknowledgments: This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N° 869467 (SEArcularMINE) and from Fundação para a Ciência e Tecnologia, I.P. under grant agreement N° PTDC/EQU-EQU/6193/2020 (Se(L)ect(i)vity). This work was also supported by the Associate Laboratory for Green Chemistry – LAQV which is financed by national Portuguese funds from FCT/MCTES (UIDB/50006/2020).

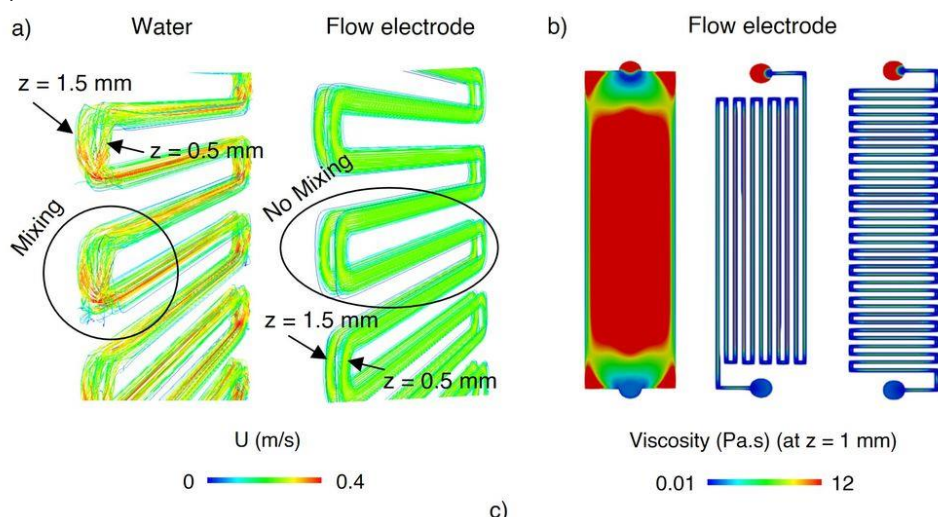


Figure 1: CFD simulations (Laminar regime, Flow rate = 47,1 ml/min, max. Re < 900), for water and flow electrode with 20 wt.% of YP50F, of a) streamlines (fluid pathways) passing through z = 0.5 and 1.5 mm in serpentine horizontal channels, b) slits of viscosity fields in channels with open, serpentine vertical and serpentine horizontal geometries at z = 1 mm (in the middle of channel thickness) and c) values of pressure drop.

| Geometry | Pressure drop (mbar) | |
|-----------------------|----------------------|-----------|
| | Water | 20 wt% AC |
| Open | 0.063 | 35.55 |
| Serpentine Vertical | 29.69 | 1007.00 |
| Serpentine Horizontal | 43.77 | 995.86 |

Organic Solvent Nanofiltration for Catalytic Recycling of Plastic Residues (iCAREPLAST)

van Lin, Rick - Co-Author¹; de Wit, Patrick - Co-Author¹; Visser, Tymen - Co-Author¹

¹EMI Twente

Main topic: Organic solvent nanofiltration

Approximately 70% of European plastic waste (18.5 Mt/year) is not being recycled due to technical or economic reasons and are thus sent to landfill (27%) or incinerated (42%). This situation affects negatively the environment in terms of pollution and greenhouse gases emissions, as well as social perception regarding waste management, consumer's products industry and policy makers.

The 'Integrated Catalytic Recycling of Plastic Residues Into Added-Value Chemicals' (iCAREPLAST) project addresses the cost and energy-efficient recycling of a large fraction of today's non-recyclable plastics and composites from urban waste. Heterogeneous plastic mixtures will be converted into valuable chemicals (alkylaromatic) via chemical routes comprising sequential catalytic and separation steps.

Organic Solvent Nanofiltration (OSN) could be an enabling technology in the downstream processing of these hydrocarbon mixtures that are obtained after initial pyrolysis of the plastic waste. Many of the traditional separation steps often require large amounts of energy. Organic Solvent Nanofiltration, or a combination of OSN with traditional techniques such as extraction or distillation, is likely to lower energy consumption and to contribute to a cost-effective technology.

Various separation steps of process will be evaluated. In the first separation step, the aim is to separate olefins and aromatics from the pyrolysis liquid; separating the impurities (e.g. oxygenates) and other hydrocarbons. The second step focusses on separating the alkylaromatics (C4-benzene and heavier) obtained at the alkylation step from unreacted olefins and aromatics and lighter by-products.

Here, we will present the evaluation of commercial organic solvent nanofiltration membranes in the upgrading of complex hydrocarbon mixtures obtained during thermal pyrolysis of urban plastic waste. Suitable membranes are evaluated using both model mixtures and real pyrolysis liquids to evaluate their performance and to yield an operating envelope for future upscaling and/or required membrane modification.

Organic solvent nanofiltration from an academic and an industrial perspective

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¹King Abdullah University of Science and Technology, ²GMT Membrantechnik GmbH, ³GMT Mebrantechnik GmbH

Main topic: Organic solvent nanofiltration

This lecture is divided into two parts: part 1 deals with academic research in the field of OSN carried out at KAUST and part 2 describes developments at GMT Membrantechnik, one of the few European companies producing modules for OSN. Problems of transferring academic research into industrial production will be highlighted.

The integration of selective cavitands into the membrane forming polymer structure is a promising approach for enhancing the selectivity of OSN membranes. One of the best studied organic cavitands is cyclodextrin, which contains defined selective cavities. Cyclodextrins are attractive for size-selective molecular separations, and cyclodextrin-based cross-linked polymers have been in preparation for some time. We performed cyclodextrin interfacial polymerization on the surface of a commercial GMT UF membrane. We started with pure and continued with aminated cyclodextrin. Mechanically and chemically stable NF membranes could be manufactured. The high reactivity of the amino-CD enables the manufacturing of coatings using standard manufacturing machines. Noteworthy is the ability of this new membrane type to discriminate between molecules with nearly identical molecular weights but different shapes. A comparison of this membrane with the best commercial and state-of-the-art membranes reveals its outstanding properties.

In spite of the superior performance of the membranes described above their implementation in industrial processes is difficult. In the case of pure cyclodextrin the reaction time for polymerization is too long for a competitive production. The reaction time is short for the aminated CD, but the synthesis makes the monomer expensive and no safety data are available. Hence, GMT focused on the modification of already available composite membranes for organic vapor separation and modified these for different OSN applications. Borsig Membrane Technology implemented the GMT modules in OSN units for industrial customers. Applications among others are conditioning of liquid hydrocarbons and fractionating of liquid process mixtures, concentration and purification of valuable fine chemicals and recycling of lube oil. The largest realized Borsig OSN unit treats a hydrocarbon mixture volume stream of more than 20 t/h.

Reference 1:

T. Huang et al., Ultrathin 2D-layered cyclodextrin membranes for high-performance organic solvent nanofiltration, *Advanced Functional Materials* 30 (4), 2020, 1906797

OSNF Membranes On Low Cost High Quality Ceramic Supports For High Temperature Applications

Sluijter, Soraya - Main Author; van Tuel, Marc - Co-Author; VRies, Frank - Co-Author; Pizzoccaro-Zilamy, Marie-Alix - Co-Author; Luiten, Mieke - Co-Author; Nijmeijer, Arian - Co-Author

Main topic: Organic solvent nanofiltration

Molecular separations account for a huge part of the energy used in the process industry. Replacing or combining traditional energy-intensive techniques like distillation, with organic solvent nanofiltration (OSNF) provides great potential for energy savings and the corresponding advantages for the environment. In the COSMOS project, we contributed to the scale-up hybrid silica and polymer based OSNF membranes using low cost, high quality ceramic supports. Two applications were investigated: separation of aromatic molecules (~200 Da) from aliphatic mixtures at <140 °C and the concentration and recovery of edible oils (~800 Da) in the food industry.

Hybrid(silica) and silica layers were prepared previously by the sol-gel route using respectively 1,2-bis(triethoxysilyl)ethane (BTESE) and tetraethoxysilane as silica source and cetyltrimethylammonium bromide (CTAB) as template for creating tailored pore sizes [1,2]. The silica membranes presented an ultrafiltration molecular weight cut-off (MWCO) values (up to 2300 Da) while the hybrid membranes showed MWCO values in the nanofiltration range (down to 180 Da). However, the permeances were limited (<0.2 kg h⁻¹ bar⁻¹ m⁻²). Recently, it was found that increasing the temperature leads to improved toluene permeance without compromising on retention.

The recipes are being translated to low cost, high quality supports of CoorsTek. A ceramic intermediate layer (γ -Al₂O₃) is required to obtain defect free membranes and this has been successfully applied both on the inside and outside of the hollow ceramic fiber supports of CoorsTek. Hybridsilica and polymeric top layers have been applied on the resulting supports. Details of the membrane preparation recipes and tests in different model mixtures mimicking industrial processes will be presented in this contribution.

Reference 1:

Paradis, G.G., Novel concepts for microporous hybrid silica membranes, PhD Thesis Univ. of Twente, 2012. ; Klotz, M., et al., Synthesis conditions for hexagonal mesoporous silica layers, J. Mat. Chem. 10: 633-669, 2000

Reference 2:

Pizzoccaro-Zilamy, MA. et al. New Generation of Mesoporous Silica Membranes Prepared by a Stöber-Solution Pore-Growth Approach, ACS Appl. Mater. Interfaces 11: 18528–18539, 2019.

Overlimiting mechanisms at ion-exchange membranes

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Main topic: Electro-membrane processes

Electrodialysis and electrodeionization are electro-membrane separation processes viewed as green technologies, allowing water desalination and industrial wastewater processing. Ion separation is provided by ion-exchange membranes (IEMs). Interesting reaction-transport phenomena, such as electroconvection or water splitting, occur on those membranes at high (overlimiting) current densities. These phenomena can enhance or deteriorate the original ion desalination process. While electroconvection intensifies the mass transfer of ions towards the membrane, water-splitting reaction affects the pH of the processed solutions, often leading to unwanted consequences (e.g., membrane scaling).

There are many theoretical and numerical papers investigating electroconvection and water splitting, but not many experimental ones. This contribution investigates the behavior of heterogeneous IEMs in batch and continuous mini-electrodialysers at high current densities experimentally.

A miniaturized homemade cell containing a piece of cation or anion-exchange membrane represents our batch system. We observe the emerging electrokinetic vortices in the solution near the membranes using fluorescein markers and polymeric tracking particles. The observation revealed two types of electroconvection differing in the characteristic length scales. The short-range electroconvection localized in the vicinity of the membrane (within 100 micrometres) is characterized by the very fast and chaotic whirring [1]. The long-range electroconvection manifests itself as two countercurrent vortices with a length scale of around 1 mm. We also determine the effect of water splitting by measuring pH values. The water splitting is of negligible importance at the cation-exchange membrane, and it attains relatively high values at anion-exchange membranes [2].

The miniaturized continuous system allows studying phenomena occurring in a desalination channel under conditions close to the ones in real electrodialysis units. We detected strong electroconvection at the cation-exchange membrane and water splitting at the anion-exchange membrane. The intensity of both processes depends on the position along the desalination channel and the applied current density.

Reference 1:

Belloň, T., et al., Experimental observation of phenomena developing on ion-exchange systems during current-voltage curve measurement. *Journal of Membrane Science*, 2019. 572: p. 607-618.

Reference 2:

Vobecká, L., T. Belloň, and Z. Slouka, Behavior of Embedded Cation-Exchange Particles in a DC Electric Field. *International Journal of Molecular Sciences*, 2019. 20(14).

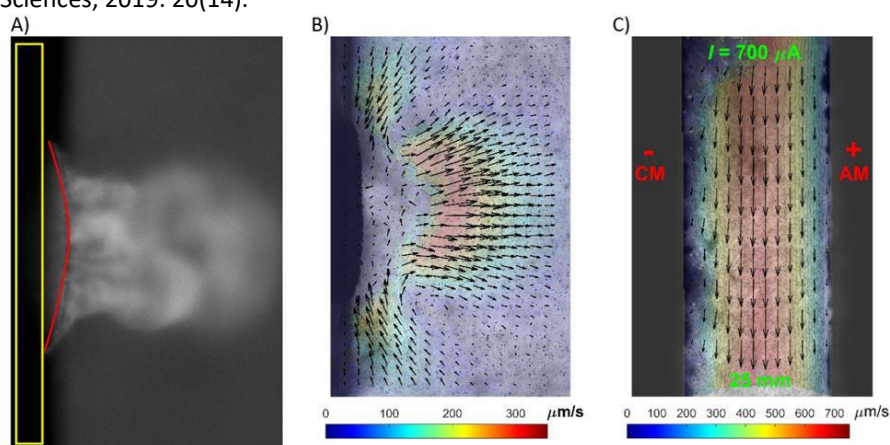


Figure 1. a) Fluorescein-tracked electroconvection on the depleted side of a CEM (red curve) in a batch system. b) PIV-reconstructed velocity vector field around a CEM. c) PIV-reconstructed velocity vector field in a desalination channel of the continuous system.

Theodorakopoulos, George - Main Author¹; Karousos, Dionysis - Co-Author¹; Sapalidis, Andreas - Co-Author¹; Forero, Stefan - Co-Author²; Schubert, Tim - Co-Author³; Favvas, Evangelos - Co-Author¹

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Main topic: Gas separation

Polymeric membranes have stimulated great attention for gas separation, primarily, thanks to their low operating and capital cost, easy fabrication and small footprint. However, polymeric membranes usually suffer from Robeson's trade-off upper bound [1]. The addition of nanofillers into polymer matrices composes mixed matrix membranes (MMMs), which can show simultaneous increase in selectivity and permeability [2].

In this study, a facile and effective method was employed in order to acquire thin film selective layer coated hollow fiber membranes (HFMs) used as support layer without gutter layer leading to improved gas separation performance membranes. The asymmetric HFMs, based on BTDA-TDI/MDI (P84) co-polyimide, were fabricated via the dry-wet phase inversion process used as porous support layer. For the thin film layer preparation, the commercial poly(ether-block-amide) (Pebax[®]-1657) was chosen as a high CO₂-selective material and the influence of the incorporation of graphene nanoplatelets (GNPs) as nanofiller in the polymeric matrix (support) and the thin film layer was evaluated. The dip coating technique was used in order to prepare the selective thin film layer (Fig. 1) onto the HFMs via a custom homemade set-up in single or/and multiple (bundle) mode (Fig. 2). The dip coating process involves the coating of the selective layer (Pebax or Pebax/GNPs) onto the stretched hollow fibers bundle or single hollow fiber at room temperature and the overnight air drying of the membranes on the corresponding scaffolds in vertical position. In order to be coated only the outer surface of the HFs, both HFMs ends were sealed. The application of tensile stress during the immersion procedure and the membrane drying process has a crucial impact to yield defect-free and uniform thin film layer.

The GNPs were characterized by LN₂ adsorption, gas adsorption measurements, SEM and Raman spectroscopy. The derived hollow fiber membranes were characterized by SEM, tensile strength and gas permeability/selectivity measurements with various binary gas mixtures. The studied membranes provide good separation factors of helium and carbon dioxide separations. Specifically, a separation factor of 20 and 56.4 for 10% He/N₂ and 10% CO₂/CH₄ feed concentrations, respectively, were achieved.

Acknowledgments

The project "GG-CO₂", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014–2020) it is acknowledged.

Reference 1:

L.M. Robeson, The upper bound revisited, J. Membr. Sci. 320 (2008) 390–400.

Reference 2:

E.P. Favvas, K.L. Stefanopoulos, J.W. Nolan, S.K. Papageorgiou, A.Ch. Mitropoulos, D. Lairez, Mixed Matrix Hollow Fiber Membranes with enhanced gas permeation properties, Separ. Purif. Technol. 132 (2014) 336–345.

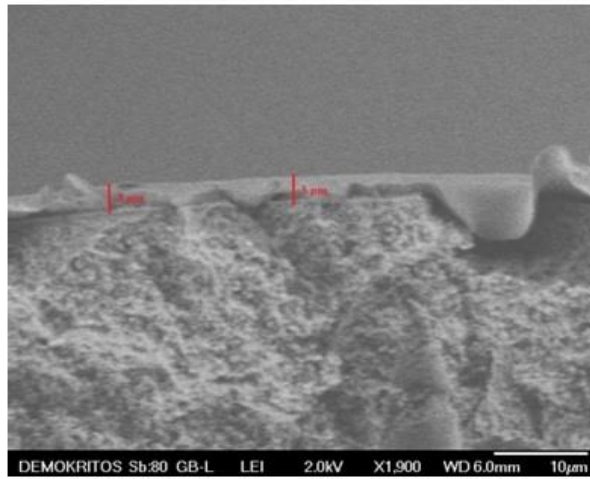


Fig. 1. SEM image of thin film selective layer.

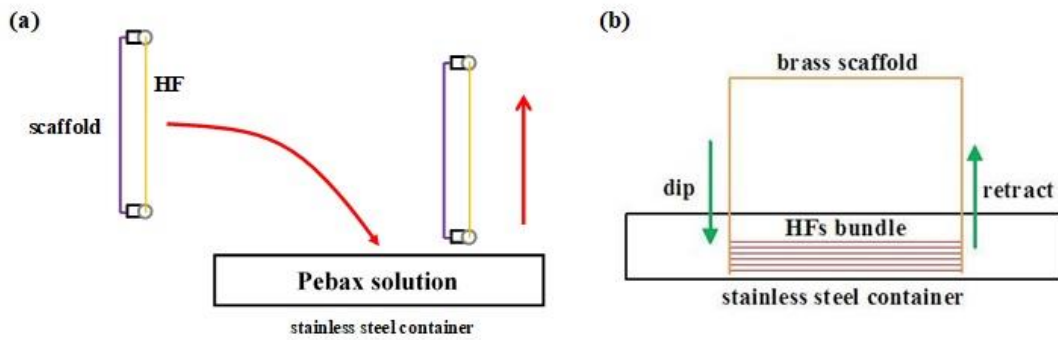


Fig. 2. Schematic diagram of the coated HF with the selective layer process in (a) single and (b) bundle mode.

PECVD surface layer prevents aging of a polymer with intrinsic microporosity

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Main topic: Ageing of polymeric membranes

In the last decades, high free volume polymers have been explored for many membrane-based gas-separation purposes. Their high permeability for various gases makes them potential next-generation membrane materials. Still, physical aging of these polymers hinders their application in industrial processes due to their time-dependent permeation behavior. Various techniques and measures are currently being explored to address this challenge, but struggle with upscalability or use in ultrathin polymer layers.

We present a highly effective method to successfully mitigate physical aging by coating the polymer with a top layer of a few nanometers using plasma-enhanced chemical vapor deposition (PECVD). In the past, such coatings have been reported as selective membrane material and showed good separation performance¹. We will present the aging behavior of PECVD coated Poly(1-trimethylsilyl-1-propyne) (PTMSP) films with a thickness of about 200 nm and compare them with uncoated PTMSP films. We show the influence of the thickness and the oxidation degree of the PECVD coating. The aging is tracked by ellipsometry where the measured refractive index directly correlates with the free volume amount of the film².

The PECVD coated films show an outstanding aging behavior with a more than 100 times slower aging rate compared to the uncoated film for highly oxidized coatings. The coating thickness has a minor impact, so that already coatings of less than 10nm show a significant aging improvement.

On the next step towards membrane applications, we present first results of the permeation behavior of the PECVD-coated PTMSP films.

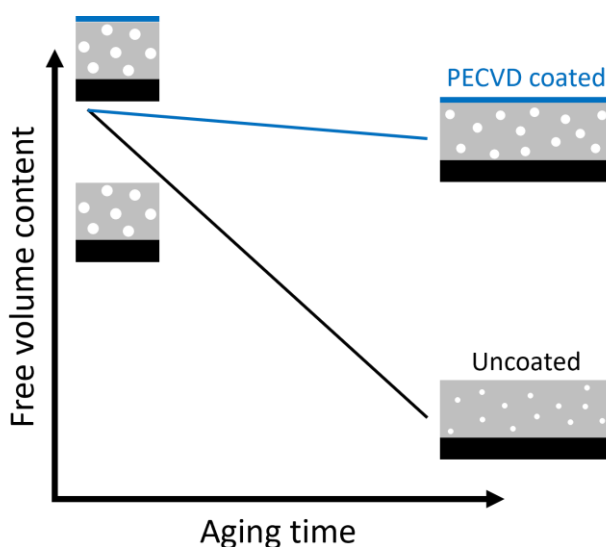
Since industrial roll-to-roll manufacturing processes already apply PECVD, our PECVD-coated PTMSP films do not only outstand technical performance in academic research, but are also expected to open a new path for a simple commercialization of high free volume polymers.

Reference 1:

Kleines, L., Jaritz, M., Wilski, S., Rubner, J., Alders, M., Wessling, M., ... & Dahlmann, R. (2020). Enhancing the separation properties of plasma polymerized membranes on polydimethylsiloxane substrates by adjusting the auxiliary gas in the PECVD processes. *Journal of Physics D: Applied Physics*, 53(44), 445301.

Reference 2:

Huang, Y.; Paul, D. R., Physical aging of thin glassy polymer films monitored by optical properties. *Macromolecules* 2006, 39 (4), 1554-1559 p



Performance and optimization of semi-industrial ultrafiltration system as wastewater tertiary treatment for water reuse

Yang, Jiaqi - Main Author; Monnot, Mathias - Co-Author; Eljaddi, Tarik - Co-Author; Simonian, Leo - Co-Author; Ercolei, Lionel - Co-Author; Moulin, Philippe - Co-Author

Main topic: Wastewater treatment

Nowadays, water reuse becomes more accepted as an approach to release water crisis. Ultrafiltration (UF) has expanded rapidly as an effective and economic technology for water treatment as it can retain suspended solids and microorganisms from water. In this context, this project aims to assess UF as a tertiary treatment of an urban wastewater treatment plant (WWTP) in France for water reuse and to find out the optimum filtration conditions for sustainable performances. The UF pilot plant (equipped with 200kDa hollow fiber membrane) is a fully automatic system with periodic cleanings of classic backwashes (CB) and air backwashes (AB). For optimization, 15 filtration conditions with different fluxes, filtration times, and air backwash frequencies were operated under constant flux mode for over 40h for each. Through comparison, one of the best conditions was a flux of $60 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$, a filtration time of 60 min, and a backwash frequency of 1 AB followed by 3 CBs. The optimized conditions stood out from the others thanks to higher water productivity ($> 92\%$), effective fouling reversibility (80% for CB and 150% for AB), better irreversible fouling control, and great permeability recovery. Moreover, the UF permeate quality was highly qualified for reuse as it met the reuse guidelines of the World Health Organization, French standards, and the last European Parliament regulations setting up minimum requirements for water reuse adopted in May 2020. In the permeate, the total suspended solids, the biochemical oxygen demand, and the turbidity were decreased to $< 2 \text{ mg}\cdot\text{L}^{-1}$, $\leq 10 \text{ mg}\cdot\text{L}^{-1}$ and, $< 0.5 \text{ NTU}$ respectively; the *Escherichia Coli* and *Enterococci* were above 5 log removal reduction, the other required microorganisms' analysis were below the detection limits. Additionally, the coronavirus SARS-CoV-2 was tested to be negative in UF feed and UF permeate. The UF membrane could also remove 91.6% microplastics from the feed. Particularly, the microplastic particles with side dimension higher than $70 \mu\text{m}$ could be almost completely removed by the 200kDa membrane. In summary, this work confirms the great interest of UF as intensified tertiary treatment for water reuse and gives operational indications for future industrial-scale production of reclaimed water.

Performances of commercial reverse osmosis membranes in the context of sunflower oil recovery after supercritical CO₂ extraction

CHABNI, Dihia - Main Author; Remigy, Jean-Christophe - Co-Author; CAMY, Séverine - Co-Author; CONDRET, Jean-Stéphane - Co-Author

Main topic: Nanofiltration/Reverse Osmosis

The development of clean processes requires the utilization of green solvents, among which supercritical CO₂ (sc-CO₂) is considered because of its biocompatibility together with modular transport properties (density, viscosity, diffusivity...). Around 200-300 bars, 40°C, sc-CO₂ has a good solvent power towards non-polar compounds such as vegetal oils for instance that makes it an interesting alternative to conventional organic solvent. After extraction, the recovery of the product is usually done by decompression (50 bars) where CO₂ spontaneously leaves the product. Then the solvent is recycled by recompression, which induces a high energy consumption.

Here, the goal is to reduce the energy consumption of sc-CO₂ processes by coupling them with a reverse osmosis membrane which allows separation of CO₂ and oil with a much lower extent of decompression (a few tenths of bars). To achieve this goal, the membrane should be both highly selective and permeable while showing good durability. In this study, commercial reverse osmosis AG and BW30 polyamide membranes were selected based on their selectivity and permeability observed with water and their mechanical resistance.

The behavior of these membranes in contact with sc-CO₂ was studied by performing physical ageing tests where membrane samples were left in sc-CO₂ atmosphere at 40°C and 200 bars for 15 days. Mass transfer properties of the membrane samples (permeability to gaseous CO₂) were characterized as well as their chemical surface properties (ATR-IRTF analysis). The results showed that neither permeability nor the chemical composition of the tested membranes were modified.

Filtration tests of pure sc-CO₂ or oil/sc-CO₂ mixtures were carried out using a home-designed filtration cell (membrane area 80 cm²) with two syringe pumps for pumping CO₂ feed and permeate. The whole setup was temperature controlled. Oil is injected into the setup using an HPLC pump and mixed with the sc-CO₂ in a static mixer.

Sc-CO₂ filtration tests, at 150 bars and 40°C using the AG membrane, showed a transmembrane pressure around 8 bars at a flux density of 33 kg/(h.m²). The sc-CO₂ permeability was then around 4 kg/(h.m².bar). In the context of solvent recycling, this would lead to a more than 80% energy consumption reduction of the process.

Performances of commercial reverse osmosis membranes in the context of sunflower oil recovery after supercritical CO₂ extraction

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Perstraction and Pervaporation: Two Approaches for Xylene Isomers Separation

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Main topic: Pervaporation and vapour permeation

The industrial importance of isolated BTEX (benzene, toluene, ethylbenzene and xylene isomers) compounds is enormous [1], however, their separation remains energetically and financially demanding. With the closest boiling points, *p*-xylene/*m*-xylene appear as the most challenging pair for separation. Nowadays, membrane techniques seem to be a suitable alternative for commonly used separation methods, nevertheless, the separation characteristics of polymeric membranes still do not fulfil the industrial standard. Although polydimethylsiloxane (PDMS) and cellulose triacetate (CTA) can be utilized to produce real-world membrane modules, their effectiveness for this mixture is insufficient. Here, we present two different membrane separation approaches: pervaporation and perstraction at 40 °C for the separation of *p*-xylene and *m*-xylene mixtures, aiming to increase the selectivity of PDMS and CTA, as two industrially relevant materials, by changing the mode of operation. We also examined the influence of the feed composition and the effect membrane entrainer added to the feed in different ratios [2]. The experiments showed that PDMS was not significantly selective to either of the xylene isomers when operated in the pervaporation mode. However, the selectivity reached up to 1.4 when operated in the perstraction mode with 40 mol.% of methanol in the feed. The CTA films were significantly less permeable but more selective towards *p*-xylene over *m*-xylene than those from PDMS at all studied experimental conditions. The highest selectivity 1.9 was observed for the CTA membrane operated in the perstraction of the feed having the molten eutectic composition (13% *p*-xylene) without additional methanol. The use of methanol as the membrane entrainer and as the perstraction receiving liquid appeared relevant as this compound could be easily separated from such mixtures using distillation or pervaporation. Moreover, the robustness of the membranes upon their exposure to methanol was verified using Dynamic Mechanical Analysis (DMA). Besides their separation characteristics, we provided spectroscopic characterization of both materials. Overall, it was shown that the efficacy of the membrane separation processes could be improved by a simple change of the mode of operation from pervaporation to perstraction, by choosing the optimized feed composition or by the addition of a membrane entrainer. This enables further exploitation of the already existing and reliable membrane materials.

This work was supported from the Czech Science Foundation, project 18-08389S, from Specific university research No. A2_FCHI_2021_021 and from MSMT 21-SVV/2021.

Reference 1:

Sholl, D. S.; Lively, R. P. Seven chemical separations to change the world. *Nature* 2016, 532, 435–437. <https://doi.org/10.1038/532435a>.

Reference 2:

Durďáková, T.-M.; Hovorka, Š.; Hrdlička, Z.; Vopička, O. Comparison of pervaporation and perstraction for the separation of *p*-xylene/*m*-xylene mixtures using PDMS and CTA membranes. *Separation and Purification Technology* 2021, 274, 118986. <https://doi.org/10.1016/j.seppur.2021.118986>.

Pesticide degradation in surface-water and vegetative-water using biohybrid regenerated-cellulose membranes

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Main topic: Membrane bio-reactors

The increasing amount of pesticides in various aqueous environments, especially due to agriculture practices, is a global still unsolved problem. In order to address this challenge, the bioremediation carried out by enzymes is appealing due to high specificity, efficiency and low energy consumption. The use of inherently stable enzymes, such as extremophiles, and their immobilization on membranes can both ensure high activity and stability, as well as the development of intensified continuous processes. The aim of this study was the development of a biocatalytic membrane reactor (BMR) for pesticides degradation in real aqueous matrices. In particular, vegetative-water (an agro-food industry waste) and surface-water, contaminated with the pesticide paraoxon were selected as model streams. A thermophilic phosphotriesterase was immobilized on polymeric membranes (polyvinylidene fluoride, polyethersulfone, nylon, regenerated-cellulose) having different chemical-physical properties. The obtained biocatalytic membranes were characterized by FT-IR, immunoelectron microscopy, water contact angle, catalytic activity and stability. The biohybrid regenerated-cellulose membrane demonstrated the better performance either in terms of retained enzyme activity or in terms of resistance to fouling phenomena during filtration, therefore this membrane was used to develop the BMR. Investigation of operative conditions showed that pesticide degradation in the BMR was a function of residence time. The full degradation of the pesticide can be obtained at 5.0 and 2.7 min of residence time when using vegetative-water and surface-water, respectively [1]. By using both matrices the deactivation constant of the immobilized enzyme resulted much lower compared to the one of the free enzyme, leading to a much higher catalytic stability. The Kinetic characterization of the enzyme demonstrated that the reduced activity towards the pesticide in vegetative-water was due to a competitive inhibition given by biophenols already present in the stream. In order to minimize the enzyme inhibition, amphiphilic molecules were used. In particular, the addition of ionic surfactants (sodium dodecyl sulphate or cetyltrimethylammonium bromide) in the reaction mixture improved the BMR performance. The high degradation capacity in both surface-water and vegetative-water as well as the good enzyme and membrane flux stability make the BMR promising for bioremediation of water streams.

Acknowledgments

The authors acknowledge the project RAVEL (prot. n.51727) supported within POR CALABRIA FESR-FSE 2014–2020.

Reference 1:

G. Vitola, R. Mazzei, L. Giorno, Enzyme-loaded membrane reactor to degrade a pesticide in vegetative waters, *J. Membr. Sci.* 2021, 119438

Photoactive polymer membranes – using photosensitizers and visible light for degradation of micropollutants

Becker-Jahn, Julia - Co-Author; Dr. Schulze, Agnes - Co-Author

Main topic: Wastewater treatment

For the removal of micropollutants in water an alternative advanced oxidation processes (AOP) was developed using immobilized photosensitizers which are well known from medical applications. A commercial polyethersulfone (PES) membrane was modified by electron beam-mediated grafting with the two different photosensitizers (PS): Eosin Y and the porphyrin-like TMPyP (5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin tetra(*p*-toluene-sulfonate)). After immobilization and subsequent excitation with light, the membranes generate the reactive oxygen species singlet oxygen ($^1\text{O}_2$), which causes a degradation of micropollutants - like pharmaceuticals - in aqueous solution.

Comparable results of degradation could be attained by irradiation the membrane systems with visible light according to the photosensitizer's specific absorption wavelength and with natural sunlight. To confirm the photoactivity of the modified membranes the generation of singlet oxygen was monitored by using the fluorescent dye ABDA (9,10-anthracenediyl-bis(methylene)dimalonic acid).

One of the pharmaceuticals we chose to test the degradation capability of the functionalized membranes was ranitidine (RAN). It is one of the most common histamine-2 blockers to medicate gastroesophageal reflux diseases, respectively. It is already reported that this drug can be found in ng-concentrations in surface water, because municipal wastewater treatment plants are not able to degrade these kinds of micropollutants.

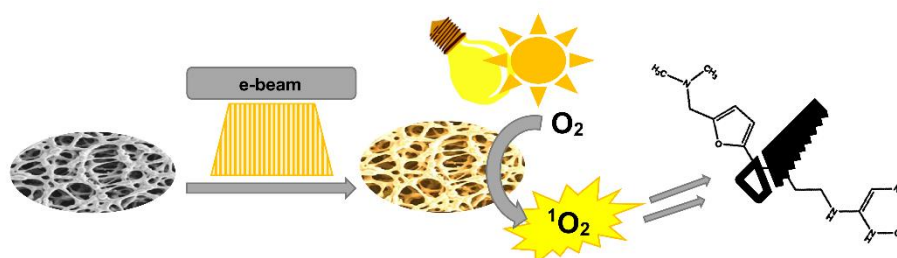
Primary, the degradation of RAN was analyzed photometrically. According the monitored UV/VIS absorbance of RAN in solution a degradation of approximately 80% was achieved for PES_TMPyP. For PES_Eosin Y ranitidine was eliminated 60 - 80%. The validation was provided by HPLC analysis. Therefore, an almost complete elimination of RAN in solution was confirmed – for both membrane systems (TMPyP and Eosin Y) and both excitation options (PS specific wavelength and sunlight). Regarding HPLC analysis RAN was degraded to various transformation products, which have to be analyzed further – especially regarding their toxicity. A mineralization was excluded by TOC analysis results. Concerning the stability of the PS-membranes the experimental results show no occurrence of membrane structure damage after modification or degradation procedure.

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Becker-Jahn et al., Catalysis Today 364 (2021) 256-262

Reference 2:

Müller et al., Photochem. Photobiol. Sci. 17 (2018) 1346-1354



Plugging of a hollow fiber capillary by gel relaxation during a cleaning step

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¹Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France, ²Solvay, Research and Innovation Center of Lyon, Saint-Fons, France

Main topic: Transport models

In membrane processes, the cleaning of gel or layers of accumulated particles on membranes is of importance. Gel formation during fouling can lead to membrane clogging during wastewater treatment [1] or to the formation of plugs in hollow fibers [2]. The gel removal procedure is often prohibited by particle agglomeration, qualified here as an irreversible phase transition. Our study aims to contribute to the understanding of the relationship between operating conditions (hydrodynamics and physicochemical properties) and gel reversibility, with the aim of predicting and optimizing the cleaning stages in filtration processes. For this purpose, we developed a model that solves the colloid transport in the frame of continuum fluid mechanics, including a description of the osmotic pressure near sol/gel phase transition applied to nanoparticles. The colloid transport is solved using the software OpenFOAM. We first considered the accumulation of particles during tangential filtration in a hollow fiber. Second, the flux was stopped, and we investigated the relaxation of particle layers, searching for the eventual occurrence of fiber plugging during the expansion stage. We studied the impact of the filtration Peclet (Pe) leading to a given initial accumulated concentration (ϕ) and of the gel reversibility on the gel relaxation time scale. We observed that, under certain conditions, the gel (defined as the region where the concentration $\phi > 0.06$) fills the entire cross-section leading to an irreversible blockage, as shown in Figure 1.

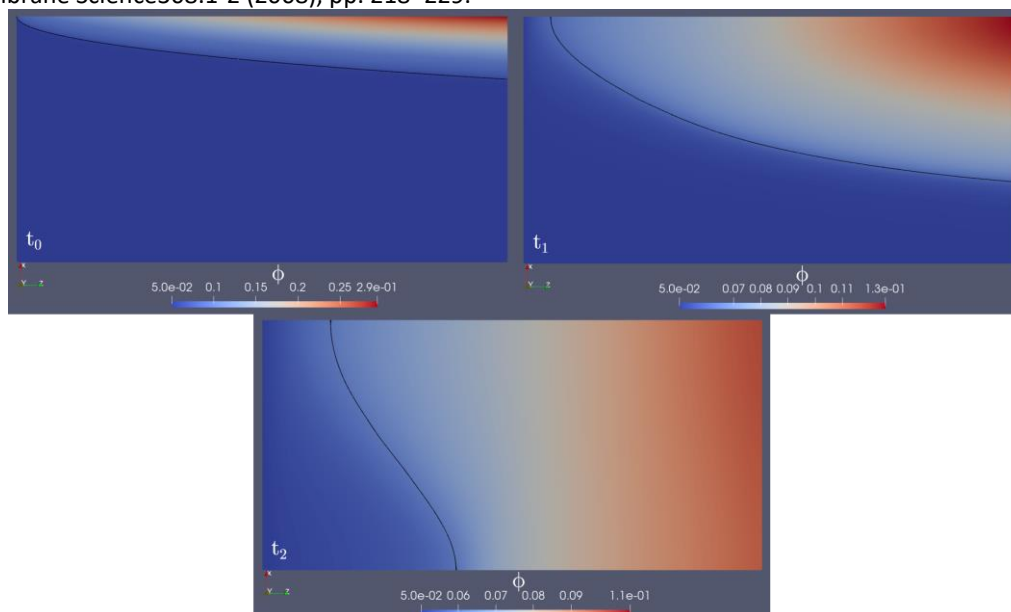
Figure 1: Contour plot of the concentrated layers inside a hollow fiber a) after filtration (t_0), b) during the relaxation (t_1) and after a plug is formed (t_2). The fiber length is scaled by a factor of 1/20 in the x-direction to ease the illustration of the concentration field. The domain width in the y-direction represents the 1-mm radius of the hollow (cylindrical) fiber. In each snapshot, the boundaries of each contour plot represent the membrane (top), the fiber center (bottom) the fiber inlet (left), and the fiber outlet (right). The black line denotes the limit of the gel phase, where the concentration is larger than $\phi = 0.06$.

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T. Zsirai et al. "Efficacy of relaxation, backflushing, chemical cleaning and clogging removal for an immersed hollow fiber membrane bioreactor". In: *Water Research* 46.14 (2012), pp. 4499–4507. issn:0043-1354.

Reference 2:

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Poly(ethylene glycol) diacrylate iongel membranes reinforced with nanoclays for gas separation

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Main topic: Novel membrane materials

The remarkable CO₂ affinity and tuneable nature of ionic liquids (ILs) allowed the exploitation of these materials through the development of membranes with distinct functionalities and separation efficiencies.

To take advantage of these ILs properties, iongel membranes were developed by combining a dispersed IL phase and a solid continuous phase. In iongel systems, the IL is usually the predominant component, which allows the preparation of CO₂ separation membranes with liquid-like gas transport properties, while the second component acts as a gelator, forming a three-dimensional network.

Even though iongel membranes have the potential to overcome the stability issues related with supported ionic liquid membranes (SILMs), the fact that the IL phase makes up for more than half of the total membrane composition, leads to problems concerning the mechanical stability of these membranes, consequently compromising their practical use for gas separation processes. The incorporation of different clays into polymeric membranes has been reported as a successful approach to improve both gas separation performance and mechanical resistance of membranes [1,2]. Having this in mind, the present work focuses, for the first time, on the preparation of solvent-free UV crosslinked poly(ethylene glycol) diacrylate-based iongels, comprising [C₂mim][TFSI] IL as the predominant component (60 wt%), reinforced with a montmorillonite (MMT) nanoclay. Different contents of MMT, between 0.2 and 1 wt%, were incorporated into the PEGDA/IL solution, as a strategy to obtain self-standing iongel membranes with improved mechanical stability, able to withstand the gas permeation experiments.

The study of the mechanical properties demonstrated that, when a homogeneous iongel structure is obtained, the addition of MMT provides a higher mechanical resistance to the iongels (up to 30% compared to the unfilled iongel) even with small concentrations. Additionally, CO₂/N₂ and CO₂/CH₄ permeation experiments showed that MMT had almost no influence in the permeability/selectivity of the prepared iongels since it doesn't possess a significant affinity towards these gases, proving that this component acts only as a mechanical reinforcement.

This initial study opens the possibility of improving the mechanical stability of the presented materials, which could eventually lead to the preparation of self-standing iongels with higher amounts of IL and, consequently, better gas separation performance

Reference 1:

Zulhairun, A. K.; Ismail, A. F.; Matsuura, T.; Abdullah, M. S.; Mustafa, A. Asymmetric Mixed Matrix Membrane Incorporating Organically Modified Clay Particle for Gas Separation. *Chem. Eng. J.* 2014, 241, 495–503

Reference 2:

Behroozi, M.; Pakizeh, M. Study the Effects of Cloisite15A Nanoclay Incorporation on the Morphology and Gas Permeation Properties of Pebax2533 Polymer. *J. Appl. Polym. Sci.* 2017, 134 (37), 1–11

Poly(vinyl alcohol) nanocomposite membranes with functionalized carbon discs for water treatment applications

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Main topic: 1D- and 2D-materials for membranes

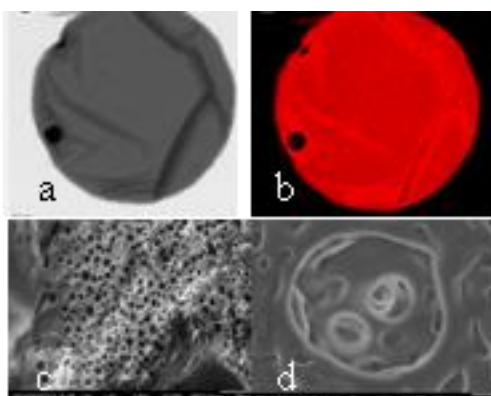
Water is an important natural resource that affects all aspects of daily life. However, the overuse of water resources constantly increases the need for clean water. Water treatment technology, aimed at removing harmful substances such as microorganisms and organic compounds, is based on the use of membranes and more commonly polymeric membranes, such as poly(vinyl alcohol) (PVA). In the present study, porous poly(vinyl alcohol) (PVA) nanocomposite membranes were developed and their performance in separations was evaluated¹. One way to improve membrane properties is by the addition of nanoparticles, based on carbon, resulting in mixed matrix structures². Since the hydrophobic nature of carbon hinders its dispersion in aqueous solutions, the following modification process was carried out: two guanidynylated derivatives of hyperbranched poly(ethylenimine) (GPEIs) having molecular weights of 5000 and 25000 Da, were used to functionalize oxidized carbon nanodiscs through covalent bonding between the functional groups of GPEIs and the oxygen containing groups of the nanodiscs. Nanocomposite PVA membranes were then prepared containing 0.1, 0.25 and 0.5 wt% of functionalized carbon nanodiscs.² Subsequently, the membranes of about 50-100 μ m thickness were crosslinked using glutaraldehyde, rendering them water stable. The hybrid nanomaterials, oxCNDs@GPEIs, were physicochemically characterized using a variety of techniques such as ¹H and ¹³C NMR, FT-IR, SEM, TEM (Fig.1a-b), RAMAN and XRD. Furthermore, the prepared membranes were studied in regards to their water permeability and their anti-fouling properties. They were also characterized by SEM (Fig.1 c-d), FTIR, water contact angle, porosity and pore size. Finally, the antibacterial properties of the membranes were assessed against a Gram-positive bacterium, Escherichia coli, where it was found that upon increase of the portion of oxCNDs@GPEIs, their antibacterial activity increased. Based on the above results, it was found that the nanocomposite membrane with 0.25% oxCNDs@GPEI-25KDa exhibited better overall properties.

Reference 1:

Sapalidis A. Porous Polyvinyl alcohol membranes: Preparation methods and applications. *Symmetry* (Basel). 2020;12(6):1-24. doi:10.3390/SYM12060960

Reference 2:

Sapalidis A, Sideratou Z, Panagiotaki KN, et al. Fabrication of antibacterial poly(vinyl alcohol) nanocomposite films containing dendritic polymer functionalized multi-walled carbon nanotubes. *Front Mater*. 2018;5(March):1-10. doi:10.3389/fmats.2018.0001



Polyelectrolyte self-assembly for the next generation of sustainable Nanofiltration membranes: From ultra-thin coatings to complete membranes

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Main topic: Nanofiltration/Reverse Osmosis

The intensification of the use and reuse of fresh water resources comes at a cost. Reports on rising levels of emerging contaminants in our water are numerous. New and better membranes are urgently needed to come to better and more sustainable water treatment processes. Over the past decade polyelectrolyte multilayers have established themselves as one of the most promising new materials in membrane Science and Technology. Novel nanofiltration membranes are prepared by the self-assembly of oppositely charged polyelectrolytes at the interfaces of a porous ultrafiltration support membrane. In this so-called Layer-by-Layer (LbL) assembly, the support membrane is alternatively exposed to polycations and polyanions, to build polyelectrolyte multilayer's (PEMs) of controllable thickness. After coating the separation properties of the membrane are completely determined by the applied PEM layer.

In this contribution, we will discuss how a novel asymmetric approach to PEM membrane preparation can lead to membranes with unique separation properties. We present a membrane with an active separation layer of just 4-6 nm in thickness. The membrane retains small organics at high fluxes, while allowing ions to easily pass through the membrane. The unique membrane properties also allow for new processes to more efficiently treat both surface and waste water [1].

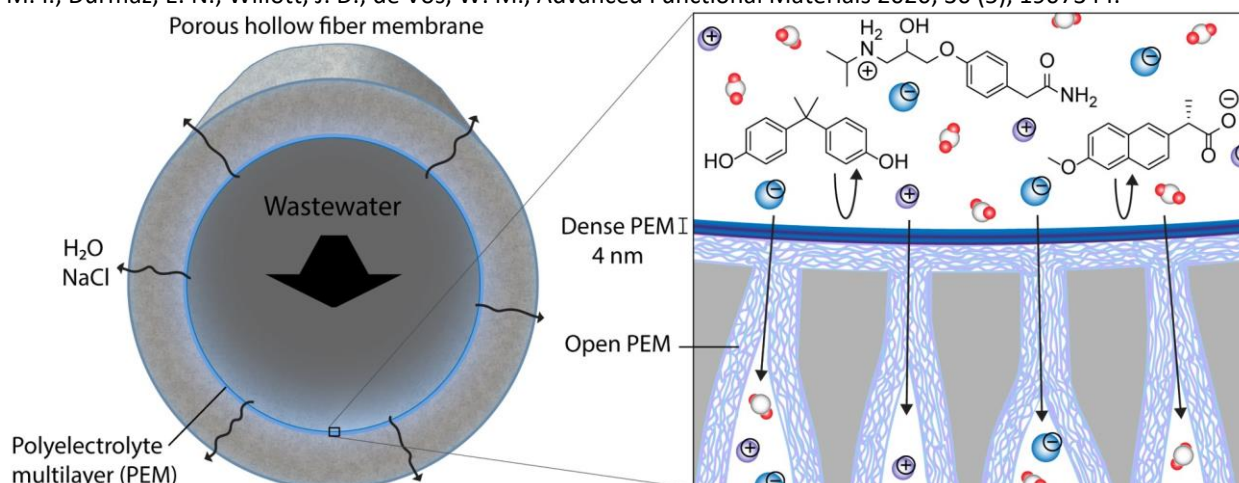
And we can even push this one step further. By a carefully controlled 1-step precipitation process, we can prepare polyelectrolyte complex based membranes, where the polyelectrolyte complex functions as the porous support membrane and as the separation layer. This aqueous phase separation (APS) approach, has strong similarities to the traditional non-solvent induced phase separation process, but without producing water streams contaminated with aprotic organic solvents. Indeed, also in APS it is possible to create very promising nanofiltration membranes [2], with excellent stability in organic solvents and at extreme pH values.

Reference 1:

te Brinke, E.; Reurink, D. M.; Achterhuis, I.; de Groot, J.; de Vos, W. M., *Applied Materials Today* 2020, 18, 100471.

Reference 2:

Baig, M. I.; Durmaz, E. N.; Willott, J. D.; de Vos, W. M., *Advanced Functional Materials* 2020, 30 (5), 1907344.



Polyethyleneimine-Carbonic Anhydrase Dynamic Constitutional Frameworks Nanoparticles With Enhanced Catalytic Turnovers

Su, Dandan - Co-Author; Ulrich, Sébastien - Co-Author; Barboiu, Mihail - Co-Author

Main topic: Environmental applications

The significant growth of carbon dioxide (CO₂) emissions causes the atmospheric pollution and the greenhouse effect. Regarding to the carbon capture and storage, many attempts have been made using electrocatalytic reduction and chemical recycling¹. Unfortunately, some barriers restrict their further application for addressing the carbon dioxide issue, such as high costs and high energy requirements. During the past decade, the use of carbonic anhydrases (CA) for CO₂ storage has attracted attention due to its high turnover rate and environmental benign property. Different molecules can be designed according to their catalytic mechanism to adjust the activity of the enzyme.

In this work, we prepared dynamic constitutional frameworks (DCF) by connecting four individual building blocks *via* the amino-carbonyl/imine reversible chemistry. The participation of reversible covalent bonds enabled the enzyme itself to select the optimal ligands, resulting in recognition of enzyme ligands from complex dynamic systems². Subsequently, the synthesized frameworks would trigger dynamic exchange of microenvironment through H-bonding interaction among the enzyme surface. The binding behavior of DCFs to CA was evaluated according to Stern-Volmer relation and the relative catalytic activity of CA was tested by hydrolysis reaction of p-nitrophenyl acetate with the addition of DCFs. The results based on Michaelis-Menten equation show that polyethylenimine (bPEI800), as the amino-rich component of DCFs, present outstanding binding phenomena towards CA with the highest association constant (K_a) 15052 M⁻¹, and display the highest catalytic proficiency with the estimated k_{cat}/K_m of 1610 M⁻¹ s⁻¹. The activation effect of the DCFs was further improved with increasing of the stoichiometry, most likely through a molecular crowding effect.

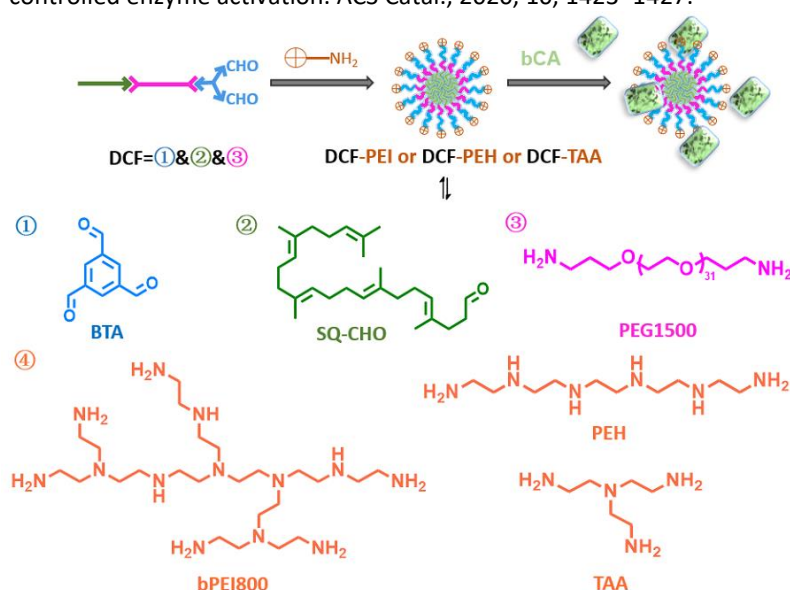
In conclusion, the use of DCFs provides a possibility to tune the enzyme catalytic activity by changing the enzyme microenvironment. A direct perspective is to immobilize encapsulated and activated enzyme in the membrane materials for enhancing CO₂ capture and conversion.

Reference 1:

E. E. Benson, C. P. Kubiak, A. J. Sathrum. Electrocatalytic and homogeneous approaches to conversion of CO₂ to liquid fuels. *Chem. Soc. Rev.*, 2009, 38, 89–99.

Reference 2:

Y. Zhang, M. Barboiu, O. Ramstrom. Surface-directed selection of dynamic constitutional frameworks as an optimized microenvironment for controlled enzyme activation. *ACS Catal.*, 2020, 10, 1423–1427.



Polymeric Membranes Incorporating Liquid Ion Exchangers: A Simple Approach For Water Pollution Control

Fontas, Claudia - Co-Author¹; Alcalde, Berta - Co-Author; Anticó, Enriqueta - Co-Author

¹University of Girona

Main topic: Facilitated transport membranes

There is a need for simple and efficient techniques to facilitate the control of pollutants in the environment. In this context, liquid ion exchangers used as specific ligands incorporated in a polymeric matrix can play an important role. Resulting materials are known as polymer inclusion membranes (PIMs), which have the ability of transporting the pollutants through the membrane that are released to a receiving phase. It is important to highlight that the high operation and high consumption of electrical energy associated to membrane technology is here avoided since the separation process is based on a chemical pumping instead of a physical rejection. Moreover, PIMs can be tailor-made depending on the characteristics of the pollutant, and incorporating either commercial extractants or specifically synthesized ligands.

In this work we want to present the latest applications of PIMs incorporating ion exchangers (such as trihexyl (tetradecyl)phosphonium chloride and trioctylmethylammonium chloride, commercially known as Aliquat 336), to show the capabilities of such membranes for the monitoring of inorganic natural contaminants in natural water, such as fluoride and arsenic [1]. Membrane composition vary depending on the pollutant to be transported. Using cellulose triacetate as the polymer, and ion-exchanger compounds as carriers, it has been seen that As(V) can be effectively preconcentrated in a special device incorporating the PIM and, therefore, facilitating its sub-sequent determination. When dealing with fluoride, the membrane needs to incorporate also tributyl phosphate (TBP) in the formulation, and it allows the removal of fluoride from different natural waters by its exchange with chloride anions used as a receiving solution. This separation system has successfully been used in different natural waters polluted with either arsenic or fluoride.

Acknowledgement: This work was supported by the Ministerio de Ciencia, Innovación y Universidades (MCIU) through project PID2019-107033GB-C22.

Reference 1:

R. Vera, E. Anticó, C. Fontàs, The use of a polymer inclusion membrane for arsenate determination in groundwater, *Water*. 10 (2018) 1–10. <https://doi.org/10.3390/w10081093>.

Polymerizable Ionic Liquid-based membrane for extraction of Co(II)

Sinoimeri, Eris - Co-Author

Main topic: Novel membrane materials

Introduction: Supported liquid membrane (SLM) has been used for several years in metal extraction processes. However, a major drawback in their use is their stability. To solve this challenge, new SLM based on ionic liquids¹ (IL) and polymerizable ionic liquids² (ILp) have been developed. Cobalt is widely used for different applications, from alloys to lithium-ion batteries. To meet this growing demand, extraction and separation of cobalt from primary and secondary sources has attracted much attention. This investigation is focused on the extraction of cobalt using SLM with ILp by conventional static mode sorption experiments.

Materials and methods: Two types of membranes (hydrophobic and hydrophilic) based on poly(vinylidene fluoride) (PVDF) are studied. Three different organic phases (O.P.) have been tested for the investigation with the SLM: a first organic phase (O.P.1) is composed of di-(2-ethylhexyl)phosphoric acid (D2EHPA) and 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX63) dissolved in eucalyptol, a second organic phase (O.P.2) consisting of the ILp named poly(diallyldimethylammonium)bis (trifluoromethanesulfonyl) imide and LIX63 dissolved in acetone and a third organic phase (O.P.3) consisting of the ILp, mentioned above, and LIX63 dissolved in eucalyptol. The SLM is prepared by immersing a membrane in O.P. for at least one night. Then, the SLM is immersed in a known volume (5 mL) of an aqueous phase (A.P.) containing 1 g/L of Co (pH=5). The stripping from the liquid membrane phase was studied by immersing the cobalt-loaded membrane in HCl (1%) (3mL) for 5 hours. The concentration of metal ions in the stripping phase is determined by ICP-OES.

Results: Figure 1 shows that the hydrophilic membranes seem to respond more effectively for the mass of O.P. immobilized in porous membrane and for the extraction of cobalt. In particular, through the system consisting of O.P.1 and hydrophilic membrane, it is possible to extract cobalt and the mass ratio cobalt / organic phase is 1.2. However, it is interesting to observe that this mass ratio is higher (4.3) for the system consisting of O.P.3 (with ILp).

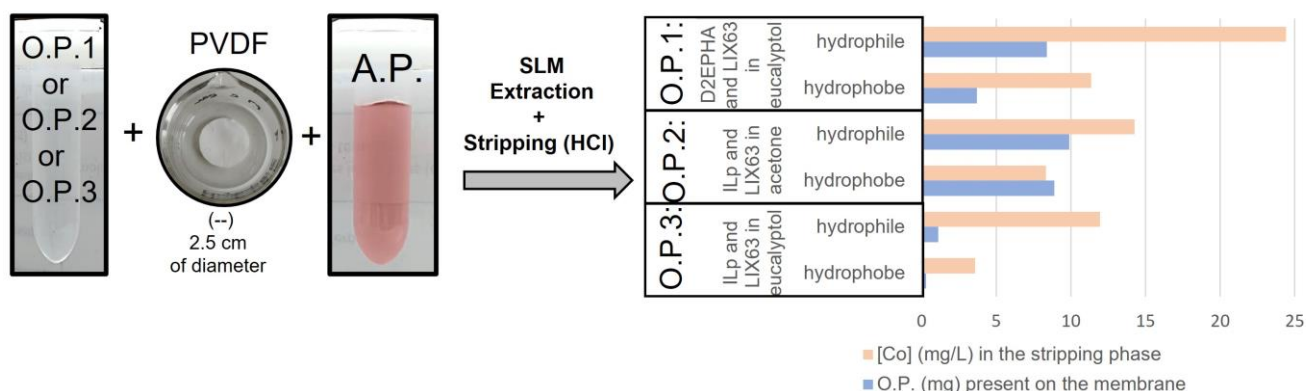
Conclusions: The investigation is going on as a function of the different parameters of the process (pH, temperature, [Me] etc.) and the aim is to develop a continuous extraction process.

Reference 1:

Zante, G.; Boltoeva, M.; Masmoudi, A.; Barillon, R.; Trébouet, D. Selective Separation of Cobalt and Nickel Using a Stable Supported Ionic Liquid Membrane. *Sep. Purif. Technol.* 2020, 252, 117477. <https://doi.org/10.1016/j.seppur.2020.117477>.

Reference 2:

Tereshatov, E. E.; Boltoeva, M.; Mazan, V.; Baley, C.; Folden, C. M. Hydrophobic Polymerized Ionic Liquids for Trace Metal Solid Phase Extraction: Thallium Transfer from Hydrochloric Acid Media. *New J. Chem.* 2019, 43 (23), 8958–8969. <https://doi.org/10.1039/C9NJ00689C>.



Polytriazole polymers as an alternative platform for organic solvent applications

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¹KAUST

Main topic: Organic solvent nanofiltration

Separation processes are essential in the chemical, pharmaceutical, and petrochemical industries. However, there is still a lack of separation materials to handle the industries conditions and the complex mixture. Therefore, more materials that are easy to process by conventional methods and can be manufactured into membranes are required to meet the industries demands.

In this paper, we report different strategies to prepare polytriazole membranes for organophilic filtration. We used the polytriazole with pendant hydroxyl (OH) groups because it can easily be synthesized in large amounts, show good mechanical properties, and has high thermal and thermal-oxidative stability. Additionally, due to the presence of the pendant OH groups, this polymer is soluble in a wide range of solvents, make it easy to process by phase inversion. By using different casting solutions in dimethylformamide (DMF) and diepoxy crosslinkers it is possible to tailor the MWCO of crosslinked polytriazole membranes to cover the range from the lower end of ultrafiltration (7000 g/mol) to the upper end of nanofiltration (3000 g/mol). Due to the versatility of this polymer, we could tune the morphology of the membrane by using ionic liquids. The performance of the crosslinked membranes prepared with ionic liquids was evaluated in DMF at 20°C, 65°C, 85°C and 105°C. The permeances were in the range of 4 - 10 L m⁻² h⁻¹ bar⁻¹, with the MWCO in the range of 1000 g/mol. In addition, by direct crosslinking of the polytriazole membrane at high temperature, the MWCO can be around 300 g/mol. Therefore, using the right strategy to prepared crosslinked polytriazole membrane, we can cover all ranges of organic solvent nanofiltration.

Acknowledgement

This research was supported by King Abdullah University of Science and Technology (KAUST)

Porosimetry of nano-pores in thin polymer films by depth resolved positron annihilation lifetime spectroscopy

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¹Institut für Angewandte Physik und Messtechnik LRT2, Universität der Bundeswehr München, Werner-Heisenberg-Weg 39, Neubiberg 85577, Germany, ²Datzmann interact & innovate GmbH, Penzoltstr. 3A, 80997 München

Main topic: New characterisation methods

The quantitative characterization of pore sizes and distributions in thin polymer layers (< 50 nm) is a challenging task, especially for free volume structures enclosed inside the material without any connection to the surface. Positron annihilation lifetime spectroscopy (PALS) offers the possibility for non-destructive investigations of nanoscopic pores in the range of $\sim 0.2 - 3$ nm. With a pulsed, monochromatic positron beam of variable energy one determines the time between positron implantation and annihilation in a certain depth (5 nm – 5 μ m) beneath the surface. In insulating materials such as polymers, positrons and electrons may form a bound state - Positronium. From the Positronium lifetime, one can calculate an effective pore radius by a semi-empirical, quantum-mechanical model (Tao-Eldrup-model). For this purpose the pulsed low-energy positron system (PLEPS) [1] was developed. It is operated at the reactor-based, high intense positron source NEPOMUC and offers the possibility for non-destructive investigations of nanoscopic free volume elements inside porous materials.

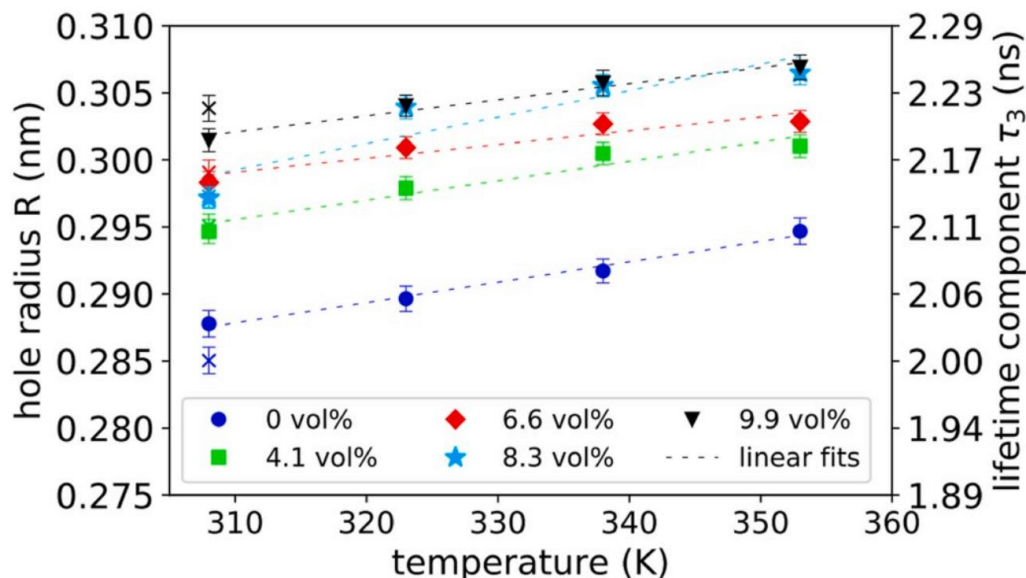
At present, it is possible with PLEPS to obtain positron and Positronium lifetime spectra of membrane samples including 4×10^6 counts in less than 10 minutes for a single implantation energy. Changing the beam energy allows positron implantation in various depths. A full depth-profile of 10 - 15 energies requires about 2 - 4 hours. The system also allows in situ manipulation of the sample temperature between 80 K and 600 K during lifetime measurements. This enables to investigate free volume elements as a function of the temperature, and thus to determine material phase transitions, e.g. the glass transition temperature. As an example, the abstract figure shows the pore radius and the respective Positronium lifetime as a function of the temperature, measured in polymer samples (poly lactic acid) with different content of dispersed nano-cellulose [2]. In the talk we describe the method and the present setup of PLEPS, its performance, and show a selection of exemplary applications to polymer problems.

Reference 1:

W. Egger, Proceedings of the International School of Physics "Enrico Fermi", CLXXIV (eds. A. Dupasquier and A. P. Mills jr.), IOS Press: Amsterdam, 419 (2010)

Reference 2:

M. Dickmann et al., Polymer 202 (2020) 122729



Practical limits of the quartz crystal microbalance for elucidating membrane phenomena

Arrizabalaga Legarra, Jon - Main Author^{1,2}; Schäfer, Thomas - Co-Author^{1,2,3}; Rafaniello Alonso, Iliane - Co-Author^{1,2}
¹SURPHASE, San Sebastián, Spain, ²POLYMAT, University of the Basque Country (UPV/EHU), San Sebastián, Spain,
³Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Main topic: New characterisation methods

Determining the partitioning of salts into polyamide (PA) reverse osmosis membranes is indispensable for optimizing their salt retention. Recently, quartz-crystal microbalance with dissipation monitoring (QCM-D) has been explored for this purpose. While this piezoelectrical technique has in theory a sensitivity in the range of pg/cm^2 , its practical sensitivity is orders of magnitude lower [1,2] and it is furthermore highly sensitive to bulk changes (e.g., viscosity). The utility of QCM-D for quantifying partitioning of salt into PA membranes was therefore systematically investigated. The experiments were complemented by multiparameter surface plasmon resonance (MP-SPR) as an optical surface-sensitive technique. During this study, sodium chloride and sucrose (as control) solutions were contacted with PA as well as gold (reference surface) and PEBAX (as control polymer). The results obtained revealed that it could not be discriminated between a supposed salt partitioning and the sensors' response to a bulk change. In fact, the response of the viscosity-sensitive sensor was found to be directly correlated with the change dynamic viscosity of the bulk solutions. MP-SPR data corroborated this observation. It was proven that while QCM-D is in practice a very convenient and easy method to study polymer-solute interactions, great care must be taken during the experimental design and interpretation of the sensor signal such as not to draw erroneous conclusions. The benefits of combining complementary surface-sensitive techniques will be shown such as to minimize the risk of pitfalls.

Reference 1:

Chem. Commun., 2012, 48, 10087-10089

Reference 2:

Chem. Sci., 2017,8, 7038-7046

Precleaning of membranes fouled with oil-in-water emulsion with NaCl: impact on the fouling structure

Couallier, Estelle - Co-Author¹; Rouquié, Camille - Co-Author; Szymczyk, Anthony - Co-Author; Rabiller-Baudry, Murielle - Co-Author; Roberge, Hélène - Co-Author; Abellan, Patricia - Co-Author; Riaublanc, Alain - Co-Author; Frappart, Matthieu - Co-Author; Álvarez-Blanco, Silvia - Co-Author

¹CNRS GEPEA

Main topic: Membrane fouling and cleaning

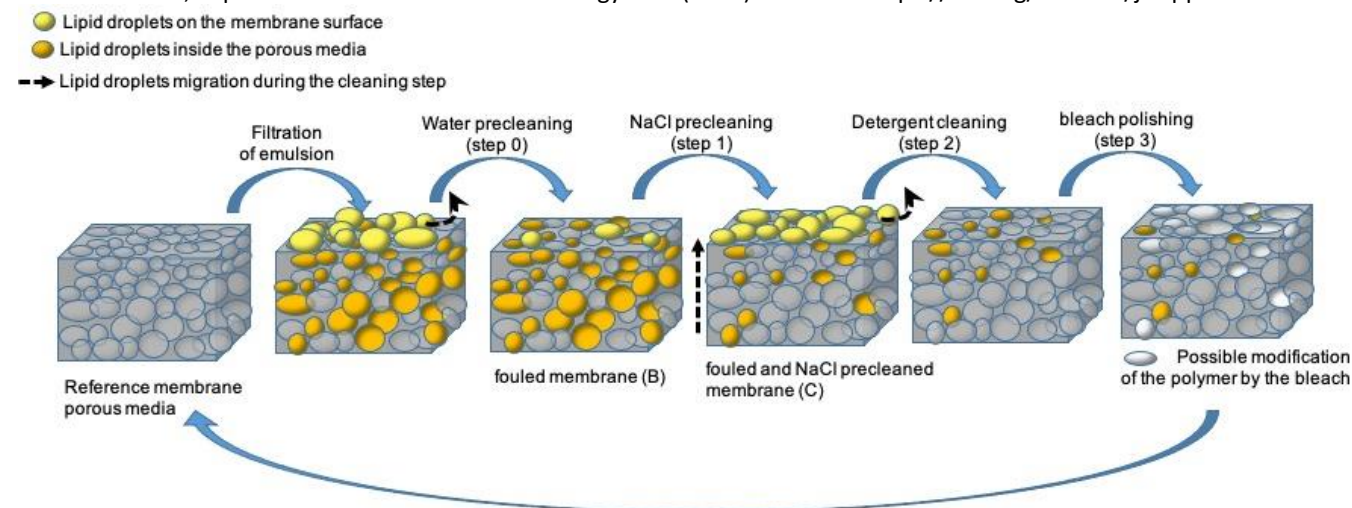
The membrane filtration is one of the most interesting processes for the fractionation of biomolecules from microalgae [1], however few works deal with membrane cleaning after treatment of such raw material. It still requires large volumes of cleaning solutions associated with energy and water consumption and environmental impact. NaCl solutions have already been used as a precleaning step to enhance the cleaning of ultrafiltration membranes fouled with whey proteins [2]. The objective of this study was to test this innovative procedure on membranes fouled with lipids representative of microalgae extracts and to evaluate its impact on the fouling structure. Polyethersulfone (PES) based 0.1 µm membranes were fouled with an emulsion, and then cleaned following several steps: water precleaning, NaCl precleaning, detergent cleaning and sodium hypochlorite polishing. Two concentrations of saline solution (5 and 7.5 mM NaCl) and 2 temperatures (37.5 °C and 50 °C) were tested and compared to control experiments. The hydraulic cleaning efficiency (HCE) was calculated to evaluate the saline solutions cleaning efficiency. 5 mM NaCl, 50 °C was the most interesting NaCl precleaning condition allowing a HCE up to 80%. Then the detergent U115 allowed removing the remaining fouling and reaching a HCE of 100%. The NaClO-NaOH polishing step was no longer required. The impact of salt on membrane fouling was then characterized comparing (i) virgin (ii) fouled and (iii) fouled and NaCl precleaned membranes, using Scanning Electron Microscopy (SEM) coupled to Energy-dispersive X-ray spectroscopy (EDX) measurements, Fourier Transform Infra-Red spectroscopy in Attenuated Total Reflection mode (ATR-FTIR) analysis, Atomic Force Microscopy (AFM) and electrokinetic measurements. It was demonstrated that the fouling of PES membranes occurred on the surface and in the porous media, irregularly organized in regions containing larger and lower quantities of lipids. Using NaCl allowed to decrease significantly the internal fouling, the lipids migrating from the internal porous media to the upper surface, thus facilitating the detergent cleaning step. This work will help developing cost-effective and eco-friendly cleaning procedures for the separation processes used for example in microalgae biorefining.

Reference 1:

E. Clavijo Rivera, L. Villafaña-López, S. Liu, R. Vinoth Kumar, M. Viau, P. Bourseau, C. Monteux, M. Frappart, E. Couallier, Cross-flow filtration for the recovery of lipids from microalgae aqueous extracts: Membrane selection and performances, *Process Biochemistry*. 89 (2020) 199–207. <https://doi.org/10.1016/j.procbio.2019.10.016>.

Reference 2:

M.-J. Corbatón-Báguena, S. Álvarez-Blanco, M.-C. Vincent-Vela, Salt cleaning of ultrafiltration membranes fouled by whey model solutions, *Separation and Purification Technology*. 132 (2014) 226–233. <https://doi.org/10.1016/j.seppur.2014.05.029>.



Preconcentration and desalination in membrane microfluidic systems

Tichy, David - Co-Author

Main topic: Electro-membrane processes

Ion concentration polarization (ICP) is a phenomenon that has been exploited in many novel technologies, contributing to biosensing, separation, ionic control and desalination. It occurs on the connection of a DC electric field to an ion-selective material of any kind. Our work introduces a novel microfluidic chip design for preconcentration and desalination integrating two cation-exchange membranes.

Ionic solution enters the chip through inlet channel which is then split into two channels. Two cation-exchange membranes are located on the top of the channel, external DC field connected to the system then causes the formation of ion-depleted and ion-concentrated regions in the bulk electrolyte. The ion-depleted zone functions as a non-mechanical ionic filter, thus resulting in desalination of the diluate flow and concentration of the concentrate flow. Experiments examining the effect of inserted voltage, volume flow rates of both outlets and salt concentration of the inlet were carried with KCl solution. Additional experiments with fluorescein solution were used to visualize the process of desalination and preconcentration.

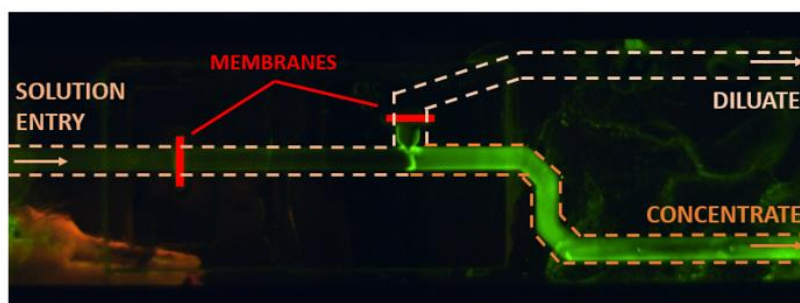
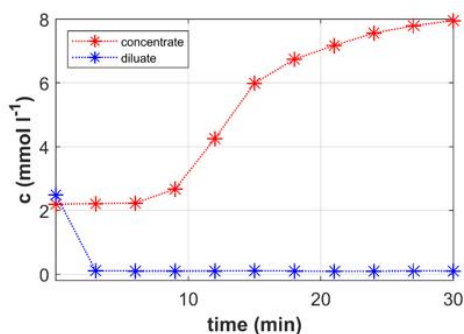
As seen in Fig. 1, experimental results confirmed that successful preconcentration and desalination of the inlet solution is performed with parameters conveniently set. Depending on the value of inserted voltage and outlet flow rates, performance of the chip can be classified either as continuous desalination (Fig. 1), unsuccessful operation or desalination by accumulation. During continuous desalination, passing of the separated ionic species directly through the membranes is prevented, which is believed to be avoiding fouling of the membranes. Thus, our novel microfluidic chip design can be a useful tool to process small volumes of samples that frequently cause membrane fouling.

Reference 1:

Kovar, P.; Tichy, D.; Slouka, Z., Effect of channel geometry on ion-concentration polarization-based preconcentration and desalination. *Biomicrofluidics* 2019, 13 (6)

Reference 2:

Tichy, D.; Slouka, Z.; Semi-continuous desalination and concentration of small-volume samples; submitted to *Desalination*, August 2021



Prediction of hydrogen gas sorption in semi-crystalline polymers through a multiscale modelling approach

Atiq, Omar - Main Author^{1,2,3,4}

¹Eleonora Ricci, Dept. of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, Italy,

²Marco Giacinti Baschetti, Dept. of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, Italy, ³Maria Grazia De Angelis, Dept. of Civil, Chemical, Environmental and Materials Engineering (DICAM),

University of Bologna, Italy; Institute for Materials and Processes, School of Engineering, University of Edinburgh.,

⁴Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, the Netherlands

Main topic: Transport models

The demand for hydrogen as an alternative energy source has grown and continues to increase with accelerating pace. The interest in hydrogen as an alternative transportation fuel stems from its ability to power fuel-cells in zero-emission electric vehicles, fast filling time, and high efficiency. Nevertheless, its low volumetric energy density implies storage at high pressures (up to 800 bar) as a compressed gas. Cost-effective and high-performance barrier materials screening for tank liner usage is therefore crucial to enable hydrogen gas technologies improvement.

In this framework, semi-crystalline polymers demonstrated to be the best candidates as barrier materials for hydrogen containment. They exhibit very low gas permeabilities, withstand the required pressures and, unlike metal tank liners, they are light weight, thus more suitable for on-board applications.

Hydrogen permeability is a critical property in the study of the performance of such materials and there is the need of developing models for its assessment in order to guide materials design and reduce the number of experimental tests required.

Penetrant solubility in amorphous rubbery polymers can be easily evaluated using an Equation of State (EoS) which describes the mixture density. On the other hand, in semicrystalline polymers, the bare EoS approach overestimates the solubility. The amorphous network shows an increased density, due to a 'constraining effect' induced by the impermeable crystals (usually represented with a constraining pressure) that results in a reduced sorption capacity [1][2].

The proposed research was aimed at modelling penetrants solubility through a multiscale approach coupling Molecular Dynamics simulations with a macroscopic model.

The model has been parametrized on CO₂ sorption experimental data in semi-crystalline polyethylene. MD simulations were applied to simulate the constrained amorphous density and its swelling behaviour for different CO₂ concentrations, pressures and temperatures.

The retrieved trends were then fed into the macroscopic Lattice Fluid model in order to find adjustable material parameters by matching the experimental solubility isotherms.

Once parametrized, the model has been tested to predict hydrogen gas sorption in the same polymer for which there's lack of experimental data.

Reference 1:

Memari, P., Lachet, V. & Rousseau, B. Molecular simulations of the solubility of gases in polyethylene below its melting temperature. *Polymer (Guildf)*. 51, 4978–4984 (2010).

Reference 2:

Minelli, M. & De Angelis, M. G. An equation of state (EoS) based model for the fluid solubility in semicrystalline polymers. *Fluid Phase Equilib.* 367, 173–181 (2014)

Preparation of a Zeolite-Based Ceramic Membrane and Its Application for Water Desalination

Chen, Xinxin - Co-Author

Main topic: Inorganic membranes

Preparation of a Zeolite-Based Ceramic Membrane and Its Application for Water Desalination

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With the expansion of industrial and agricultural activities, many country suffering from water shortage. In face of the huge ocean water, membrane desalination play a key role as it combine high water permeability, high selectivity towards dissolved salts, and high stability in the working conditions. Among the membranes, zeolites have been widely used in separation, owing to their regular network structure provide their high stability and defined pore structure¹. The zeolites possess nonporous with optimized pore size and pore structure, hence, high permeability and selectivity concerning water desalination. In this project, we focus on the development of high-performance water desalination membranes through a combination of crystals zeolites sol-gel derived amorphous silica². Specifically, a well-selected zeolite based thin layer (<1 μ m) was deposited on a porous alumina substrate. The defects in boundaries between particles could be eliminated by combining the amorphous silica with the zeolite crystals. We used the sol-gel method to deposit amorphous silica thin films onto the substrate, in which the particles are uniformly distributed. The template N,N-Dimethylformamide (DMF) was added to silica during the sol-gel process in order to control the pore structure, and thereby to optimize water permeability and salt rejection. Finally, the membrane thickness was minimized to be less than 1 μ m, while formation of defects was avoided, thus allowing fast water permeation rates and rejecting salts. This research provides a new way to make a high-performance membrane for water desalination through a combination of amorphous-crystalline materials.

Keywords: Ceramic membranes; Zeolite; Desalination; Sol-gel

Reference 1:

Wang, X.; Yang, Z.; Yu, C.; Yin, L.; Zhang, C.; Gu, X., Preparation of T-type zeolite membranes using a dip-coating seeding suspension containing colloidal SiO₂. *Microporous and mesoporous materials* 2014, 197, 17-25.

Reference 2:

Ma, X. Z.; Janowska, K.; Boffa V., ; Fabbri, D.; Magnacca, G.; Calza, P.; Yue, Y. Z., Surfactant-Assisted Fabrication of Alumina-Doped Amorphous Silica Nanofiltration Membranes with Enhanced Water Purification Performances. *Nanomaterials* 2019, 9, 1368

Preparation of mixed matrix hydrophobic PVDF membranes for distillation using carbon black

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Main topic: Membrane contactors and membrane distillation

Background

Mixed matrix membranes are prepared dispersing fillers into the dope solution to improve some membrane property (e.g. hydrophobicity, mechanical properties, fouling etc.). The nanoparticles modify the solution characteristics leading to different coagulation mechanism during the phase inversion process.

Porous PVDF membranes were prepared exploiting the nonsolvent induced phase separation (NIPS) technique. Based on previous work [1], a weak nonsolvent was exploited to increase the membrane hydrophobicity.

Different types of carbon fillers are currently investigated for the preparation of membranes for distillation [2]. Here further efforts to improve the performance of the membranes were made adding different amounts of carbon black (CB) to the dope solution, analysing the effect on the membrane structure and distillation ability.

Materials and methods

A 300 kDa PVDF (Solvay Speciality Polymers – Italy) was dissolved in a green solvent (Triethylphosphate, TEP, Merck – Germany) containing the CB for 24 hours at 70°C.

The solution was cast on a nonwoven support using a casting knife with a 300 µm gap and immediately immersed in a 96v% ethanol coagulation bath. The membranes were then washed with deionized water and dried.

Several membrane characterizations were carried out, such as scanning electron microscopy, liquid entry pressure (LEP-), liquid-liquid displacement porometry (LLDP), surface roughness and contact angle measurements. The membranes performance in vacuum membrane distillation (VMD) process was assessed using both pure water and a concentrated NaCl solution (90 g/L).

Results

The introduction of CB increased the viscosity of the casting solutions changing the morphology of the final membrane as reported in the figure attached.

When no filler was added to the solution, a highly porous surface with interconnected spherulites was formed during the phase inversion process. Instead, even with really small amounts of CB the membrane surface was characterized by a denser sponge-like structure and the spherulites disappeared.

Further increase of the CB loading did not modify the membrane morphology but caused a decrease of the mean pore size and increase of the membrane porosity.

Conclusions

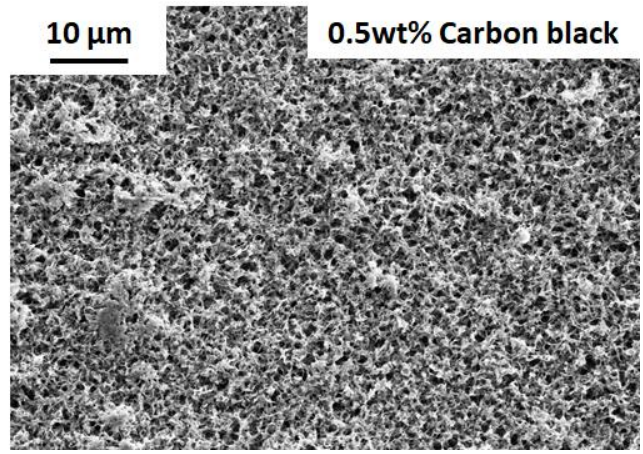
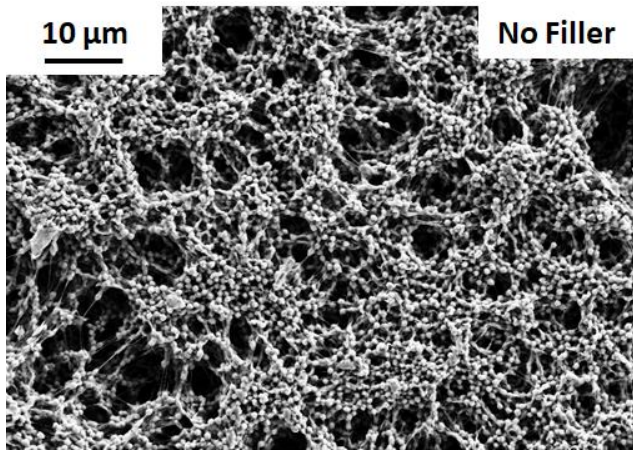
Hydrophobic PVDF membranes were prepared using a green solvent. The addition of different amounts of CB modified the characteristics and distillation performance of the membranes.

Reference 1:

[1] M. Pagliero, A. Bottino, A. Comite, C. Costa, Novel hydrophobic PVDF membranes prepared by nonsolvent induced phase separation for membrane distillation, *J. Memb. Sci.* 596 (2020) 117575. <https://doi.org/10.1016/j.memsci.2019.117575>.

Reference 2:

[2] S. Leaper, A. Abdel-Karim, P. Gorgojo, The use of carbon nanomaterials in membrane distillation membranes: a review, *Front. Chem. Sci. Eng.* 2021 154. 15 (2021) 755–774. <https://doi.org/10.1007/S11705-020-1993-Y>.



Preparation of novel composite membranes for lithium recovery from saline streams via flow capacitive deionization (FCDI)

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¹Universidade NOVA de Lisboa, Portugal

Main topic: Novel membrane materials

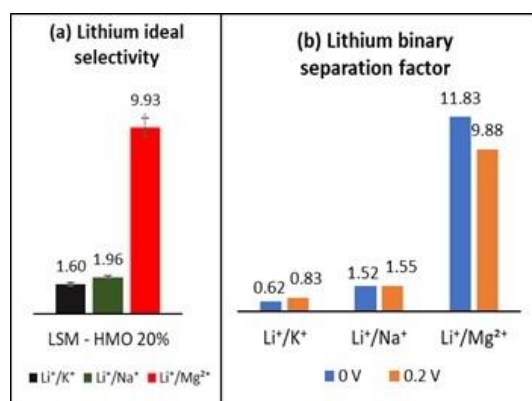
Membrane technologies provide promising possibilities to recover lithium from aqueous resources, like saline natural and/or industrial brines and sea water, in a green and eco-friendly way [1]. However, there are still limitations to fully exploit this technology, such as membrane's low lithium ion permselectivity, low flux and challenging scale-up. In this presentation, we will present and discuss a novel and easier approach to synthesize lithium selective membranes (LSM). The membranes were prepared by mixing of hydrogen manganese oxide (HMO), used as lithium selective adsorbent, into a homogeneous blend of sulfonated polyether sulfone (SPES) and Nafion resin as a polymeric matrix. The effect of HMO loading, varying from 0 to 30 wt. %, its distribution in the membrane matrix, as well as the physical, structural/morphological, chemical, thermal, and electrochemical properties of the membranes were comprehensively investigated. The most promising membrane (LSM-HMO 20 %), containing 20 % (w/w) of HMO with respect to the polymer, showed an almost 8 times higher Li^+ ionic conductivity (12.9 mS/cm) compared to the control composite membrane without HMO (1.6 mS/cm) and an average lithium ideal selectivity (LIS) of 1.60, 1.96, and 9.93 towards Li^+/K^+ , Li^+/Na^+ , and $\text{Li}^+/\text{Mg}^{2+}$ respectively. The binary separation factor (BSF) assessed under natural diffusion was 0.62, 1.52, and 11.83 while in electro-diffusion it was 0.83, 1.55, and 9.88 for the Li^+/K^+ , Li^+/Na^+ , and $\text{Li}^+/\text{Mg}^{2+}$ pairs respectively. All in all, the prepared membranes showed promising lithium recovery and this study paves a path to the design and development of large-scale lithium selective composite membranes. Moreover, such membranes are suitable to be used in flow capacitive deionization (FCDI) devices according to our ongoing studies.

Acknowledgments:

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869467 (SEArctularMINE) and from Fundação para a Ciência e Tecnologia, I.P. under grant agreement No PTDC/EQU-EQU/6193/2020 (Se(L)ect(i)vity). This work was also supported by the Associate Laboratory for Green Chemistry – LAQV which is financed by national Portuguese funds from FCT/MCTES (UIDB/50006/2020).

Reference 1:

Saif et al., Development of highly selective composite polymeric membranes for $\text{Li}^+/\text{Mg}^{2+}$ separation, J. Membr. Sci. 620 (2021) 118891.



$$LIS \left(\frac{\text{Li}^+}{\text{M}^{n+}} \right) = \frac{\text{Membrane's LiCl conductance}}{\text{Membrane's MCl}_n \text{ conductance}} \quad (1)$$

$$BSF \left(\frac{\text{Li}^+}{\text{M}^{n+}} \right) = \frac{\frac{[\text{Li}^+]_{\text{Receiver}}}{[\text{Li}^+]_{\text{Feed}}}}{\frac{[\text{M}^{n+}]_{\text{Receiver}}}{[\text{M}^{n+}]_{\text{Feed}}}} \quad (2)$$

where **M** is a competing counter-ion and **n** is its valence.

Figure 1: Lithium ideal selectivity (LIS) (a) and binary separation factor (BSF) (b) of a LSM – HMO 20 % membrane, as calculated by Eq. 1 and 2, respectively.

Preparation of pure β -phase PVDF membrane by using bio-based solvents; experiment, molecular dynamic simulation and life-cycle assessment

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Main topic: Novel membrane materials

The use of extremely toxic solvents raises substantial health and environmental threats. It would be beneficial to adopt green solvent for sustainable membrane processing. This study discusses the development of PVDF membranes using inexpensive environmentally friendly biobased and biodegradable cyclic carbonate solvents, namely ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC). The morphology, crystalline structures, and polymorphism of the prepared PVDF membranes with a different type of solvents were studied. Polymorph analysis showed that PVDF membrane fabrication in EC or PC produced pure β -phase material, while PVDF membrane fabrication in BC produced a mixture of α and β -phase material. Molecular dynamics simulation was used to explore the mechanism of polymorph phase formation, which was found to be based on the formation of hydrogen bonding at the polymer-solvent interface. Since the PVDF membrane fabricated in EC had the highest porosity and pure water permeability, it was further tested in direct contact membrane distillation (DCMD) application, yielding promising results in terms of permeate flux and salt rejection. Life-cycle research was used to determine the influence of the solvents used (common vs. EC) on global warming, marine ecotoxicity, human carcinogenic and non-carcinogenic toxicity, land use potential, and fossil fuel scarcity. Toxic solvents, such as NMP, are largely responsible for membrane production's harmful environmental effects, accounting for 40–60% of the overall impact. Meanwhile, the use of EC as a renewable solvent alternative will save up to 35% on environmental costs and impacts. These findings present a sustainable alternative for preparing pure β -phase PVDF membrane that large-scale processing of piezoelectric PVDF membranes using green solvents is feasible.

Reference 1:

Ismail, N., Essalhi, M., Rahmati, M., Cui, Z., Khayet, M., & Tavajohi, N. (2021). Experimental and theoretical studies on the formation of pure β -phase polymorphs during fabrication of polyvinylidene fluoride membranes by cyclic carbonate solvents. *Green Chemistry*.

Reference 2:

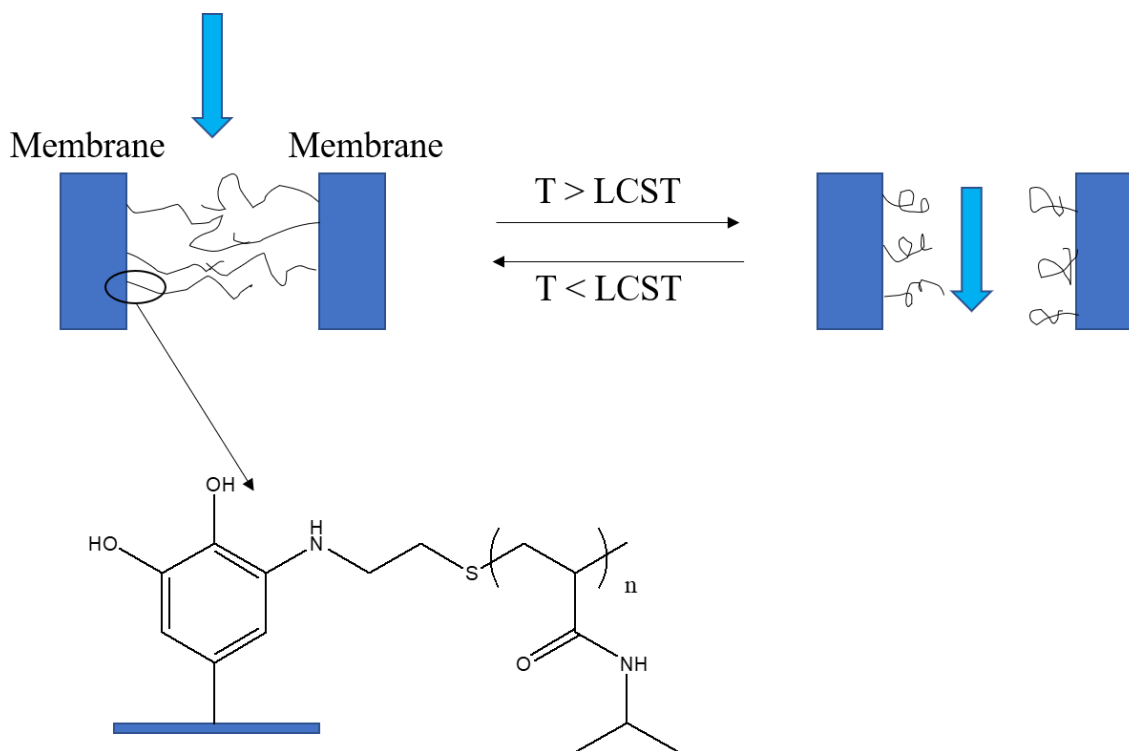
Yadav, P., Ismail, N., Essalhi, M., Tysklind, M., Athanassiadis, D., & Tavajohi, N. (2021). Assessment of the environmental impact of polymeric membrane production. *Journal of Membrane Science*, 622, 118987.

Preparation of Thermally Responsive PVDF Membrane via Dopamine Co-deposition with PNIPAM

Xiong, Chen - Main Author; Ulbricht, Mathias - Co-Author

Main topic: Microfiltration/Ultrafiltration

Abstract: Poly(N-isopropylacrylamide) (PNIPAM), a typical thermally responsive polymer, could show a volume change at its lower critical solution temperature (LCST), a property which is widely used in the preparation of the thermally responsive membranes that has attracted a significant attention in microfiltration and ultrafiltration. In this work, a thermally responsive polyvinylidene difluoride (PVDF) microfiltration membrane was accomplished via dopamine co-deposition with amino-functional PNIPAM synthesized by free radical polymerization using 2-aminoethanethiol hydrochloride as a chain transfer agent (Fig. 1). ATR-FTIR spectra illustrated the successful introduction of PNIPAM on the PVDF microfiltration membrane surface via dopamine co-deposition. The PVDF membrane after dopamine co-deposition with PNIPAM improved its hydrophilicity, and there was a rough polydopamine (PDA) with PNIPAM nanoparticles coating layer on the surface of the membrane. The water permeance of the PVDF membrane coated with dopamine and PNIPAM for 16 h reached 55 000 and 37 000 L/m² h bar at 45 and 25 °C, which indicated the role of the thermally responsive property of PNIPAM in the membrane. Therefore, dopamine co-deposition could be used as a facile and convenient method to prepare a thermally responsive PVDF microfiltration membrane, and it can be extended to preparation of other types of surface-functionalized membranes.



Production of a food acidifier from acid whey using nanofiltration and electro dialysis

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¹Department of Food Science, University of Copenhagen, Rolighedsvej 26, 1958 Frederiksberg, Denmark, ²Toulouse INP-ENSIACET, 4 Allée Emile Monso, 31030 Toulouse Cedex 4, France, ³Department of Food Science, University of Denmark, Rolighedsvej 26, 1958 Frederiksberg, Denmark, ⁴Arla Foods Amba, Agro Food Park 19, 8200 Aarhus N, Denmark, ⁵MemBrain s.r.o. (Membrane Innovation Centre), Pod Vinicí 87, 471 27 Stráž pod Ralskem, Czech Republic

Main topic: Electro-membrane processes

Acid whey is a side-stream from the production of skyr, Greek yoghurt, quark and cottage cheese. It contains high concentrations of valuable compounds, such as calcium, magnesium and lactic acid. However, it also contains sodium and potassium, which the health authorities recommend limited intake, since they can cause health problems, such as high blood pressure and calcium deficiency. Several studies have shown that electro dialysis (ED) is an efficient technology to recover charged compounds from acid whey. Nevertheless most studies have focused on demineralizing acid whey to produce more stable whey powders (Merkel et al., 2021).

Monovalent ions from acid whey can be removed by nanofiltration (NF) prior to ED, potentially improving the separation efficiency of the divalent ions during ED. Consequently, a retentate solution containing mainly calcium, magnesium, lactose and lactic acid can be obtained. Thus, the objective of this study was to investigate the processing conditions needed during NF and ED to produce a stream rich in lactic acid, calcium and magnesium, but low in sodium and potassium, which can be used as acidifier and mineral fortifier in the food industry. The results have shown, that calcium and magnesium are completely retained by the NF membrane, while 50% of the sodium and potassium and 35% of the lactic acid are removed. ED processing of the NF retentate, which contains high concentrations of lactic acid, calcium, magnesium and lactose (approx. 12 g/L, 3 g/L, 0.3 g/L and 70 g/L, respectively) have shown that it was possible to effectively produce two streams: one rich in lactic acid, calcium and magnesium and one rich in lactose.

Reference 1:

Merkel, A.; Voropaeva, D.; Ondrusek, M. The impact of integrated nanofiltration and electro dialytic processes on the chemical composition of sweet and acid whey streams. *Journal of Food Engineering* 2021, 298. Article 110500.

Production of food for oyster by ultrafiltration

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¹aix marseille university

Main topic: Food processing

The production of oyster spat in a commercial hatchery requires control over the seawater quality for the food production of fodder microalgae. An ultrafiltration pilot was used from lab to industrial scales in *Vendée Naissain* company. The aim of this work is to use ultrafiltered seawater (UFSW) for a sustainable production of the microalga *Isochrysis lutea* (T-Iso) and to determine if a better growth than on borehole water (BW), historically used by the producers, can be observed. A comparison between autoclaved seawater (ASW) and UFSW is also realized. In all these cases, UFSW has shown a definite efficiency for culturing T-Iso with rapid growth and significant reduction in contaminations compared to cultivation on BW. Indeed, during the experiments, all the cultures of T-Iso were evaluated according to four criteria: appearance, mobility, contamination, and effective use to produce a larger volume (Figure 1). It was observed that the appearance of the cultures is considered satisfactory (>90%) or perfect (100%) for UFSW and only 56% for BW. A greater mobility of T-Iso cells is observed in UFSW. Contamination i.e. ciliates in cultures is 8% for UFSW against 40% for BW. It should be noted that a crop that grows at a rate of one division per day, has a doubling time of one day, and an instantaneous growth rate of 0.693 d^{-1} . The average growth rates of cultures show a greater growth of UFSW compared to BW during the first day with $0.92\text{-}1.1 \text{ doubling.d}^{-1}$ for UFSW against $0.55\text{-}0.83 \text{ doubling.d}^{-1}$ for the BW as the function of the volume. The feasibility study is validated [1] by a comparison of UFSW with ASW in an iso nutrient concentration experiment: whatever the initial concentration, 1 or 2 million cell.mL⁻¹, a faster growth of cultures on UFSW than with ASW is observed after 4 days, x1.7 and 1.5 respectively. A similar growth rate is obtained for a higher concentration limited at 22 million cell.mL⁻¹. As conclusion, culture on UFSW, a one-step treatment, allows a better protection, and a reduction in growth cycles, thus limiting glassware and daily transplanting time.

Reference 1:

Cordier, C., C. Stavrakakis, K. Guyomard, F. Coelho, P. Sauvade et P. Moulin, Culture of microalgae by ultrafiltered seawater, *SCI - Medicine* vol 2-2 (2020) 56-62.

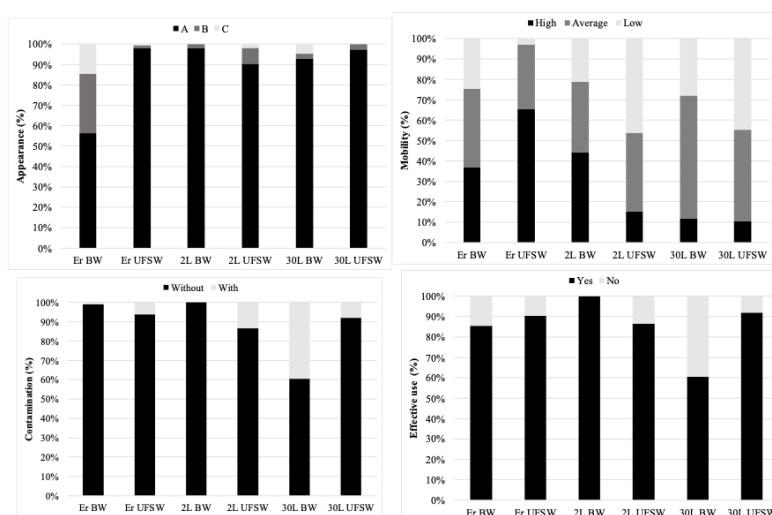


Figure 1: Appearance, mobility, contamination and effective use of T-Iso cultures in the different containers as a percentage of scores assigned on all replicates

Promoted sodium carbonate solution by amino acids for post combustion CO₂ capture using membrane contactors

Sang Sefidi, Vida - Main Author; Luis, Patricia - Co-Author

Main topic: CO₂ capture

Introduction:

Burning fossil fuels for energy production and transport has caused a significant increase in CO₂ emissions leading to catastrophic problems for the environment. One potential approach to reduce CO₂ emissions from power plants is to use CO₂ capture and storage/utilization technologies. Membrane gas absorption (MGA) using a membrane contactor has recently appeared as one of those technologies, in which the membrane acts as a non-selective barrier providing the contacting surface for gas and liquid phases. Carbonate solutions are studied as a green solvent in MGA. However, due to low absorption rate of the solvent which increases the capital cost of the process, a promoter such as amino acids is introduced to increase the absorption rate. In this study, arginine and sarcosine are studied as promoters. In addition, several operational parameters have been evaluated to find the optimal process conditions.

Material and methods:

Arginine (Sigma Aldrich,99%), Na₂CO₃ (Sigma Aldrich, Germany) enters membrane contactor in recirculation in lumen side of a hollow fiber membrane contactor (MiniModule 1x5.5 G543, liquid-Cel, Membrane GmbH, Germany) and 15% of CO₂ and air is entering shell side. CO₂ percentage of outlet gas is analyzed via a CO₂ gas analyzer (Rosemount™ X-stream enhanced XEGK continuous gas analyzer, Emerson, Germany). The total mass transfer coefficient (K_{ov}) is calculated as follows:

$$K_{ov} = \frac{C_m}{V_g(C_{i,g,out} - C_{i,g,in})} A_m \cdot \Delta$$

(1)

Results:

Several operational parameters such as liquid and gas flow rates, amino acids concentration, CO₂ concentration, presence of impurities, and temperature of the solution, are studied. It was found that with an increase of gas and liquid velocity, K_{ov} will increase due to a reduction in gas boundary layer resistance. On the other hand, the liquid temperature influence on K_{ov} is negligible. However, the effect of impurities in the solution cannot be overlooked since there is a significant decrease in K_{ov} when the concentration of impurities decreases in the solution.

Conclusion:

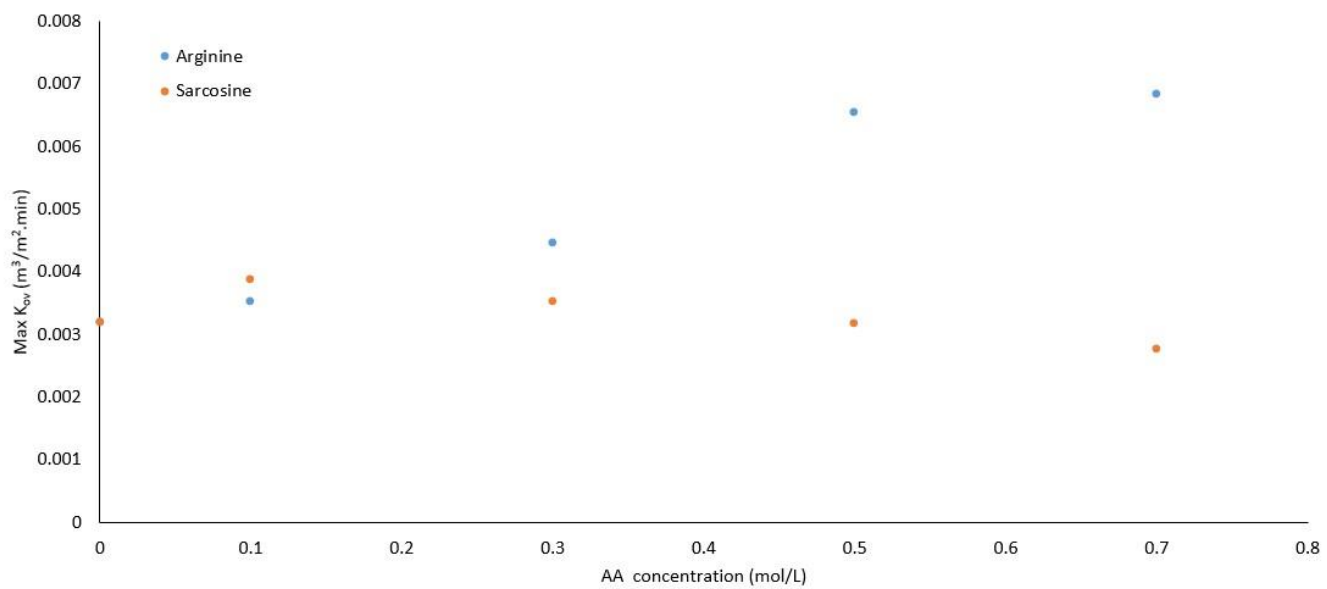
The addition of amino acids clearly increases the mass transfer coefficient. In this study, the operational operation conditions have been found: 400 ml/min for liquid flow rate, 0.5 mol/l of arginine and 0.3 mol/l of sarcosine, operating at room temperature, and without the presence of sodium bicarbonate.

Reference 1:

P. Luis, V. Sang Sefidi, M. Sparenberg, M. Garcia Alvarez. (2021), continuous process and system for the production of sodium bicarbonate crystals, 20211693.5-1108, universite catholique de louvain.

Reference 2:

V. Sang Sefidi and P. Luis, "Advanced Amino Acid-Based Technologies for CO₂ Capture: A Review," Industrial and Engineering Chemistry Research. 2019.



Prospects of industrial membrane concentrates: zero waste hybrid process combining membrane filtration and wet air oxidation

Gout, Emilie - Main Author¹; Loisir, Steevens - Co-Author¹; Vanloot, Pierre - Co-Author¹; Boutin, Olivier - Co-Author¹; Moulin, Philippe - Co-Author¹

¹Aix-Marseille University

Main topic: Environmental applications

Industrial development has led to the generation of higher volumes of wastewater. Depending on the industry, wastewater volume and quality can considerably vary. Recalcitrant organic pollution is found in these effluents. Proper treatment to comply with stringent regulation for environmental discharge remains a challenge. The hybrid process study was set to treat ultrafiltration or reverse osmosis (RO) concentrates with wet air oxidation (WAO) to generate a global outlet, including permeate, safe for environmental discharge. Membrane separation is a process of choice for wastewater remediation as it permits the production of a significant volume of good quality permeate. However, the main drawback of membranes is the concentration of a highly polluted stream that cannot be discharged. WAO is suited for small volumes of concentrated effluents with a chemical oxygen demand (COD) typically between 10 – 100 g.L⁻¹ for autothermicity. This treatment path combines pros and cons of both processes by lowering the volume of concentrates while obtaining the right COD with filtration for further low energy WAO treatment. High intensification potential has been shown in previous works on both synthetic and real industrial effluents. High concentration factors were obtained (between 17 and 40) without affecting a good regeneration of the membrane. Moreover, for total organic carbon (TOC), removals by WAO were above 80% and filtration retention reached at least 75% [1]. Performance of the global process depends on efficiency of filtration (concentration factor and permeate quality) and of WAO (pressure, temperature, concentration criterion (mainly COD) and residence time). Experimental design methodology was used to determine best operating conditions for pollution removal. Characterizations were performed to highlight process performances such as pH, conductivity, turbidity, COD, TOC and humic acid-like reduction by emission-excitation fluorescence spectroscopy. The first test campaign was on real RO landfill leachates concentrates (1.5 concentration factor and 99% TOC retention) ; a TOC removal of 88% was achieved after lab-scale WAO at 300°C – 21 MPa. The goal is to work on all operating parameters to enable sufficient pollution reductions to meet with discharge regulation. To validate industrial-scale process intensification, experiments in a bubble column reactor working in continuous are foreseen.

Reference 1:

C. Pinchai, M. Monnot, S. Lefèvre, O. Boutin, and P. Moulin, « Coupling membrane filtration and wet air oxidation for advanced wastewater treatment: Performance at the pilot scale and process intensification potential », *Can. J. Chem. Eng.*, dec. 2019, doi: 10.1002/cjce.23688

Purification of galactoglucomannan in the liquid fraction from steam pretreatment of soft wood using ultrafiltration membranes

Sjölin, Mikael - Main Author¹; Herrlin, Svante - Co-Author¹; Wallberg, Ola - Co-Author¹; Thuvander, Johan - Co-Author¹; Lipnizki, Frank - Co-Author¹

¹Lund University

Main topic: Bio-separations and bio-refinery

Fractionation of biomass by steam explosion (STEX) is a growing research area, e.g. for bioethanol production. When softwood is pre-treated, galactoglucomannan (GGM) is dissolved in the liquid fraction. This polymeric hemicellulose compound has been identified as a valuable resource and can be used in fields such as oxygen barrier films, food coatings, hydrogels or biomedical applications [1]. Since severity during STEX affects the GGM chain length and thereby its properties, two different severities were evaluated based on previous studies: (1) STEX pre-treatment at 190°C for 5 minutes and (2) 200°C for 2 minutes [2]. The two pre-treatment processes were evaluated based on GGM size, yield and purity. Even though, the results showed only minor differences between the two severities, the option using 200°C for 2 minutes was slightly superior with a GGM yield of 17.6 % and a purity of 27.1% and was thus chosen for the subsequent purification which is required for its full utilisation. The impurities are mainly comprised of lignin derivatives, organic acids, salts and other dissolved components. To achieve purification, ultrafiltration was chosen and four polymeric flat-sheet membranes – GR90PP, RC70PP, ETNA01PP and ETNA10PP (Alfa Laval, Denmark) with molecular weight cut-off of 5kD, 10kD, 1kD and 10kD respectively - were investigated in recirculating batch-crossflow mode at 60°C and 0.5-3 bar of transmembrane pressure. All membranes were evaluated with respect to flux and GGM retention. The best membrane was the GR90PP with a flux of 11 L/m²h at 3 bar transmembrane pressure and a GGM retention of 96%. Furthermore, it was possible to completely recover the pure water flux of the GR90PP membrane with a one stage alkaline cleaning after the membrane was heavily fouled with a pure water flux reduction of 95% compared to the pristine membrane. Hence, it is planned to use this membrane for future concentration and purification studies of GGM.

Reference 1:

Natanya M. L. Hansen and David Plackett *Biomacromolecules*, 2008, 9 (6), 1493-1505 DOI: 10.1021/bm800053z

Reference 2:

Magnus Palm and Guido Zacchi *Biomacromolecules*, 2003, 4 (3), 617-623 DOI: 10.1021/bm020112d

PVDF membranes prepared by the combined crystallisation and diffusion (CCD) method- a breakthrough in ultrafiltration membrane fabrication

Shah, Vatsal - Main Author; Li, Kang - Co-Author

Main topic: Microfiltration/Ultrafiltration

The innovative technique of membrane fabrication, Combined Crystallisation and Diffusion (CCD), produces membranes that are intrinsically asymmetric and generates much higher fluxes at similar pore sizes compared to those achieved by membranes fabricated via non-solvent induced phase separation (NIPS) and thermal induced phase separation (TIPS) (Wang et al., 2016). The CCD method is inspired by the freeze-drying method as it involves unidirectional cooling of the polymer cast solution using a solid media to freeze the solvent molecules into crystals. These crystals, after being leached out in an icy water bath, serve as pore templates in the final membrane.

The pore sizes of CCD based PVDF membranes so far were limited by the cooling conditions and the total polymer dope concentration, with the smallest pore size achieved was 33 nm. The purpose of this study was to decrease the pore size further, without changing the total polymer concentration or the cooling conditions. To achieve this blending modification was applied using poly(methyl methacrylate) (PMMA) as an additive (Shah et al., 2021).

PVDF flat sheet membranes were prepared via CCD and NIPS with dope concentration varying from 10 to 20wt.%. PMMA modified PVDF membranes were prepared with total polymer concentration fixed at 20wt.% while changing the PMMA concentration from 0-4wt.%. The temperature of the cooling plate was kept fixed at -40°C. Various characteristic properties of the membranes were analysed via SEM, liquid-liquid displacement porometer, dead end filtration cell, FTIR and tensile strength testing machine.

For pristine PVDF membranes, CCD and NIPS, both showed similar pore sizes but former had much higher pure water permeation fluxes (by 10x), owing to the interconnected microchannels in the support layer along with the high pore density as seen in the SEM images (Fig.1). For PMMA modified PVDF membranes, despite maintaining the total polymer content at 20wt.% but increasing the PMMA content from 0 to 4wt.%, the pore size decreases from 30 nm to 15 nm. This result was attributed to change in the gelation curve (thermodynamics) and possible reduction in diffusion rates (kinetics) that would limit the growth of solvent crystals.

Reference 1:

Wang, B., J. Jing and K. Li, Porous membranes prepared by a combined crystallisation and diffusion (CCD) method: Study on formation mechanisms. *Journal of Membrane Science*, 2018. 548: p. 136-148.

Reference 2:

Shah, V., B. Wang, and K. Li, Blending modification to porous polyvinylidene fluoride (PVDF) membranes prepared via combined crystallisation and diffusion (CCD) technique. *Journal of Membrane Science*, 2021. 618: p. 118708.

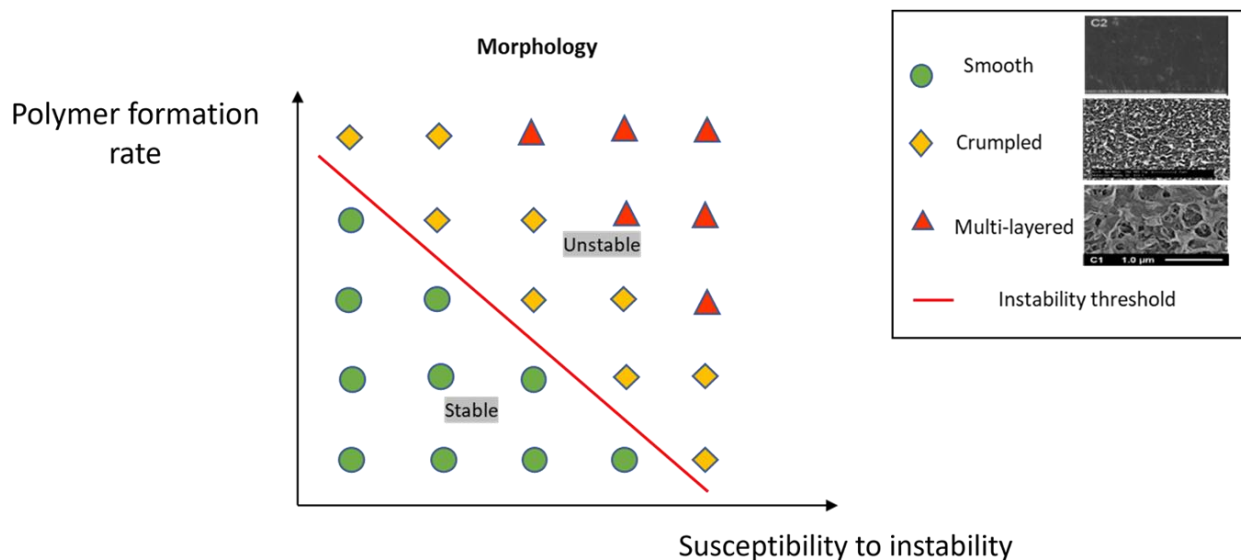
Re-thinking polyamide thin film formation: Interfacial destabilization and resultant morphology.

Nulens, Ines - Main Author¹; Ben-Zvi, Adi - Co-Author²; Vankelecom, Ivo - Co-Author¹; Ramon, Guy - Co-Author³
¹KU Leuven, ²Technion-Isreal Institute of Technology, ³Technion-Israel Institute of Technology

Main topic: Nanofiltration/Reverse Osmosis

Thin-film polyamide (PA) selective layers fabricated via interfacial polymerization (IP), form the core of membrane-based water purification. Despite widespread commercial application, the link between synthesis conditions and resultant film properties is not fully understood. Unravelling this fundamental knowledge is essential for designing better membranes for different applications. Much experimental work has been reported, where synthesis conditions are varied, and the resultant performance and morphology are discussed. However, contradicting trends are often observed, primarily due to lack of a rigorous theoretical description. Here, we outline an approach that considers the interfacial stability of a system undergoing IP, with the notion that a transition from stable to unstable state corresponds to a morphological shift of the resultant film, from smooth to crumpled. Within the proposed framework, we re-examine data reported in the literature, encompassing a wide variety of synthesis conditions. Specifically, we identify and classify physical parameters that affect either the polymer formation rate and/or the system's susceptibility to instability. A conceptual 'phase diagram' maps the morphological 'regimes' with respect to the relevant parameter space. Our analysis illustrates how PA morphology, observed by SEM images collected from the literature, transitions from smooth to crumpled, with remarkable correlation with the defined parameter space. Re-casting results in this manner highlights not only the underlying physics, but also potential pitfalls where variations of synthesis conditions result in conflicting effects, making it difficult to define clear trends. New experimental data, cast within the developed physical framework and supplemented by theoretical quantification, will strengthen the fundamental understanding of the process for a given chemistry, with the goal of providing a clear physical toolbox for IP-based membrane design.

A conceptual 'phase diagram'



Real-time Monitoring of Membrane Wetting Progression in using Impedance Spectroscopy

Wong, Pak Wai - Main Author¹; An, Kyoung Jin - Co-Author¹

¹City University of Hong Kong

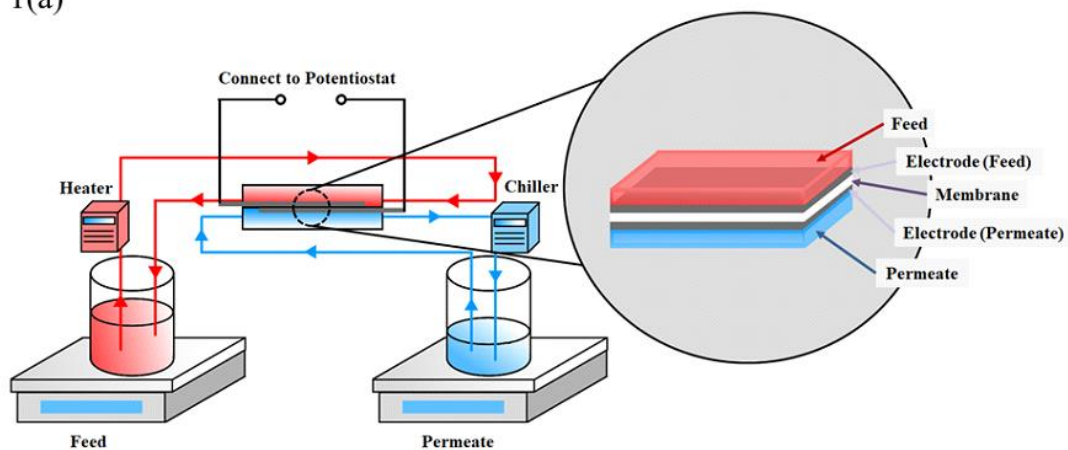
Main topic: Membrane contactors and membrane distillation

Surfactants pose a serious challenge in membrane distillation as they can cause wetting. The mechanisms and wetting progression during wetting is not yet well defined as changes in salt rejection only provide a signal after permeate quality has been deteriorated.

To quantify the wetting progression rate by surfactants in membrane distillation, we applied a new impedance analysing technique to real-time monitoring wetting proportion based on data obtained from Electrochemical Impedance Spectroscopy (EIS) which has been proposed as a wetting detection method by providing earlier signal warning and in a broader compared to measuring flux and conductivity.

With the proposed technique, we discovered the instant wetting and progressive wetting stages under different concentration of surfactant 0.1 ~ 0.4 mM Sodium Dodecyl Sulfate (SDS) with commercial PVDF (C-PVDF) membrane. It was found that instant wetting could still occur at low concentrations 0.1 mM SDS with wetting front reached 18%, suggesting surface tension is not the only cause of membrane wetting, as adsorption of surfactant on the membrane surface altered the membrane's hydrophobicity. The instant change of feed concentration at the wetting front caused immediate adsorption of SDS into the membrane channels until the concentration at neared the adsorption and desorption rate. The slow wetting stage may be caused by the replenishment of SDS from the feed solution to wetting front. Under 0.1 mM SDS, wetting front increased by 2% in 1.5 hr. Further addition of SDS brings cumulative effect on wetting progression with wetting front increased by 50% within an hour after further addition of 0.1 mM SDS. Modelling result were verified by examining the cross section of a partially wetted membrane at different time intervals using FE-SEM with EDX. These results suggest that this analysis approach can assist in identifying optimal membrane replacement times by real-time monitoring of membrane wetting proportion, while also demonstrating new direction for proving how membranes are wetted during membrane distillation.

1(a)



1(b)

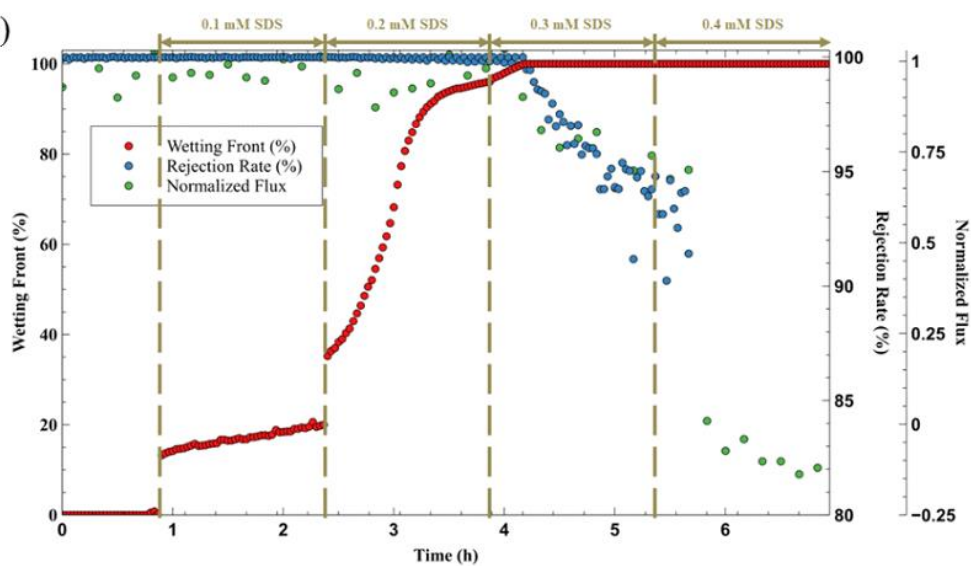


Figure 1. (a) DCMD setup with potentiostat to detect the change of impedance during the experiment. The small circle shows 3-dimensional illustration of module configuration. Carbon cloth electrodes were set on both the feed and permeate sides of the membrane. (b) Decline of normalized flux and rejection rate was not significant before 0.3 mM SDS was added. Wetting front reached 100% after 0.3 mM SDS was added for C-PVDF with pore size 0.22 μm . Normalized flux and rejection rate started to decrease significantly when the wetting front was 100%. At 0.4 mM SDS, negative normalized flux occurred indicating the membrane was not performing any salt rejection process.

Real-time particle imaging reveals morphological effects in calcium phosphate membrane fouling

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Main topic: Membrane fouling and cleaning

Wastewater effluent is a critical water resource to tackle water scarcity, as effects of climate change and population growth degrade existing water resources. However, filtration of effluent in nanofiltration/reverse osmosis systems is limited to ~80% water recovery by specifically calcium phosphate (CaP) mineral fouling; and further complicated by the various polymeric forms of phosphate salts. More so, the use of anti-scalants have proved ineffective in CaP fouling mitigation. In this study, we used a novel new combination of real-time inline microscopy, electrical impedance spectroscopy (EIS), post SEM analysis and filtration metrics (water flux and rejection) to delineate CaP fouling mechanisms and the consequent morphological effects in high recovery synthetic effluent nanofiltration (NF). We used an NF polyelectrolyte multilayer (PEM) membrane, prepared by static layer-by-layer (LbL) coating of a cationic polymer - polydiallyl dimethylammonium chloride, and anionic polymer - poly styrenesulfonate (six bi-layer) on a polyethersulfone (PES) ultrafiltration (UF) membrane. Increasing permeate recovery over filtration time was simulated through additions of CaCl_2 with $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$. Using this new technique(s), we characterised mechanisms governing CaP fouling development with time. An evolution between fouling by amorphous particles to fouling by crystalline particles was identified, and this phase-change was captured in real-time images using in-line microscope. CaP fouling was detrimental to water flux with 86% decrease, due to the voluminous amorphous phase. The delineated mechanism(s) highlight CaP fouling as independent of membrane surface chemistry, since it is bulk-solution controlled. We showed inline microscopy as a new effective technique to study mineral fouling, as it gives invaluable information on the onset of bulk crystallization and the crystallized particles' morphological evolution in real-time. Combining it with EIS gives complementary information on mineral accumulation on the membrane surface. Findings from this study and further use of these techniques can guide the development of future mitigation strategies for sustainable higher effluent recovery by membrane filtration.

Reference 1:

Bunani, S., Yörükoğlu, E., Sert, G., Yüksel, Ü., Yüksel, M., Kabay, N., 2013. Application of nanofiltration for reuse of municipal wastewater and quality analysis of product water. *Desalination* 315, 33–36. <https://doi.org/10.1016/J.DESAL.2012.11.015>

Reference 2:

Mangal, M.N., Salinas-Rodriguez, S.G., Dusseldorp, J., Kemperman, A.J.B., Schippers, J.C., Kennedy, M.D., van der Meer, W.G.J., 2021. Effectiveness of antiscalants in preventing calcium phosphate scaling in reverse osmosis applications. *J. Memb. Sci.* 623, 119090. <https://doi.org/10.1016/j.memsci.2021.119090>

Recovering high-value P-K fertilizer from effluents by integrating adsorption and electro dialysis with bipolar membranes

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Main topic: Electro-membrane processes

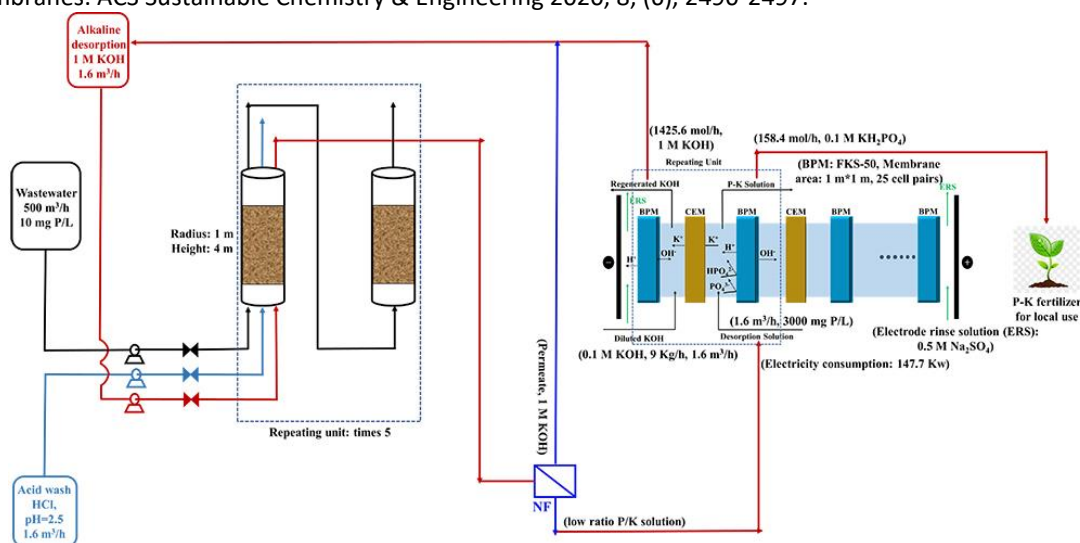
Recently, phosphorus (P) recovery from wastewater has attracted widespread attention, as worldwide food production is largely dependent on this non-renewable resource. Although effective phosphate removal and recovery was demonstrated using adsorption, these studies mainly focused on adsorbent regeneration and reuse, while very few studies addressed the recycling of the regeneration solution. As a result, obtaining a high-value P fertilizer is still a standing technological challenge. To address these challenges, we developed a novel combination of bipolar membranes electro dialysis (BMED) with phosphate sorption by granular-ferric-hydroxide. The BMED is utilized to further treat the exhausted KOH eluent and to produce KH_2PO_4 solution. The BMED stack is composed of repeating units of cell pairs, each containing a bipolar membrane (BPM), and a cation exchange membrane (CEM). The BPM induces water dissociation under electric current, providing H^+ and OH^- to the spent eluent and the regenerated KOH compartments, respectively. Excess K^+ ions are driven through the CEM while phosphate species are retained in the spent eluent compartment. At the end of the process, a high purity KH_2PO_4 solution — a valuable P-K fertilizer— and concentrated KOH, which can be reused as eluent in the desorption step, are obtained. We found that under the optimal operating conditions (*i.e.* column adsorption experiments with single-pass of the up-flow mode with the flow rate 45 ml/min; acid cleaning using HCl of the pH 2.5; pH of the eluent desorption KOH solution = 13.4~13.9, concentration = 2.29 M), the satisfactory accumulated concentration of P (3545.45 mg P/L) in the regeneration solution was obtained after adsorption, acid cleaning and alkaline desorption of continuous operation. The P-rich eluate is used as a source for subsequent BMED step for recycling the regeneration solution to obtain high-value liquid P fertilizer. Experimental results indicate that high current efficiency (>90%), low energy consumption (<0.1 KWh/mol- K_2HPO_4), and high P recovery (99%) can be achieved in the BMED step. The new approach can be used as a sustainable, economical, and environment-friendly method for P recovery from effluents.

Reference 1:

Nir, O.; Sengpiel, R.; Wessling, M., Closing the cycle: Phosphorus removal and recovery from diluted rinse effluents using acid resistive membranes. *Chemical Engineering Journal* 2018, 346, 640-648.

Reference 2:

Monat, L.; Chaudhury, S.; Nir, O., Enhancing the Sustainability of Phosphogypsum Recycling by Integrating Electro dialysis with Bipolar Membranes. *ACS Sustainable Chemistry & Engineering* 2020, 8, (6), 2490-2497.



Recovery and purification of polyphenols from fruits and vegetables by membrane technology

MONTENEGRO, MARIA FERNANDA - Main Author; CORTINA, JOSE LUIS - Co-Author; TAPIA, PAULINA - Co-Author; VECINO, XANEL - Co-Author; REIG, MONICA - Co-Author; VALDERRAMA, CESAR - Co-Author; Saurina, Xavier - Main Author; GRANADOS, MERCE - Main Author

Main topic: Bio-separations and bio-refinery

The growing interest and consumer demand for additives of natural origin in food, pharmaceutical and cosmetic industries have promoted the search for different sources of bioactive compounds. Polyphenols have been one of the additives that have attracted the most attention in recent decades, due to their antioxidant activity [1]. Polyphenols are present in plants as part of the defense mechanism against solar radiation and infections.

The optimization of operational conditions to maximize polyphenols extraction yield from spinach and orange wastes were previously studied [2], modifying time, temperature, solid-to-solvent ratios and pH. Then, the purification and concentration of the polyphenols obtained by the extraction, under the optimum conditions (5 min, 50 °C, 1:50 and pH 6 for spinach matrix, and for orange matrix 15 min, 70 °C, 1:100 and pH 4), were done by membrane technology.

Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) technologies were studied. The type of the membranes MF was: 0.22 and 0.45 µm; UF: 30 and 50 kDa; NF: NF90, NF270, DURACID, TFCS and TFC-HR; and RO: BW30LE, SW30HR and XLE.

The membrane experiments were carried out by collecting 1 mL of the permeate stream after increasing the flow rate from 1-10 mL/min, the extracts were analyzed by high performance liquid chromatography with diode array detection (HPLC-DAD). Results shown that the transmembrane flux depended on the feed flow rate for MF, UF and NF; whereas for RO it was independent. For spinach matrix, 50 kDa (UF) and TFC-HR (NF) membranes could be used to separate polyphenols and BW30 (RO) to concentrate them. On the other hand, for orange waste, 0.22 µm (MF), 50 kDa (UF), DURACID (NF) and BW30 (RO) could be used for separate.

Reference 1:

M. Derrien, A. Badr, A. Gosselin, Y. Desjardins, and P. Angers, "Optimization of a green process for the extraction of lutein and chlorophyll from spinach by-products using response surface methodology (RSM)," *LWT - Food Sci. Technol.*, vol. 79, pp. 170–177, 2017, doi: 10.1016/j.lwt.2017.01.010.

Reference 2:

M. F. Montenegro-Landívar et al., "Fruit and vegetable processing wastes as natural sources of antioxidant-rich extracts : Evaluation of advanced extraction technologies by surface response methodology," *J. Environ. Chem. Eng.*, no. November 2020, 2021, doi: <https://doi.org/10.1016/j.jece.2021.105330>.

Recovery of nitrogen from Pharmaceutical wastewater effluent as fertilizer using hollow fiber liquid-liquid membrane contactors

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¹Zuckerberg Institute for Water Research, Blaustein Institutes for Desert Research, Ben Gurion University of the Negev, Sde Boker 84990, Israel

Main topic: Membrane contactors and membrane distillation

The competence to recover ammonia from Pharmaceutical wastewater effluent is significant to ensure eco-efficiency and to reduce wastewater treatment costs. To recover the dissolved ammonia from wastewater effluent, a hollow fiber membrane contactor is considered as prospective technology. This membrane technology has been shown to generate value-added and affordable fertilizer economically. The novelty of this study is to apply this technology to the pharma industry wastewater. Furthermore, a mathematical model is proposed in this paper to represent the ammonia concentration profile for both continuous and batch recovery processes. The experiments performed involved ammonia synthetic solution (4.25 g/L), and nitric acid (0.4M) as a stripping solution, streaming counter - currently in the membrane contactor. The effect of different operational parameters was investigated: the ammonia feed flow rate (from 50 to 100 L/hr) and the ammonia feed stream inputs (shell and lumen). The application of low ammonia feed flow rate, and shell side ammonia feed stream input shows an increase in ammonia recovery efficiency. The obtained ammonia recovery efficiency was greater than 97%, with a mass transfer coefficient of 22.84 ± 3.39 m/hr, and liquid fertilizer composition of 6,200 ppm-N- NH_4^+ . The mathematical model was validated against the experimental data. The experimental data and the analytical solution are consistent for both the batch and continuous processes, therefore, the mathematical model can be applied to evaluate the anticipated ammonia concentration in the outlet of the membrane contactor over a range of inlet concentrations and ammonia feed flow rates. Moreover, the mathematical model is also helpful to predict the required number of membrane contactor modules and the operational costs for the industrial-scale recovery of ammonia from Pharmaceutical wastewater effluent.

Reference 1:

Reig, M., Vecino, X., Gibert, O., Valderrama, C., Cortina, J.L., 2021. Study of the operational parameters in the hollow fibre liquid-liquid membrane contactors process for ammonia valorisation as liquid fertiliser. *Sep. Purif. Technol.* 255, 117768. <https://doi.org/10.1016/j.seppur.2020.117768>

Reference 2:

Noriega-Hevia, G., Serralta, J., Borrás, L., Seco, A., Ferrer, J., 2020. Nitrogen recovery using a membrane contactor: Modelling nitrogen and pH evolution. *J. Environ. Chem. Eng.* 8, 103880. <https://doi.org/10.1016/j.jece.2020.103880>

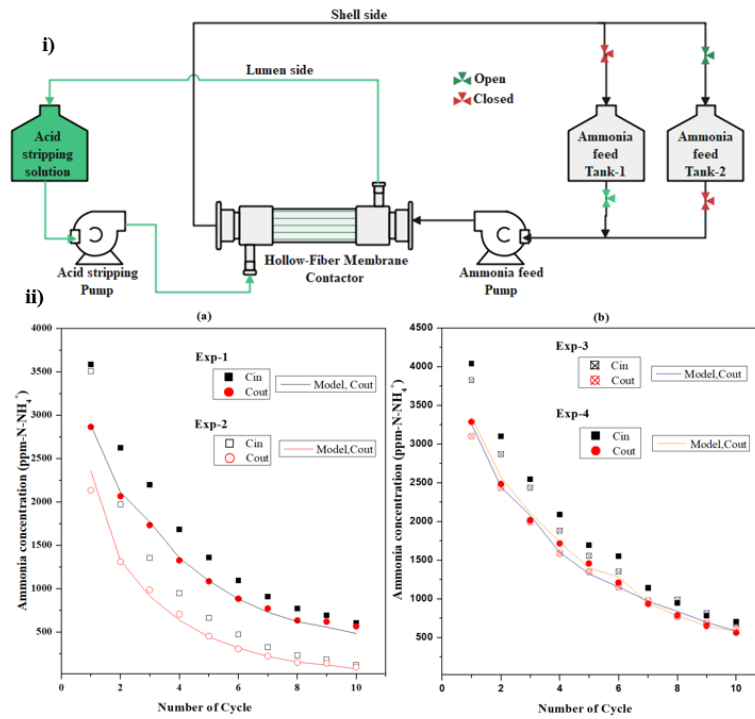


Figure 1 – i) Experimental setup of the ammonia recovery using Hollow Fiber Liquid-Liquid Membrane Contactor (HLLMC) for the continuous, and batch mode. **Figure 1 – ii)** Comparison of ammonia concentration in the inlet and outlet of the membrane contactor over different cycles between the experimental data (dots) and the analytical solution (line) in the ammonia feed stream: (a) effect of ammonia feed flow rate (100 and 50 L/hr, Exp-1, and Exp-2 respectively), and (b) effect of ammonia feed stream input (lumen and shell, Exp-3, and Exp-4 respectively).

Reducing water footprint in evaporative cooling towers with hollow fiber nanofiltration membranes

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¹Grundfos Holding A/S, ²NX Filtration B.V., ³University of Twente

Main topic: Industrial applications and scale-up

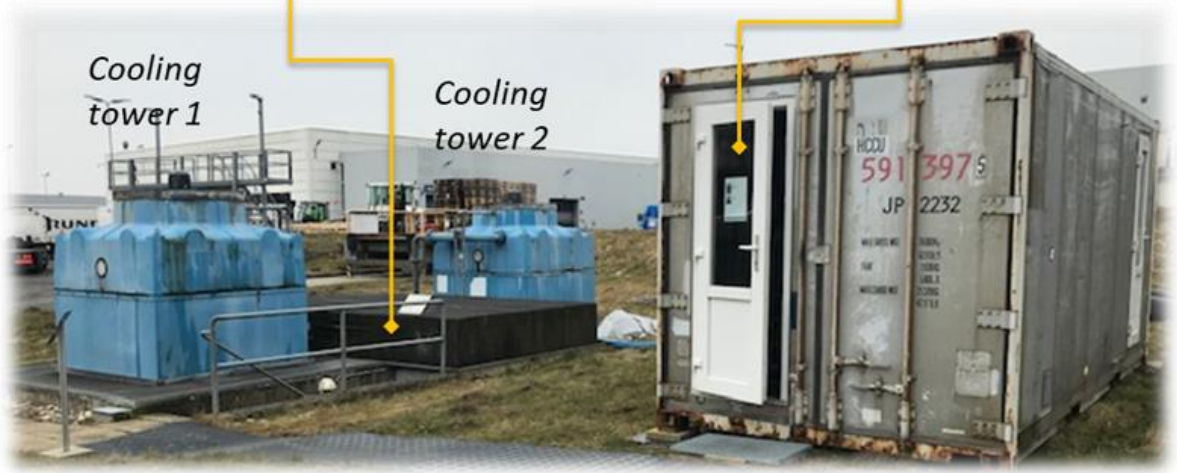
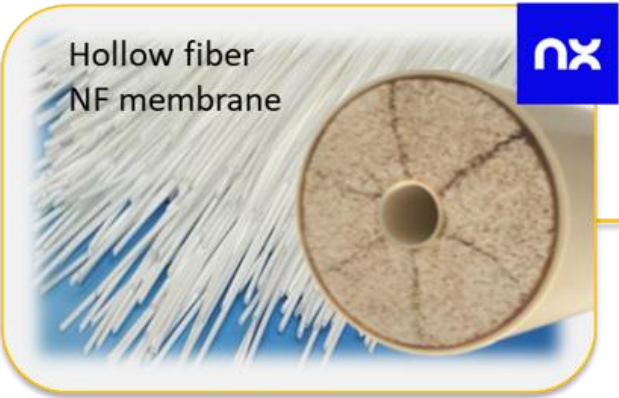
Evaporative cooling towers are critical to the operation of various industrial facilities and large buildings. It is also one of the largest water consuming processes because it dissipates excess process heat by evaporation of water circulated for cooling. Besides water usage (make-up), it also discharges large volumes of saline wastewater (blowdown) that can be harmful to the environment. Typical cooling towers operate at a specific make-up to blowdown ratio or cycle of concentration (COC) of 2-4, to maintain water quality within the guideline limits for minimizing scaling and corrosion issues. In this work, we investigated the possibility to reduce the water footprint of cooling towers without exceeding cooling water quality limits, through application of hollow fiber nanofiltration (HFNF) for side-stream filtration of cooling water.

The concept was tested in pilot scale using a polyelectrolyte multilayer (PEM) HFNF membrane (dNF40) from NX Filtration to treat cooling tower water in a Grundfos facility in Denmark. Since PEM membranes has high tolerance to chlorine (de Grooth *et al.*, 2015), which is a common biocide applied in cooling towers, makes dNF40 a suitable NF membrane for cooling tower applications. Our results show that dNF40 can maintain concentrations of critical ions (i.e., calcium, sulphate) in cooling water down to a safe level, while the low membrane rejections of chloride and dissolved silica define the maximum water savings attainable in the cooling tower. Consequently, increasing the COC of the cooling tower from 3 to 8 was possible. Experimental and modelling data projected that make-up water savings of 20-27% and blowdown discharge reduction of 60-80% are attainable, depending on the size of the cooling tower and quality of the make-up water. The side-stream HFNF can also remove particles, nutrients, organics and planktonic bacteria (including *Legionella*) in the cooling loop, thereby reducing fouling and biological risk during cooling tower operation.

Longer term testing with a modular unit has just been initiated in a cooling tower, to demonstrate actual water savings and operational robustness of the solution. We will show the technical and economic feasibility of the application of HFNF to reduce the water footprint of cooling towers.

Reference 1:

de Grooth J., Haakmeester B., Wever C., Potreck J., deVos W.M., Nijmeijer K. (2015) Long term physical and chemical stability of polyelectrolyte multilayer membranes. *Journal of Membrane Science* 489, 153–159.



REINFORCED BRAIDED HOLLOW FIBER MEMBRANES FOR WELL WATER TREATMENT

Bildyukevich, Alexandr - Main Author¹; Hliavitskaya, Tatsiana - Co-Author¹; Liubimova, Alena - Main Author¹; Tatiana, Plisko - Co-Author²

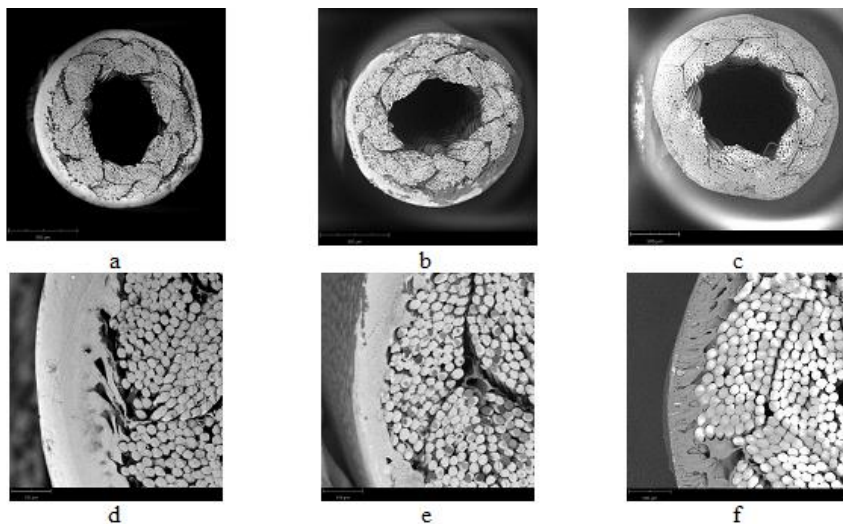
¹Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, Minsk, Belarus, ²Institute of Physical Organic Chemistry of the National Academy of Sciences of Belarus, Minsk, Belarus

Main topic: Novel membrane materials

The reinforced braided hollow fiber membranes from polysulfone (PSf), cellulose acetate (CA) and polyacrylonitrile (PAN) were fabricated via dry-jet wet spinning process. The two-dimensional commercial polyester (PET) braid (density - 1.35 g/m and outer diameter - 2.0 mm) was used as a support. The performance of prepared membranes was characterized in terms of pure water flux (PWF), water contact angle (WCA) and polyvinylpyrrolidone (PVP K-30, $M_n=40\ 000\ \text{g}\cdot\text{mol}^{-1}$) rejection, % (Table). Membrane structure was studied by SEM (Figure).

It was found that the developed membranes are moderately hydrophilic. Moreover, PSf/PET and CA/PET feature relatively high PWF of 390-690 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, while PWF for PAN/PET doesn't exceed 140 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. For that reason the most high-performance developed membranes (PSf/PET and CA/PET) were selected as membranes for submerged membrane module preparation for well water treatment. Feed well water had the following characteristics: total iron content - 10.7 $\text{mg}\cdot\text{L}^{-1}$, turbidity - 145 $\text{mg}\cdot\text{L}^{-1}$, colour $>150^\circ$. The membrane modules were operating for 190 hours in dead-end mode without back flush and air bubbling. The permeate characteristics were found to be similar for both developed membranes: total iron content - 0.35-0.50 $\text{mg}\cdot\text{L}^{-1}$, turbidity - 0.1-0.2 $\text{mg}\cdot\text{L}^{-1}$, colour - 15-17°. Although PWF for PSf/PET membrane is 25-50% higher compared to the PWF for CA/PET membrane, the latter membrane has 50% higher initial well water flux (WWF) (Table). It was found that after 190 hours of filtration, the CA/PET membrane module featured 5 times higher flux compared to PSf/PET submerged membrane module. These results indicate that the CA/PET membranes are characterized by excellent antifouling stability in well water treatment.

Figure. The structure of reinforced braided PSf/PET (a,d), CA/PET (b,e) and PAN/PET (c,f) membranes. Table. Membrane properties and performance in water treatment.



Relating Uncharged Solute Retention of Polyelectrolyte Multilayer Nanofiltration Membranes to Effective Structural Properties

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¹University of Twente

Main topic: Nanofiltration/Reverse Osmosis

Since its first appearance end of the 80s, Nanofiltration (NF) has been a field of intensive research and is nowadays widely applied in a variety of fields such as water treatment, biotechnology, and food processing. One of the ongoing research directions is the development of novel membranes with maximum separation efficiency and minimum hydraulic resistance. These membranes are typically built of two parts: a porous support structure and a denser separation layer. As a rule of thumb, reducing the separation layer thickness reduces the hydraulic resistance of the membrane. A relatively young method of making NF membranes is to apply the Layer-by-Layer (LBL) method, developed by Decher et al. in 1991, on top of a porous support membrane. In this method, polyelectrolytes are alternately coated on a surface to form a film with a controllable thickness in the nanometer range, also known as a Polyelectrolyte Multilayer (PEM). Due to its simplicity and versatility, LBL offers a toolbox for membrane scientists to fine-tune membrane properties for specific applications. Structural properties of PEMs and their relation to coating conditions as well as membrane performance is an ongoing field of research.

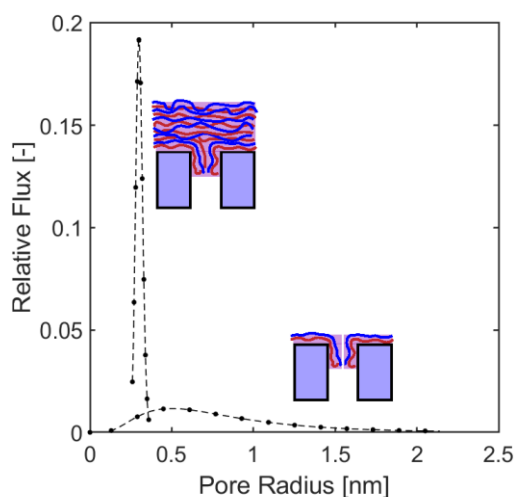
In this work, the separation performance of NF PEM membranes towards uncharged molecules is related to film structure and its dependency on coating conditions. The structure of the membrane is hereby represented by a nanoporous film with distribution in pore size [1]. As, up to date, no experimental technique is available to directly measure pore sizes in the nanometer range of a wet film, a representative pore size distribution is estimated via the use of a theoretical transport description. Here, a standard pore model, which accounts for distribution in pore size as well as the presence of imperfections, is being applied. Using this methodology the critical step of defect-free film formation is monitored [2]. The narrow pore size distribution in the sub-nanometer range for the studied PEM systems (PDADMAC/PSS and PAH/PAA), which is comparable to that of commercial polyamide-based membranes, describes observed retentions well. The presented method offers a novel approach to obtain a more complete understanding of PEM properties.

Reference 1:

Fabián Vaca Chávez and Monika Schönhoff, "Pore size distributions in polyelectrolyte multilayers determined by nuclear magnetic resonance cryoporometry", *The Journal of Chemical Physics* 126, 104705 (2007) <https://doi.org/10.1063/1.2565841>

Reference 2:

J. de Grooth, R. Oborný, J. Potreck, K. Nijmeijer, W.M. de Vos, "The role of ionic strength and odd–even effects on the properties of polyelectrolyte multilayer nanofiltration membranes", *Journal of Membrane Science* 475 (2015) 311–319 <http://dx.doi.org/10.1016/j.memsci.2014.10.044>



Remotely controlled magneto-responsive polymeric membranes for controlled release of biomacromolecules

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Main topic: Bio-medical applications

Between 2010 and 2020, FDA has approved 97 new therapeutic proteins with subcutaneous injection as the main route of administration. Responsive membranes can offer an alternative route with high reproducibility and dosing flexibility to increase patient's compliance. Previous work in our group had demonstrated stimuli-responsive membranes with excellent switchable rejection for dextran 2000 kDa [1]. This work aims at developing membranes with switchable sieving for much smaller biomacromolecules such as insulin (5.8 kDa).

Thermo-responsive pore-filled membranes were developed through a two-steps approach. Polyethersulfone (PES) was used to create different porous supports which were subsequently pore-filled with poly(*N*-isopropylacrylamide) hydrogel that acts as the sieving medium. Membranes demonstrated reversible increase in water permeability by about 380 times (Figure 1) in response to increased temperature (from ~25 to 40°C). Furthermore, rejection of dextran (4 kDa, which has a comparable Stoke's diameter to that of insulin) under ultrafiltration conditions decreased from 91% to 10%; diffusion rate increased by a factor of 21. This increase in diffusion rate opens up the possibility of pulsatile biomacromolecules release. As an example, a membrane with a radius of 2 cm (12.6 cm²) could deliver from a reservoir the average insulin daily requirement in 2 hours of membrane stimulation.

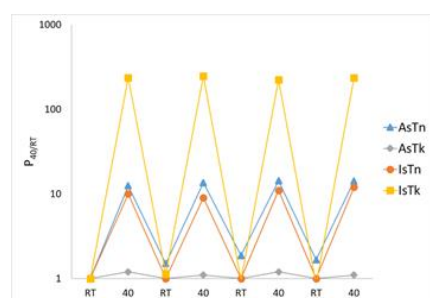


Figure 1: Reproducibility shown by relative permeability $P_{40/RT}$ of different hydrogel pore-filled membranes. IsTn, AsTn, IsTk and AsTk represent isotropic thin, anisotropic thin, isotropic thick and anisotropic thick membranes, respectively.

To add remote control functionality, iron oxide nanoparticles were incorporated into the porous PES support to create nanohybrid membranes. In response to an external alternating magnetic field (AMF), nanohybrid membrane temperature increases beyond the hydrogel volume phase transition temperature (Figure 2). Following functionalization resulted in pore-filled nanohybrid membranes that demonstrated reversible increase in water permeability about 400 times.

Overall, highly responsive remotely controlled membranes are available for controlled release of biomacromolecules as small as insulin. To the best of our knowledge, for the first time in literature such performance is to be reported.

Reference 1:

Lin, X., Huang, R. and Ulbricht, M. (2016). Novel magneto-responsive membrane for remote control switchable molecular sieving. *Journal of Materials Chemistry B*, 4(5), pp.867-879.

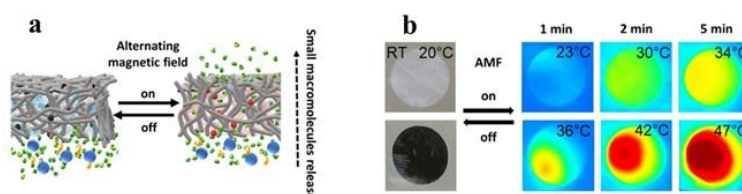


Figure 2: (a) Schematic representation of thermo-responsive membrane for biomacromolecule release via remote control by AMF. (b) IR camera images showing the pristine and nanohybrid membrane temperature changes upon exposure to an AMF (magnetic field strength = 20 kA/m) for 1, 2 and 5 min

Removal of 17 α -Ethinylstadiol and Estrogenic Activity by a novel Hybrid UV-LED-Membrane Distillation system

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Main topic: Membrane contactors and membrane distillation

Endocrine-disrupting compounds (EDCs) are increasingly released into aquatic environments. Among EDCs, 17 α -Ethinylstadiol (EE2) potential for endocrine-disrupting is much higher than other synthetic EDC, besides being less biodegradable. As EDCs can cause several damages to health, advanced technologies are required to remove them from water. In this context, membrane distillation (MD) is a technology that generates high-quality water and effectively removes micropollutants [1]. As many organic molecules absorb radiation in the UVC range, coupling MD and UV radiation is a promising alternative. EE2 photolysis is faster than other EDCs due to the ethynyl group, which can quickly absorb UV radiation [2]. Light-emitting diodes (LEDs) can be used as a radiation source as they are more environmentally friendly than mercury lamps. Although LEDs release energy through heat, coupling LEDs and MD may not be disadvantageous since the feed must be heated. Therefore, this study investigated the removal of EE2 and estrogenicity in a new hybrid UV-LED-MD module. The module was designed with a quartz plate placed in the feed compartment. A NaCl (10 mmol.L^{-1}) solution containing EE2 ($100 \text{ }\mu\text{g.L}^{-1}$) was maintained at $40 \text{ }^\circ\text{C}$, while permeate was kept at $20 \text{ }^\circ\text{C}$. Flux in the UV-LED-MD system tended to stabilize at an average value of 3.5 LMH. In the MD test, the flux tended to stability at an average value of 3.1 LMH. Although LED had provided 60 kJ of heat to the system, it did not significantly change the membrane surface temperature from UV-LED-MD since temperatures were controlled automatically. As LED provides heat, there is a saving on the heating system, which was activated fewer times. Permeate conductivity differences were minimal between both systems. The estrogenicity removal was 99.2% and 99.0% for MD and UV-LED-MD. EE2 removal efficiencies were higher than 97.7 % for both systems. Since the hybrid module provided a permeate free of EE2 and estrogenic by-products, the new module has great potential for treating hormone-contaminated water, with the promising capacity of degrading organic molecules in the concentrate, which deserves further studies.

Reference 1:

1 - COUTO, C.F.; SANTOS, A.V.; AMARAL, M.C.S.; LANGE, L.C.; ANDRADE, L.H.; FOUREAUX, A.F.S.; FERNANDES, B.S. Assessing potential of nanofiltration, reverse osmosis and membrane distillation drinking water treatment for pharmaceutically active compounds (PhACs) removal. *Journal of Water Process Engineering*, v. 33, p. 101029, 2020.

Reference 2:

3 - SORNALINGAM, K.; MCDONAGH, A.; ZHOU, J. L. Photodegradation of estrogenic endocrine disrupting steroidal hormones in aqueous systems: progress and future challenges. *Science of the Total Environment*, v. 550, p. 209-224, 2016.

Removal of human noroviruses in seawater by ultrafiltration for closed shellfish production systems

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Main topic: Environmental applications

Shellfish production must comply with sanitary quality objectives for the consumers and this is linked to the coastal seawater quality. Indeed, bivalve molluscs are mostly raised in coastal areas where the seawater they filtrate can be contaminated by wastewaters containing various microbial pathogens, including human enteric viruses such as Noroviruses (NoV). Noroviruses, major cause of acute viral gastroenteritis linked to consumption of contaminated oysters, are actively accumulated in digestive tissues *via* specific ligands during filter feeding. This specific fixation results in low reduction rates during standard post harvesting depuration process (oysters placed in tanks continuously supplied with treated seawater for 48h). The aim of this work is to evaluate the performances of the ultrafiltration (UF) process to retain NoV in seawater and closed epuration systems. The objectives are to understand the potential transfer of NoV through the membranes as a function of the water quality (salinity, suspended solids, organic matters...) and the initial virus concentration. First, preliminary experiments were carried out with Tulane virus, a NoV surrogate, at different initial concentrations varying from 10^4 to 5×10^{10} RNA copies.mL⁻¹. For this feasibility study two types of water were used (Evian and seawater). A multi-channel hollow-fiber polyethersulfone UF membrane (pore size - 0.02 mm) was used at a constant transmembrane pressure of 0.3 bar. As expected, whatever the initial concentration and the volumic concentration factor, the fouling resistance increased with the virus concentrations but remained far under the value of the membrane resistance. The experiments were reproducible (three experiments for each concentration) in terms of permeability decrease. Electronic microscopy of the membrane surface after filtration confirmed the retention of Tulane virus. The analysis of the permeate will be made in terms of RNA concentrations and infectious virus titer (TCID₅₀) to calculate the log retention values of each parameter. The virus retention factor is calculated as the function of the concentration and compared to other virus with similar size [1]. Experiments will also be made with NoV to confirm the efficiency of UF as a treatment process for shellfish depuration system.

Reference 1:

Jacquet, N., Y. Wyart, G. Darracq, S. Wurtzer, L. Moulin and P. Moulin, Retention and integrity of drinking water production membranes towards nanoparticles and viruses, IWA 2019, 23-27 Juin 2019, Toulouse, France.

Removal of microplastic particles in water by ultrafiltration: assessment of process performances using a new characterization and quantification analytical technique

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Main topic: Microfiltration/Ultrafiltration

The production of plastic grew exponentially since 1950 and unfortunately, about 80% of this production ends up in landfills or in the environment. This issue has gained popularity since oceanic gyres recovered of plastic wastes and microplastic particles (MP) have been revealed to the population. This pollution leads to harmful effects on marine fauna and organisms and to a risk of bioaccumulation. One of the main sources of MPs in the water bodies is wastewater sometimes unefficiently treated in wastewater treatment plants. In this context, the scientific community is now clearly involved to find solutions. However, an adequate analytical tool is needed to assess the number of MPs, their size and the type of polymer in order to accurately evaluate the efficiency of treatment processes. Traditional techniques such as stereomicroscopy fluorescence illumination after sample's pretreatment, classical Raman and infrared spectroscopy, or pyrolysis GC-MS all lead to numerous limitations. Therefore, in this work, a new high throughput analytical technique is developed for characterization and quantification of MPs in water using Fourier-transform infrared spectroscopy imaging system from PerkinElmer. Data treatment for polymer identification is realized by siMPle (Systematic Identification of MicroPlastics in the Environment) software developed by Aalborg University and Wegener Institute. This technique enabled to quantify and characterize MPs in wastewater secondary effluent and evaluate the efficiency of 200 kDa ultrafiltration (UF) to retain MPs. The polymer types in the secondary effluent were identified and quantified. The result showed the excellent removal capacity of UF membrane on MPs of all types with side dimension higher than 70 μm , which is above 95%. The MP retention rates by UF will decrease as the particle size becomes smaller, for example 17% for MPs' side dimension under 40 μm . In global, there were 207.5 $\text{MPs}\cdot\text{L}^{-1}$ in the feed and 17.5 $\text{MPs}\cdot\text{L}^{-1}$ in the permeate, resulting in 91.6% removal rate of MPs. These conclusions is function of the type of effluent and the number of MP. The analytical technique will be tested on other water matrices and industrial effluents and UF will also be studied as a potential MPs remediation technology.

Removal of the Pharmaceuticals Diclofenac, Carbamazepine and Paracetamol from Wastewater through Multi-channel Capillary Membranes with Embedded Powdered Activated Carbon

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Main topic: Wastewater treatment

Background

Water contamination with pharmaceuticals, such as diclofenac, carbamazepine and paracetamol, is an emerging threat to the eco-system and, consequently, for human health. The elimination of these substances during the wastewater treatment process is challenging. Therefore, a combination of filtration, using a multi-channel capillary membrane, and adsorption, through embedded powdered activated carbon (PAC), is applied to water with an initial drug concentration of 15 mg/l.

Materials and Methods

These mixed-matrix-membranes (MMM) were spun in a steam-dry-wet spinning process using a polymeric solution containing 19 wt.% polyethersulfone, 5 wt.% polyvinylpyrrolidone ($M_w = 360\,000$ g/mol), 15 wt.% 1,2-propandiol and 61 wt.% *N,N*-dimethylacetamide. 10 g PAC per 100 g polymeric solution were added and the PAC-polymer solution was homogenized before spinning. Filtration tests were performed over 60 min for diclofenac, carbamazepine and paracetamol separately, as well as with a combined solution containing 15 mg/l of each drug. Additionally, the efficiency of the membrane over 8 h was investigated.

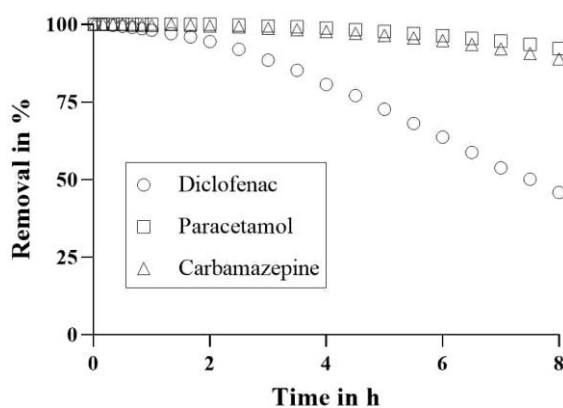
Results

The results of the filtration experiments showed a mean removal of 99 % over 60 min, with the lowest retention for diclofenac and the highest for carbamazepine. Also, for the combined experiment of all three substances, a mean retention of the drugs over one hour of 99 % was achieved. After 8 h of filtration, retentions of 46 % of the initial concentration of diclofenac, 89 % of carbamazepine and 92 % of paracetamol were measured for the combined solution (Figure 1). The fluctuations of permeability and flux, over both 1 h and 8 h, were negligible. Therefore, it is assumed that the flow characteristics of the MMM are not affected by the combined filtration and adsorption process over the investigated time-period.

Conclusion

Based on the obtained results, it can be stated that a combination of filtration and adsorption in the form of a mixed-matrix multi-channel capillary membrane with embedded PAC may be a viable alternative for the removal of these pharmaceuticals. However, the MMM should be tested under realistic wastewater concentrations and conditions, as well as in a pilot scale to better understand the applicability.

Figure 1: Removal of diclofenac, carbamazepine and paracetamol using mixed-matrix multi-channel capillary membranes with embedded powdered activated carbon over 8 h



Retention and inactivation of antibiotic-resistant bacteria present in river water using a novel hybrid system

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Main topic: Microfiltration/Ultrafiltration

According to the World Health Organization, antibiotic resistance is one of the main threats to global health. The excessive use of several antibiotics led to the widespread distribution of antibiotic-resistant bacteria in various environment matrices, such as surface water. Hence, there is an urgent need for the development of effective treatment solutions to upgrade conventional wastewater treatment processes and avoid the release of antibiotic resistant bacteria in the aquatic environment.

Membrane filtration and ultraviolet (UV) photolysis are effective treatment processes to retain and inactivate pathogenic bacteria from different water sources.

A new hybrid photocatalytic membrane reactor [1] was used to test the efficiency of membrane filtration (unmodified and modified with titanium dioxide and copper), direct photolysis (using UV-C low pressure mercury lamps that emit light at 254 nm, UV-C light emitting diodes that emit light at 265 nm and UV-A light emitting diodes that emit light at 385 nm) and the combination of both processes to ensure the retention and inactivation of antibiotic resistant bacteria present in river water at occurrence levels.

Enzyme specific microbial methods (Colilert and Enterolert from IDEXX) were modified by addition of different antibiotics (ciprofloxacin, levofloxacin, imipenem, ampicillin, and streptomycin) to quantify antibiotic resistant bacteria before and after river water treatment.

A sustainable sol–gel procedure was followed to obtain photocatalytic membranes using low temperature and under solvent free conditions [2]. This procedure was further modified with the addition of copper that was found to be the most promising material to extend the light absorbing capacity of the materials.

This hybrid system effectively retains microorganisms that can then be successfully inactivated by photolysis and advanced oxidation processes. The new hybrid reactor could be a promising approach to treat drinking water and wastewater in small scale systems.

João Sérgio and Ana Paula Marques contributed equally for this work. **This work was supported by the Associate Laboratory for Green Chemistry – LAQV (UIDB/50006/2020 and UIDP/50006/2020)**

Reference 1:

[1] C. Fraga, R. Huertas, J.G. Crespo, V.J. Pereira. 2019. Novel submerged photocatalytic membrane reactor for treatment of olive mill wastewaters, *Catalysts*. Special Issue Photocatalytic Membrane Reactors. 9(9), 769.

Reference 2:

[2] R.M. Huertas, M.C. Fraga, J.G. Crespo, V. J. Pereira. 2019. Solvent Free Process for the Development of Photocatalytic Membranes, *Molecules*. 24, 4481.

Reuse of petrochemical condensate: pilot MABR for the treatment of a real waste stream

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Main topic: Industrial applications and scale-up

Treating petrochemical waste streams can be tricky, the organics load and toxicity can often impact traditional biological treatment. Here, membrane aerated biofilm reactors (MABR) were evaluated for the treatment of a waste stream containing organic acids, phenol, BTEX and other organics. A pilot scale set-up with two reactors in series was operated for over a year to assess removal efficiency, final water quality, and suitability and robustness of the MABR technology compared to conventional activated sludge treatment.

Materials and methods

Two identical MABRs, supplied by OxyMem DuPont (Athlon, Ireland), in series treated a heavily polluted petrochemical condensate.

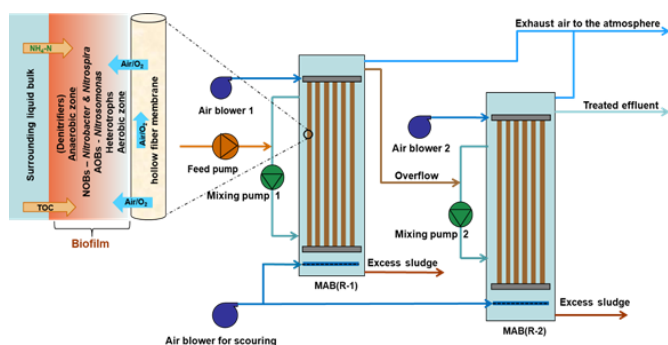


Figure 1. Schematic representation of the pilot scale MABR system in series. Own figure.

In short, the reactors were inoculated using on site WWTP sludge, biofilm thickness was controlled through regular scouring, macro and micronutrients were dosed, and an HRT of 10 h/reactor was initially maintained. The concentration of phenol, acetate, propionate, formate, total organic carbon, ammonia, and phosphate was monitored as well as dissolved oxygen, conductivity, and pH. Based on these measurements, removal efficiencies and oxygen transfer rates were determined.

Results and conclusions

At stable operations, the pilot in series achieved a total removal efficiency of 85% TOC, 95% BOD₅, >98% organic acids, 98% phenol, and 90% ammonia. The formed biofilm was able to remove C and N and both nitrification and denitrification were observed without traces of intermediate byproducts (NO₂⁻ and NO₃⁻). Although removal efficiencies were comparable to that of a traditional activated sludge system, the aeration efficiency of the MABR is higher because of the more effective and flexible aeration.

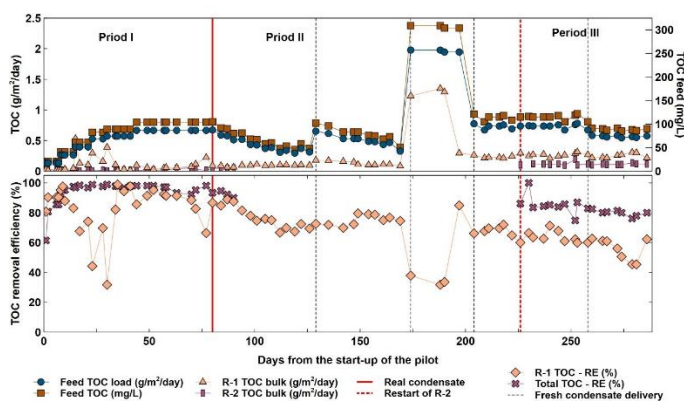


Figure 2. Total organic carbon (TOC) load and removal efficiency (RE) in the first (R-1) and second (R-2) reactor

The system was able to handle shock loads and feed fluctuations in TOC, ammonia, and organic acids. This is attributed to the rich microbial community and abundance in the MABR biofilm and indicated the value of the system for treatment of complex industrial streams. Although polishing of the effluent is required to reuse the effluent as high-quality water, this study clearly demonstrates the applicability and advantages of the MABR system.

Rotation in a spinneret integrates static mixers inside hollow fiber membranes

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¹DWI – Leibniz Institute for Interactive Materials, ²AVT.CVT – Chemical Process Engineering, RWTH Aachen University

Main topic: Advanced fabrication methods

Turbulence promotion plays key in boosting the efficiency and sustainability of membrane applications as they share one major drawback: mass transfer limitations due to boundary layer formation known as concentration polarization. To break these limitations, static mixers established as state-of-the-art technology for robust and large diameter tubular heat exchangers and chemical flow reactors. Bellhouse et al. pioneered in the membrane field installing static mixers into tubular membranes. However, large tubular size, low number of membranes per module, and tedious assembly limit the approach for large-scale applicability. Especially, this renders vision for hollow fiber membranes, as modules consist of thousands of fibers featuring fragile separation layers of small size. We resolve this issue by presenting a single-step technology to simultaneously fabricate and integrate static mixers inside hollow fiber membranes.

The fabrication technology bases on dry-jet wet spinning with phase inversion of polyvinylidene fluoride polymer solutions. Heart of our technology builds the rotation in a spinneret device featuring a 3D printed spinneret and microstructured rotating needle in its center. The needle exhibits an 8-shaped orifice creating a twisted tape static mixer upon rotation. The device simultaneously co-extrudes a membrane forming and a static mixer forming polymer solution, separated by a bore solution in between. Hence, the static mixer precipitates inside the hollow fiber membrane for single-step fabrication and integration with a separate, decoupled arrangement.

We elucidate how conventional and new fabrication parameters influence intrinsic hollow fiber membrane properties and static mixer appearance. Adjustment of needle microstructure and rotation speed allows for free tunability of the static mixer geometry. A gas-liquid membrane contactor oxygenation showcase demonstrates the impact of static mixer membranes. Ultimately, static mixers enhance the oxygen flux up to 300%.

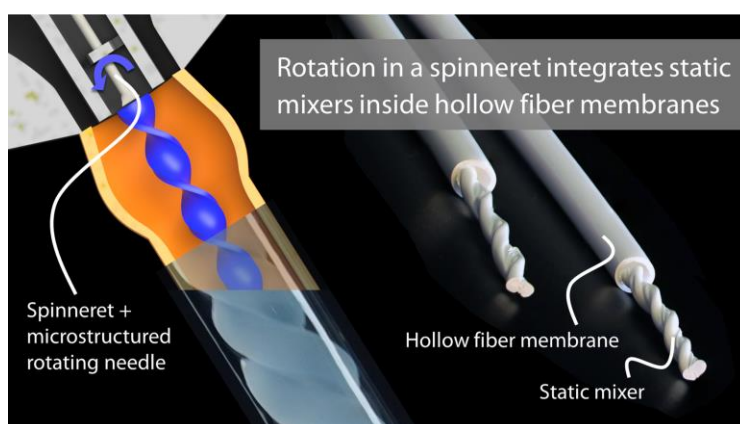
We highlight our novel static mixer membranes and single-step fabrication and integration technology. Our concept wipes out limitations to apply static mixers inside hollow fiber membranes. An oxygenation showcase reveals up to 300% increase in mass transfer pointing out disruptive influence on membrane technology. We envision overcoming mass transfer limitations in various applications. The static mixer being microporous empowers further advanced functionality, we provide first insight to equip the static mixer with functional particles.

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Tepper, M., Walorski, J., & Wessling, M. (2019). Membrane system, spinneret for manufacturing the membrane system, device including the spinneret and method for forming the membrane system. EP19203629

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Salt concentration via Membrane Distillation – performance results and influences on membranes tested via real industrial waste waters

Meitz, Sarah - Co-Author

Main topic: Membrane contactors and membrane distillation

Salt concentration via Membrane Distillation – performance results and influences on membranes tested via real industrial waste waters

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Membrane distillation (MD) is a thermally driven membrane process for various applications in desalination, process and waste water treatment as well as resource recovery. [1] [2] In various industrial applications like for example in the refractory industry, MD could be integrated to process highly concentrated aqueous solutions in order to recover water (Permeate side) and concentrate salts (Feed side). Depending on desired concentration factors (CF) supersaturation and crystal formation is possible.

In the presented work experimental studies have been elaborated with the target to (1) concentrate and in further consequence reduce the amount of wash water contaminated with salts - ideally a volume reduction by a factor of 20 should be reached - and (2) reuse the separated water in the washing process.

Membrane distillation was tested in Direct-Contact-Configuration (DCMD) at laboratory scale (membrane area 0,0375 m²) in batch mode. The initial conductivity of the Feed (washing water from refractory industry) was 22,5 mS/cm. The flux behavior was investigated up to CF 14, quantified via conductivity measurement and mass balances as well as analytically validated via ICP (Inductively Coupled Plasma) spectroscopy. It was observed that MD was operable at high concentrations at feed temperatures of 70°C. High transmembrane fluxes up to 40 – 50 L/m²-h could be reached during the experiments. Salt rejection of 99,9 % was identified throughout the whole experimental studies. Reduction in transmembrane flux only occurred during crystal formation on the membrane. The influence of salt concentration and crystal formation on the hydrophobic PTFE membrane was evaluated. With reference to this, optimization potential for the crystallization were defined for a targeted final system integration.

Concluding, the experiments have proven the high application potential in treating high saline waste waters. Huge savings in waste water amounts derive in huge monetary savings.

Reference 1:

Woo et al. (2019): Introduction: Membrane Distillation Today, Past and Future, Current Trends and Future Developments on (Bio-) Membranes, Elsevier.

Reference 2:

Tijing et al. (2015): Fouling and its control in membrane distillation—A review, Journal of Membrane Science, Pages 215-244.

Scrubber water treatment from marine vessels by ultrafiltration process

Drouin, maryse - Main Author; Nasser, Samy - Co-Author; Adolphe, Cyril - Co-Author; Moulin, Philippe - Co-Author

Main topic: Industrial applications and scale-up

Current sulfur oxide (SO_x) atmospheric emission regulation implies a modification of marine vessels to stay within air rejection compliance. To limit pollution impacts on population, port and coastal navigation zones have stricter SO_x air concentration regulations. In controlled areas, the gas emission ratio (SO_x/CO_2) is reduced by a factor 5 regarding the other navigation zones. Several solutions are proposed to reduce the SO_x concentration in rejected ship exhaust gas. Among them, the less expensive one for vessels studied, is fitting gas treatment unit. The exhaust gas treatment unit installed is gas-liquid absorption process using a liquid alkaline suspension as absorbent. In controlled navigation areas, the liquid is continuously circulated in the column, is absorbed SO_x , heavy metals, and is concentrated with suspended solids. Then this effluent is treated by a membrane process which allows it rejection in agreement with seawater discharged criteria. First filtration tests highlight interesting membrane properties in terms of effluent flux, pollutants retention and recovery rates. In January 2022, 45 vessels will be retrofitted with absorption column and 70% of them will be operational for membrane filtration. Objectives of this study is to develop the on-board filtration by limiting concentrate volume, limiting membrane fouling, and improving pollutant retention. Taking into consideration the great variability of scrubber water, different filtration campaigns are realized. For each one, marine water treated is directly sampled on a new ship. The final filtration conditions chose for scale-up must be fitted for all ships studied. First results obtained show similar behavior for membrane fouling. In most of the case, irreversible fouling rate of silicon carbide membrane noted is close to $8 \cdot 10^{-4} \text{ bar} \cdot \text{min}^{-1}$. In terms of membrane retention, permeate turbidity is always lower than 5 NTU even for high turbidity value on the loop (500 NTU) and sample analysis shows a heavy metal retention higher than 80%. However, permeate volume loss needed to be stored on board is quite important, around 30% of the feed flow. Thus, filtration parameters must be adapted to respect ship constrain and improve the filtration behavior: backpulses and backwashes are compared.

Separation of calcium and lactose in dairy streams with polyelectrolyte multilayer membranes

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Main topic: Nanofiltration/Reverse Osmosis

In the dairy industry, lactose is separated from milk and other dairy products for numerous reasons. For example, separation is needed to produce low-lactose or lactose-free dairy products for those who are lactose intolerant, or for recovering lactose from whey in cheese production. After the separation, the lactose gets purified through crystallization. A known strategy to remove lactose from milk and other liquid dairy products is ultrafiltration, where the lactose can pass through the membrane while proteins and oil droplets are retained [1]. However, during ultrafiltration, dissolved minerals (such as calcium and phosphates) will also end up in the permeate stream, impeding the recovery of lactose. Polyelectrolyte multilayer (PEM) membranes could be a good addition to this process. In particular asymmetric PEM membranes, that have demonstrated efficient retention of small molecules while maintaining a high water permeability and a low salt retention [2]. In this work we use PEM membranes with an asymmetric coating to retain lactose while allowing calcium and other ions to pass through. Initial experiments with membranes coated with a bottom layer of poly(4-aminostyrene) (PAS)/poly(4-styrene sulfonate) (PSS) and a thin separation layer on top of /poly(allylamine hydrochloric acid) (PAH)/poly(acrylic acid) (PAA) have shown promising results. With asymmetric coating we achieved low molecular weight cut offs while maintaining a decent permeability up to $8 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. For model solutions we observe lactose retentions well over 95%, while CaCl_2 retentions were as low as 30%. Such a membrane would thus allow simultaneous de-watering and desalination of lactose containing waste stream such as whey. Unfortunately, when these components are mixed together and with other salts that are present in dairy streams, the separation is not as effective as with model solutions. Still, tuning the membrane performance by changing the pH of the feed solution allows an easy way to improve the separation. Understanding this separation system will be key to the further design of PEM based nanofiltration membranes for lactose/salt separations.

Reference 1:

[1] J.L. Maubois, G. Mocquot Application of Membrane Ultrafiltration to Preparation of Various Types of Cheese, *J. Dairy Sci.*, 58 (1975)

Reference 2:

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Silicalite Zeolite Membranes for Water Desalination

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Main topic: Inorganic membranes

MFI zeolite membrane with a length of 30 cm has been synthesized by the secondary growth method [1], and using a fast heating profile for the removal of the template [2]. The performance of the membrane in water desalination has been evaluated by the vacuum membrane distillation process varying both the distilled water flow rate (from 65 Lh⁻¹ to 120 Lh⁻¹) and the temperature (from 60 °C to 70 °C) and using sodium chloride solutions at different concentrations (0.2 M-1.2 M) [2]. Results evidenced as increasing the salt concentration up to 0.9 M, at the various temperatures used, the flux of the permeate slightly decreased and the rejection was almost constant and with interesting values (about 99.9%). A significant decrease of flux and rejection has been detected with the brine concentration of 1.2 M. Nevertheless, the membrane rejection has been improved operating at the highest temperature and feed flow rate (70 °C and 120 Lh⁻¹, respectively), reaching the value of 97.13%. The zeolite membrane exhibited a good performance for water desalination by producing permeates with conductivity values lower than those requested for drinking/agricultural purposes, when treating feeds ranging from 0.2 M to 0.9 M. Whilst, a further permeate treatment (e.g., by RO) is required for 1.2 M feeds.

Reference 1:

A. Garofalo, M.C. Carnevale, L. Donato, E. Drioli, O. Alharbi, S.A. Aljlil, A. Criscuoli, C. Algieri Scale-up of MFI zeolite membranes for desalination by vacuum membrane distillation, *Desalination* 397 (2016) 205-212.

Reference 2:

L. Donato, A. Garofalo, E. Drioli, O. Alharbi, S.A. Aljlil, A. Criscuoli, C. Algieri, Improved performance of vacuum membrane distillation in desalination with zeolite membranes, *Sep. Purif. Technol.* 237 (2020) 116376.

Silicon carbide (SiC) membranes applied in wine clarification

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Main topic: Food processing

In a winery, the winemaker may have to filter very different matrices such as musts, wines, lees, containing from 1 to 400 g.L⁻¹ of suspended solids and having undergone various oenological treatments. These processes of wine clarification and stabilization by tangential microfiltration are limited by the phenomenon of fouling, which reduces production flows and can alter the aromatic potential of the wines, obliging professionals to use several successive filtering media. The objective of this work is to study the influence of the characteristics of SiC material on this fouling phenomenon. The efficiency and reliability of SiC membranes (Saint Gobain, France) were tested from the laboratory scale to Vignobles Ducourt's winery (Bordeaux, France) and validated on all matrices tested. The SiC membrane was tested on different matrices with a large variety of fouling agents (grape juice, lees, sweet wine, white, rose and red wines) ranging from very low to very high filterability. In general, SiC membranes have shown significantly greater and constant hydraulic performances, on average 3.8 times greater than that conventional polymeric membranes. The microbiological stabilization by SiC membranes, whatever the microorganisms (type and concentration), was ensured with concentrations in the permeate below the limit of quantification. Reductions of up to 2 and 5 log respectively for bacteria and yeast were obtained. Furthermore, the SiC membranes have been tested on matrices which cannot be filtered by classical polymeric hollow fiber membranes without prior treatment such as lees sedimentation or a wine with a high quantity of bentonite. It appears that SiC membranes are able to filter these matrices with very satisfactory production flow and retention efficiency. This process was optimized in particular by developing an efficient regeneration protocol. The clarification and stabilization of the matrices by SiC membranes allow (i) the preparation of clear and brilliant wines, (ii) the retention of wine microorganisms, (iii) operation at significantly higher production flows than other filter media, while conserving the tested compounds of interest in wines. The knowledge of the surface and structural properties of SiC membranes has made it possible to explain the superior filtration efficiency of matrices from the wine industry.

Simulating the ion transport through inorganic ion-exchange membranes: influence of pore size, surface charge and pH on selectivity

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Main topic: Inorganic membranes

The growth and price reduction of wind and solar renewable energies has stimulated development of electrochemical conversion processes, such as water and CO₂ electrolysis, electrodialysis, and fuel cells. These processes rely on ion-exchange membranes (IEMs) to separate the products and provide a conductive medium between the electrodes. While ion-exchange polymers have been widely developed in the past decades, it is hard to further improve the charge density (up to approx. 6M) and to maintain selectivity in highly acidic/alkaline environments. As both water electrolysis and CO₂ conversion often use highly alkaline media, new membranes that are chemically stable, selective and highly conducting are demanded.

Charged inorganic nanoporous materials can be used as an alternative to polymeric IEMs. Their ion selectivity relies on the fact that the nanopores' radius is of equal magnitude as the electrical double layer's thickness. Therefore, the charge within the nanopore allows the transport of only counter-ions, rejecting co-ions. However, this is a fairly unexplored concept and the details on how properties of the membranes and parameters of the process affect their selectivity.

Our research explores the relation between the pore size and surface charge of a material, the electrolyte's concentration and pH, applied external current and selectivity of the developed membrane. This is done by employing a modified space-charge model. The model was experimentally verified using anodized aluminum oxide membranes and a permselectivity setup.

Ultimately, this method could allow a membrane to be completely selective by using just an ultra-thin layer. This could reduce the electrical resistance of a membrane, on top of potentially increasing chemical stability and the concentrations up to which the membrane can remain selective. This would be of great advantage, as increasing the conductivity of the membrane can potentially increase the productivity of all the mentioned processes.

Simulation and design of a membrane process based on hybrid ionic liquid and polymer membranes for the separation of close boiling point refrigerant mixtures

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Main topic: Gas separation

Background

Membrane technology exhibits an important stage of maturity in different industrial applications (CO₂ from CH₄ in natural gas and hydrogen recovery). Recently, our experimental work has proved that membranes can also offer outstanding performance for the separation of target refrigerant gases from mixtures with azeotropic or near azeotropic behavior employed in refrigeration applications. This sort of separations is in line with the objectives established in new environmental regulations to reduce emissions of fluorinated gases with high global warming potential (GWP) and to promote their recycling.

We present the simulation and design of a two-stage membrane process to undertake the separation of two refrigerant mixtures, namely R410A, a mixture with 50 wt% R32 (difluoromethane, GWP: 677) and R125 (pentafluoroethane, GWP: 3170) and mixture R454B, with 68.9 wt % R32 and 31.1 wt % R1234yf (2,3,3,3-tetrafluoropropene, GWP: 1). The separation strategies have been designed towards the recovery of R32, which is an HFC qualified as mid-GWP, and is being used in the formulation of new environmentally-friendly refrigerant blends. In addition, R32 gas has significantly higher permeability than R125 and R1234yf in Pebax-based ionic liquid membranes, which means that R32 will be the major component in the permeate streams [1,2].

Materials and Methods

The permeation properties for R32, R125 and R1234yf were experimentally obtained in our recent works^{1,2}. A mathematical model describing gas permeation through the membrane module has been implemented in Aspen Custom Modeler and the permeation of gases through the hybrid material is described by the solution-diffusion model. Accordingly, this model was then exported to Aspen Plus to study the influence of critical variables such as feed pressure, permeation area and membrane thickness on product purity and recovery.

Results and conclusions

In light of the results, 98% R32 purity can be obtained in the product stream using a 2-stages system for the 2 mixtures studied (R410A and R454B). The configuration selected improves remarkably the recovery and purity of the product, which is one of the more critical limitations found in single stage membrane systems.

Acknowledgements

Juan de la Cierva-Formación 2017 postdoctoral contract (FJCI-2017-32884) and AEI-Spain (PID2019-105827RB-I00).

Reference 1:

[1] Pardo et al., *J. Memb. Sci.* (2021). 618, 118744

Reference 2:

[2] Pardo et al., *ACS Sustain. Chem. Eng.* (2021). 9 (20), 7012-7021

Single-Step Application of Polyelectrolyte Complex Films as Gas Barrier Coatings

Li, Jiaying - Main Author¹; van Dijken, Derk Jan - Co-Author²; van Ewijk, Gerard - Co-Author³; van der Gucht, Jasper - Co-Author⁴; de Vos, Wiebe - Co-Author¹

¹University of Twente, ²BASF Nederland B.V., ³AkzoNobel, ⁴Wageningen University and Research

Main topic: Gas separation

Polyelectrolytes (PE) and their complexes (PEC) as coating materials have demonstrated versatile functionalities, however, mainly at the nanometer scale. The conventional Layer-by-Layer method of preparing complexes makes it difficult for industrialization. To bring PEC and their functionalities to the micrometer range, it is necessary to establish a one-step method. Here, we introduce a new method to make polyethylenimine (PEI) and polyacrylic acid (PAA) complex films by evaporating a volatile base, ammonia.¹ Ammonia was first added into PAA to increase the pH which prevents direct complexation between PEI and PAA. PEI was kept uncharged that it can be homogeneously mixed with PAA in different ratios. These solutions then can be cast onto different substrates with controlled thicknesses. Biaxially orientated polypropylene (BOPP) sheets were used here for further testing gas barrier property. This combination has been proved to show excellent oxygen properties.² These PEC-based films can be a good substitute for traditional Aluminum oxides based oxygen barrier layer in food packaging.

The resulting films all showed good oxygen barrier properties (PEI:PAA 2:1 OTR lower than $4 \text{ cm}^3/\text{m}^2 \cdot \text{day} \cdot \text{atm}$) that indeed can be potentially used for food packaging. In this work, we have shown successful phase transitions from solution to solid complex that also achieves the functionality in one step. To improve and understand the current system, we are now working on potential additives, meanwhile searching for other PE systems.

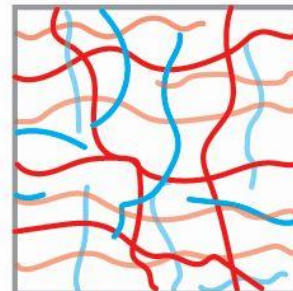
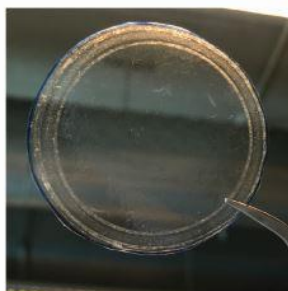
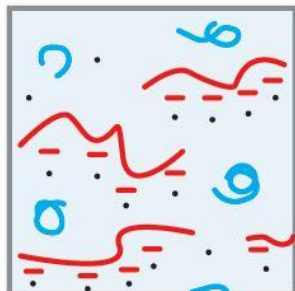
Reference 1:

Li, J.; van Ewijk, G.; van Dijken, D. J.; van der Gucht, J.; de Vos, W. M., ACS Applied Materials & Interfaces, 2021, 13(18), 21844-21853.

Reference 2:

R. J. Smith, C. T. Long and J. C. Grunlan, Transparent Polyelectrolyte Complex Thin Films with Ultralow Oxygen Transmission Rate. Langmuir 34, 11086-11091 (2018).

PEI + PAA + NH₃ → Evaporation → Dense polyelectrolyte network as O₂ barrier
homogenous solution



Single-use membrane bioreactor to produce polyhydroxyalkanoate (PHA) from CO₂

Akkoyunlu, Burcu - Main Author; Daly, Sorcha - Co-Author; Horvat, Tomislav - Co-Author; Casey, Eoin - Co-Author

Main topic: Membrane bio-reactors

Polyhydroxyalkanoate (PHA) is a promising alternative to petroleum-derived plastics due to their comparable physical and chemical properties and biodegradability. Many microorganisms can produce PHA as an intracellular energy and carbon storage material. Microorganisms such as *Cupriavidus necator* can metabolize CO₂ as a carbon source and produce PHA when a mixture of H₂, CO₂ and O₂ gas is supplied. Thus, it is possible to produce PHA directly from CO₂ which would reduce greenhouse gas emissions. However, the optimum gas composition ratio for cell growth is 7:2:1 for H₂:O₂:CO₂ which is within the gas-explosion range [1]. To eliminate the explosion risk, the oxygen concentration should be maintained below the lower explosion limit however this limits the growth and productivity due to oxygen limitation. Furthermore, gas fermentation faces substrate limitation due to the low solubility of gases in the culture medium. Membranes have the potential to help achieve high gas transfer efficiencies at low gas supply rates due to the high specific surface area available for transfer. Thus, membrane bioreactors are promising reactor systems for gas fermentation process. Our contribution will demonstrate the applicability of membrane bioreactors to deliver gaseous substrates for the production of PHA. To accomplish this, single-use systems were constructed using plastic centrifugal tubes and gas-permeable polydimethylsiloxane (PDMS) membrane fibres. Preliminary results indicate that comparable cell concentrations can be reached when membranes are used for provision of gaseous substrates. Further research will include investigating the effect of operational parameters such as the specific surface area of the fibers, composition of gas and recirculation flowrate on the production of PHA in a membrane bioreactor in order to develop a scale-up strategy.

Reference 1:

[1] L.-G. Md. Salatul Islam Mozumder, Heleen DeWeveraEveline I.P. Volcke, "Poly(3-hydroxybutyrate) (PHB) production from CO₂: Model development and process optimization," *Biochem Eng J*, vol. 98, pp. 107-116, 2015.

Single, dual, and triple-layered mixed matrix electrospun nanofibrous membranes: a strategic improvement for desalination by direct contact distillation membranes

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¹Department of Chemistry, Umeå University, Umeå, Sweden, ²Department of Structure of Matter, Thermal Physics and Electronics, Faculty of Physics, University Complutense, Madrid, Spain

Main topic: Membrane contactors and membrane distillation

The electrospinning technique easily fulfills the requirements for developing optimum direct contact membrane distillation (DCMD) membranes by fabricating single-, dual- and triple-layered electrospun nanofibrous membranes (ENMs).

Firstly, a systematic study using Polyvinylidene fluoride (PVDF) was carried out to determine the optimum electrospinning preparation condition, explored in terms of polymer solution flow rate, air gap distance, and applied voltage, to prepare an adequate ENM for DCMD.

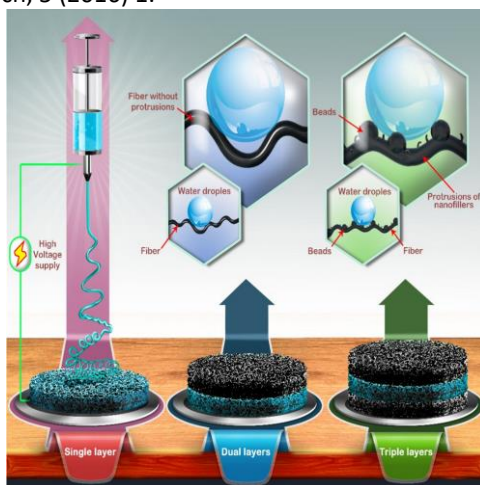
Beyond optimizing the electrospinning parameters to develop an optimum ENM, our achieved results using the proposed optimum ENM demonstrated that the DCMD technology possesses a potential application for desalination and could become a promising candidate for developing a portable system to produce drinkable water in emerging situations and remote areas without access to distilled water to be used on the membrane permeate side. For the first time, a long-term (100 h) DCMD experiment using a 30 g/L (NaCl) aqueous solution on both the feed and permeate sides of the optimum ENM was performed to evaluate its potential to produce drinkable water. After only 28 h DCMD operation, the experiment resulted in water permeate production with electrical conductivity below 400 $\mu\text{S}/\text{cm}$, recommended by World Health Organization (WHO) as drinkable water [1]. The obtained flux remained constant around $\sim 57.5 \text{ kg}/\text{m}^2\text{h}$ during the next 72 h of DCMD operation with separation factor $> 99.9\%$, indicating the robustness of this optimum ENM.

Secondly, Polysulfone (PSF), PVDF with different molecular weights, various concentrations of multi-walled carbon nanotubes, and graphene oxide were used to develop robust, single-, dual-, and triple-layered superhydrophobic mixed matrix (MM-ENMs) without any post-modification step. Based on the polymer solution's properties (i.e., electrical conductivity, viscosity, and surface tension), MM-ENMs were characterized in terms of morphology, hydrophobicity, structural, mechanical properties, and DCMD performance.

The optimum dual-layered MM-ENM produced an ultra-high permeate flux compared to previously published of up to $74.7 \text{ kg}/\text{m}^2\cdot\text{h}$, with stable electrical conductivity around $7.63 \mu\text{S}/\text{cm}$, and (NaCl) rejection factor of up to 99.995%, maintaining a stable electrical conductivity over 10 h DCMD operation. However, sandwiching a hydrophilic layer between two hydrophobic layers promotes water pocket formation. Consequently, DCMD performance became compromised.

Reference 1:

Y. Meride, B. Ayenew, Drinking water quality assessment and its effects on residents health in Wondo genet campus, Ethiopia, Environmental Systems Research, 5 (2016) 1.



Dedvukaj, Angela - Co-Author

Main topic: Nanofiltration/Reverse Osmosis

Polyamide (PA) thin-film composite (TFC) membranes are commonly applied in nanofiltration and reverse osmosis, thanks to their thin, selective top layer, rendering a high selectivity and flux. Interfacial polymerisation (IP) is the conventional method to synthesise TFC membranes. However, some drawbacks are associated with IP as it requires the utilisation of toxic solvents, generates much waste and is a very time-consuming process. In this research, a new approach is introduced to synthesise TFC membranes, called spray-based interfacial polymerisation prior to solidification (s-IPS). Here, first, a polymer solution containing a first monomer is cast. Next, the cast, still liquid polymer film is sprayed with a solution containing a second monomer. Subsequently, these two monomers can react at the interface and are expected to form a thin, selective layer on top of the still liquid polymer film. Solidification of the membrane occurs by placing the membrane in a non-solvent bath to undergo phase inversion (PI). s-IPS is more time-efficient, since fewer synthesis steps are needed, uses less solvents and produces less waste than the conventional process. Therefore, the membrane production cost will be lower and up-scaling will be easier. Additionally, problems associated with non wetted support pores and bad adhesion of the IP layer to the support should be eliminated. A very thin, defect free and smooth top-layer is expected which leads to increased flux, selectivity and fouling.

Membranes with good performances (98% RB retention and water permeances up to $3 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) were obtained. Filtration data, SEM pictures and ATR-FTIR spectra all indicated PA layer formation. Overall, high-performance membranes were synthesised, indicating that s-IPS is a potential alternative for the conventional synthesis of TFC membranes.

Reference 1:

Hermans, S. & Vankelecom, I. Membranes synthesized via interfacial polymerization: from aqueous to solvent resistant nanofiltration. (2014).

Stability of graphene oxide (GO) composite membranes in an aqueous environment: a molecular view

Tocci, Elena - Co-Author¹; Muzzi, Chiara - Co-Author; Gotzias, Anastasios - Co-Author²; Fontananova, Enrica - Co-Author
¹Institute on Membrane Technology (CNR-ITM), ²Institute of Nanoscience and Nanotechnology INN

Main topic: 1D- and 2D-materials for membranes

Climate change, the rapid growth of urban populations together with poor water management and decarbonization, will worsen water shortage in the next future. Alternative water sources are necessary for sustainable development. Since freshwater is already lacking in many countries, the biggest natural water resource on Earth is now exploited: seawater. To this day, there are 1200 operating desalination plants located in the EU Member States across the Mediterranean region. 91% of them rely on membrane-based technologies. One promising candidate for water treatment are Graphene Oxide (GO) membranes, because of their great performances in terms of selectivity and permeation. GO membranes need substrates to increase their stability and avoid swelling or delamination. In this work, we investigate the stability of GO membranes on different polymeric substrates via Molecular Dynamics (MD). MD can give an atomic insight on the mechanisms that lead to GO membrane great features. The simulation results are compared with experimental data.

Acknowledgements:

This work was supported by the Italian Ministry of Education University and Research (prot. MIUR no. 10912, 06/06/2016; concession grant decree no. 3366, 12/18/2018; IDEA-ERANETMED2-72-357.

Standardised processing of large datasets to characterise porous polymeric membranes using machine learning and automatable workflows within the research data infrastructure

Kadi4Mat

Griem, Lars - Main Author¹; Koepe, Arnd - Co-Author¹; Altschuh, Patrick - Co-Author²; Schoof, Ephraim - Co-Author³; Brandt, Nico - Co-Author¹; Zschumme, Philipp - Co-Author¹; Selzer, Michael - Co-Author^{1,4}; Nestler, Britta - Co-Author^{1,4}
¹Karlsruhe Institute of Technology (KIT) - Institute for Applied Materials - Computational Materials Science (IAM-CMS),
²Karlsruhe University for Applied Sciences (HKA) - Institute for Digital Materials Research (IDM), ³Karlsruhe Institute of Technology (KIT), ⁴Karlsruhe University of Applied Sciences (HKA) - Institute for Digital Materials Research (IDM)

Main topic: New characterisation methods

The synthesis and evaluation of synthesized membrane structures as virtual parts of digital twins provide a data basis for training machine learning algorithms and for enabling them to predict structure-property correlations when applied to real structures. The research data infrastructure Kadi4Mat [1] developed at KIT offers a platform for combining both, data management and data processing as a prerequisite for structured data storage as a database for machine learning.

The present work introduces a workflow that models the development process of a machine learning algorithm for the determination of the geometric anisotropy in porous polymer membranes and is implemented in Kadi4Mat in an automatable way. In the current use case, the structures to be investigated are diagnostic membranes used in lateral flow tests.

As a basis for the machine learning approach, more than 12,500 structures with a specifically configured microstructure are generated algorithmically. These synthesized microstructures are designed to mimic the macroscopic properties of the real diagnostic membranes and are additionally imprinted with different geometric anisotropies.

The generated structures are prepared for the CIDS [2] machine learning framework, an integrated part of Kadi4Mat. A supervised learning algorithm is selected and trained with the prepared structures aiming to predict anisotropic physical properties of the specific membrane structure. We show that the resulting anisotropy measurement tool can be applied to the digitally reconstructed images of the real diagnostic membranes.

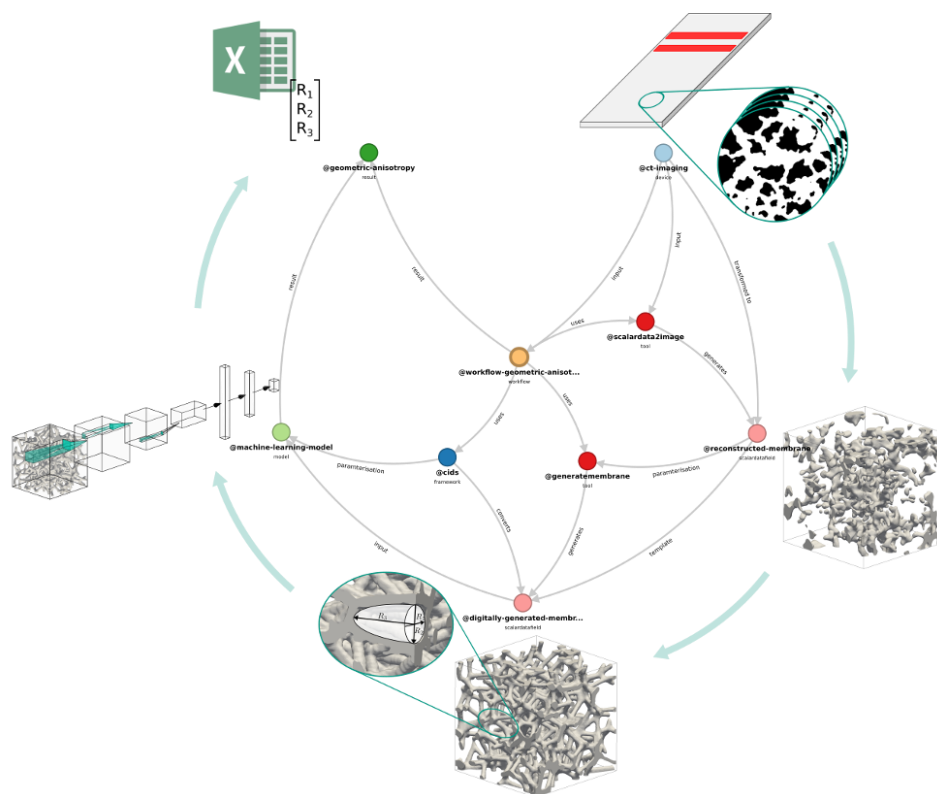
In order to save the process knowledge and keep it accessible for similar applications, a digital workflow holistically models the development process of the ML tool from the generation and preprocessing of the data to the training of the ML architecture. The KadiStudio workflow editor, an integral part of the research data infrastructure, allows the creation, visualisation and recording of the workflow. The focus of this contribution lies on the implementation of such a reproducible and automatable workflow for the characterization of porous microstructures by means of machine learning. The relevance of a research data infrastructure for accelerating and archiving research efforts will also be addressed.

Reference 1:

Brandt, N., Griem, L., Herrmann, C., Schoof, E., Tosato, G., Zhao, Y., ... & Selzer, M. (2021). Kadi4Mat: A Research Data Infrastructure for Materials Science. *Data Science Journal*, 20(1)

Reference 2:

Koepe, A., Bamer, F., Markert, B., 2019. An efficient Monte Carlo strategy for elasto-plastic structures based on recurrent neural networks. *Acta Mech* 230, 3279–3293.



Study of essential oils transport in nanocellulose films

Casalini, Sara - Co-Author; Giacinti, Marco - Co-Author; Montanari, Federico - Co-Author

Main topic: 1D- and 2D-materials for membranes

Nanocellulose is a 1-D material with continuously growing applications, due to its large availability, renewability and stable mechanical properties. Thanks to its peculiar transport properties, it has been used recently both as a barrier material and as a membrane for liquid and gas separation [1,2]. In this work, to further understand the potential application of this material, the sorption and diffusion of essential oils in different nanocellulose matrices has been studied, in view of its use as antimicrobial agent. The knowledge of essential oil transport is fundamental to control the release of the active substances, thus optimizing the antimicrobial effect, for example in active packaging systems. In particular, the diffusivities of Thyme, Cinnamon and Oregano in nanocellulose, obtained from Eucalyptus pulp, with different carboxymethylation degree (surface charge ranging from 30 to 1600 $\mu\text{eq/mol}$) have been measured and compared. The behavior is investigated through both liquid absorption and vapor desorption tests, to study conditions relevant for both active film preparation and essential oil release. The nanocellulose films were prepared by solvent casting and then immersed in the oils for the absorption measurements. The mass absorption ranged from 14% to 20% for the different oils, with Cinnamon being the most soluble.

The diffusion coefficient estimated from liquid absorption increases with the carboxymethylation degree, going from 2.3×10^{-9} to 1.0×10^{-8} cm^2/s with maximum values observed for Cinnamon oil. The desorption in the gas phase showed a complex release kinetics, which was described by considering two diffusion processes having different diffusion coefficients: the faster one, ranging from 1.1×10^{-9} to 3.0×10^{-11} cm^2/s , and the slower one, which becomes prevalent at long times, ranging from 4.0×10^{-11} to 1.0×10^{-12} cm^2/s . Interestingly, they both resulted lower than the ones related to the liquid absorption process, suggesting non-negligible plasticization effect of the liquid oils on nanocellulose films, also confirmed by the FTIR analysis.

The study therefore suggests that the release kinetics of the essential oils from nanocellulose can be controlled by changing the surface charge of the matrix and its plasticization, related to the loading of essential oil. This information can give useful guidelines for the production of more effective bio-based active packaging solutions.

Reference 1:

Z. Karima S. Claudpierre, M. Grahn, K. Oksman, A.P. Mathew, Nanocellulose based functional membranes for water cleaning: Tailoring of mechanical properties, porosity and metal ion capture, *Journal of Membrane Science*, 514 (2016) 418-428

Reference 2:

D. Venturi, D. Grupkovic, L. Sisti, M.G. Baschetti, Effect of humidity and nanocellulose content on Polyvinylamine-nanocellulose hybrid membranes for CO₂ capture, *J. Memb. Sci.* 548 (2018) 263–274

Studying fouling behavior of layer-by-layer modified nanofiltration capillary membranes in water treatment and its impact on separation performance

Abuelgasim, Hussein - Main Author¹; ElSherbiny, Ibrahim - Co-Author¹; Meshki-Zadeh, Nikta - Co-Author¹; Niestroj-Pahl, Robert - Co-Author²; Staaks, Christian - Co-Author³; Panglisch, Stefan - Co-Author^{1,4,5}

¹Chair of Mechanical Process Engineering & Water Technology, University of Duisburg-Essen, ²Surflay Nanotec GmbH, ³inge GmbH-DuPont, ⁴Center for Water and Environmental Research, University of Duisburg-Essen, ⁵DGMT German Society of Membrane Technology

Main topic: Novel membrane materials

Nanofiltration (NF) membranes can separate divalent ions rather than monovalent ions as well as organic matter compounds (including several micropollutants), more or less completely, which makes them interesting option for drinking and wastewater treatment. Besides, NF membranes are less susceptible to internal (pore) fouling that is one of the most common fouling scenarios for ultrafiltration membranes. Recently, capillary NF membranes are gaining attention because they allow operation without spacers resulting in better fouling control and cleanability compared to spiral-wound membranes. Nevertheless, there are very limited literature reporting on the fouling behavior of capillary NF membranes and its impact on the retention of monovalent and divalent salts.

In this study, the fouling propensity and separation performance of novel capillary NF membranes (MWCO ~ 400 Da) during mini-plant filtration experiments employing synthetic model feed water, imitating moderately loaded surface water, are investigated. The capillary NF membranes were prepared via layer-by-layer modification of polyether sulfone-based hollow fiber modules [1]. The model feed water comprised salts mixture and potting soil extract solution (mimicking natural organic matter, e.g., humic substances, biopolymers, and hydrophobic organic carbon). The filtration experiments were conducted at crossflow and dead-end operation modes employing different operating conditions to imitate different fouling scenarios at industrial scale-applications.

Capillary NF membranes have shown consistent antifouling performance during crossflow and dead-end experiments at the applied conditions. The organic fouling was found to be considerably hydraulic reversible, by simple mechanical cleaning, indicating that it is dominated by cake filtration mechanism. Particulate organic matter was completely retained at low concentration factor (CF), while retention of dissolved organic matter was promoted at high CF due to stronger fouling layer formation. Additionally, high retention of divalent species was measured at low CF, whereas a decrease in retention was observed at high CF, most likely because of cake-enhanced concentration polarization mechanism. Furthermore, retention of dissolved organic matter decreased with increasing the permeate flux, whereas retention of both monovalent and divalent salts was promoted. The results of this study are believed to boost our knowledge concerning performance of capillary NF membranes at different operating conditions toward wide application in drinking water and surface water treatment.

Reference 1:

Niestroj-Pahl, R.; Stelmaszyk, L.; ElSherbiny, I.M.A.; Abuelgasim, H.; Krug, M.; Staaks, C.; Birkholz, G.; Horn, H.; Li, T.; Dong, B.; Dähne, L.; Tiehm, A.; Panglisch, S. *Membranes* 2020, 10, 398. <https://doi.org/10.3390/membranes10120398>

Submerged-Helical Module: A conceptual, loosely-packed module design for minimal pressure drop in PRO

Aschmoneit, Fynn - Main Author^{1,2}; Hélix-Nielsen, Claus - Co-Author²

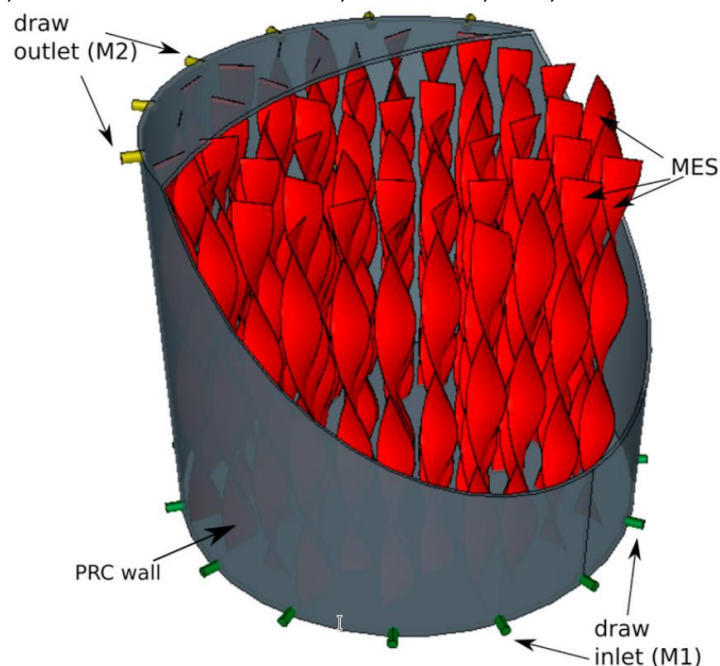
¹Aalborg University, Department of Mathematical Sciences, ²Technical University of Denmark, Department of Environmental Engineering

Main topic: Forward osmosis/Pressure retarded osmosis

Pressure retarded osmosis remains an outsider in green energy generation, despite the enormous theoretical energy potential. Besides the lack of high water flux membranes, one limiting aspect of PRO performance is related to the energy consumption of the system, which is crucially depending on the pressure drop along the PRO module. Traditional module designs for forward osmosis or reverse osmosis seem not ideal for PRO processes, since they are generally densely-packed, which, in turn, leads to high pressure drops, hence increasing the operation costs. Here we introduce our work on an alternative module design, in which, as opposed to the more traditional designs, the membranes are loosely-packed. The Submerged-Helical Module (SHM) design is a cylindrical drum holding several membrane envelope sheets (MES). The inside of the drum holds the pressurized draw solute. The MES are sealed double layers of membranes enclosing the feed channel. The central feature of the design are the twisted MES, which will locally deflect the flow field and impose a solute mixing effect, reducing ECP. The SHM design was analyzed through computational fluid dynamics, where the energy generation and the pressure drop in the draw channel were evaluated against several geometry- and operational conditions. The simulation results indicate explicit advantages and disadvantages of the SHM: The loosely packed design leads to a much decreased pressure drop and the twisting of the MES efficiently reduce the ECP, both increasing the net energy generation. However, the loose packing of the MES also leads to a large volume of draw solute, which must be pressurized, which decreases the net energy generation. This disadvantage was addressed by recirculating a share pressurized draw solution. It was found that for recirculation rates of >90% the SHM yields a higher net power generation rate than densely packed plate-and-frame or spiral-wound module types. In conclusion, this study indicates that the SHM could make the PRO process more efficient and may contribute to make PRO commercially viable. However, the SHM is conceptual and has solely been analyzed by computational means. An experimental setup would have to be developed, in order to validate the presented results and support the design concepts.

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F.J. Aschmoneit, C. Hélix-Nielsen, Submerged-helical module design for pressure retarded osmosis: A conceptual study using computational fluid dynamics, *Journal of Membrane Science*, Volume 620, 2021, 118704



Supercritical CO₂ for the sterilization of ultrafiltration membranes

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Main topic: Bio-medical applications

Ultrafiltration, a process widely used for water treatment is known for its performance in retaining microorganisms such as bacteria and virus. This study aims to evaluate the feasibility of organic membrane sterilization using supercritical CO₂ (CO₂SC). Supercritical fluids, especially CO₂SC, can be used as a sterilizing agent in order to kill or inactivate microorganisms. Compared to organic solvents sterilisation processes, CO₂SC sterilization has the advantage of being a "green", totally neutral, non-toxic, non-polluting and non-flammable process. Moreover, CO₂SC allows sterilization of thermosensitive materials thus limiting the thermal and/or chemical degradations linked to conventional sterilization methods. But, as a function of the microorganism resistances (bacteria < virus < bacterial spores) and sensitivity of treated material, a compromise on treatment conditions must be found between the sterilization performances and the membrane integrity. The objectives of this study are then (i) to control the membrane performances after treatment in different supercritical conditions and (ii) to evaluate the performances of sterilization toward a virus for the tested conditions. Sterilization temperature was fixed at 35 °C to take into account the membrane resistance. Different contact times [20 min- 11h30] in batch or continuous process and pressures of CO₂SC [100-150 bar] are tested on 2 membrane materials (PES, PVDF). The Molecular Weight Cut Off has been selected to stop the virus on the ultrafiltration membrane surface. To control membrane integrity, potentially altered by CO₂SC sterilization, permeability measurements and retentions to Dextran solution were performed before and after sterilization. Regarding the sterilization efficiency, membranes were fouled with a virus. Fouled membranes were then sterilized with CO₂SC and backwashed with pure water to recover the retentate containing the sterilized virus analysed with qPCR to measure virus concentration and activity. Those analyses are coupled with Transmission Electron Microscopy (TEM) observations to assess virus integrity. The results obtained on native membranes highlight the absence of impact of the CO₂SC sterilization on membrane integrity whatever the operating conditions. Indeed, the retention and hydraulic performances are similar before and after sterilization treatments (Figure 1). Virus inactivation was also validated and CO₂SC emerges as a viable and effective solution for membrane sterilization.

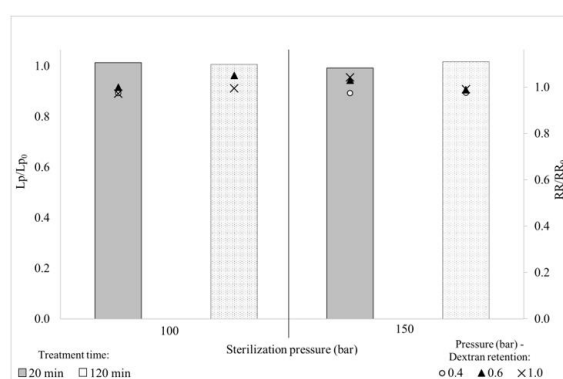


Figure 1: Sterilization of native membrane - Impact of CO₂SC sterilization on permeability and retention for different treatment conditions (RR : Retention Rate)

Supported Green Solvents Membranes for Bio-based Organic Acid Recovery

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Main topic: Bio-separations and bio-refinery

The search for green routes for chemical production has boosted the interest in bio-based organic acids as fundamental building blocks. Bio-based organic acids are produced by fermentation starting from renewable feedstock, e.g., starch, hemicellulose, cellulose, and lignin or sugars; and commonly purified by liquid-liquid extraction, using hazardous volatile organic solvents, which is opposed to initial green efforts. Thus, the use of green solvent alternatives must be promoted to establish a complete eco-friendly production that competes with petrochemical routes.¹ In addition, developing separation methods with low energy demand and solvent consumption, along with higher efficiency and selectivity is key. Within this framework, Supported Liquid Membranes (SLMs) have been broadly proposed as a promising alternative for the selective recovery of target compounds from diluted solutions. This work aims to address both features by studying the bio-based organic acid recovery using supported green solvent membranes.

Novel green solvents, such as ionic liquids (ILs), eutectic solvents (ESs), and bio-based solvents (BSs), were selected based on their solvent performance, solvent-water affinity, and energetic contributions in the organic acid extraction process from aqueous solutions.² Green solvents were impregnated into polymeric flat sheet porous supports, such as polyvinylidene fluoride (PVDF), and experimentally tested in terms of solute permeability and membrane stability. An activity-based flux model was ensemble to describe the solute transport employing quantum chemical COSMO-RS calculations and experimental data. Experiments were carried out at room temperature in a diffusion cell, Figure 1.a, by measuring the organic acid concentration at different time intervals up to 120 h by HPLC analysis. A sodium hydroxide solution was used as the receiving phase to enhance mass transport. Preliminary results for the activity-based model fixed to the experimental data give an organic acid permeability within a range of $5 \cdot 10^{-7}$ to $3 \cdot 10^{-6} \text{ m} \cdot \text{s}^{-1}$, as depicted in Figure 1.b.

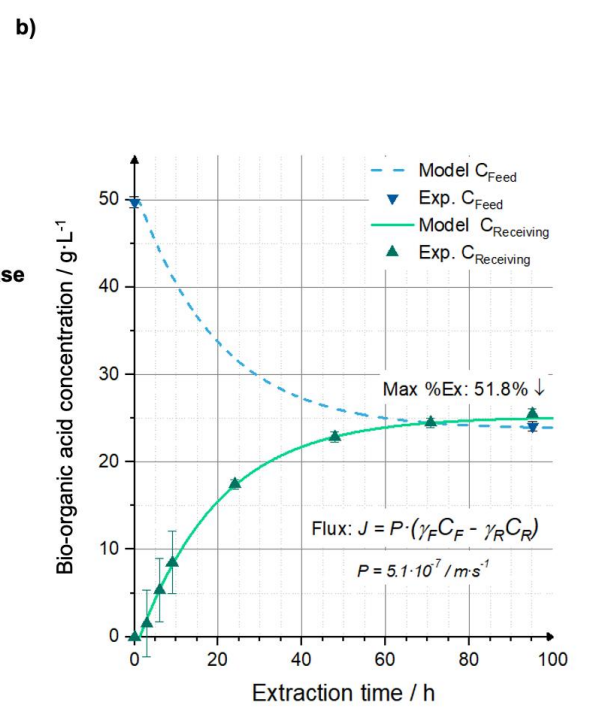
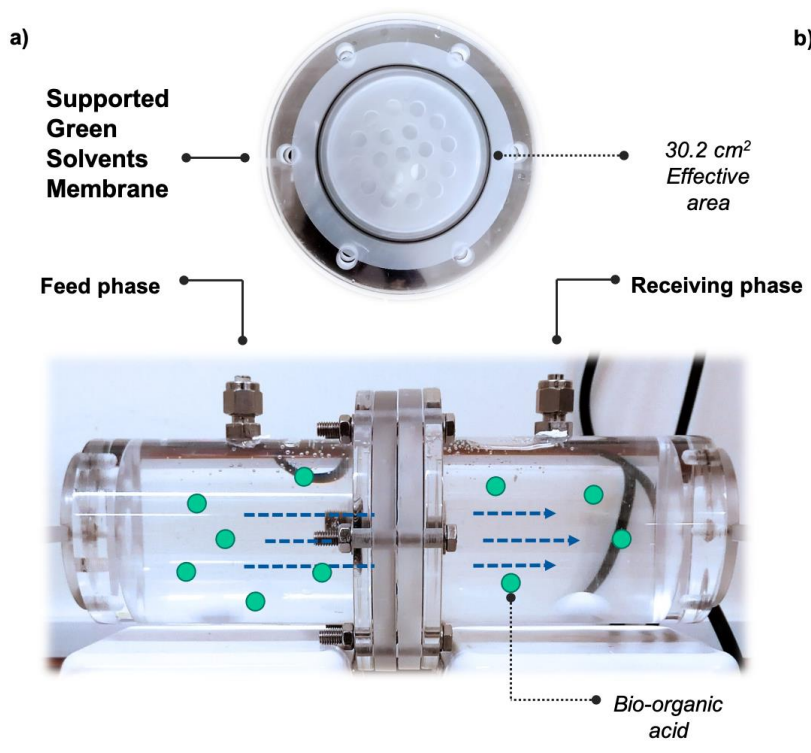
Results will provide fundamental insights into the development of sustainable separation processes of bio-based organic acids considering the underlying transport phenomenon through the SLM, ultimately promoting novel downstream technologies for the bio-refinery industry.

Reference 1:

J. M. Pinazo, M. E. Domine, V. Parvulescu, and F. Petru, "Sustainability metrics for succinic acid production: A comparison between biomass-based and petrochemical routes," *Catal. Today*, vol. 239, pp. 17–24, 2015.

Reference 2:

P. López-Porfiri, P. Gorgojo, and M. Gonzalez-Miquel, "Green Solvent Selection Guide for Biobased Organic Acid Recovery," *ACS Sustain. Chem. Eng.*, vol. 8, no. 24, pp. 8958–8969, Jun. 2020.



Suppression of Crack Formation in Mesoporous Metallic Foams

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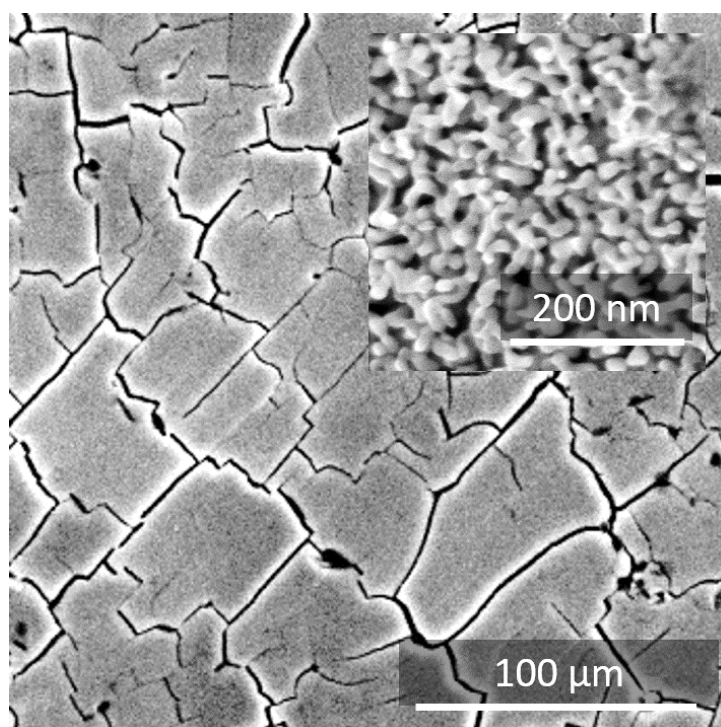
Main topic: Inorganic membranes

Polymers but also ceramics or glasses are usually used as membrane materials. The former material class is characterized by simple, cost-effective production and high degree of flexibility. Ceramics and glasses, on the other hand, offer pressure resistance, are chemically stable and temperature resistant. Metals, in contrast, are rarely employed. Their high reactivity and tendency to form oxides are only sufficiently suppressed in noble metals such as gold or platinum. In addition, pore networks in metals are less stable because of their high surface energy. Lastly, there are only a few established manufacturing methods for selectively introducing interconnected pore networks into metals. However, the alleged disadvantages of metallic materials can also be used to give membranes new functionalities. Many (transition) metals and their oxides are catalytically active and the high surface energy offers the potential to effectively functionalize or cover the pore surfaces (even down to monolayers).

A scalable process to generate mesoporous metal foams with unique properties is wet-chemical dealloying of suited bulk alloys and alloy foils. In this process, pores with adjustable characteristics are created in the more noble metal by self-organization, while the less noble alloy component is chemically dissolved. Except for ultra-thin Au foams, crack networks typically form in other metallic foams during dealloying. Those cracks so far impede the application as membranes or scaffolds.

We aim at the fundamental understanding of the crack formation and, more importantly, at the development of fabrication routines in order to produce mechanically stable mesoporous metallic foams on large scales. In this study, copper was chosen as an abundant, inexpensive, nonhazardous transition metal with catalytically active oxides. By *in situ* light microscopy in conjunction with advanced FIB/SEM and TEM, the material evolution, in particular cracking, during the dealloying process can be correlated to the applied process parameters. Besides the chosen electrolyte, the temperature and an applied bias are parameters that need to be adjusted for controlling pore and crack formation. Moreover, appropriate homogenization of the bulk starting material turned out to be mandatory to improve the cracking behavior.

Image caption: SEM-image of a crack network formed during dealloying. Inset: High magnification image of the pore network.



Surface modification using a photo-responsive copolymer for bioinspired anti-biofouling membrane

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Main topic: Biomimetic and bioinspired membranes

Biofouling remains a severe problem to be addressed in water treatment systems affecting membrane processes performance and cost.

Several amphiphilic coatings have been combined to antibacterial molecules for biofouling release [1]. However, antibacterials have to be used cautiously because of the risk to develop antibiotic resistance. Over the recent years, stimuli responsive materials, which have the potential to reverse their chemical/physical properties in response to external stimuli, e.g. light, have attracted great attention to achieve versatile bio-interfaces. As well, a trans–cis–trans photoisomerization of azobenzene-coated substrate can induce photofluidization and provide morphological changes at a local scale on surfaces [2].

Herein, we turn that photoisomerization concept around to detach biofilms from membrane surface just by applying light as an external stimulus. For this purpose, we combined a zwitterionic molecule to a photoresponsive azobenzene molecule to formulate a new copolymer (AZO-copolymer). This AZO-copolymer could resist fouling during wastewater filtration and detach fouling using light irradiation. A polyethersulfone (PES) membrane was modified with this AZO-copolymer by a one-step dip-coating method. The physicochemical and antifouling properties of the membrane surfaces were characterized. The fouling by bovin serum albumine (BSA) and bacteria (*P. aeruginosa*) was quantified and its reversibility evaluated.

UV-vis absorption spectra of the AZO-copolymer in solution were recorded before and after UV light irradiation (365 nm). The changes in UV spectra demonstrated that the azobenzene groups switch from trans to cis conformation. The phenomenon is reversible under visible light illumination.

The AZO-copolymer modified membranes were evaluated for their filtration performances through a pure water/BSA/pure water cycle. A complete reversibility of the flux was almost obtained with the highest AZO-copolymer coating densities (figure 1a). IR mapping allowed the observation of the static and dynamic effect of the coated AZO-copolymer on the BSA fouling layer. Epifluorescent microscopy images confirmed that bacteria were removed from the modified membrane surface (figure 1b). No significant effect of UV light was observed on bacteria for the pristine membrane.

Thus, we provided a new bioinspired membrane that presents preventive and curative effect against fouling, thanks to the fluttering of an AZO-copolymer at membrane/biofilm interface induced by opto-mechanical forces.

Reference 1:

[1] Zhu, J., Hou, J., Zhang, Y., Tian, M., He, T., Liu, J., Chen, V., 2018. Polymeric antimicrobial membranes enabled by nanomaterials for water treatment. *Journal of Membrane Science* 550, 173-197.
<https://doi.org/10.1016/j.memsci.2017.12.071>

Reference 2:

[2] Kehe, G.M., Mori, D.I., Schurr, M.J., Nair, D.P., 2019. Optically Responsive, Smart Anti-Bacterial Coatings via the Photofluidization of Azobenzenes. *ACS Applied Materials & Interfaces* 11, 1760-1765.
<https://doi.org/10.1021/acsami.8b21058>

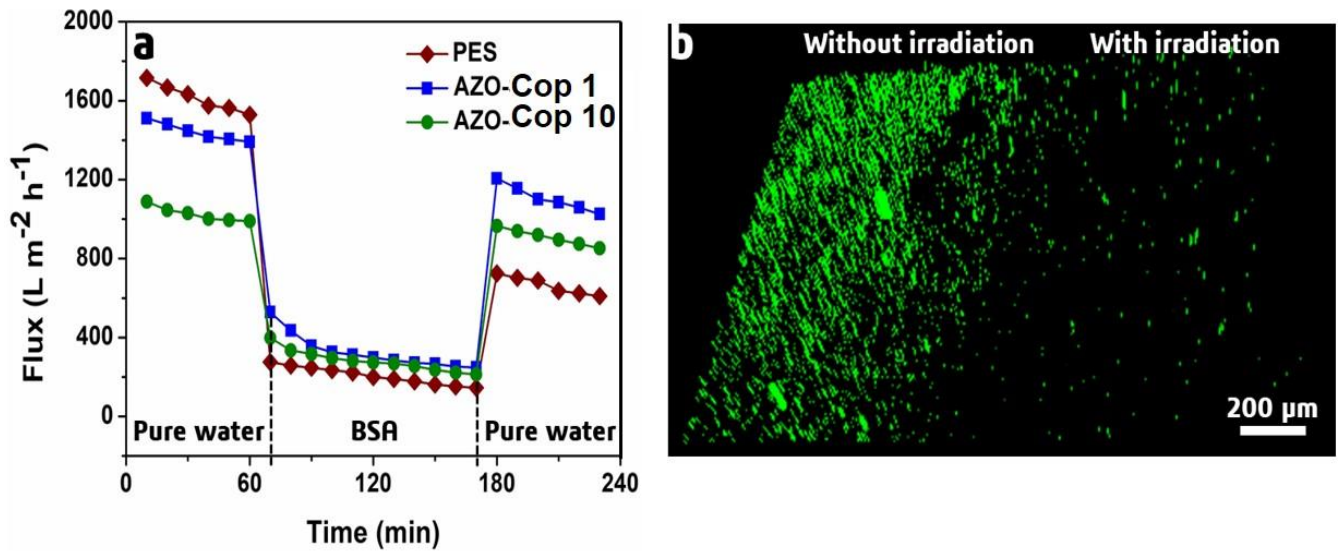


Figure 1: a/ Pure water and BSA fluxes on virgin (PES) and AZO-copolymer modified membranes at two level of coating densities (AZO-cop 1 and 10). b/ Epifluorescent microscope images of AZO-copolymer modified PES membranes after 3h of bacterial adhesion (bacteria marked with SybrGreen), without and with UV and vis irradiation cycles.

Surface-modified polyetherimide hollow fiber membrane with a fluorinated polyurethane for long-term desalination by membrane distillation

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Main topic: Membrane contactors and membrane distillation

Several methods for developing composite hollow fiber membranes are available, i.e., plasma treatment, coating, physical or vapor deposition, grafting [1]. However, the challenge with these suggested methods is how to prepare a robust surface-modified membrane without altering its structural integrity and surface pores size.

A simple approach for developing membranes for direct contact membrane distillation (DCMD) in one-step was proposed. Polyetherimide (PEI) robust surface-modified hollow fibers were developed using surface segregation of a fluorinated polyurethane additive (FPA). Three different hollow fibers were prepared by changing PEI concentration from 14 to 17 wt%, maintaining FPA concentration at 2 wt%. The liquid entry pressure (*LEP*), internal and external hydrophobicity, mechanical properties, average pore size, pore size distribution, effective porosity, average membrane roughness were determined by various characterization techniques, as well as DCMD performance, which was carried out by conducting DCMD experiments using pure water and different NaCl aqueous solutions as feed.

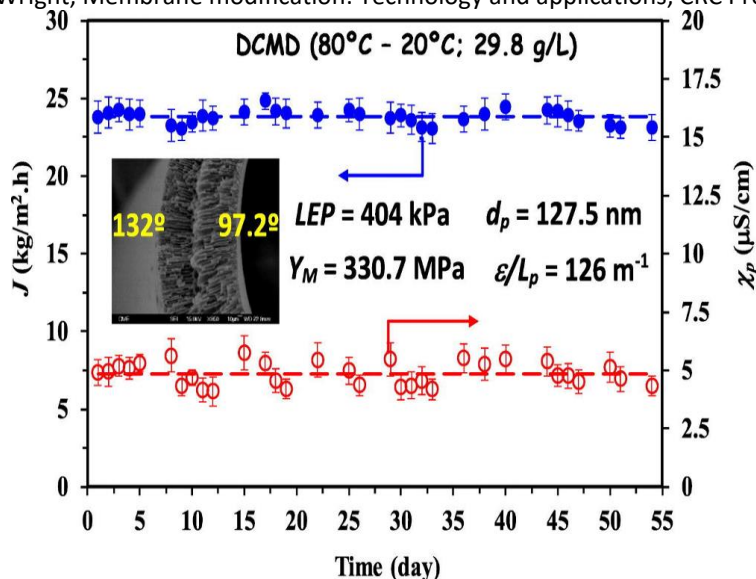
The addition of FPA to the spinning solution significantly improved the mechanical strength and *LEP* properties of the hollow fibers while reducing inner and outer pore size. Furthermore, increasing the PEI concentration in FPA/PEI hollow fibers resulted in improved *LEP* and reduced maximum pore size. Therefore, all the prepared membranes fulfill both conditions and properties required for membrane DCMD membranes.

The hollow fibers were successfully tested for desalination. Among them, FPA/PEI-14 (14 wt% PEI) showed excellent performance and was then subjected to a long-term desalination experiment for 54 days, during which no permeate flux decline was observed (i.e., an average value of 23.79 ± 0.45 kg/m².h) without any alteration of its quality (i.e., the average electrical conductivity value of 4.9 μ S/cm) over two months period.

Compared with single-layer composite hollow fibers and double-layer composite hollow fibers proposed for DM desalination, the FPA/PEI-14 hollow fiber is among those exhibiting reasonable permeate flux with low permeate electrical conductivity over long-term DMCD experiments. Moreover, the prepared membrane's exceptional advantage resulted in long-term durability during the desalination test resulting from its high *LEP* value. Consequently, FPA/PEI-14 hollow fibers are more suitable for desalination of DCMD regarding their long-term durability and desalination performance without risk regarding pore wetting.

Reference 1:

[1] N. Hilal, M. Khayet, C.J. Wright, Membrane modification: Technology and applications, CRC Press, 2012.



Sustainable dry-jet wet spinning of polyelectrolyte complex membranes via an all aqueous salt dilution induced phase inversion

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¹DWI - Leibniz Institute for Interactive Materials e.V., ²RWTH Aachen University, AVT.CVT - Chemical Process Engineering

Main topic: Novel membrane materials

Tubular and hollow fiber membranes are important elements of industrial filtration processes, dialysis and artificial organs. Established production processes require organic solvents that are prone to be phased out due to stricter regulations. The fabrication of polyelectrolyte complex (PEC) membranes via salt dilution induced phase separation represents a promising alternative. Flat-sheet membranes were successfully fabricated, while tubular and hollow fiber geometries remain a challenge. We present for the first time the organic solvent free dry-jet wet spinning of PEC complex tubular and hollow fiber membranes using a salt dilution induced phase separation. The aqueous polymer solution with PSS, PDADMAC and KBr is extruded with an aqueous bore fluid through a single orifice spinneret passing the air gap before immersed in the aqueous coagulation bath. Through contacting polymer solution with bore fluid and coagulation bath, the salt concentration in the polymer solution decreases, which induces phase inversion on the lumen and shell side, forming the tubular and hollow fiber membrane structures. The combination of the strong polyelectrolytes PSS and PDADMAC was proven to be stable in acids, alkaline and sodium hypochlorite solution. Moreover, no harmful acids are required in the coagulation bath compared to a pH shift induced phase separation of weak polyelectrolytes. Glycerol in the bore fluid stabilizes the forming fiber and allows tuning of the phase inversion kinetics on the lumen side resulting in a defect free selective layer. Tubular membranes reveal reproducible nanofiltration properties featuring a molecular weight cut-off (MWCO) of 320 Da and a salt retention hierarchy typical for a positive charge dominated retention behavior. While the filtration with tubular membranes requires a mechanical support, the produced hollow fibers are covalently cross linked resulting in stable fibers, so an additional support is not required. The cross linked hollow fibers show larger permeances of 18 LMH/bar and MWCOs of 30000 Da, which classifies them as ultrafiltration membranes. This promising sustainable fabrication strategy motivates to continue tubular and hollow fiber PEC membrane development. The all aqueous fabrication offers novel opportunities to outstand existing technologies related to the incorporation of sensitive additives such as biofunctional materials into the spinning process.

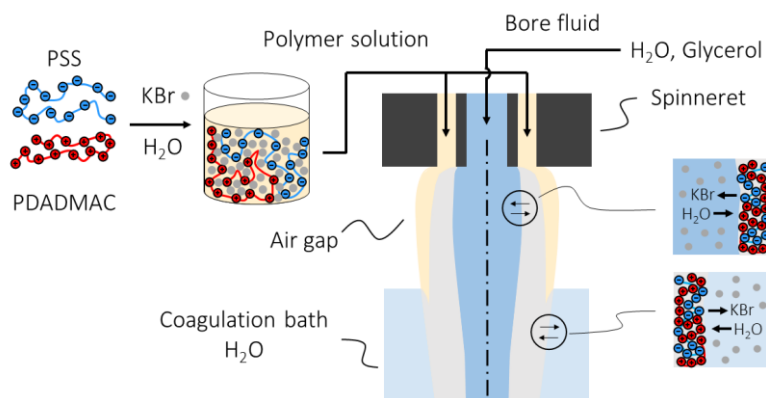
Reference 1:

J. Kamp, S. Emonds, J. Borowec, M. A. Restrepo Toro, M. Wessling, On the organic solvent free preparation of ultrafiltration and nanofiltration membranes using polyelectrolyte complexation in an all aqueous phase inversion process, *Journal of Membrane Science* 618 (4) (2021) 118632. doi:10.1016/j.memsci.2020.118632.

Reference 2:

S. Emonds, J. Kamp, J. Borowec, H. Roth, M. Wessling, Polyelectrolyte complex tubular membranes via a salt dilution induced phase inversion process, *Advanced Engineering Materials*-doi:10.1002/adem.202001401.

Fabrication of polyelectrolyte complex tubular and hollow fiber membranes



Sustainable, room temperature, acid-free processability of polyaryletherketones for solvent-resistant membrane applications

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Main topic: Organic solvent nanofiltration

Poly(ether ether ketone) (PEEK) and poly(ether ketone ketone) (PEKK) are both in the polyaryletherketone family of ultra-high performance polymers, known for its high thermal and organic solvent resistance. However, the processability of them have been limited to high temperature/pressure methods or by using harsh and corrosive solvents, such as methanesulfonic and sulfuric acid, which can lead to sulfonation of the polymer backbone, compromising the chemical stability of the material. Here, we report the preparation of PEEK and PEKK membranes for organic solvent filtration by using common organic solvents at room temperature, without the polymer solubilization in strong acids. The preparation method consisted in a chemical modification of the pristine polymer into a soluble derivative that allows the electrospinning, or the cast of the material in order to obtain different morphologies such as hollow fiber and flat sheet membranes. The resulting membranes were regenerated to the non-soluble polymers, displaying high stability over 90 day immersion in organic solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), toluene, concentrated hydrochloric acid and base solutions. The flat-sheet membranes showed a rejection of Methyl Orange (327 g mol^{-1}) of 82% with a permeance of $4.5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for DMF, while the rejection increased to 97% with a $0.8 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ permeance by changing the solvent mixture ratio of the polymer dope solution. Moreover, after the performance of the membranes, they were re-processed using the same methodology, making the whole process sustainable. This procedure opens many possibilities for processing PEEK and PEKK into membranes by using common techniques to obtain flat sheet membranes or hollow fibers for a broad range of applications requiring high chemical and thermal stability without the risk of corrosion or the use of high temperatures or pressure during the membrane manufacture.

Keywords: Poly(ether ether ketone), and Poly(ether ketone ketone), solvent resistant membranes, organic solvent nanofiltration, high temperature filtration, high-performance polymer, chemical modification.

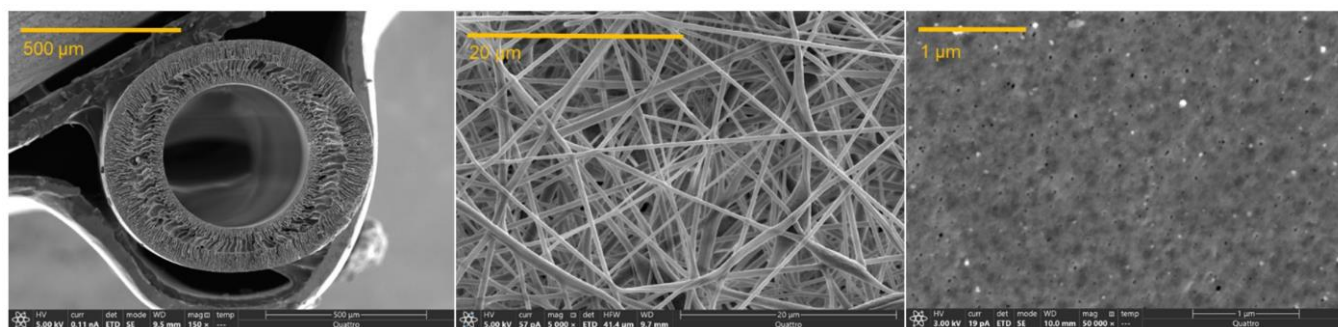


Figure 1. Different morphologies of the Poly(ether ether ketone) membranes (left: hollow fiber, center: electrospinning, right: flat sheet).

Synthesis of solvent stable UV-cured polysulfone-based support membranes using a green solvent approach

Dedvukaj, Angela - Co-Author

Main topic: Microfiltration/Ultrafiltration

Solvent stable UV-cured support membranes consisting of a semi-interpenetrating network of polysulfone (PSU) and cross-linked penta-acrylate were successfully synthesised for the first time using an alternative non-reprotoxic and biodegradable solvent. Tamisolve® NxG is a high-boiling, dipolar aprotic solvent with similar solubility parameters to those of DMF and NMP, which makes it an eco-friendly alternative. The support membranes, prepared via UV-curing and non-solvent induced phase inversion, serve as a universal solvent resistant support for the synthesis of a broad set of membranes containing organic solvents. Different parameters such as UV irradiation and the concentration of PSU, penta-acrylate and photo-initiator were varied to obtain suitable support membranes. The characteristics of the resulting support membranes were investigated in terms of separation performance, hydrophobicity, porosity, conversion and pure water permeability. The resulting membranes showed improved chemical resistance in solvents such as ethyl acetate, NMP, THF and toluene. Solvent stable support membranes with different pore sizes were synthesized and used for the preparation of TFC membranes to demonstrate its potential. Promising separation performance with RB retention up to 98% and water permeance up to $1.5 \text{ L m}^{-2}\text{h}^{-1}\text{bar}^{-1}$ were reached.

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Strużyńska-Piron, J. Loccufier, L. Vanmaele, I.F.J. Vankelecom, Parameter study on the preparation of UV depth-cured chemically resistant polysulfone-based membranes, *Macromol. Chem. Phys.* 215 (2014) 614–623

Tailoring the Selective Permeation Properties of Asymmetric Cellulose Acetate/Silica Hybrid Membranes. Deuterium and Proton Nuclear Magnetic Resonance Characterization

de Pinho, Maria Norberta - Main Author¹; Pereira da Silva, Miguel - Co-Author¹; Sebastião, Pedro - Co-Author¹; Figueirinhas, João - Co-Author¹

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Main topic: New characterisation methods

Asymmetric cellulose acetate (CA)/silica, CA/SiO₂, hybrid membranes with three distinct ultrafiltration porous structures and increasing permeation fluxes, herein denoted as CA22/SiO₂, CA30/SiO₂ and CA34/SiO₂, were synthesized by coupling the wet phase inversion and sol-gel techniques [1]. Pos-treatments of solvent exchange and surfactant mixtures conditioning were assessed in terms of their effect on the hydraulic permeability, selective permeation properties, molecular weight cut-off (MWCO) and average pore radius at the active layer's surface. These results were correlated with the ordering and dynamics of water in their porous structures by deuterium and proton Nuclear Magnetic Resonance (NMR) spectroscopy and relaxometry [2]. In the membranes CA22/SiO₂, CA30/SiO₂ and CA34/SiO₂, the number 22, 30 and 34, corresponds to the wt. % of formamide in the casting solutions where the solvent system is composed of acetone and formamide. Their hydraulic permeabilities are 7.8±0.3, 24±2 and 62±3 kg h⁻¹ m⁻² bar⁻¹ and their molecular weight cut-off (MWCO) is equal to 10, 17 and 21 kDa, respectively. It was found that the pos-treatment by solvent exchange caused membrane shrinkage and leads to very different permeation characteristics typically associated to nanofiltration, namely a decline in hydraulic permeabilities to 1.29±0.12, 0.95±0.10 and 1.59±0.09 kg h⁻¹ m⁻² bar⁻¹, a reduction of their MWCO to 2, 2 and 1 kDa, respectively, and a total rejection to Na₂SO₄ and MgSO₄ salts. In contrast, the conditioning with surfactant solutions presented minimal dissimilarities on the membrane's permeation properties and structure. NMR results pointed to the existence, in all membranes, of two distinct spectral components with different degrees of order and relaxation times, T1 and T2, compatible with two distinct water populations that may be associated with the asymmetric nature of the membranes and their respective pore sizes. This work provides an essential indication that NMR spectroscopy and relaxometry are reliable tools to characterise the effects of the pos-treatments on the asymmetric CA/SiO₂ hybrid membranes.

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[1] G. Mendes, M. Faria, A. Carvalho, M.C. Gonçalves, M.N. de Pinho, Structure of water in hybrid cellulose acetate-silica ultrafiltration membranes and permeation properties, *Carbohydr. Polym.* 189 (2018) 342–351. doi:10.1016/j.carbpol.2018.02.030.

Reference 2:

[2] M.J. Beira, M.P. Silva, M. Condesso, P. Cosme, P.L. Almeida, M.C. Corvo, P.J. Sebastião, J.L. Figueirinhas, M.N. de Pinho, Molecular order and dynamics of water in hybrid cellulose acetate–silica asymmetric membranes, *Mol. Phys.* 117 (2019) 975–982. doi:10.1080/00268976.2018.1537526

Technical assessment of electro dialysis system for potassium recovery from sugarcane vinasse treatment

Ramos, Ramatisa Ladeia - Main Author; Barros, Laura Braz Monteiro - Co-Author; Silva, Ana Flávia Rezende - Co-Author; Brasil, Yara Luiza - Co-Author; Lange, Liséte Celina - Co-Author; Moravia, Míriam Cristina Santos Amaral - Co-Author

Main topic: Wastewater treatment

Brazil is the second-largest ethanol producer in the world with a production of 30 million m³ in 2020 (RFA, 2021), making the sector of great relevance for the country. Large volumes of wastewater, especially vinasse, are generated during the ethanol production process. The main use of vinasse is in fertigation, returning to the crops bringing beneficial results. However, if applied in excess, it can cause serious negative impacts. Potassium is the predominant ion in the vinasse, and because of its high concentration, there are legislations that limit the application of vinasse in agricultural soil. The use of electro dialysis, a membrane separation process in which there is ionic transport under the influence of an electric field, enables the reduction of potassium content of the vinasse. This allows an increase in the application rate of this effluent without compromising the soil, the crop, and the quality of water. In addition, it is possible to concentrate the salts of the vinasse, among which the potassium, enabling its usage as concentrated fertilizer in agriculture. In this work aspects such as vinasse pre-treatment, use of different membranes and configurations, and use of different electrolyte solutions were evaluated in order to achieve maximum potassium recovery and vinasse desalination. Regarding pretreatment, ultrafiltration was efficient in the removal of solids, reducing membrane fouling. Of the configurations tested, mixed configuration (one monovalent selective cationic membrane and others non-monoselective membranes) was able to recover, after 8 hours, with a current of 0.11A, 72% of potassium with the lowest energy consumption (0.5 kWh.m⁻³) and the best current efficiency (54%). The potassium removal allows an increase of 5 times the dose of vinasse application and consequently reduction of the transport cost in the fields. Electrolyte solutions of sodium sulfate, magnesium sulfate, ammonium nitrate, and potassium sulfate were tested. Solutions of magnesium sulphate and ammonium nitrate provided better conditions, considering the greater recovery and removal of potassium and greater potential use of vinasse as fertilizer. The treatment route proposed for vinasse treatment is in line with the principles of circular economy, guided by its valuation through the recovery of by-products and agricultural reuse of water.

Reference 1:

RFA – Renewable Fuels Association. (2021, September 01). Market & Statistics: World Fuel Ethanol Production. Retrieved from <http://ethanolrfa.org/resources/industry/statistics/>

The application of sulfomethylated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene ion exchange membrane in microbial electrochemical technologies: efficiency and operational stability

Koók, László - Main Author¹; Zitka, Jan - Co-Author²; Rózsenszki, Tamás - Co-Author¹; Otmar, Miroslav - Co-Author²; Nemestóthy, Nándor - Co-Author¹; Bélafi-Bakó, Katalin - Co-Author¹; Bakonyi, Péter - Co-Author¹

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Main topic: Fuel cells

In this work, a novel cation exchange membrane, PSEBS SU was deployed in various microbial and conventional electrochemical systems (ECs), including microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) to examine system efficacy in line with membrane characteristics. Compared to a reference material (Nafion), using PSEBS SU resulted in improved current density and electricity generation kinetics in MFCs, together with similar electron recovery efficiency (19–28%). These outcomes indicated more beneficial ion transfer features and lower mass transfer-related losses in the PSEBS SU-MFCs, supported by water uptake, ion exchange capacity (IEC), ionic conductivity and permselectivity values. By re-activating the membranes after (bio)foulant removal, PSEBS SU regained nearly its initial conductivity, highlighting a salient functional stability. The operational stability of PSEBS SU membrane was further demonstrated in MECs and abiotic ECs. 10 days long low current density MEC operation (1 A m^{-2}) did not alter significantly the conductivity and IEC of the membrane, while the performance decrease caused by the increased current density (up to 50 A m^{-2}) in ECs could be mostly regained after the acid-base re-activation of the polymer. Considering all the findings, the PSEBS SU seems to be promising for bioelectricity generation, hydrogen production, as well as for resource recovery using electro-membrane technologies.

Acknowledgement

László Koók was supported by the ÚNKP-20-3 New National Excellence Program of the Ministry for Innovation and Technology from the source of the National Research, Development and Innovation Fund. This research was supported by the National Research, Development and Innovation Fund project NKFIH OTKA K 119940 entitled “Study on the electrochemical effects of bioproduct separation by electrodialysis.

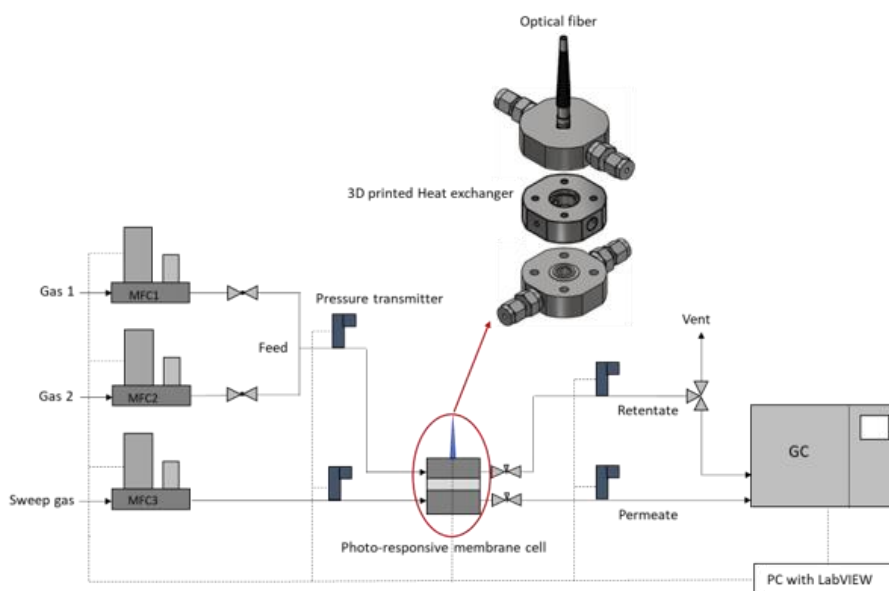
The development and application of a remarkable photo-responsive gas separation system

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Main topic: Gas separation

Light-responsive membranes have attracted considerable attention in terms of gas separation due to its abundance and rarely generate any side products. However, to precisely characterize and determine the mixed gas separation performance of the photo-responsive membranes, a reliable and stable test system is crucial. In this work, a new automatically online mixed gas separation test system are designed basing on the Wicke-Kallenbach technique and applied to investigate the performance of photo-responsive membranes under controlled-temperature and pressure. For the experimental setup of mixed gas separation measurement, the custom-made photo-responsive membrane test cell plays a core role and is applied to evaluate the photo-responsive ability of the membranes during continuously gas permeation process by switching on/off the light, thereby making it is possible to dynamically investigate the permeability and selectively of the photo-responsive membrane. The remarkable 'sandwich' structured test cell consists of three parts. The top chamber incorporated with an external light source that bring light in with a high NA (numerical aperture) polymer optical fiber. The high power optical fiber coupled multi-wavelength LED light sources (such as UV, Violet, Blue, Green and Red light) illuminate the photo-responsive membrane at a certain distance, and the light density of each channel could be precisely controlled. A 3D printed heat exchanger inserted between top and bottom chamber with metal grid inside, supplied high surface area density and combined with optimized multi-channel fluid pathways, effectively transfers heat caused by the adsorbed light from membrane surface and maintain a specific test temperature of the membrane. During the measurement, a binary feed compositions are controlled by MFCs and simultaneously introduced through the upper chamber of the membrane cell, while the lower chamber is swept by helium with an equal flow of the upper to eliminate concentration polarization in the permeate side. The permeate outlet composition is continually online determined by gas chromatography (GC 2010 Plus, Schimadzu) equipped with a ShinCarbon micropacked column from RESTEK. Following a software (LabVIEW) controlled the MFCs, and measured the pressures and temperature, realizing the online automatically process.



The effect of different degassing methods on polysulfone membranes

Bozorgmehr, Zahra - Co-Author

Main topic: New characterisation methods

Air bubbles are the main source of pinholes in membranes. To reduce the pinholes in a membrane, degassing of the casting solution before membrane preparation is a critical step. This study evaluates first the optimal polymer dissolution method, and then the efficiencies of various degassing methods, including ultrasonic water bath, probe sonication, vacuum, oven treatments at different temperatures, and degassing under simple hood ventilation at room temperature. The effects on the pore size of two kinds of polysulfone membranes are studied: 20wt% S3010 and Udel 1700P, both cast from dimethylformamide.

Flat sheet polysulfone membranes were prepared using an automatic casting device, with a thickness of 200 μm at a speed of 0.02 ms^{-1} using the phase inversion technique in a water containing coagulation bath. A high-throughput filtration with eight membrane positions using a $35 \mu\text{M}$ Rose Bengal (RB) in Milli-Q water feed solution, was conducted. Fourier transform-infrared (FT-IR) spectroscopy was applied to investigate the membranes. Membrane pinholes were visually detected using a lightbox.

Degassing using the ultrasonic water bath led to retention of 90% and 65% RB for S3010 and Udel 1700P, respectively,. The vacuum-treated solutions showed the fastest degassing rate and retentions of about 75% for S3010 and 60% for Udel 1700P. The retentions were 70% (S3010) and 50% (Udel 1700P) for the oven-based procedure and about 65% (S3010) and 10% (Udel 1700P) for the room temperature hood ventilation.

Heating proved crucial to dissolve the polymer powder properly before the degassing. The ultrasonic and vacuum methods were found to be most effective to accelerate the removal of gas.

Reference 1:

<https://doi.org/10.1016/j.matlet.2006.07.012>

Reference 2:

<https://doi.org/10.1016/j.vacuum.2009.03.032>

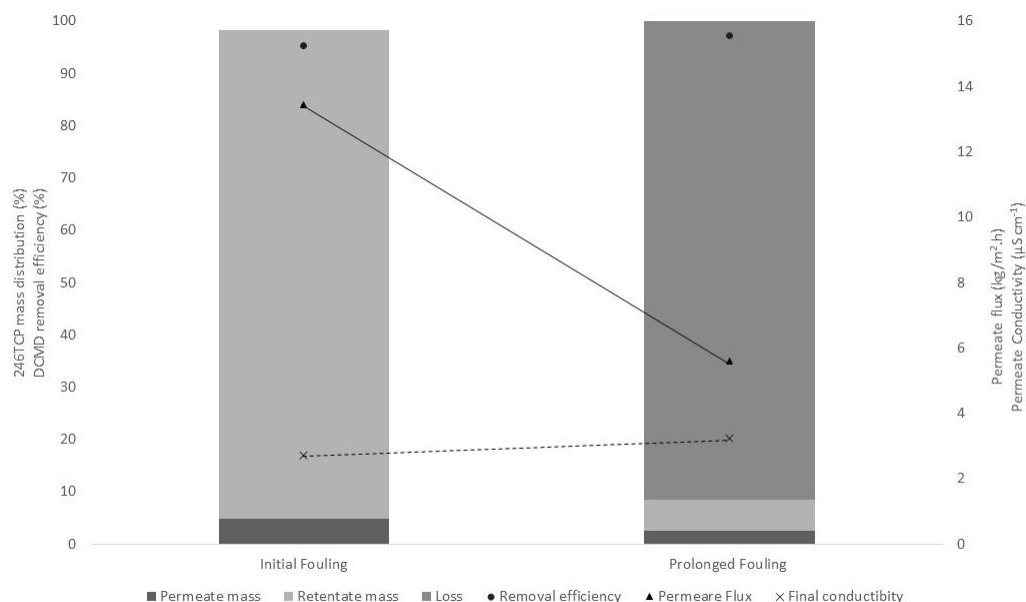
The effect of fouling in membrane distillation treating surface water with 2,4,6 trichlorophenol

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¹Universidade Federal de Minas Gerais

Main topic: Membrane contactors and membrane distillation

The presence of chlorophenols in surface water is of great interest, due to the variety of contaminant sources and the physicochemical properties of these substances. The process of disinfecting water for human consumption by chlorination in the presence of phenolic compounds can result in the chlorophenols formation. The 246-Trichlorophenol (246TCP) is the main isomer formed through this process. As a fungicide, herbicide, insecticide, and antiseptic substance, it is widely used. Chlorophenols are especially toxic and potentially carcinogenic. Many are considered priority pollutants for monitoring in water by the European Union and the US Environmental Protection Agency. The development of effective methods for removing these phenols from water is still an important topic and direct contact membrane distillation (DCMD) has attracted attention for the removal of micropollutants present in water. In this sense, this study evaluated a surface water spiked with 246TCP in the concentration of $5 \mu\text{g L}^{-1}$ used to feed a DCMD system. Distilled water was used in the permeate tank. In addition, the test was continuously monitored to observe the membrane fouling process. The streams were recirculated in counter-current mode at 1.0 L min^{-1} and the permeate and feed temperatures were set as 25°C and 60°C , respectively. As can be seen in Figure 1, the magnitude of DCMD permeate flux was strongly affected by the fouling process, but the permeate conductivity was not compromised, remaining practically constant over time. This result suggests that there was no episode of total membrane wetting. Furthermore, it is remarkable that the fouling process favored the retention of 246TCP (Removal efficiency IF = 95.32% and PF = 97.63%). The 246TCP has moderate volatility ($\text{pK}_a = 5.377$) and more hydrophilic characteristics ($\text{Log D} = 2.78$), showed less passage to the permeate side during the fouling process. The compound loss in the prolonged fouling process were more significant since the test time was longer compared to the initial fouling. In that case, may have occurred thermal degradation, adsorption, and a lower contribution volatilization and photodegradation. Therefore, the DCMD demonstrating the great potential for remove this compound in trace concentration in surface water, which has volatile and hydrophilic characteristics.



The role of absorbent temperature on mass transfer in microporous and dense-film hollow fibre membrane contactors for CO₂ absorption

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Main topic: CO₂ capture

Hollow fibre membrane contactors (HFMC) are an emerging technology for CO₂ capture from industrial flue gases and for purifying biogas into biomethane. While microporous hollow fibres promote high mass transfer, they are vulnerable to pore wetting which increases membrane resistance over time[1]. Incorporation of dense gas-permeable films within the hollow fibre geometry can prevent wetting to improve resilience, but membrane resistance of the virgin fibre will increase, dependent upon the thickness and permeance of the polymer employed[1]. Flue gas treatment occurs at raised temperatures (> 35°C), whilst biogas treatment favours low temperatures (5-10°C) to limit solvent slip into biomethane. While studies have sought to establish the impact of absorbent temperature on CO₂ flux within HFMC, the implications on dense-film HFMC resistance through varying polymer permeability and thus suitability for different applications has not been explored. Consequently, this study evaluates 1µm dense-film polymethylpentene hollow fibres across absorbent temperatures 5-35°C, benchmarking performance against microporous hollow fibres within commercial HFMC of comparable scale.

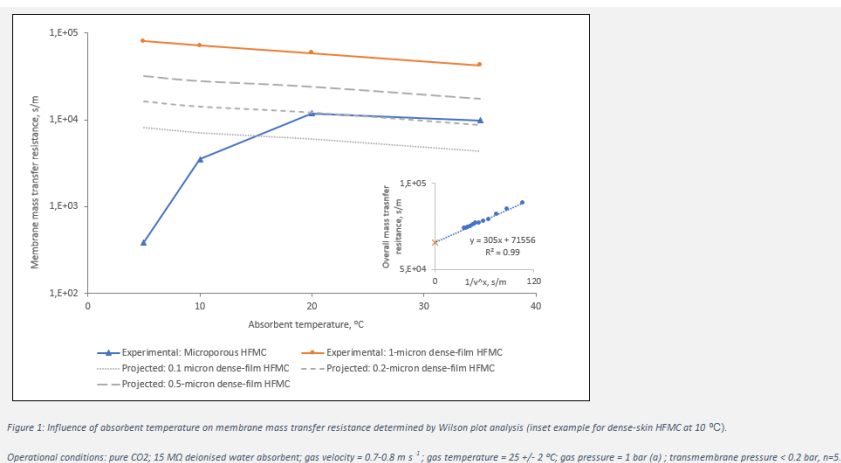
Resistance within dense-film HFMC decreased exponentially with temperature (Figure 1) driven by the decline of dense-film permeability in accordance to an Arrhenius relationship. Interestingly, permeability was 53% lower than polymethylpentene under dry conditions[2] leading to higher resistance values. This may result from sorption by water vapour which competes with CO₂ transport through the dense-film, underlining the importance of permeability evaluation in the presence of a solvent. Resistance within microporous HFMC should decrease marginally with increasing temperature due to increasing CO₂ diffusivity within gas-filled pores. However, increasing resistance occurred due to pore wetting via capillary condensation under increasing solvent vapour pressure, highlighting its vulnerability. Above 20°C, increasing diffusivity of CO₂ in water offset further impacts of pore wetting (Figure 1). Resultantly, from 5 to 35°C the difference in resistance between the HFMC reduced by almost two orders of magnitude (Figure 1). This greatly favours suitability of the dense-film HFMC for flue gas treatment, whilst indicating that it is practically unviable for chilled biogas treatment. Future development of commercial HFMCs incorporating < 1 µm dense-films or utilising polymers resistant to water sorption could further reduce resistance and strengthen viability over microporous HFMC for all CO₂ capture applications.

Reference 1:

Belaissaoui, B. et al. (2016) 'Potentialities of a dense skin hollow fiber membrane contactor for biogas purification by pressurized water absorption', *Journal of Membrane Science*, 513, 236–24

Reference 2:

Mohd Shafie, Z. M. H. et al. (2019). Prospect of Oxyplus hollow fibre membrane with dense polymethylpentene (PMP) skin as support-gutter layer of thin film composite (TFC) for biogas upgrading. *J. Phys. Sci.*, 30(Supp. 2), 179–189



The role of Anion Exchange Membranes for CO₂ electroreduction in alkaline media

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¹University of Cantabria, ²Universidad de Cantabria, ³University of Cantabria

Main topic: Electro-membrane processes

Electrochemical reduction of CO₂ (CO₂RR) is a promising technology for coupling CO₂ conversion into value added products and energy storage from renewable sources. Mass transport limitations in electrochemical cell reactors are noticed as one of the mayor challenges, due to the poor solubility of CO₂ in aqueous electrolytes. In this regard, polyelectrolyte membrane reactors (PEMER) are gaining relevance, because they allow the elimination of the liquid electrolytes. Thus, the study of the role of the ion exchange membrane (IEM) is an important issue in the electrochemical reactor configuration, as they provide the ionic media in which the reaction takes place, controlling the pH and facilitating ion transport (and hindering product crossover) between the electrodes. In particular, alkaline media present several advantages by reducing the competition of Hydrogen Evolution Reaction (HER) compared to acid media, lower ohmic losses than neutral and a high concentration of hydroxide anions in the surroundings of the catalyst to improve the kinetics of the CO₂RR, favoring the formation of C₂ products.

In this work, we studied the behavior of two commercial alkaline anion exchange membranes (AAEM) suitable for the construction of a PEMER for CO₂RR: Sustainion and FAA-3. Electro reduction experiments were conducted in alkaline conditions (initial pH=14, pH=10 during process) with Cu as catalyst to distinguish the product distribution and calculate the kinetic parameters of the reactions via Tafel plots. Formate was obtained from the CO₂RR with the Sustainion AAEM, but the highest Faraday Efficiencies were for ethanol (50.91 %) with the FAA-3 and ethylene (67.22 %) with the Sustainion membrane, respectively, which agrees with the influence of the alkaline media in the generation of C₂ products. Also, diffusion experiments were carried out in the same reaction cell to study the crossover of products through the AAEM. These results were validated by a mathematical model of the electrochemical cell developed for CO₂ electrolyzers in slightly acid media, comprising reactions and transport phenomena occurring at the cathode compartment, AAEM, and anode compartment in order to increase the understanding of the influence of the role of the membrane in CO₂ electrolysis in alkaline media.

Reference 1:

C. Dinh, T. Burdyny, G. Kibria, A. Seifitokaldani, C.M. Gabardo, F.P.G. De Arquer, A. Kiani, J.P. Edwards, P. De Luna, O.S. Bushuyev, C. Zou, R. Quintero-bermudez, Y. Pang, D. Sinton, E.H. Sargent, CO₂ electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface, *Science*, 787 (2018) 783–787.

Reference 2:

L.C. Brée, M. Wessling, A. Mitsos, Modular modeling of electrochemical reactors: Comparison of CO₂-electrolyzers, *Comput. Chem. Eng.*, 139 (2020) 106890..

The role of membranes in the continuous production of lactic acid with cell recycle: Productivity and economics

Daly, Sorcha - Co-Author

Main topic: Membrane bio-reactors

Introduction: Two major challenges facing our planet are inherently linked: the decline of our natural resources and the accumulation of plastic in our environment. The production of petroleum based plastics is also a key contributor to climate change. Both of these challenges can be tackled simultaneously thanks to engineering. Waste that was once allowed to accumulate in our environment now has the potential to be reused as something of value that is not harmful to the planet. For example, whey permeate from the dairy industry can be converted into lactic acid and then polylactic acid, a biodegradable plastic. This is conventionally done using batch fermentation, however, integrating membranes with the bioreactor can facilitate a more efficient continuous process, the focus of this study.

Materials and methods: The use of cell recycle via membranes in fermentation processes can increase cell density and lactic acid yield, (Xu et al., 2006). The continuous fermentation of *Lactobacillus lactis* to produce lactic acid with hollow fibre ultrafiltration membranes for cell recycle is examined in this study with a particular focus on membrane fouling and mitigation.

Results: Preliminary results show that higher recycle flowrates can help delay flux losses due to membrane fouling. Cell recycle at a flowrates of 0.09, and 0.14 L/min resulted in a 97% and 70% decrease in flux after just 5 minutes respectively. Cell recycle at a flowrate of 0.18 L/min managed to maintain the flux for over an hour. This is an opportunity for research in the optimal flowrate required to maintain performance.

Future work: Further work is required to examine damage, if any, to cells caused by cell recycle flowrate. The optimum flowrate must be identified, and an effective fouling control strategy developed. Technoeconomic analysis will be undertaken to compare the continuous process to the batch process.

Reference 1:

Xu, G.-q., Chu, J., Wang, Y.-h., Zhuang, Y.-p., Zhang, S.-l., Peng, H.-q. 2006. Development of a continuous cell-recycle fermentation system for production of lactic acid by *Lactobacillus paracasei*. *Process Biochemistry*, 41(12), 2458-2463.

Thermally rearranged mixed matrix membranes for hydrogen separations

Soto, Cenit - Main Author; Torres-Cuevas, Edwin S. - Co-Author; González-Ortega, Alfonso - Co-Author; Palacio, Laura - Co-Author; Lozano, Ángel E. - Co-Author; Freeman, Benny D. - Co-Author; Prádanos, Pedro - Co-Author; Hernández, Antonio - Co-Author

Main topic: Gas separation

Nowadays, hydrogen is considered to be one of the most promising alternative energy sources to fossil fuels, which can be derived from renewable electricity and sustainable organic feedstock. High purity hydrogen has many applications in the hydrogen fuel cell industry or as clean fuel but requires a preliminary purification step when obtained from the dark fermentation of organic waste (typically named as biohydrogen). This work reports the preparation of mixed matrix membranes (MMMs) by incorporating porous polymer networks (tritycene-trifluoroacetophenone, PPN-2) using a hydroxypolyamide (HPA) as polymeric matrix for hydrogen separation¹. PPN-2 has excellent CO₂ adsorption properties due to the strong interaction between PPN and CO₂ molecules. The HPA herein used was manufactured from 2,2-bis(3-amino-4-hydroxy phenyl)-hexafluoropropane (APAF) diamine and 5'-terbutyl-m-terphenyl-4,4''-dicarboxylic acid chloride (tBTpCl) and a copolyimide (HPA-PA) made by the stoichiometric copolymerization of APAF and 4,4'-(hexafluoroisopropylidene) diamine (6FpDA), using the same diacid chloride. The MMMs prepared were subjected to a heat treatment to remove the solvent (up to 180°C). Subsequently, the MMMs were thermally treated to convert the HPA matrix to polybenzoxazole (β -TR-PBO) at 375 °C under a nitrogen atmosphere, thus generating the corresponding TR-MMMs. The chemical structure and thermal stability of the membranes were characterized by FTIR and TGA. Gas transport properties of the MMMs, TR-MMMs and the pure polyamide membranes were determined in constant-volume variable-pressure permeation systems at 3 bar and 35 °C.

The permeabilities of H₂, N₂, O₂, CH₄ and CO₂ notably increased with the addition of 20% PPN-2 to the polymeric matrix by a factor of 4.0-10.2 for the HPA, 3.1-4.3 for the HPA-PA. TR and the addition of porous polymer networks increased permeability with a slight decrease in selectivity for H₂/CH₄ and H₂/N₂ gas pairs. In both cases, results approached the 2008 Robeson's limit line². The values of permeability coefficients and the ideal selectivity are plotted at the Robeson upper bound (Figure 1). The most important improvement in gas permeabilities was recorded for TR-MMMs, particularly for those manufactured from HPA. This study confirmed the outstanding performance of β -TR-MMMs for biohydrogen purification.

Figure 1. Permeability-selectivity Robeson's plot for the H₂/CH₄ (left) and H₂/N₂ (right) gas pairs.

Reference 1:

Soto, C. et al. (2020). Separation and Purification Technology, 247, 116895

Reference 2:

Robeson, L. M. (2008). Journal of membrane science, 320 (2), 390-400

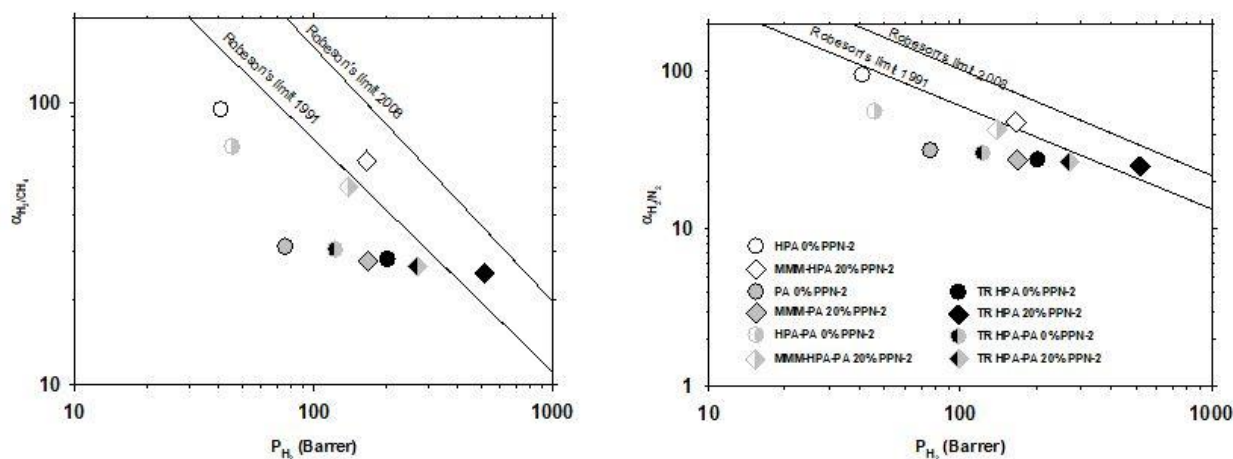


Figure 1. Permeability-selectivity Robeson's plot for the H₂/CH₄ (left) and H₂/N₂ (right) gas pairs.

Thin Film Composite (TFC) with a MOF layer on Single Walled Carbon Nanotubes buckypaper (SWCNT-bp) for Nanofiltration (NF) and Organic Solvent Nanofiltration (NF)

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¹INMA (Instituto de Nanociencia y Materiales de Aragon)

Main topic: Drinking water

Nowadays, in the chemical and pharmaceutical industries, the nanofiltration membrane system is gaining importance in both aqueous and organic solvents due to its flexibility, energy efficiency, and low-cost technology[1]. Usually, these membranes are constituted by porous polymeric supports and a selective polyamide layer, which can be improved by the introduction of a filler. Between other materials, MOFs (metal-organic frameworks) have been used as fillers as they have outstanding features (high specific surface area, adsorption properties, molecular sieving, flexibility, organic-inorganic nature, and possibility of functionalization). Typically, the filler has been included during the interfacial polymerization of the polyamide layer but other different methodologies to position the MOF in the membrane have been developed like interfacial synthesis[2] or Langmuir-Schaefer. In this work, we report a nanofiltration membrane with good performance in both organic and aqueous feeds based in SWCNT-bp support in which a MOF (ZIF-8 and ZIF-93) has been grown via a layer by layer method, on top of which a polyamide layer is synthesized by an interfacial polymerization method.

Acknowledgments

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P. Marchetti, M.F. Jimenez Solomon, G. Szekely, A.G. Livingston, *Chem. Rev.* 114(21) (2014) 10735–806. 10.1021/cr500006j.

Reference 2:

L. Paseta,, D. Antorán,, J. Coronas,, C. Téllez, *Ind. Eng. Chem. Res.* 58(10) (2019) 4222–30. 10.1021/acs.iecr.8b06017.

Thin film composite hollow fiber membranes for O₂/N₂ separation

Liubimova, Alena - Main Author¹; Bilyukevich, Alexandr - Co-Author¹; Hliavitskaya, Tatsiana - Co-Author¹; Tatiana, Plisko - Co-Author²

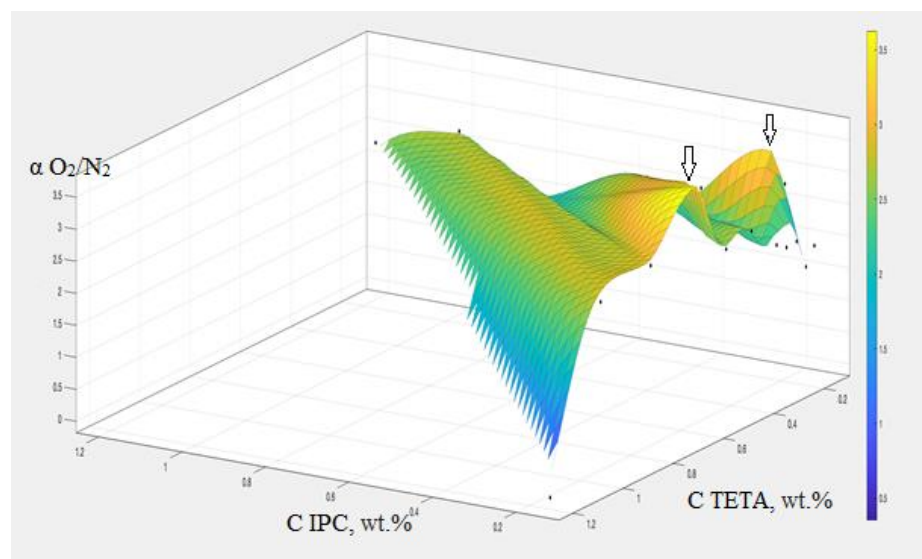
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Main topic: Gas separation

The study deals with the development of thin film composite (TFC) membranes for gas separation using interfacial polymerization (IP) on the inner surface of polysulfone hollow fiber membrane support (in the lumen), followed by the dip-coating of polydimethylsiloxane (PDMS). The effect of the nature and ratio of amine (m-phenylenediamine (MPD) and triethylenetetramine (TETA)) and acyl (isophthaloyl chloride (IPC) and trimesoyl chloride (TMC)) components in IP, as well as the concentration and conditions of the PDMS layer deposition on the oxygen and nitrogen gas permeances of TFC membranes was studied.

It was found that after formation of a selective layer by IP, regardless of the monomers used and their concentration, hollow fiber membranes with high gas permeance (GPU >1000) were obtained, the oxygen/nitrogen separation factor (α_{O_2/N_2}) was about 1. After subjecting the membranes to dip-coating process using PDMS (1-3 wt.%), the oxygen/nitrogen separation factor increases and was found to be in the range of 1.5-3.7. The best results were obtained in the case of using TETA and IPC as monomers for IP and for membranes double coated with 1 wt.% PDMS solution. The maximum values of O₂/N₂ separation factor are fixed in a rather narrow range of TETA concentrations (0.15-0.6%) and a certain equivalent TETA/IPC ratio (Figure). The first maximum (α_{O_2/N_2}) = 3.5 is observed at an equivalent ratio TETA/IPC = 1.8, the second one (α_{O_2/N_2}) = 3.5 at the TETA / IPC ratio = 11.8, the oxygen permeance of the TFC membranes was 107 and 77 GPU, respectively. Comparison of the characteristics of polysulfone hollow fiber ultrafiltration membranes, modified by IP with a surface coating of PDMS, obtained in this work, with the literature data indicate that they are promising for the process of oxygen enrichment.

Figure. Dependence of the separation factor (O₂/N₂) of composite membranes on the concentration of TETA and IPC.



TiO₂ and ZnO as dopants in bioinspired low-cost microbial fuel cell membranes

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Main topic: Membrane bio-reactors

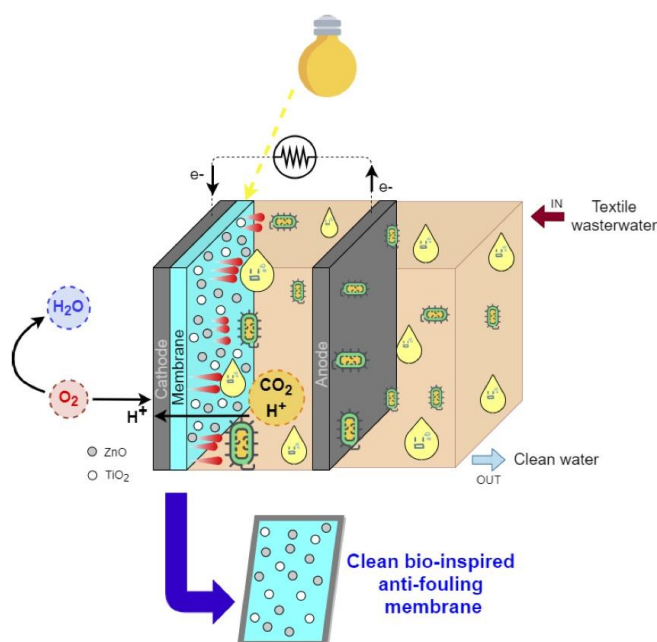
Microbial fuel cells (MFCs) are a novel technique for converting biodegradable materials into electricity¹. In recent years, low-cost membranes, such as cellophane have been used as ion exchange membranes in microbial fuel cells (MFCs). The main problem with low-cost membranes is biofouling and durability. In this work, three one-compartment microbial fuel cells (MFCs)², equipped with the same components except for the membranes, were operated with the same operation conditions, in order to evaluate the effects of the modification. Results obtained showed that a MFC equipped with a polydopamine modified cellophane membrane (PDA) and a mixture of TiO₂ and ZnO in ratios (1:1) 0,03 wt. %. the modified MFCs increased 2.5 times the power and 5,7 times the current compared to the unmodified cell (MFCs equipped the Cellophane or cellophane PDA membrane). The MFCs were tested with synthetic textile wastewater and the MFC with PDA and catalyst was also evaluated with real textile wastewater. The modified membrane helped to decrease the cycle work time of the MFCs from 5 days to 3 days, doubled the lifetime of the membranes and demonstrated higher COD removal efficiency and colour removal. These results showed that membrane modification could increase the lifetime of low-cost membranes and could be an alternative to improve the efficiency of MFCs. Finally, this modification could be an interesting alternative modification for other potential membranes for use in MFCs, due to the fact that the catalyst activation was only performed with visible light (artificial and solar), which could decrease operating costs.

Reference 1:

Logan, B. E. Exoelectrogenic Bacteria That Power Microbial Fuel Cells. *Nat. Rev. Microbiol.* 2009, 7 (5), 375–381. <https://doi.org/10.1038/nrmicro2113>.

Reference 2:

Oliot, M.; Galier, S.; Roux de Balmain, H.; Bergel, A. Ion Transport in Microbial Fuel Cells: Key Roles, Theory and Critical Review. *Appl. Energy* 2016, 183, 1682–1704. <https://doi.org/10.1016/j.apenergy.2016.09.043>.



Towards a mechanistic understanding of mass transfer in ion exchange membrane using Maxwell-Stefan equation

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¹The University of Edinburgh

Main topic: Transport models

Ion exchange membrane plays an important role in extensive applications for sustainability. Understanding the mass transfer process in the membrane gives both theoretical and practical guidelines in developing membranes with high electrical performance. Numerical models provide a fundamental approach to describe the transfer phenomena across the membrane. The Nernst-Planck equation is commonly used to describe the mass transfer characteristics in ion exchange membranes. However, comparing to the Maxwell-Stefan relation, the Nernst-Planck equation uses one overall diffusivity to represent the mass transfer resistance. The simplifications of the Nernst-Planck equation conceal the detailed contribution of friction between species and restrict us from achieving a thorough understanding of the process. Herein, a numerical model coupling Maxwell-Stefan relation with Poisson equation, mass conservation equation and Pitzer's law is built to gain a comprehensive description of mass transfer in both membrane and liquid electrolytes. Through the comparisons between the Nernst-Planck and Maxwell-Stefan models, the Nernst-Planck model is found to overestimate the conductivity of the liquid electrolyte and underestimate the ionic mobility of the membrane. The Nernst-Planck model could only provide acceptable approximation in dilute solutions, i.e., less than 50 mol m⁻³. The effects of water content on membrane conductivity and permselectivity are interpreted numerically by using the Maxwell-Stefan model. Moreover, the Maxwell-Stefan diffusivity between ion and membrane matrix in the membrane is determined on the basis of the model. Electrical performances of an electrodialysis process are measured, which provide inputs and baselines for the modelling. Through comparing the calculated results and measured data, the Maxwell-Stefan diffusivities between ion and matrix are obtained, which is in the order of 10⁻¹⁴ m² s⁻¹.

Towards more rational mixed-matrix membrane (MMM) development: Correlation of MOF-808 parameters with MMM CO₂ permeation

Thür, Raymond - Co-Author¹; Thür, Raymond - Main Author; Van Havere, Daan - Co-Author; Van Velthoven, Niels - Co-Author; Smolders, Simon - Co-Author; Lataire, Aran - Co-Author; Wieme, Jelle - Co-Author; Van Speybroeck, Veronique - Co-Author; De Vos, Dirk - Co-Author; Vankelecom, Ivo - Co-Author
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Main topic: Gas separation

Consistent structure-performance relationships for the design of MOF (metal-organic framework)-based mixed-matrix membranes (MMMs) for gas separation are currently scarce in MMM literature. An important step in establishing such relationships could be to correlate intrinsic MOF parameters, such as CO₂ uptake and the CO₂ adsorption enthalpy (Q_{st}), with the separation performance indicators of the MMM (i.e. separation factor and permeability). Such a study presumes the availability of a platform MOF, which allows systematic comparison of the relevant MOF parameters. MOF-808 can take up the role of such platform MOF, owing to its unique cluster coordination and subsequent ease of introducing additional functional molecules. For this purpose, formic acid (FA) modulated MOF-808 (MOF-FA) was post-synthetically functionalized with five different ligands (histidine (His), benzoic acid (BA), glycolic acid (GA), lithium sulfate (Li₂SO₄) and trifluoroacetic acid (TFA)) to create a series of isostructural MOFs with varying affinity/diffusivity properties but as constant as possible remaining properties (e.g. particles size distribution). Traditional MOF parameters such as BET surface area, pore volume and CO₂ uptake were determined while the MOF CO₂ adsorption enthalpy was calculated with a Clausius-Clapeyron analysis. These MOF properties were subsequently linked to the CO₂/N₂ separation factor and CO₂ permeability of the corresponding MMM. Unlike what is often assumed in literature, MOF-808 CO₂ uptake proved to be a poor indicator for MMM performance. In contrast, a strong correlation was observed between Q_{st} at high CO₂ loadings on one hand and CO₂ permeability under varying feed conditions on the other hand. Furthermore, correlation coefficients of $Q_{st,15}$ and $Q_{st,30}$ (Q_{st} at 15 and 30 cm³ (STP)/g) with the separation factor were significantly better than those calculated for CO₂ uptake. The surprising lack of correlation between membrane performance and CO₂ uptake and the strong correlation with Q_{st} opens possibilities to rationally design MMMs and stresses the need for more fundamental research focused on finding consistent relationships between filler properties and the final membrane performance.

*based on *Journal of Materials Chemistry A*, R. Thür et al., *Correlating MOF-808 parameters with mixed-matrix membrane (MMM) CO₂ permeation for a more rational MMM development*, just accepted, 2021

Towards the next generation of supported liquid membranes for CO₂ capture

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¹Delft University of Technology, ²Imperial college London

Main topic: Gas separation

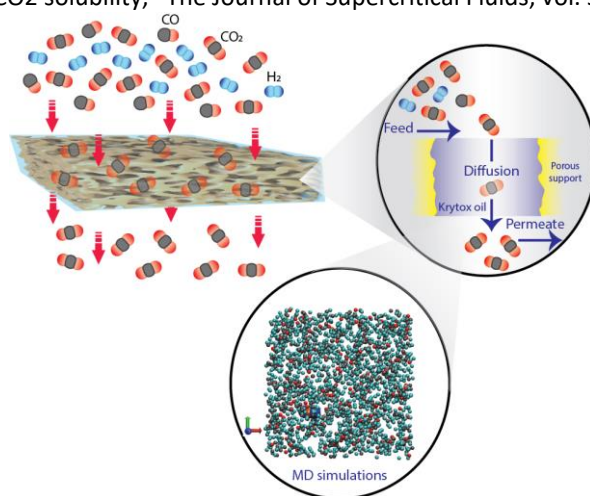
Membrane gas separation is an important part of various industrial processes, and can be implemented for CO₂ capture. Supported liquid membranes (SLMs) are considered one of the most efficient gas separation membrane processes due to potential higher permeability and ease of scalability. In SLM, the separation takes place via the solution-diffusion mechanism, in which the diffusion coefficient is about three-four times higher than that in polymer membranes [1]. The most widely-studied organic liquids for this purpose are fluorinated ionic liquids (ILs). It has been shown that fluorination of ILs can lead to increased CO₂ solubility [2]. High cost, high viscosity, and environmental issues of ILs further curtail the commercial implementation of IL-based SLMs for gas separation. Here, we study the applicability of an organic liquid, namely, perfluoropolyether oil (Krytox™ oil), as the liquid medium in SLMs for CO₂ capture. The CO₂ absorption and solubility in the oil are measured experimentally using a magnetic suspension balance. The transport properties of the oil, i.e., the viscosity and diffusivity of CO₂ in the oil for varying conditions of temperature, pressure and polymer chain length are further studied using equilibrium molecular dynamics simulations. The SLMs, are fabricated by infusing porous flat sheet PVDF membranes (pore diameter of approximately 30 nm) with 15.5 μL cm⁻² of oil using a micropipette. The gas separation performance of SLMs is tested by measuring single gas permeability and ideal selectivity using pure CO₂, N₂, CO, CH₄ and H₂ gas using an in-house gas separation set-up at various pressures and temperatures. The mixed gas separation performance is also studied with some common gas pairs, e.g., CO₂/CH₄, CO₂/N₂ and CO₂/H₂. Higher CO₂ solubility and diffusivity are observed in Krytox™ oil compared to those in fluorinated ILs at the same temperature and pressure. The experimental Henry's constant is 4 times lower, and the computed diffusion coefficient is 2 times higher than those in fluorinated ILs. The highest gas permeability is observed for CO₂ which is almost 2 times higher than that of fluorinated ILs. Comparing the selectivity results to the upper-bound values for the selectivity vs. permeability of polymer membranes (Robeson plot), it can be concluded that these novel SLMs have better ideal-selection properties than the commonly used, industrial polymer membranes.

Reference 1:

P. Cserjési, N. Nemestóthy, and K. Bélafi-Bakó, "Gas separation properties of supported liquid membranes prepared with unconventional ionic liquids," *Journal of Membrane Science*, vol. 349, no. 1-2, pp. 6–11, 2010.

Reference 2:

T. Hoefling, D. Stofesky, M. Reid, E. Beckman, and R. M. Enick, "The incorporation of a fluorinated ether functionality into a polymer or surfactant to enhance CO₂ solubility," *The Journal of Supercritical Fluids*, vol. 5, no. 4, pp. 237–241, 1992.



Towards to green chemistry: comparative study of effective composite hollow fiber membranes preparation for CO₂ separation

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Main topic: Gas separation

During last decades polymeric membranes have been considered as promising technology for gas separation. The most used technique for polymeric membranes fabrication is based on the phase inversion process and the most common used solvent is n-methyl-2-pyrrolidone (NMP) due to its high boiling point and strong dissolving power. But its toxic and hazardous nature [1] requires special treatment during labor use and before disposal as waste. Upon the green chemistry guidelines and directives, the reduction or complete elimination of hazardous substances would be mostly preferred. Subsequently, in this study, NMP was partially or completely substituted by γ -butyrolactone (GBL), a nontoxic solvent with similar characteristics with NMP, in dope solution and bore liquid, respectively. The successful hollow fibers (HFs) preparation was based on Hansen solubility parameters and cloud point data from the ternary polyimide/solvent/non-solvent diagrams evaluation.

After the asymmetric HFs preparation, the dip coating technique (Fig. 1) was employed yielding to composite hollow fiber membranes, which are considered more competitive for large-scale industrial applications [2]. These membranes consist of a highly permeable gutter layer and a thin selective layer, which are coated on the porous substrate [BTDA-TDI/MDI (P84) co-polyimide]. Polydimethylsiloxane (PDMS) was investigated as gutter layer applied on the porous support and for the thin separation layer, the commercial poly(ether-block-amide) (Pebax[®]-1657) was chosen as a high CO₂-selective material evaluating, in parallel, the effect of the embedment of graphene nanoplatelets (GNPs) as promising filler in the polymeric matrix (substrate) and the selective layer, respectively.

The composite hollow fiber membranes were characterized by SEM, tensile strength and contact angle measurements and their performance was studied under elevated pressure conditions employing CO₂/CH₄ mixture (10% concentration) as feed gas. In addition, pressurization-depressurization cycle was applied in order to conceive the stability and the possible reversibility of the membranes' structure change by the pressure application. Overall, the GNPs presentation both in support and separation layer enhances the gas permeance/selectivity of the composite membranes (almost twofold values) and the gutter layer offers stability to the membrane performance under pressure healing possible defects of the substrate.

Acknowledgments

The project "GG-CO₂", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014–2020) it is acknowledged.

Reference 1:

[1] Y. Alqaheem, A. Alomair, A. Alhendi, S. Alkandari, N. Tanoli, N. Alnajdi, A. Quesada-Peréz, Preparation of polyetherimide membrane from non-toxic solvents for the separation of hydrogen from methane, *Chem. Centr. J.* 12 (2018) 80.

Reference 2:

[2] P.D. Sutrisna, J. Hou, H. Li, Y. Zhang, V. Chen, Improved operational stability of Pebax-based gas separation membranes with ZIF-8: A comparative study of flat sheet and composite hollow fibre membranes, *J. Membr. Sci.* 524 (2017) 266–279.

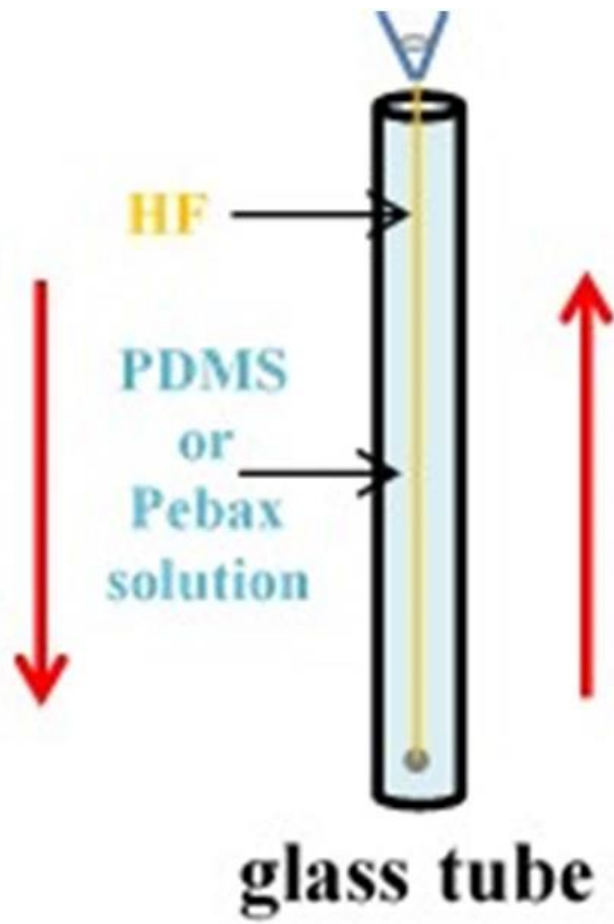


Fig. 1. Schematic diagram of the preparation process of the composite HF membranes.

Transport mechanisms behind enhanced solute rejection in forward osmosis compared to reverse osmosis mode

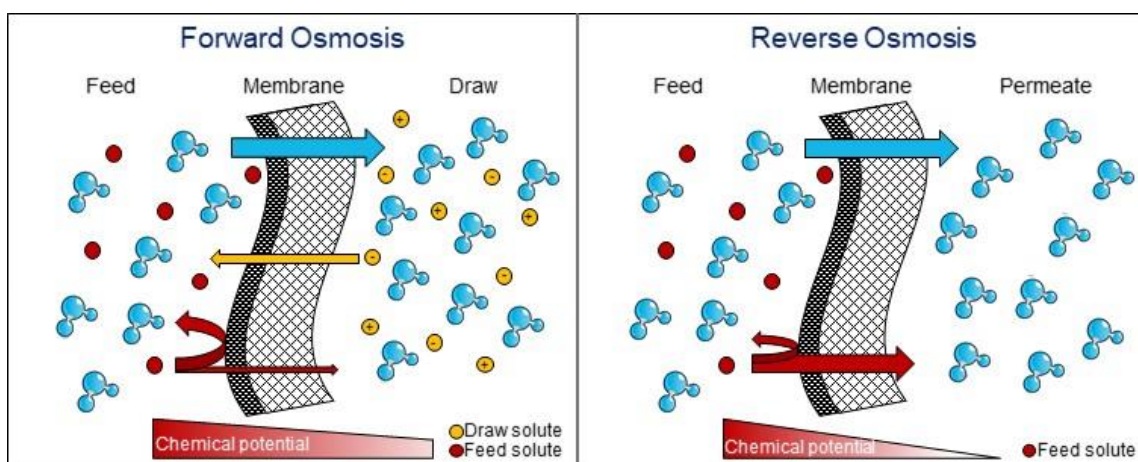
Frauholz, Jan - Co-Author

Main topic: Forward osmosis/Pressure retarded osmosis

Forward osmosis (FO) as emerging technology for water treatment was reported to exhibit higher solute rejections compared to reverse osmosis (RO). In this work, the rejection of two uncharged organic compounds (nicotinamide, caffeine) were investigated the first time in low-pressure reverse osmosis (LPRO) mode and FO under similar process conditions utilizing the same hollow fiber forward osmosis membrane modules. FO consistently showed higher rejection than LPRO mode for both nicotinamide (FO: 94.8%, LPRO: 85.5%) and caffeine (FO: 99.9%, LPRO: 99.2%). To elucidate the influence of draw solute on the rejection, different salts (NaCl, MgCl₂, MgSO₄), concentrations, and draw flow rates were investigated. A rise in draw concentration increased rejection in FO for all salts indicating an enhancement of rejection due to the presence of salt on the permeate side of the membrane. Two theories are proposed: While the resistance for feed solute transport could be increased due to the counter-directed reverse solute flux and the presence of salt in the support layer, the driving force for feed solute diffusion might be lowered due to the presence of a secondary ionic compound on the permeate side of the membrane.

Reference 1:

<https://doi.org/10.1016/j.memsci.2021.119561>



Transport Mechanisms in Vapor--Gap Membranes

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Main topic: Membrane contactors and membrane distillation

Contaminated liquids can be cleaned by membrane distillation (MD) using so-called vapor-gap membranes [1]. When a temperature difference is applied to a membrane with repulsive walls, fluid is allowed to pass in the vapor phase. This occurs by evaporation on one side and condensation on the other side, thereby producing clean fluid transport across the vapor gap, away from the contaminated fluid [1].

Conventional descriptions of transport in vapor--gap membranes account for the temperature difference by considering the equilibrium vapor pressure difference inside the membrane as the driving force for the mass flux. Most of the models developed for the mass and heat transfer in MD have in common that they neglect the contributions of the two liquid--vapor interfaces as well as the fluid--solid interaction inside the pore. However, for a precise control of the flow, it is not only important to distinguish between independent and dependent driving forces but also to account for each local resistivity. While the evaporation area was shown to play an important role [2], little has been said about the local mechanisms behind it. Also, the effect of the fluid--solid interaction inside the pore on the mass transport of vapor--gap membranes has not yet been dealt with extensively.

In this work, we elaborate on the impact of the local resistivities on the mass transport in vapor gap membranes. We use non--equilibrium molecular dynamics simulations to investigate the mechanisms of the temperature-driven transport. We show the interplay between evaporation/condensation area and transport of vapor through the pore.

Reference 1:

[1] G. Meindersma et al. *Desalination*, vol. 187, no. 1-3, pp. 291–301, 2006.

Reference 2:

[2] J. Liu, Q. Wang, H. Shan, H. Guo, and B. Li, "Surface hydrophobicity based heat and mass transfer mechanism in membrane distillation," *Journal of Membrane Science*, vol. 580, pp. 275–288, 2019.

TREATMENT OF OLIVE MILL WASTEWATER BY MEANS OF MEMBRANE PROCESSES: AN OVERVIEW”

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Main topic: Wastewater treatment

In this paper an overview to treatment possibilities and difficulties by means of membrane processes is presented. In the framework of many EU project, boundary fluxes on a pilot scale membrane process treating a stream of olive mill wastewater were studied by changing operating conditions and pre-treatment processes. In its standard configuration, olive mill wastewater is first pre-treated by an acid coagulation, followed by ultrafiltration and nanofiltration. In the actually ongoing MEWLIFE project, target of the treatment is to concentrate organic matter from the wastewater stream to feed bio algae production processes.

It is important to keep boundary flux values high to inhibit severe fouling of the membrane. Experiments were performed by using the pressure cycle approach and then validated by more days of process operation. In detail, the importance of UF will be reported, in comparison to alternative process as use of only NF. Parallel to this, basic economic evaluation will be presented, to estimate the requirements of membrane area, the capacity of the plant and the outcome of the separation in terms of quantity and quality. Finally, some small insight about advanced process control will be provided.

Reference 1:

Stoller, M., Ochando-Pulido, J.M., Field, R., On operating a nanofiltration membrane for olive mill wastewater purification at sub- and super-boundary conditions, (2017) *Membranes*, 7 (3), art. no. 36

True lifetime of Polymeric & Ceramic membranes – a Case study

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Main topic: Membrane fouling and cleaning

Membrane life is one of the biggest drivers in life cycle costs for any membrane-based water or wastewater treatment plant. Shorter than expected membrane life not only increase life cycle costs, but it also generates a negative perception of membranes. Ultra- and Micro filtration membranes are critical for ensuring access to safe water due to the extremely high effluent quality they provide.

Membrane cleaning is a normal part of membrane plant operations regardless of application type. Unfortunately, chemical cleaning often dictates membrane life either by not fully recovering or by changing the properties of the membrane itself.

To ensure membrane life is not compromised, it is necessary for membrane systems to operate, without disruption or failure, in ever changing environments. This means being able to fully recover membrane permeability over its entire life, even when influent quality changes. Unfortunately, most membranes experience a gradual decline in permeability over time that accelerates as the membrane ages. The inability to completely recover a membrane can result in premature membrane replacement.

A comprehensive study by Brehant et al. from 2015 on membrane life of three different polymeric membrane installations treating surface water, demonstrated a membrane permeability loss after only 3-years of operation of 36% for the PVDF membrane, 22% for the PES membrane & 13% for the CTA membrane. With a NaOCl exposure of 388.174 ppm hours, 6.160 ppm hours and 104.772 ppm hours respectively.

This study demonstrates the impact of membrane permeability and physical properties of a SiC membrane treating primary wastewater from a Sewage facility during a two-year period. The membranes underwent Clean In Place (CIP) 60 times amounting to 1,9 million ppm hours of NaOCl and 1,9 million ppm hours of NaOH. The case study shows no sign of degradation of membrane permeability, mechanical strength, or membrane hardness.

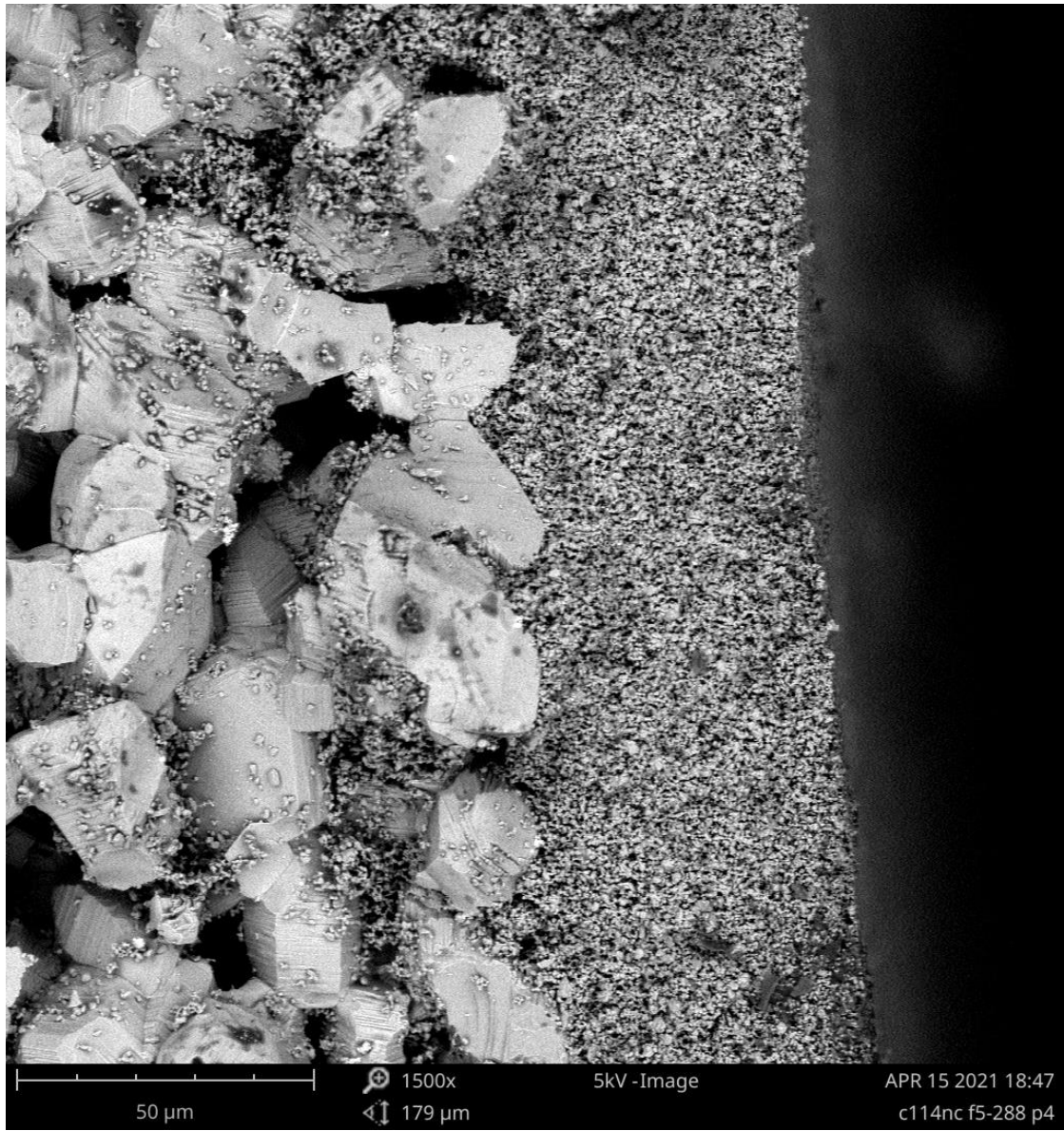
Silicon carbide (SiC) is a relatively new membrane material that helps solve many of the challenges associated with chemical cleaning. With a completely different set of material properties, compared to conventional polymeric membranes, hence SiC membranes do not experience the same degradation in permeability over time.

Reference 1:

Comparison of ceramic and polymeric membrane permeability and fouling using surface water. Bas Hof, Julien Ogier, DirkVriesErwin, F. Beerendonk, Emile R.Cornelissen. 2011

Reference 2:

WHAT IS THE REAL TOTAL COST OF OWNERSHIP OF A LOW-PRESSURE MEMBRANE PLANT FOR DRINKING WATER PRODUCTION? THE COMPARISON OF THREE MEMBRANE MATERIALS: PVDF, PES & CTA. Anne BREHANT*, Angélique FABRE*, Reynald BONNARD. 2015



TRUST PROJECT: Management of industrial Treated wastewater ReUse as mitigation measures to water Scarcity in climate change context in two Mediterranean regions

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¹University of Calabria - Department of Computer Engineering, Modeling, Electronic and System Engineering, ²Institute for Membrane Technology (ITM–CNR), ³Economic Structure Dept. Valencia, ⁴CATALIST Service provider, ⁵Teriva environment Service provider, ⁶Institut Européen des Membranes – University of Montpellier, ⁷Laboratory of hydrology and geochemistry of Strasbourg, ⁸University of Sfax - Faculty of Science, ⁹University of Carthage, ¹⁰Department of Chemical Engineering, Ege University, ¹¹Van Yüzüncü Yıl University, ¹²Dokuz Eylül University. Geological Engineering Department, ¹³Laboratory of civil Engineering and Hydraulics University of Guelma

Main topic: Wastewater treatment

According to reports of the World Water Council 2018 based on global projections, water demand will increase by 50% in many Middle East and North African countries already submitted to high water stress. Currently, underground available water resources are in high demand due to irrigation, urban and industrial needs in relation to demographic increase and imperatives to maintain the regional economic fabric. Added to this is the problem of increasing water scarcity linked to climate change. In line with the [Integrated Water Resources Management](#) approaches, TRUST will apply in an integrated way, environmental and economic friendly technical solutions to allow sustainable treatment of wastewater, reuse of water in a relevant allocation strategy recovery of useful substances, and savings of energy. Everything following circular economy strategy. The sustainable treatment and safe reuse of water will be considered integrating various scales, from pilot demonstration sites to basin scale, integrating the constraint of climate change adaptation. Moreover, TRUST will consider the economic feasibility of the actions including energy efficiency and social acceptance of depolluted wastewater reuse. TRUST will focus on challenging cases in terms of efficient wastewater treatment of the textile and pharmaceutical industries from Tunisia and Turkey where water scarcity is a major concern and irrigation is a large water-consuming sector [1]. TRUST will also focus on recovery of valuable substances for reuse.

Acknowledgment: This work has received funding from PRIMA Foundation under grant agreement no. *Grant Agreement number: [2024] [TRUST] [Call 2020 Section 1 Water IA]*.

Reference 1:

<http://www.trust-prima-project.eu>

Tuning 6FDA-DABA membrane performance for CO₂ removal by physical densification and decarboxylation cross-linking during simple thermal treatment[1]

Van Havere, Daan - Main Author; Thür, Raymond - Co-Author; Lemmens, Vincent - Co-Author; Van Essen, Machiel - Co-Author; Nijmeijer, Kitty - Co-Author; Vankelecom, Ivo - Co-Author

Main topic: Gas separation

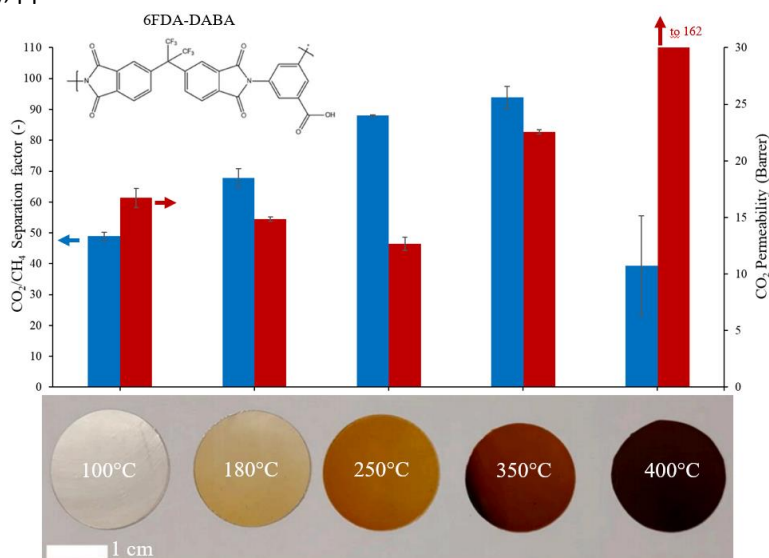
Thermally induced decarboxylation cross-linking of carboxylic acid bearing polyimides has recently been introduced as a novel strategy to create cross-linked polymer membranes with enhanced gas permeability. The main focus has been on the cross-linking of high permeability/low selectivity 6FDA (4,4'-(hexafluoroisopropylidene)-diphthalic anhydride) copolymers with a relatively low amount of carboxylic acid groups.^[2] In contrast, decarboxylation cross-linking was applied in this work on 6FDA-DABA (3,5-diaminobenzoic acid), a low permeability/high selectivity polymer with a large amount of –COOH groups. 6FDA-DABA membranes were thermally treated at different temperatures (100 °C, 180 °C, 250 °C, 350 °C and 400 °C), tested for CO₂/CH₄ and CO₂/N₂ gas separations and thoroughly characterized by infrared spectroscopy, thermogravimetric analysis coupled to mass spectroscopy, differential scanning calorimetry, energy dispersive X-ray analysis, X-ray diffraction, density measurements, fluorescence spectroscopy and gas sorption measurements. Two counteracting mechanisms defined the overall performance of the cured membranes. Physical tightening of the membrane significantly enhanced the CO₂/CH₄ separation factor with increasing annealing temperature, due to an improved polymer chain packing efficiency, which was confirmed by fluorescence spectroscopy and membrane density experiments. In contrast, cross-linking through decarboxylation occurred from 330 °C onward and induced a more open polymer structure for 6FDA-DABA-350 and 6FDA-DABA-400. Consequently, the more open polymer structure resulted in an increase in permeability for all tested gases. For 6FDA-DABA-350, a synergy was observed between the dilation effect of cross-linking and the tightening effect, causing a simultaneous, strong improvement of both separation factor (+100%) and permeability (+40%). As a result, the membrane performance crossed the 2018 mixed-gas upper bound and scored very close to the 2008 Robeson upper bound. Moreover, the cross-linked 6FDA-DABA-350 showed an increased resistance to CO₂-induced plasticization thanks to covalent cross-linking.

Reference 1:

R. Thür, V. Lemmens, D. Van Havere, M. van Essen, K. Nijmeijer, I.F. Vankelecom Tuning 6FDA-DABA membrane performance for CO₂ removal by physical densification and decarboxylation cross-linking during simple thermal treatment *J. Membr. Sci.*, 610 (2020), p. 118195

Reference 2:

A.M. Kratochvil, W.J. Koros Decarboxylation-induced cross-linking of a polyimide for enhanced CO₂ plasticization resistance *Macromolecules*, 41 (2008), pp. 7920-7927



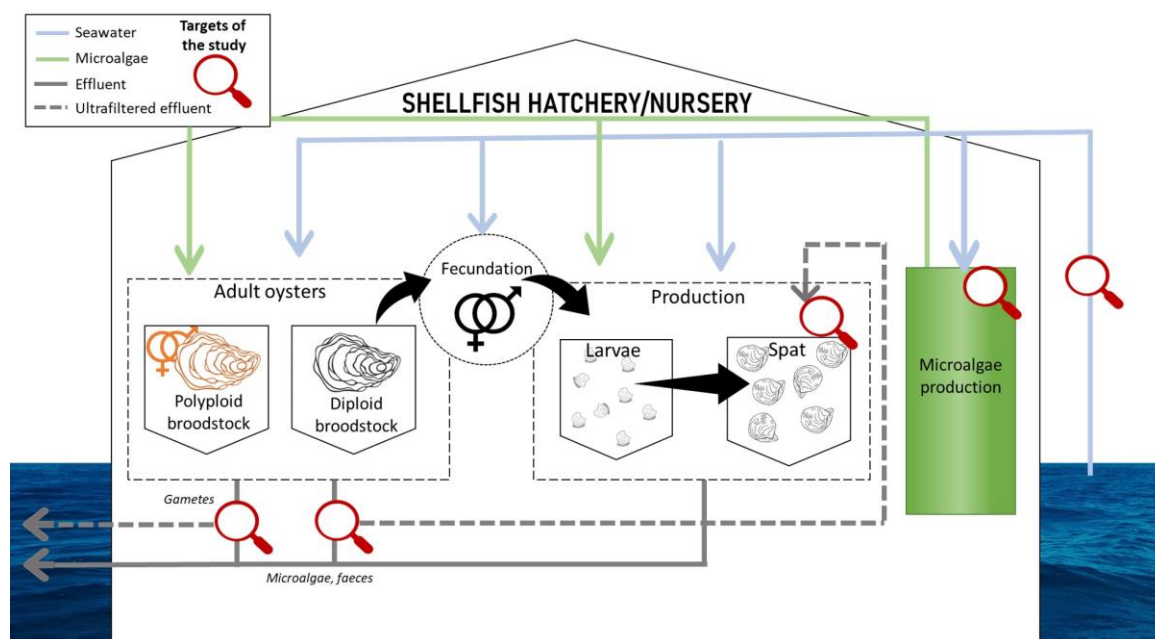
Ultrafiltration for shellfish hatchery: industrial applications and scale up

Cordier, Clémence - Co-Author; Stavrakakis, Christophe - Co-Author¹; Moulin, Philippe - Co-Author²

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Main topic: Industrial applications and scale-up

The aim of the study was to develop the ultrafiltration process in shellfish hatchery/nursery to answer all problematics encountered in those establishments: from the inlet feed to outlet effluents and also the use of purified water. This objective to treat different waters in hatchery nursery at an industrial scale was carried with 2 ultrafiltration pilots, which continuously treated seawater and real effluents from oyster breedings for almost 4 years at industrial scale (20 m³.day⁻¹ and 360 m³.day⁻¹). First, ultrafiltration was evaluated on its performance as a treatment of water to supply hatchery/nursery with the objective to protect oyster breedings towards contaminants, bacteria and virus, even when confronted to a bloom. In the case of bacteria, the quantity of *V. aestuarianus* in ultrafiltered water was at least, 400 times inferior to the threshold known to induce mortalities in oysters (higher than 3log removal). The quality of the water produced was then controlled and used for hatchery/nursery applications: oyster fecundation, spat breeding and culture of microalgae. For example, the daily monitoring of microalgae culture in ultrafiltered water highlights a faster growth on UF sea water i.e. 25 % time savings in the global process. Finally, effluents generated in those establishments were treated in order to control the capacity of the process to protect the environment when facing discharges containing biological materials, suspended solids and bacteria. Ultrafiltration appears efficient (> 3 log) to treat effluent from a real oyster breeding with a better removal (bacteria, virus, suspended matter) than classical treatment. Also, for the specific case of oocytes and spermatozoa in effluents, ultrafiltration demonstrates its capacity to protect the environment from aquaculture pollutions containing biological material, metabolic products and bacteriological contamination. Considering these results, the reuse by ultrafiltration of effluents from breedings to feed others seems a feasible solution with a water quality adapted to supply juveniles. In parallel with these studies, the hydraulic performances of the membrane process were controlled to evaluate the sustainability and the resistance of ultrafiltration over time facing the numerous matrices tested. The different procedures to clean the membranes were optimized to adapt the process to this application.



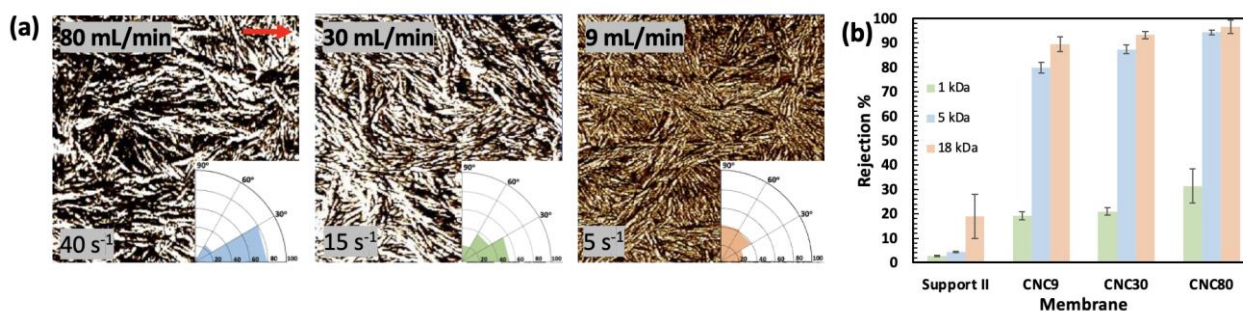
Ultrafiltration membranes fabricated by shear-aligned deposition of cellulose nanocrystals with easily tunable rejection

Kocaman, Ceren - Main Author; Culfaz-Emecen, Zeynep - Co-Author; Bukusoglu, emre - Co-Author

Main topic: Advanced fabrication methods

Controlling separation performance of membranes using easily adjustable parameters is highly desirable. We fabricated ultrafiltration membranes by shear aligned deposition of cellulose nanocrystals (CNCs). CNCs of 180 nm length and 8 nm diameter, prepared by sulfuric acid hydrolysis of cotton linters, were filtered through a porous support in cross-flow at different flowrates followed by AlCl_3 solution permeation for stabilizing the deposit. Concentrated CNC aqueous suspensions are known to show lyotropic phase behavior where nanocrystals self-assemble with cholesteric symmetry. With the shear applied on the support surface during cross-flow filtration, nanocrystals aligned in the direction of flow, as shown by polarized optical microscopy and atomic force microscopy (Figure 1.a). AlCl_3 solution permeation through the shear-aligned CNC deposit was used to screen repulsive interactions between nanocrystals and destroy the colloidal stability of accumulated CNCs on the support, thereby forming a stable CNC deposit to act as the selective membrane. CNC membranes' stability was also confirmed upon dissolving the support layer to obtain a free-standing CNC membrane. CNC alignment in the deposit was controlled by changing the hydrodynamic conditions during cross-flow filtration. Order parameter increased from 0.17 to 0.7 by increasing shear rate on the support surface from 10 s^{-1} to 50 s^{-1} which increased Blue Dextran (5 kDa) rejection from 79.9% to 94.3% β - immunoglobulin (18 kDa) rejection from 89.6% to 96.5% (Figure 1.b). It was shown that the acquired control over directional assembly of CNCs provided by an easily changeable parameter, feed flow rate, enabled adjustment of rejection of the CNC membrane.

Figure 1. (a) AFM top view phase images of CNC membranes fabricated at various feed flow rates and surface shear rates (80 mL/min, 40 s^{-1} ; 30 mL/min, 15 s^{-1} ; 9 mL/min, 5 s^{-1}). Inset polar histograms for each membrane for the % aligned nanocrystals where the reference axis is CNCs flow direction. Red arrow indicates feed flow direction. (b) Probe rejection of empty support and membranes fabricated at CNC suspension feed flow rates of 9 mL/min (CNC9), 30 mL/min (CNC30), 80 mL/min (CNC80).



Ultrafiltration of Process Streams from Lignocellulosic Biorefineries: Insights on Membrane Fouling and Cleaning

Rudolph, Gregor - Main Author¹; Schagerlöf, Herje - Co-Author¹; Jönsson, Ann-Sofi - Co-Author¹; Lipnizki, Frank - Co-Author¹

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Main topic: Membrane fouling and cleaning

The transformation of pulp and paper mills into lignocellulosic biorefineries is a cornerstone for the bio-based circular economy. Lignocellulosic biorefineries allow not only the production of pulp, paper, and electricity, but also novel biochemicals. In order to achieve this, pulp mills have to close their loops and focus on the optimal utilisation of the lignocellulosic raw material. For this, highly selective, electrifiable, and low-energy-consuming separation technologies such as pressure-driven membrane processes, e.g., ultrafiltration (UF), are needed. However, the greatest challenge to a broad implementation of these processes is still membrane fouling, which does not only alter the capacity and selectivity of the membrane, but also increases the investment and operational costs and can only be overcome by regular chemical cleaning.

In the work presented, fouling and cleaning of membranes used for the UF of process streams from lignocellulosic biorefineries were investigated. This was done with the help of various *ex situ* analytical methods, and *in situ* studies with quartz crystal microbalance with dissipation (QCM-D). Valuable insights on membrane fouling depending on the filtration conditions were gained with traditional analytic methods such as scanning electron microscopy (SEM), atomic force microscopy (AFM), and Fourier transform infrared spectroscopy (FTIR). New knowledge on the impact of membrane fouling on the inner structure of the membranes was gained with Brunauer-Emmett-Teller (BET) surface analysis. QCM-D was used for adsorption studies and provided further understanding on the underlying processes leading to fouling. Membrane cleaning was analysed based on permeability recovery and *ex situ* analysis.

This presentation gives an overview of challenges and insights from membrane fouling and cleaning studies related to lignocellulosic biorefineries. Overall, the findings presented will help improve membrane processes. Comprehensive knowledge of the causes of membrane fouling will make it easier to tailor membrane cleaning, which will prolong the membrane lifetime, reduce plant downtime and the usage of chemicals and water. Thus, the findings contribute to the wider implementation of membrane processes in the transition from a fossil-based economy to a fossil-free bio-based circular economy.

ULTRAFILTRATION OF TWO-PHASE OLIVE MILL WASTE TO OBTAIN A PERMEATE ENRICHED IN PHENOLIC COMPOUNDS

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Main topic: Wastewater treatment

The two-phase olive mill waste or *alperujo* (TPOMW) is a by-product derived from the olive oil production. It is hugely generated in the Mediterranean countries and represents an important environmental concern, because of its high-organic load, phytotoxicity and reducing power. Its retirement and reutilization are of the utmost importance. Despite its related ecological risk, the TPOMW contains a plethora of interesting bioactive molecules, such as phenolic compounds, whose health benefits can be exploited by the pharmaceutical, cosmetic and food industry [1]. Considering the double benefit of its employment, a process to extract phenolic compounds from TPOMW and purify them by ultrafiltration has been developed.

First, the residue was submitted to a solid-liquid extraction in which the extraction of the maximum concentration of bioactive compounds (belonging to different chemical families) was pursued. To avoid organic solvents, water was used as extractant. The combination of temperature, ultrasounds and reaction time permitted the recovery of a satisfying phenolic content.

Afterwards, the obtained extract was submitted to ultrafiltration. Two membranes, UH030 and UP005 (Microdyn Nadir) were compared. Three cross-flow velocities (1.5, 2.5 and 3.5 m/s) and three transmembrane pressures (0.75, 1.5 and 2.5 bar) were studied. Additionally, different cleaning protocols were tested: water (at two different temperatures, 20 and 35°C) and P3 Ultrasil 115 0.7% (v/v) (at three different temperatures, 20, 35 and 40°C).

The steady-state permeate flux reached 15 L·h⁻¹·m⁻² (UP005) and 39 L·h⁻¹·m⁻² (UH030). A total phenolic content higher than 5 g/kg was obtained in the extraction step. Both membranes satisfactory rejected colour (64-95%), total dissolved solids (27-55%) and COD (23-59%), whereas the majority of phenolic compounds was retrieved in the permeate, with an increased purity. From the five phenolic families found in TPOMW, lignans, secoiridoids and simple phenols were highly recovered.

A powerful separative methodology based on liquid chromatography coupled to mass spectrometry was applied to better understand the distribution of the different families of phenolic compounds obtained in the permeate. More than 30 compounds were identified and quantified, including elenolic acid (and several derivatives), oleuropein and hydroxytyrosol, all of them having a vast number of health benefits.

Reference 1:

[1] M.Á. Fernández-Prior, J.C.P. Fatuarte, A.B. Oria, I. Viera-Alcaide, J. Fernández-Bolaños, G. Rodríguez-Gutiérrez, New Liquid Source of Antioxidant Phenolic Compounds in the Olive Oil Industry: Alperujo Water, *Foods*. 9 (2020). <https://doi.org/10.3390/foods9070962>.

Ultrafiltration-based diafiltration for lignin-DES separation in the paper industry

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Main topic: Paper and pulp industries

The isolation of lignin from deep eutectic solvents (DES) after biomass delignification requires a cost-efficient, energy-efficient and sustainable separation and purification process. Membrane separation, mainly ultrafiltration (UF) or nanofiltration (NF), as an economical and environmentally sustainable process, has showed great potential for treatment of black liquor and separation of pure lignin [1][2].

This work aims to study the UF process in diafiltration (DF) mode for recovery and purification of lignin dissolved in DES consisting of lactic acid and choline chloride after delignification. Due to the viscosity of this so-called DES-dark liquor, dilution of this stream with organic solvents is required prior to membrane separations. The high solubility of lignin in a 70:30 (v:v) acetone:water mixture can be exploited to wash lignin effectively from the fibers after delignification. Such operation results in DES/lignin mixtures diluted in acetone:water. To study on UF-DF applicability on such mixtures, various concentrations of lignin and DES in 70:30 acetone:water were applied. The experiments were done in a stirred dead-end cell setup. Membrane resistance was measured over time to indicate the fouling during filtration.

Furthermore, experimental results were used to model a continuous UF-DF process as would be applied in an industrial system.

The results showed high lignin rejection for different lignin concentrations (w:w) in the feed (>90% lignin rejection). On the other hand, membrane fouling and flux decline were found to be dependent not only on lignin concentration but also on DES concentration. Feed with higher DES concentration leads to de-swelling of the membrane polymer, leading to smaller pores in the membrane and consequently more pore blocking and sharper flux decline.

The experimental results were applied to model a continuous UF-DF system for lignin recovery from DES to give insight on the effect of operating conditions on DF and optimization of the system design.

Reference 1:

C. A. E. Costa, P. C. R. Pinto, and A. E. Rodrigues, "Lignin fractionation from E. Globulus kraft liquor by ultrafiltration in a three stage membrane sequence," *Sep. Purif. Technol.*, vol. 192, pp. 140–151, 2018, doi: 10.1016/j.seppur.2017.09.066.

Reference 2:

K. Servaes et al., "Purification and concentration of lignin from the spent liquor of the alkaline oxidation of woody biomass through membrane separation technology," *Ind. Crops Prod.*, vol. 106, pp. 86–96, 2017, doi: 10.1016/j.indcrop.2016.10.005.

Uncovering the hidden potential of online data in Reverse Osmosis: a data-driven model to predict fouling

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Main topic: Nanofiltration/Reverse Osmosis

Background

Models can help gaining better insights in pressure driven membrane processes, such as reverse osmosis (RO), and the challenges that come with their use in full-scale installations, such as fouling. The solution-diffusion model is the most popular mechanistic model used for modelling RO processes. However, prediction of fouling remains a bottleneck in mechanistic models. As more data of full-scale installations becomes available, data-driven models can help to overcome this bottleneck.

A mechanistic model for a full-scale RO installation, based on the solution-diffusion model, was already developed (Gaublomme et. al, 2020). However, the model lacks the prediction of fouling. Therefore, the goal of this work, was to develop a data-driven model that can predict the influence of fouling on the full-scale RO process.

Materials and Methods

Online data of a full-scale installation, operated by the water utility FARYS, was collected and processed, hereby removing outliers. Two types of data-driven time series models were developed for prediction of the additional membrane resistance due to fouling: (1) linear ARIMAX models and (2) non-linear recurrent neural networks (RNN) with long short-term memory (LSTM). The time component in these models is of importance, since fouling occurs and increases over time.

The predictions of the data-driven models (ARIMAX and RNN) are compared to the mechanistic model that uses a temperature correction factor (TCF) or a simple fouling model (SFM) as described by Lee et al. (2012).

Results

In Figure 1.1, the predictions of the additional membrane resistance, during the validation and testing period, are shown. The RNN model showed better results for the testing period compared to the ARIMAX model, and compared to the mechanistic models (TCF and SFM). Nevertheless, including the impact of a cleaning-in-place (CIP) can still be improved since including this effect is not yet optimal, but essential to interpret the dynamics of fouling build-up. To further improve the data-driven models, more detailed information on the feed water and a better monitoring of the CIP procedures might be needed.

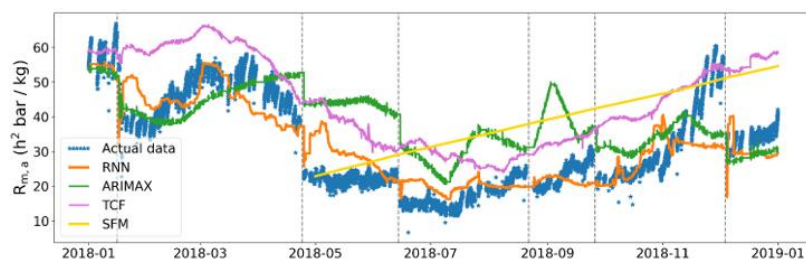


Figure 1.1 The predictions of the additional membrane resistance $R_{m,a}$ during the validation and testing period: (blue) actual data, the data-driven models: (orange - RNN) non-linear recurrent neural networks with long short-term memory and (green - ARIMAX) linear autoregressive integrated moving average models, and the mechanistic models: (pink - TCF) with temperature correction factor and (yellow - SFM) a simple fouling model. The cleaning-in-place (CIP) dates are indicated by dashed lines. Remark: the SFM was only plotted for the testing period.

Conclusions

The data-driven RNN model showed the best results for the predictions of fouling in RO, compared to the data-driven ARIMAX model and the mechanistic models.

Reference 1:

Gaublomme, D., Strubbe, L., Vanoppen, M., Torfs, E., Mortier, S., Cornelissen, E., De Gusseme, B., Verliefde, A., Nopens, I. 2020 A generic reverse osmosis model for full-scale operation, *Desalination*. 490, 114509.

Reference 2:

Lee, Y.G., Lee, Y.S., Kim, D.Y., Park, M., Yang, D.R., Kim, J.H. 2012 A fouling model for simulating long-term performance of SWRO desalination process, *Journal of Membrane Science*. 401-402, 282-291.

Unraveling the degradation pathway of polybenzimidazoles in alkaline environment

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¹Technical University of Denmark, Department of Energy Conversion and Storage

Main topic: Electro-membrane processes

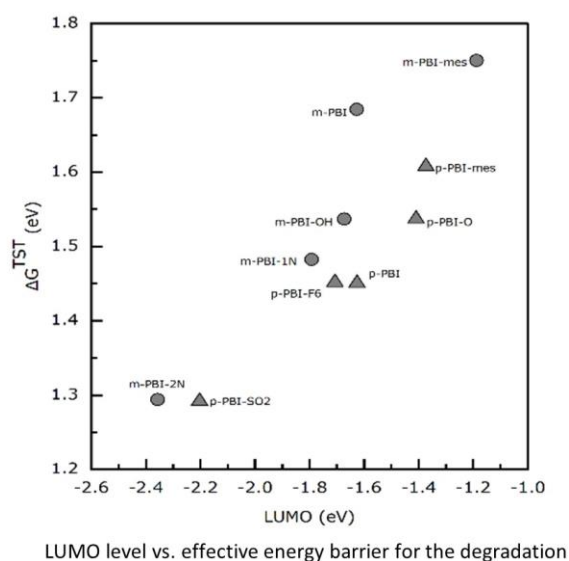
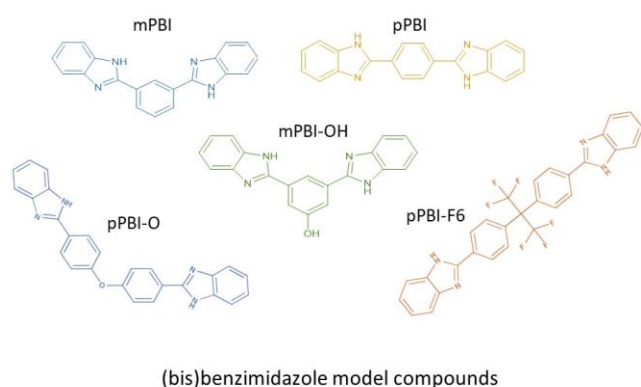
Polybenzimidazoles (PBIs) have gained increasing attention in recent years in the form of membranes in diverse fields of application such as water treatment, gas separation, pervaporation, organic solvent nanofiltration, and as electrolyte material for electrochemical systems operating in a wide pH range. [1] Their application in alkaline water electrolyzers is especially promising since PBI membranes possess remarkably high ion conductivity in alkaline environment, which allows for superior cell performance. [2] However, the chemical stability of common PBI derivatives remains insufficient in aqueous KOH. However, the main degradation mechanism that ultimately results in chain scission of PBI is not widely studied. This study aims at shedding new light on the stability and degradation of PBIs in alkaline environment as a basis for new design strategies of stable PBI chemistries. Towards this target, the alkaline stability of five (PBI-like) (bis)benzimidazole derivatives was studied in 25 wt% potassium deuteroxide at 80 °C for a prolonged period of time and the results were analyzed using ¹H and ¹³C NMR spectroscopy as well as LC-MS. After 192 hours the tested compounds did not show any signs of degradation. DFT calculations showed that the LUMO energy correlated with the effective energy barrier for the assumed degradation pathway. On this basis, the stability order was calculated m-PBI > p-PBI-O ≈ mPBI-OH > p-PBI ≈ pPBI-F6.

Reference 1:

D. Aili, J. Yang, K. Jankova, D. Henkensmeier, Q. Li, J. Mater. Chem. A 2020, 8, 12854

Reference 2:

Kraglund, M.R., Carmo, M., Schiller, G., Ansar, S.A., Aili, D., Christensen, E., Jensen, J.O., Energy & Environmental Science 2019, 12, 3313–3318.



Unravelling soft matter filter cake motions by microfluidic fouling analysis

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Main topic: Membrane fouling and cleaning

Soft matter colloid ultrafiltration processes suffer from filtrate agglomeration on the membrane surface as cake layer. This undesirable cake layer raises the resistance for the fluid permeating the membrane and, thus, increases the filtration process's energy consumption. Particularly in soft matter filtration, cake compression induces morphology changes in the inner cake structure leading to higher packing densities, increasing fluid resistances, and gel layer formation.

In this work, we visualize soft colloid cake layers during filtration and cleaning procedures using in-situ microscopy methods. We developed two microfluidic filtration cells for visualizing different orientations of the filter cake on particle scale. We filter soft micron-sized hydrogel particles (microgels) and analyze the filter cake's inner morphology during cake built-up, cake compression, and cleaning procedures.

The microgel filter cake's inner organization during cake built up presents single-particle movements that affect the whole cake's morphology and its filtration resistance. In the ongoing filtration, the morphology remains in a geometrical frustration which yields a steady-state for the filter cake resistance on the macroscopic level. A cake compression promotes further rearrangements, such that the cake history is of major importance for the inner morphology [1]. Additionally, we analyze the filter cake's dynamic motions while performing backflushing and crossflow flushing cleaning procedures. Herewith, the cake movements during backflushing confirm the process history-dependent cake morphology. On the other hand, crossflow flushing reveals a longitudinal 3D-pattern appearing on the cake surface, which accelerates the cake removal [2].

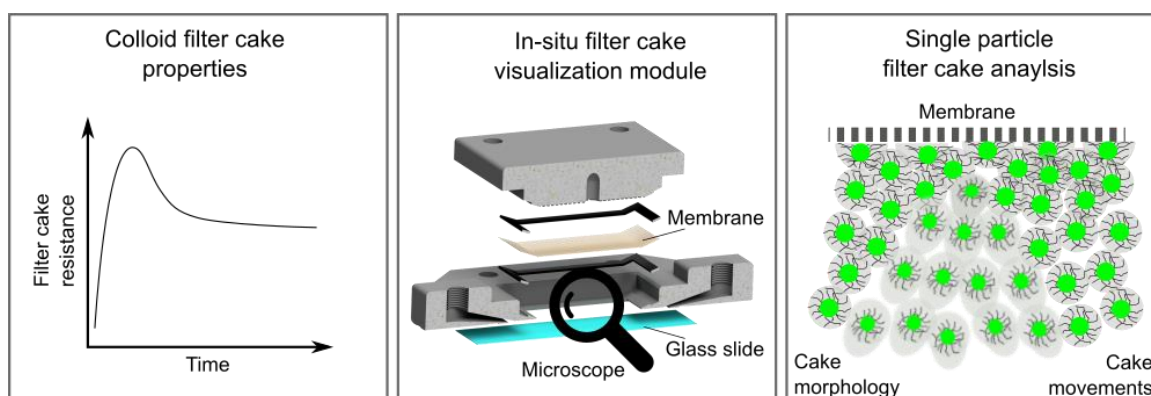
The filter cake fouling analysis presented in this study links macroscopic cake resistances to the microscopic cake morphology and single-particle behavior in the filter cake. It gives a rigorous understanding of fundamental phenomena inside a filter cake and narrows the gap from filtration models to empirical observations.

Reference 1:

[1] Lüken, A., Stüwe, L., Lohaus, J., Linkhorst, J., & Wessling, M. (2021). Particle Movements Provoke Avalanche-like Compaction in Soft Colloid Filter Cakes. [Preprint on Researchsquare]

Reference 2:

[2] Lüken, A., Linkhorst, J., Fröhlingsdorf, R., Lippert, L., Rommel, D., De Laporte, L., & Wessling, M. (2020). Unravelling colloid filter cake motions in membrane cleaning procedures. *Scientific reports*, 10(1), 1-11.



Utilization of the waste lavender residue from the essential oil industry via extraction and membrane filtration

Chilev, Chavdar - Main Author; Peshev, Dimitar - Co-Author

Main topic: Environmental applications

The possibility for utilization of WLR from the essential oil industry by combination of extraction and membrane filtration were studied. The WLR from the essential oil industry is *Lavandula angustifolia* from which the lavender oil is extracted by steam distillation. Thus, the residue contains KBAC -rosmarinic acid, caffeic acid, quercetin and luteolin. Extraction of KBAC from WLR by extraction under different conditions was investigated. By studying the equilibrium and kinetics, the parameters of the extraction process (solid-liquid ratio, time, type of solvent) were experimentally optimized. The time intervals to extract the KBAC from 600 to 10800s were studied. The results showed that equilibrium was reached at approximately 7000s after the start of the experiment. Thus, a time of 7200s for performing the extraction is selected. Two liquid-solid ratios, respectively: 0.01 and 0.03, were tested. A faster kinetics and more complete extraction of KBAC at solid-liquid ratio 0.01 are observed. To determine the optimal solvent, four solvents were tested, respectively: pure water, 99.99% Ethanol and mixtures between them - 40% and 60% Ethanol. Maximum amounts of KBAC in 40% Ethanol were found. Thus, the optimal conditions under which the experiments were performed were determined: temperature - 40°C, solid-liquid ratio - and the solvent - 40% Ethanol.

The extracts are aqueous-alcoholic solutions containing both hydrophobic and hydrophilic compounds. A range of commercial NF (DL, SUEZ (GE); NP030, NADIR, Puramem 200, Evonik MET) and RO (X201, TriSep) membranes were tested for their capability to fractionate or concentrate the KBAC in the obtained extracts. The use of membranes with different structure and composition of the selective layer, and with different hydrophobicity respectively, allowed for qualitative conclusions on the effects from the KBAC components interactions with the membranes. The adverse depot effect due to the adsorption of solutes in the membranes during batch filtration was evaluated. The membrane materials included modified polyimide (Duramem 200), polyethersulfone (NP030), polyamide (DL) and polyamide-urea (X201).

Keywords: essential oil, nanofiltration, membrane, fractionation, extraction.

Abbreviations:

WLR - Waste Lavender Residue

KBAC - Key Biologically Active Components

RO - Reverse Osmosis

NF - Nanofiltration

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UV-cross-linked iongel membranes with azo-functionalized porous organic polymers for CO₂ separation

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Main topic: Gas separation

Ionic liquids (ILs) have undoubtedly been one of the most explored class of materials for membrane-based gas separation processes, especially due to their remarkable affinity for CO₂. The development of iongel membranes, with a high IL content is a promising strategy to obtain high gas separation performances, while at the same time overcome the stability issues reported for supported IL membranes or the limitation in the IL/polymer composition of poly(ionic liquid)-based membranes. Moreover, a third component, such as a porous organic polymer (POP), which is a highly crosslinked, amorphous polymer, constructed from organic covalent bonds, can be incorporated in the membrane to further increase its separation efficiency.

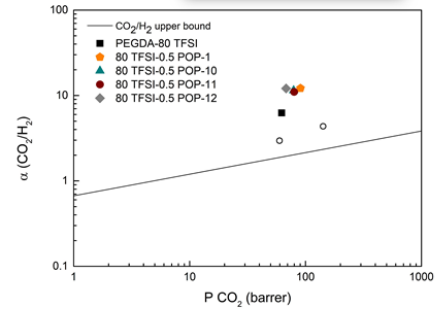
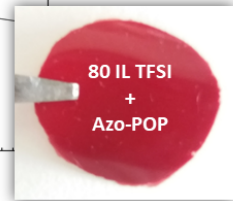
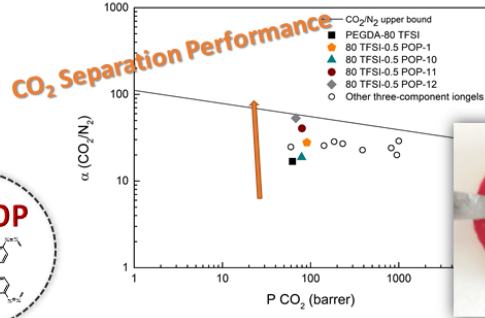
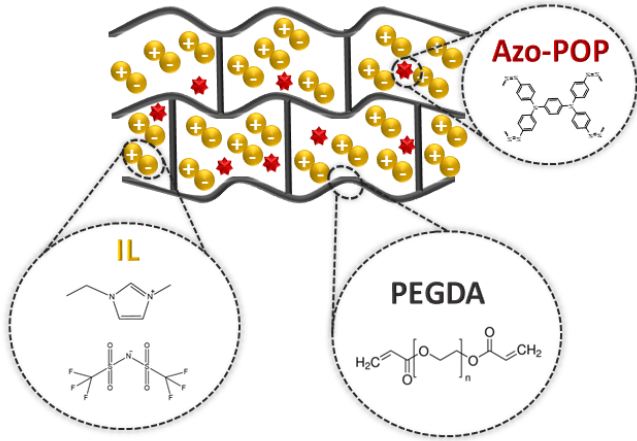
With the purpose of maximizing the potential of IL-based materials, crosslinked iongel membranes using solvent-free UV polymerization were prepared and characterized, combining 80 wt% [C₂mim][TFSI] IL with a polymer network (poly(ethylene glycol) diacrylate, PEGDA), that presents structural features relevant for CO₂ removal, and a small concentration (0.5 wt%) of azo-linked POPs, also known for their CO₂-philic nature.^[1] The aim of this communication is to show, for the first time, how the combination of high CO₂ solubility in fluorinated ILs and the CO₂-philic properties of the azo functional groups in iongels can unveil the possibility of developing membranes with high separation efficiency for gas separation processes.

A full membrane characterization revealed good compatibility between the solid and liquid phases and good dispersion of azo-POP particles in the iongels, with dense and defect-free structures and suitable thermal stability towards the proposed application. Pure gas permeation experiments for CO₂, CH₄, H₂ and N₂, showed that azo-POP-containing iongels outperformed the PEGDA/IL iongel. For the CO₂/N₂ separation the obtained data came close to the upper bound limit, and it was possible to relate the different azo-POPs structures with the variations in selectivity. Remarkably, for CO₂/H₂ all experimental results were able to surpass the respective upper bound limit. Moreover, CO₂/CH₄, CO₂/H₂ and CO₂/N₂ gas mixtures revealed that the CO₂ permeability is enhanced by an increase in temperature while the addition of azo-POPs resulted in unchanged gas selectivity, due to the N₂-phobic nature of their functional groups, unveiling the potential of these materials for the proposed application.

Reference 1:

[1] L. Zou, Y. Sun, S. Che, X. Yang, X. Wang, M. Bosch, Q. Wang, H. Li, M. Smith, S. Yuan, Z. Perry, H. C. Zhou, *Adv. Mater.* 2017, 29, 1

Ionogel Membranes



Valorization of vegetable oily refinery wastewater using ultrafiltration technology : water treatment and raw oily material recovery

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Main topic: Bio-separations and bio-refinery

Abstract

Refining of crude vegetable oils needs a significant amount of water and produces huge amounts of wastewater, which come from the degumming, de-acidification, deodorization and neutralization steps [1]. Vegetable Oil Refinery Wastewater (VORW) represents a serious environmental impact on land and water bodies if not properly handled [2]. The conventional methods have several limitations for the treatment of VORW since the oil fraction can cause pipe clogging and biomass washout during the biological step. Therefore, it is highly essential to separate the oily component before being released into the environment. Membrane based technology is one of the most effective separation processes since it can make it possible to obtain not only purified process water, but also, it might yield some value-added products that can be recovered and reused in the process itself or in other applications.

Within this framework, investigations were carried out to treatment VORW using commercial ultrafiltration (UF) membrane with a molecular weight cut-off of about 150 kDa under cross-flow mode. The obtained results confirm a promising application of the ceramic UF membrane (Orelis, France) in treatment of wastewater from the edible oil industry. Positive results regarding turbidity removal, chemical oxygen demand (COD), total organic carbon (TOC) and oil and grease reduction were noticed. UF was able to remove 99.97%, 93.7%, 94.1% and 100% of turbidity, COD, TOC and oil and grease respectively. Whereas, water permeability remained stable at a value close to $150 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ as a function of the volumetric concentration ratio (VCR).

The characterization of recovered oil in the UF retentate showed similar percentage of the major five fatty acids. Thus, cross flow UF treatment was a successful oil-water separation without being destructive to the nature of oil. Overall, this study strongly demonstrates that the UF process was able to produce treated water suitable for reuse and offers the advantage for vegetable oil valorization.

The experiments showed that UF of this type of wastewater is a convenient process for a possible large-scale industrial application in treating wastewater from the vegetable oil Refining.

Reference 1:

[1] Dkhissi, O., El Hakmaoui, A., Souabi, S., Chatoui, M., Jada, A., & Akssira, M. (2018). Treatment of vegetable oil refinery wastewater by coagulation-flocculation process using the cactus as a bio-flocculant. *J Mater Environ Sci*, 9(1), 18-25.

Reference 2:

[2] Sharghi, E. A., Shourgashti, A., & Bonakdarpour, B. (2020). Considering a membrane bioreactor for the treatment of vegetable oil refinery wastewaters at industrially relevant organic loading rates. *Bioprocess and biosystems engineering*, 43(6), 981-995.



Fig 1. Performance of UF as a function of volumetric concentration ratio (VCR) in the VORW treatment

VAPOR-PHASE DEPOSITION OF METAL-ORGANIC FRAMEWORK MEMBRANES FOR GAS SEPARATIONS

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Main topic: Gas separation

Metal-organic frameworks (MOFs) show high potential to exceed the separation properties of polymers. The structural and functional diversity of MOFs enables the possibility to achieve molecular sieving and specific adsorptive interactions for industrially relevant gas mixtures. Although the intrinsic MOF properties can be ideal, the performance of a MOF membrane depends on the quality and the thickness of the MOF layer. Ideally, the selective membrane top layer would be as thin as possible (< 100 nm) but at the same time has to remain defect-free. However, poor MOF-support interactions, heterogeneous nucleation, extensive solvent use, *etc.*, typical for conventional wet methods, makes the development of ultra-thin, pinhole-free MOF layers on porous supports a formidable challenge. Vapor-phase deposition of MOFs, pioneered by our research group, allows ultra-thin MOF films on dense substrates in a controlled and reproducible manner.¹ This method can be extended to porous substrates, resulting in pinhole-free MOF membranes combined with high separation performances.²

The fabrication process of MOF membranes consists of first depositing a metal-oxide precursor layer via a vapor deposition method (sputtering or atomic layer deposition), from which the thickness can be precisely controlled in the nanometer range. Subsequently, the precursor layer is converted into the MOF structure by exposing it to the vapor phase of the organic linker. During this conversion, the dense precursor layer expands into the porous MOF structure by which the pores of the substrate are fully blocked. The nature of the top surface and interlayers can be altered by the vapor phase treatment of the ZIF membranes. In this way, the gas separation performance can be fine-tuned for different gas mixtures (CO₂/N₂, CO₂/CH₄, and propylene/propane). Different treatment protocols are explored, and the chemical and structural changes following the treatment process are investigated in detail.

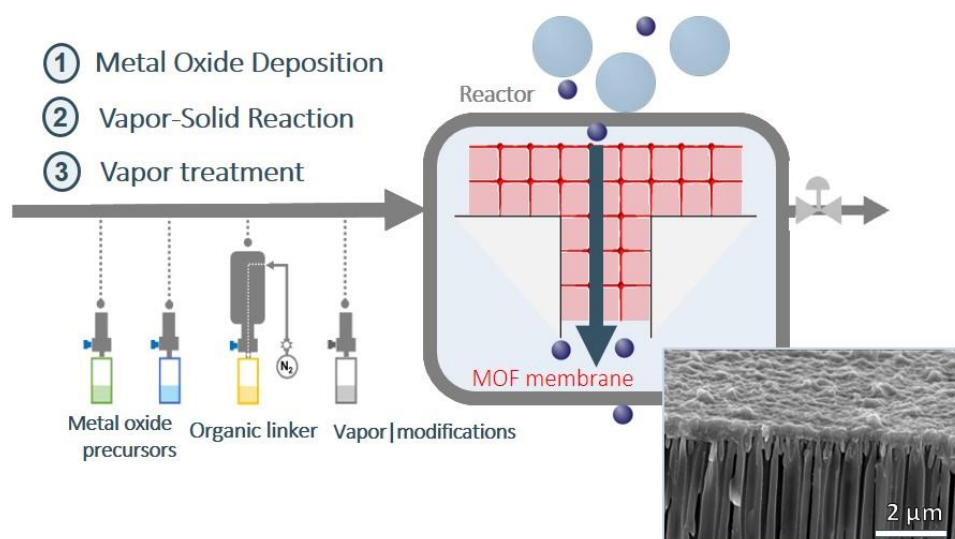
The findings obtained in this work showcase a facile route to high-performance gas separating membranes from which the performance can be enhanced even further by vapor-phase modifications. Additionally, the demonstrated all-vapor-phase approach holds great promise for scalability.

Reference 1:

Stassen, I. et al. Chemical vapour deposition of zeolitic imidazolate framework thin films. *Nature Materials* 15, 304–310 (2016).

Reference 2:

Ma, X. et al. Zeolitic imidazolate framework membranes made by ligand-induced permselectivation. *Science* 361, 1008–1011 (2018).



Vibro Filtration – new and disruptive solution for micro and ultrafiltration

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Main topic: Microfiltration/Ultrafiltration

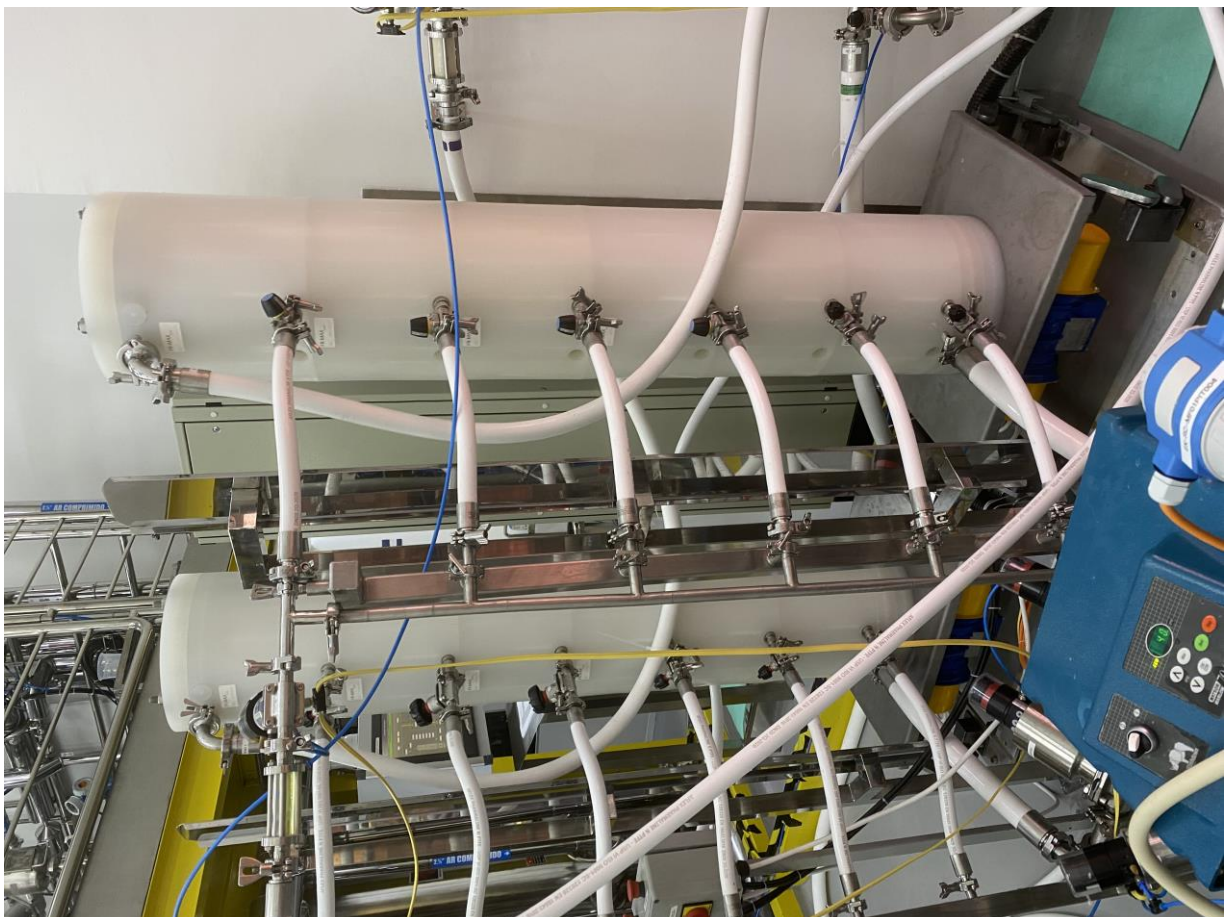
SANI Membranes will present a new and patented membrane filtration technology based on the Free Flow Plate modules and the Vibro technology. The Vibro technology delivers efficient continuous micro- and ultrafiltration with less fouling, less energy consumption and with a simple and sanitary design.

The Vibro technology is based on the crossflow filtration principle, but the cleansing turbulence at the membrane surface is here created by vibrating the membrane relative to the feed instead of applying a fast cross flow. The turbulence is only produced at the membrane surface and the huge pressure loss from a traditional cross flow is eliminated. Consequently, the transmembrane pressure (TMP) becomes close to uniform throughout the system - making unique process control and sharper separations possible.

The key features of the Vibro technology that will be explained are improved separation due to a uniform TMP obtained through fouling reducing turbulence achieved by moving the membrane relative to the media. The design opens for operation at very low TMP in the entire system (e.g. 0.10 bar) and this is the key to continuous fouling free microfiltration with high transmission of target molecules. Several test underlines that in many applications higher pressures reduce flux in microfiltration and always higher pressure seems to reduce transmission.

The open plate design supports operation with high concentration, viscosity and solid loads, and this combined with vibro technology leads to very high savings in pumping energy and cooling.

The technology is successfully implemented in continuous microfiltration of fermentation broths with exceptional transmission of target molecules even at high cell/cell-debris concentrations. The technology is also as a subsequent step implemented in UF concentration of proteins and other target molecules to remarkably high concentrations with extremely low shear on the media.



Wastewater reuse for agriculture irrigation: could nanofiltration be used as tertiary treatment?

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Main topic: Nanofiltration/Reverse Osmosis

Nowadays, 72% of all water withdrawals are utilized by agriculture, making this the sector with the highest pressure over freshwater resources [1]. By 2050, the global food production is expected to increase by 50% to feed an estimated 9.7 billion people, leading to even higher water consumption. Hence, it is crucial to explore new solutions and water sources for agriculture irrigation, such as domestic wastewater effluents. Nevertheless, prior to the irrigation with wastewater effluents, it is important to evaluate the presence of micropollutants (e.g. antibiotics) and pathogens (e.g. antibiotic resistant bacteria and viruses) in the effluents as well as to address the potential uptake of contaminants by food crops after irrigation. If necessary, effective treatments should also be explored to cope with the presence of these contaminants.

In this study, analytical and molecular methods were developed to detect the presence of antibiotics, antibiotic resistance genes and pathogenic viral genomes in wastewater effluents as well as in solid matrices (soil, leaves and fruits). Broad-spectrum fluoroquinolone antibiotics (ciprofloxacin and levofloxacin), carbapenem and fluoroquinolone resistance genes, as well as viral genomes, were detected in grab samples of wastewater effluent collected throughout a year [2]. Passive samplers (Pharmaceutical Polar Organic Chemical Integrative Samplers), which are easier to use and provide information about the concentrations of contaminants present in a fluid matrix over time, proved to be extremely promising devices to monitor the presence of the target antibiotics in wastewater effluent [2].

Additionally, pilot scale nanofiltration assays using a Desal 5DK membrane were conducted at a domestic wastewater treatment facility to test the feasibility of using nanofiltration as tertiary treatment and achieve a high-quality water that could be more suitable for irrigation. High rejections of the target contaminants were obtained in all the experiments, showing no influence of the different operating conditions tested [2]. Regarding fouling, the best operating conditions were found to be working under a controlled transmembrane pressure of 6 bar and recovery rate of 73% [2]. The wastewater effluent and the nanofiltration permeate will be used for irrigation of raspberries to evaluate the potential uptake of the target contaminants by these fruits.

Reference 1:

FAO, IFAD, UNICEF, WFP and WHO. 2017. The State of Food Security and Nutrition in the World. Building resilience for peace and food security, 2017

Reference 2:

M. B. Cristóvão, S. Tela, A. F. Silva, M. Oliveira, A. Bento-Silva, M. R. Bronze, M. T. B. Crespo, J. G. Crespo, M. Nunes, V. J. Pereira, *Membranes* 2021, 11 (1), 9

What is the molecular weight limit to have a systematic full rejection of organics in reverse osmosis of salty & sea waters?

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Main topic: Nanofiltration/Reverse Osmosis

Seawater desalination is an alternative for providing drinking water. However, in certain developing countries, the sea is still used as a dumping ground for effluents, and can be polluted by several toxics due to human and industrial activities. RO is the dominating technology for desalination; however, organics' traces have to be evaluated in the permeates of polluted seawater. Literature reported on the partial rejection of small organics (MW < 200 g.mol⁻¹, drugs, pesticides...) and transmission of lactose (neutral, 342 g.mol⁻¹) was evidenced [1, 2]. Finally, the MW limit (and associated RO conditions) leading to a systematic full rejection is not clearly known.

This work addressed this question by filtering molecules dissolved in deionized water, 30 g.L⁻¹ NaCl or seawater at pH= 7.5-8.2. A set of anionic azo-dyes were selected as model micropollutants (textile industry is one of the most polluting). They cover a MW range up to about 1000 g.mol⁻¹, own backbone with rigid and planar domains limiting their deformability, and exhibit significant differences in their hydrophobicity. To account for the impact of long term solute accumulation at the membrane wall, dyes were dissolved at "high" concentration (0.5x10⁻³ mol.L⁻¹ each) for RO by the SW30 membrane (Filmtec) in the 30-40 bar applied pressure range (no flux decrease associated with the dye).

Among the selected molecules were Tropaeolin O (TO, 293 g.mol⁻¹, z = -2, LogKow= 1.53) and Brilliant Blue G (BB, 831 g.mol⁻¹, z = -1, LogKow= -2.55).

Despite their negative charges that could increase rejection by electrostatic repulsion, TO and BB filtered as single pollutant were partially transmitted in the permeate regardless of the salt environment (DI water, NaCl, seawater). Whereas BB transmission was constant at 0.01, TO transmission varied in the 0.03-0.06 range

When TO and BB were filtered in mixture, TO transmission was not modified when compared to single TO whereas BB transmission increased up to 0.08 in 30 g.L⁻¹ NaCl. The MW limit for full rejection was thus greater than 831 g.mol⁻¹ for such a hydrophilic compound. RO of dyes with higher MW will be shown and transfer mechanisms discussed for a better fundamental understanding.

Reference 1:

[1] M. Rabiller-Baudry, H. Bouzid, B. Chaufer, L. Paugam, D. Delaunay, O. Mekmene, S. Ahmad, F. Gaucheron, On the origin of flux dependence in pH-modified skim milk filtration, *Dairy Sci. Technol.* 89 (2009) 363–385. <https://doi.org/10.1051/dst/2009018>.

Reference 2:

[2] M.G. Shin, W. Choi, S.-J. Park, S. Jeon, S. Hong, J.-H. Lee, Critical review and comprehensive analysis of trace organic compound (TOC) removal with polyamide RO/NF membranes: Mechanisms and materials, *Chem. Eng. J.* 427 (2022) 130957. <https://doi.org/10.1016/j.cej.2021.130957>.

ZIF-8 incorporated into chitosan membrane to enhance separation in organic-organic pervaporation

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Main topic: Pervaporation and vapour permeation

Separation of organic-organic mixtures using pervaporation is a current challenge that has attracted the interest of the research community due to the enormous potential of this technology considering its low energy consumption [1]. For example, valorisation of glycerol as a platform molecule to produce glycerol carbonate is of utmost interest, but it involves the reaction of glycerol with dimethyl carbonate to produce glycerol carbonate and methanol as byproduct [2]. This reaction is limited by the equilibrium and an azeotrope between dimethyl carbonate and methanol is also present. Thus, the low yield and high separation costs using conventional technology make this process uninteresting for a real application.

In this work, we present pervaporation as the alternative technology to minimise energy consumption. Novel membranes are proposed to selectively separate methanol from the organic mixture. With porous metal-organic frameworks as fillers, mixed matrix membranes (MMMs) can significantly improve the separation performance in contrast with corresponding pristine polymeric membranes. ZIF-8 particles were embedded uniformly into chitosan (CS) matrix to prepare CS/ZIF-8 MMMs and were used for the pervaporation separation of methanol-dimethyl carbonate mixtures. Benefiting from the flexible framework, high surface area and high affinity of ZIF-8 crystals with CS matrix, the methanol permeance of CS/ZIF-8 MMMs was significantly increased without compromising the membrane selectivity. The results depicted that CS membrane loaded with 15 wt% ZIF-8 showed a high methanol permeance of 82.9 GPU and selectivity of methanol/DMC of 18.42 which was 361.3 % and 9.4% higher when compared to pristine CS membrane. Thus ZIF-8 doped CS mixed matrix membrane serves as a potential candidate for industrial pervaporation studies.

Reference 1:

Smitha, B., et al., Separation of organic–organic mixtures by pervaporation—a review. *Journal of membrane science*, 2004. 241(1): p. 1-21.

Reference 2:

Li, W., et al., Sorption and pervaporation study of methanol/dimethyl carbonate mixture with poly (etheretherketone)(PEEK-WC) membrane. *Journal of Membrane Science*, 2018. 567: p. 303-310.