Programma della conferenza

Sessione

ANA-3B: Divisione di Chimica Analitica - Parte 3B

Ora: **Giovedì, 29.08.2024: 10:30 - 13:00**

Luogo, sala: **Orange2**

Level -1; 132 seats

Presentazioni

10:30 - 10:45

A “white” analytical method for the determination of emerging contaminants in water: optimization of the analytes’ extraction by a bio-degradable polymeric film

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The growing interest in greener approaches in many scientific fields generated the need for a green analytical chemistry. Nevertheless, in many analytical applications, essential method requirements cannot be overlooked, such as performance and time and cost-effectiveness. These aspects are not always easily fulfilled through the greenest strategies. Therefore, Nowak et al recently introduced the concept of “White analytical chemistry”1(WAC), which highlights the importance of being “greener” without neglecting the value of method performance (accuracy, precision, specificity…) and feasibility. In the environmental analysis of emerging contaminants (ECs), WAC embodies the use of green and sustainable sample preparation, coupled to reliable, accurate and sensitive analytical determinations.

In this framework, the present work deals with the multivariate optimization of an extraction method based on the use of a biodegradable polymeric film (Mater-Bi), coupled to analysis by liquid chromatography-tandem mass spectrometry, for the determination of ECs in treated wastewater.

The interaction among 39 ECs with varying chemico-physical properties and the Mater-Bi film (a patented blend of polybutylene-terephthalate, starch and fatty acids) was investigated by two sequential experimental designs2, to simultaneously study several factors and optimize extraction efficiency. The results indicated that hydrophobic and weakly acidic analytes were the most prone to interact with the material, resulting in good recovery from water samples. The final method, which basically resembled a fabric phase sorptive extraction, involved pH and ionic strength modification of the sample, 1 h extraction and desorption in ethanol. Satisfactory recoveries from real wastewater were obtained for sixteen analytes (56-116%), as well as excellent precision (inter-day relative standard deviations below 10% for most compounds). Matrix effect was investigated at two dilution factors, with good or acceptable results in both cases. Limits of detection in matrix, from 0.004 to 0.159 µg L-1, were lower than or comparable to those from recent studies employing green extraction procedures. The method demonstrated its applicability to samples from wastewater treatment plants, allowing quantification of pharmaceuticals and UV filters at the µg L-1 and ng L-1 levels, respectively.

The optimized protocol allows a green, simple and extremely cheap extraction of several ECs from treated wastewater, by using a material so-far unexplored in analytical chemistry. The method guarantees very good analytical performance and demonstrated to comply with WAC principles.

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[2] B. Benedetti, V. Caponigro, F. Ardini, Critical Reviews in Analytical Chemistry 2022, 52, 1015-1028.

10:45 - 11:00

Wood-derived biochar in biodegradable membrane for pharmaceuticals thin-film microextraction in environmental waters

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The occurrence of organic contaminants, particularly antimicrobials, in aquatic environments is a global threat due to the growing evidence of adverse effects, such as the selection and spread of multidrug resistant bacteria and genes. Sensitive and accurate monitoring studies are a challenge with important but also contradictory aspects, since they help to detect the presence of such pollutants even at very low concentrations, but at the same time they can have an inherent environmental impact due to the resources involved. Recent trends pursue the goal of the sustainability through a simplification of the sample treatments and the use of natural and/or renewable materials1. In such a scenario, the focus of this work is the synthesis of efficient, green and biodegradable polymeric membranes for the multiclass thin film microextraction (TF-ME) of antimicrobials, namely fluoroquinolones, sulphonamides, tetracyclines, macrolides, diaminopyrimidines and glycopeptides. With the aim of not only serving the purpose of sample preparation but also avoiding secondary pollution, polycaprolactone has been selected as polymer due to its biodegradability, whereas a wood-derived biochar (Cabot) and a wood-derived activated biochar (Nuchar) have been tested as carbon precursors with the added benefit of extending the life-cycle. The films are home-made prepared, studying different compositions based on the solvent (chloroform or acetic acid) for solubilizing the polymer, the type and amount of char entrapped in the polymeric matrix. The preliminary TF-ME tests allow to evaluate the extraction efficiency (EE%) at different times (5 min ÷ 24 h) for each membrane. The use of acetic acid causes a partial acid hydrolysis of the lactone ring making the membrane less stable and hence less efficient, thus CHCl3 has been selected despite its toxicity which is mitigated by its low consumption (1 mL). The adsorption capacity of the neat polymer was negligible (EE% < 8%) for all analytes, but it increased significantly in presence of Nuchar (15%w/w, EE% ≥ 80% at 8h). This biochar possesses a higher affinity in respect to Cabot (15% w/w, EE% < 15% at 8h) ascribable to the different functional groups and surface area. The results also show that the extraction efficiency is strictly dependent on the amount (15-30% w/w) of Nuchar incorporated in the polymeric matrix, and finally the film with 24% of Nuchar has been chosen as it guarantees quantitative extraction of all compounds in 4h. Different elution conditions, viz. solvent type and volume, type and time of stirring are being studied together with the analytical evaluation of the method in river and wastewater samples.

References:

[1] Á.I. López-Lorente, F. Pena-Pereira, S. Pedersen-Bjergaard, V.G. Zuin, S.A. Ozkan, E. Psillakis, Trend. Anal. Chem. 2022, 148, 116530.

11:00 - 11:15

Controlled Periodic Illumination (CPI) for enhancing the photonic efficiency of a photocatalytic system

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Semiconductor photocatalysis for water treatment and water photo splitting is plagued by low photonic efficiency and slow mass transfer, hindering its exploitation.

Photonic efficiency measurements at semiconductor surfaces for pollutant abatement and H2 evolution (HER) are usually carried out under continuous irradiation of the catalyst.

Controlled Periodic Illumination (CPI) was proposed to increase the photonic efficiency of irradiated semiconductor systems. CPI consists in the modulation of the incident radiant power, alternating light and dark periods with given duty cycle, intensity, and frequency.

In this work we demonstrated that CPI:

i - in the photocatalytic abatement of organic pollutants in aerobic conditions using semiconductor nanoparticles (usually TiO2) it is not able to increase the photonic efficiency at the same average photon flux compared with continuous illumination;

ii – conversely, it is effective in the HER using metals like Pt, Pd and Rh alone or in combination with TiO2. The supposed mechanisms fall under the surface catalytic resonance theory and the differences between active and not-active metals can be explained invoking the Volmer-Tafel or Volmer-Heyrovsky mechanisms.

11:15 - 11:30

Electrochemical degradation of oxolinic acid on BDD electrodes

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Oxolinic acid (OA)belongs to the first generation of quinolone antibiotics that are widely used in veterinary medicine and aquaculture. OA can be employed both as a prophylactic to prevent diseases and as a chemotherapy agent, because it is effective against the most common bacterial infections. However, the overuse and misuse of antibiotics have led to increased antibiotic resistance in pathogenic bacteria. The residues of OA and other antibiotics have been found in the environment, waste and urban waters due to incomplete elimination of these compounds in wastewater treatment plants. In this study, we studied the electrochemical degradation of OA in galvanostatic mode simulating real aquaculture effluents. Two boron-doped diamond (BDD) - electrodes with 9 cm² area were used as working electrode (anode) and counter electrode (cathode) along with OA concentration of 10 µM. Supporting electrolytes were chosen to understand the role of the different components of sea water, e.g. NaCl, NaBr, Na2SO4, NaHCO3, NaBO2 and their interactions. HPLC-UV results showed that degradation efficiencies were between 50 and 100% within 2 hours depending on the electrolyte tested. OA degradation was almost independent on current density, whereas larger currents generally led to improved mineralization at the expense of energy consumption. Degradations were particularly effective (> 90%) in NaBr-containing electrolytes already at 1 mA cm-2 current density with the least amount of energy supplied to the system (1.9 kWh m-3). The addition of supporting electrolyte to Br-containing solutions led to similar degradation and mineralization efficiency but significantly reduced energy input, improving efficiency. While Br- can improve OA degradation, reactive bromine species can also be responsible for the formation of harmful compounds. In fact, we detected bromate ion through ion chromatography and we hypothesize the formation of a brominated intermediate, but its identity will be investigated in future tests.

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11:30 - 11:45

Debunking the need (and existence) of “pure” g-C3N4 to optimize its photocatalytic properties for environmental applications

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Graphitic carbon nitride (g-CN) is a metal-free semiconductor gaining interest within the scientific community for its simple preparation, low cost, and photo-electrochemical properties.1 Noteworthy, there is no clear consensus on its optimal synthesis due to the several parameters affecting it, such as, precursor, employed gas on the oven, temperature, or even if the precursor should be compressed or covered to reduce sublimation.2 In views of standardizing its preparation and optimize its properties for environmental applications, in this work, we have calcinated melamine at different temperatures within the range 350 – 650 °C under anoxic controlled atmosphere and in presence and absence of an aluminium cover to reduce or enhance melamine sublimation, respectively.

Obtained materials were characterised by several techniques, and their photocatalytic performance evaluated as H2O2 generation (with methanol as hole scavenger) and phenol oxidative degradation under UVA and visible light, respectively. Results indicated that under UVA light, the best performance was obtained with the g-CN prepared at 425°C with the aluminium cover, leading to 6 mM production of H2O2 in 3 h, as well as a 3.4×10-2 min-1 phenol oxidation rate with an initial concentration of the organic substrate of 100 µM. To correlate the huge amount of data (21 variables analysed for 10 types of g-CN) a Principal Component Analysis was carried out3, indicating that to maximize the photocatalytic performance under UVA light irradiation, employed temperatures should not exceed the 500 °C, contrarily to what is currently found in literature. On the contrary, for visible light experiments, reduction of band gap by doping the g-CN with nitrogen (employing higher temperatures, thus, observing a higher polymerisation degree and a C:N ratio close to stoichiometric 3/4 value) is required as usually observed in other works.

This work intends to shed light into the basic properties of g-CN and into the correlation between its photocatalytic properties and its physico-chemical features, as well as to promote the use of UVA light in views of saving synthesis costs of this semiconductor.

11:45 - 12:00

Principal Component Analysis describes soil features through Rare Earth Element distributions overcoming normalization challenges

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Exploration of Rare Earth Elements (REE) as potential biogeochemical tracers is constantly gaining attention across various fields of research, thanks to their unique properties. The common method for investigating the data coming from REE quantification by ICP-MS typically involves a visual evaluation of REE distribution, after normalization to a lithological reference. However, this approach has an inherent limitation because the choice of such lithological reference is subjective and therefore the interpretation of the distribution and identification of anomalies may depend on this choice.

In the present study, a new approach for analysing REE concentration profiles is proposed, applying Principal Component Analysis (PCA) for the creation of REE chemometric maps, which allow a simple and direct evaluation of similarities and differences to be performed in the geographical region under study. Moreover, PCA describes the profiles of REE in soils, facilitating the interpretability of results to exploit the chemical information embedded in concentration profiles. Results reveal that loading plots of PC1, PC2, and PC3 distinguish between light and heavy REE while highlighting anomalies of specific elements and REE groups. Data compression allows visualization of REE behaviour using an RGB colour scale (PC1= red channel; PC2= green channel; PC3= blue channel) directly on a geographical map.

Interestingly, similarities in agrochemical conditions were observed among soils belonging to the same lithological family when exhibiting similar REE distribution patterns. This underlines relationships between REE distribution and the diverse array of soil characteristics, supporting traceability studies and environmental monitoring.

Of particular significance is the fact that the application of the proposed methodology to non-normalized data yields results consistent with those derived from normalized datasets. For the first time, it was shown that similarities and differences in distributions can be found starting from raw concentration data, devoid of preconceived normalization biases.

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12:00 - 12:15

Self-Organizing Maps: An AI Tool for Identifying Unexpected Source Signatures in Non-Target Screening Analysis of Urban Wastewater by HPLC-HRMS

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The monitoring of effluent in water treatment plants has a key role in identifying possible pollutants that can be released into the environment. A non-target analysis approach can be used to identify unknown substances and isolate multipollutant signatures related to specific sources using powerful analytical techniques such as high performance liquid chromatography-high resolution mass spectrometry (HPLC-HRMS). However, HPLC-HRMS techniques focused on non-target screening (NTS) produce a huge amount of high-dimensional data, often with noisy and collinear structures; thus, it is necessary to use multi-step workflows involving extensive data processing and multivariate data analysis techniques to handle data sets appropriately and to further obtain interpretable results. Here we present the results from a case study in which urban and industrial wastewater effluent were examined by HPLC-HRMS for NTS1. The anomalous infiltration of industrial wastewater into urban wastewater was detected by analysing the information-rich mass spectrometry data of “unknown common” compounds using principal component analysis (PCA) and Self-Organizing Maps (SOMs). SOMs are a rather old type of artificial intelligence (AI) that employs unsupervised learning to convert high-dimensional input data into a lower-dimensional grid composed of nodes or neurons.

SOMs have several advantages over classical chemometrics methods such as PCA, including the ability to capture non-linear relationships and structure in the data, the ability to deal with complex high-dimensional datasets, meaningful visualisation of the outcomes in 2D maps, tolerance and robustness to outliers, the ease with which the latter can be identified, and the simplicity with which the results can be related to the experimental variable importance. In this case study, we compared the outcomes from PCA and SOMs, demonstrating that the PCA model could not fully perceive the differences among the different samples. Moreover, since PCA involves the calculation of new variables based on the original experimental ones, it is not possible to reconstruct a chromatogram that displays the recurring patterns in the urban wastewater samples. This can be easily achieved using the SOM outcomes.

12:15 - 12:30

OPTIMIZATION OF AN LC-MS ANALYTICAL METHOD FOR THE DETERMINATION OF MULTI-CLASS POLAR EMERGING CONTAMINANTS IN RECLAIMED WATER

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Food and agriculture account for most of the human demand for water, due to the huge amounts required for crops and livestock. Within the whole agricultural, municipal, industrial and energy sectors, 70% of water is used for cultures and farming. The current available water resources need an aware management to meet the growing global demand for food [1]. Thus, the possible use of reclaimed water for irrigation represents a great opportunity for water conservation and fits in the circular economy approach.

In this study, the optimization of an analytical method based on liquid chromatography-mass spectrometry (LC-MS) was carried out for the determination of 33 polar emerging contaminants in wastewater. The contaminants encompassed various classes including pharmaceuticals, personal care products, and other emerging pollutants.

Due to the high polarity of the analytes under study, hydrophilic interaction liquid chromatography (HILIC) was employed, by testing a zwitterionic stationary phase. To enhance the efficiency of the analysis, response surface methodology (RSM) utilizing a Fractional Factorial Design [2] was employed to optimize the experimental parameters. Indeed, multiple factors influence the chromatographic separation in HILIC, such as initial mobile phase percentage, gradient time, column temperature, type and concentration of salt and flow rate, which were investigated to achieve the best separation and sensitivity for the target analytes. Finally, the optimized method was combined to a suitable sample pre-treatment and applied

to different reclaimed water samples. Thus, the method performance could be evaluated in real matrices and the presence of the considered contaminants in treated water was investigated.

References:

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12:30 - 12:45

Multivariate analysis of the photoaging of four types of microplastics by Micro-IR spectroscopy

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Understanding the origins of microplastics and evaluating the consequences of plastic pollution hinges upon precise chemical information. In this regard, a remarkable challenge lies in the chemical changes that microplastics undergo due to photoaging, which could hinder spectroscopic matching and identification.1 Micro-IR is currently one of the go-to techniques for the screening of microplastics, coupling the possibility of collecting optical images of the particles with the chemical information provided by the IR spectra. The sensitivity of reflectance Micro-IR spectroscopy to the thickness of the particles and to chemical changes induced by photodegradation on one hand hinders the automated recognition by spectral matching, but on the other hand contains layers of information that lie beyond the reaching of conventional data analysis. In this study, we conducted multivariate analysis on four types of microplastics obtained by common objects: two conventional (PE and PS) and two compostable bioplastics (PLA and PBAT). These microplastics underwent artificially accelerated photoaging and were analysed by Micro-IR spectroscopy in the medium infrared range. Principal component analysis (PCA) was able to classify the polymers and show degradation trends, highlighting even subtle changes in the spectra. The issue of reflection “artifacts” in spectra obtained from particles thicker than 100 µm was also addressed.

12:45 - 13:00

Accurate pH monitoring of highly concentrated saline aqueous solutions (Seawater-like) with a pH Colorimetric Sensor Array

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The increase in the atmospheric CO2 concentration is causing a decrease in surface ocean pH by ≈ 0.002 pH units per year with a long-term pH decrease from 8.25 to 8.10 in the last two centuries. Caldeira and Wicket predicted further decreases in seawater pH of up to 0.80 pH units by 2300. Monitoring the seawater pH is therefore more and more important to determine negative effects on the environment. In particular, “in situ” real-time pH sensors are more and more necessary. In this context, a pH Colorimetric Sensor Array (CSA) was prepared on a nitrocellulose membrane and used for accurate pH measurement in highly concentrated saline solutions. The CSAs consisted of sensing spots made of a suitable OrMoSil polymer prepared from organo-fluorinated-silane precursors and/or organo-silane with tetraethyl orthosilicate hosting an acid-base indicator. Four CSAs were prepared: D, 1F, 2F, and 3F. In D a non-fluorinated organo-silane was present. From 1F to 3F the concentration of the fluorinated organo-silane increased and improved the pH measurement accuracy in highly saline concentrations. No re-calibrations were required and the analytical signal was stable in time. D, 1F, 2F, and 3F were deposited in triplicate and they were prepared to work in the seawater pH interval (7.50-8.50). The use of fluorinated precursors led to a lower pH prediction error and tailored the interval of the CSA at more basic pH values so that the inflection points of the sigmoidal calibrations of D, 1F, 2F, and 3F moved from 6.97 to 7.98. The overall pH prediction error was 0.10 pH units (1F), 0.02 pH units (2F), and 0.04 pH units (3F). The CSAs were stable, reversible, reusable, and independent of salinity (S) between 20 and 40. The performances of the CSA were compared with those of the glass electrode whose pHNIST values were converted in the pHSWS scale through a conversion equation. Being unaffected by the typical drawback of the glass electrode, the CSAs can be used directly in seawater real samples and it validated the proposed conversion equation.

References:

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