Title: A chain for the treatment of oilfield produced waters: case study and experimental analysis

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Keyword(s): Produced Waters (PWs), Assisted- Reverse Electrodialysis (A-RED), Sequencing Batch Moving Bed Biofilm Reactor (SBMBBR), Experimental treatment chain.

Abstract

Produced water are salty and organic polluted waters that are drilled out during the extraction of oil. Typically, these waters are re-injected into the extraction well, without any treatment or valorisation. In this work, a more sustainable and environmental friendly solution is proposed consisting of an innovative PWs treatment scheme: Assisted Reverse Electrodialysis (ARED) is used to reduce the PWs salinity to make them compatible with the downstream Sequencing Batch Moving Bed Biofilm Reactor (SBMBBR), aimed at removing the organic content. To this purpose, a 20-cell pair ARED unit was continuously operated for 24 hours to desalinate PWs down to a target concentration of 20 g L^{-1} of NaCl. Then, the desalinated stream was treated in a 50 L bioreactor and an abatement up to 40 % of the Total Petroleum Hydrocarbon (TPH) was achieved.

Introduction

Due to the depth of the reservoir, the fluid pressure of the oil certainly helps the drilling techniques, but over time this pressure difference decreases, and water is used to enhance the oil recovery (waterflooding method). As a result, downstream separation processes are used to separate the water from the organic component. The latter, referred to as produced water (PW), is characterised by (i) high salinity due to contact with subsurface rocks and (ii) hydrocarbon compound contaminants [1]. Overall, PWs present a complex and variable composition depending on oil maturity, extraction methods, well depth and site morphology [2]. Due to all these variables, it is not possible to standardise the characteristics of PWs, and consequently, their treatment must be defined on a case-by-case basis through ad-hoc studies and experimental investigations. Their complex nature is further complicated by the large volumes involved. Estimates suggest an annual generation of 11.2 million of m^3, with production increasing progressively with the well age, generating at least 3 barrels of PWs for every barrel of oil produced [3]. The management of PWs usually consists of re-injection into the well, but due to increased public and legislative attention, this might not be longer possible. This would require to treat these PWs appropriately, with treatment chains leading to (i) the Minimum Liquid Discharge (MLD) target and to (ii) the reuse for potable or irrigation purpose [4].
Environmental awareness has increased in recent years, attracting the interest and efforts of the scientific community to propose new technologies and treatment chains capable of handling PWs. Typically, three main process categories are employed to treat PWs: physical treatment (e.g., evaporation, filtration), chemical processes (e.g., oxidants, electrochemistry), and biological remediation [5]. Physical and chemical treatments are the most efficient, but also the most expensive. Conversely,

biological treatments are among the most cost-effective and efficient technology to deal with wastewaters. Traditionally used for urban wastewaters, biological remediation has the main limit of the high salinity, i.e., PWs high salinity is detrimental for conventional bio-remediation treatment processes [6]. For this reason, a low-cost pre-treatment for the salinity reduction represents an appealing way to economically manage this kind of wastewaters.

Plant proposal/ Treatment chain

Reverse Electrodialysis (RED) is a process exploiting the salinity gradient between two streams to move the salt ions from a concentrated solution to a diluted one, generating electric energy. The ions migrations can be boosted with ARED, by the application of an external electric field. In this new scheme, PWs are fed to the ARED unit for the salinity reduction, to make them compliant with the downstream biological section. The ARED stack is constituted by repetitive modules units as cell pairs, each comprising of two channels and two Ion Exchange Membranes (IEMs): an Anion Exchange Membrane (AEM) and a Cation Exchange Membrane (CEM). Spacers were placed between the membranes to create the channels where a concentrated solution (H) and a low-concentrated solution (L) are alternately fed. Electrode compartments are positioned at both ends of the stack. In these compartments an Electrode Rinse Solution (ERS) containing redox couples (Fe^{3+}/Fe^{2+}) continuously circulates, allowing the conversion of electric current into ionic current. After the dilution up to an equivalent NaCl concentration target of 20 g L^{-1} (see **Figure *1***), the PWs are sent to a biological section consisted of a biological reactor with IFAS (Integrated Fixed Film Activated Sludge) technology operating in a batch cycle, hereafter named SBMBBR (Sequencing Batch Moving Bed Biofilm Reactor). The latter has the purpose to reduce the organic content of PWs and make the PWs respectful of the legislative limit for discharge. The same effluent could be addressed to a valorisation section for a subsequent recovery of the high-value minerals present or to produce freshwater.

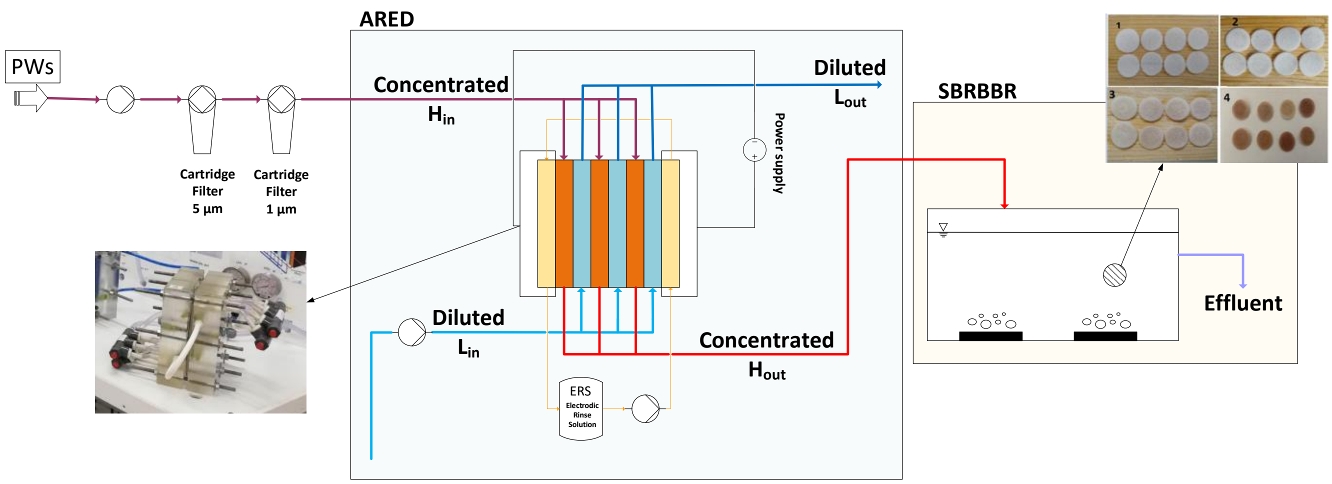

Figure 1. Scheme of the proposed treatment chain.

Methodology

The experimental tests were performed with real PW solutions by coupling the two units described in the previous section. PWs feed was firstly filtered in 2 cartridge filters in series (5 and 1 µm) to avoid clogging phenomena. The ARED unit has a 10x10 cm^2 active area constituted by 10 cell pairs, assembled with Fujifilm membranes Type 10 and separated by 300 µm woven spacers. PW presented a conductivity of 95 mS cm^{-1} and is recirculated in the stack to reduce its concentration to 20 g L^{-1}. Recirculation is necessary due to the use of a laboratory unit that is not able to lead to the target concentration in a single pass. The diluted solution was also recirculated in a separated tank. Each load

of PW had a volume of approximately 4 L, while the diluted solution had a volume of 50 L and a test lasted approximately 24 hours. The treated PW was then collected in a buffer reservoir and transferred to the biological reactor once the previous cycle was completed. The bioreactor (capacity of 20 L) started to operate without an active sludge inoculum to allow the development of autochthonous halophilic biomass present in the PWs on the carriers. The carriers used were the Mutag BioChipsal type (surface area of 5,500 m^2/m^3). The total volume of carriers used was 5 L, corresponding to approximately 5000 carriers. The reactor was equipped with a blower connected to two porous stone diffusers for air supply (flow rate of 5 L min^{-1}) and two peristaltic pumps for the PW feeding and effluent discharging. All the equipment were connected to a PLC for cycle phase management.
The biological reactor operated in continuous mode, by alternating cycles with a duration of 6 hour. The volumetric exchange ratio was set to 5 % to avoid organic overloading. Consequently, the treatment capacity of the plant was 4 L day^{-1}. Each cycle was divided into the following phases: a feeding phase lasting 1 hour; a reaction phase lasting 3 hours; a settling phase lasting 2 hours; and a discharge phase lasting 30 minutes. Biological performances were evaluated by measuring the total organic carbon (TOC) and total petroleum hydrocarbons (TPH) removal efficiencies. TOC was measured in surface water samples at the inlet and outlet of the ARED and the biological reactor using a Shimadzu TOC-V analyser. Additionally, total petroleum hydrocarbons (TPH) were also measured in samples taken upstream and downstream the units. Specifically, liquid/liquid extraction with hexane was performed, followed by measurement of C10-C40 hydrocarbons using a GC-FID (Gas Chromatography-Flame Ionization Detector).

Results and Discussions

Conductivity, TOC and TPH were monitored for each 4 L-charge of PW. The trend for one cycle of treatment is described in **Figure 2**, where it is possible to observe the inlet and the outlet values in each unit. The PW entered in the ARED unit with a conductivity of about 95 mS cm^{-1}, showing some variability, and after 24 hours of treatment, the outlet conductivity was always lower than 33 mS cm^{-1}, corresponding to a salinity concentration of 20 g L^{-1}. As stated before, this value was considered tolerable for the biomass and favourable for its growth. Inside the ARED unit the TOC concentration remained constant at the initial value of about 95 mg L^{-1}, meanwhile the TPH concentration decreased by about 15 % (value at the inlet of the integrated system was 34 mg L^{-1} on average), probably due to the adhesion of hydrocarbons on the ARED components due to continuous recirculation of PW. The total applied energy for the salinity reduction until the goal conductivity was of about 7.4 Wh (i.e., 1.84 kWh m^{-3}). The PW, then, enters the SBMBBR for the biological treatment where an abatement of 80% was achieved (from 95 to 19 mg L^{-1}). This good result allows to consider the SBMBBR as a system capable of producing a consistently high-quality effluent even with varying organic load inputs, demonstrating excellent resilience to load fluctuations. This was likely due to both the low volumetric exchange ratio applied in the reactor and the predominant presence of attached biomass, which is more effective at withstanding load fluctuations compared to suspended biomass. As further evidence of the efficiency of the bioreactor, the gradual development of the biofilm on the carriers is shown in **Figure *1***. Overall, the bacterial mass per unit surface area was 38.17 g m^{-2}, after approximately 180 days from the start-up of the plant, indicating good development of the autochthonous halophilic biomass in the system. Additionally, the attached biomass exhibited a good biological activity measured as the consumption rate of dissolved oxygen, which averaged about 5 mgO_2 $L^{-1}\cdot h^{-1}$. In contrast, the concentration of suspended biomass was quite modest, averaging around 400-500 mgTSS L^{-1}. In the biological unit, the TPH concentration was reduced to an average of 18 mg L^{-1}, contributing to an additional reduction of about 30 %. Overall, the integrated system could remove about 35-40 % of the TPH present in the produced water.

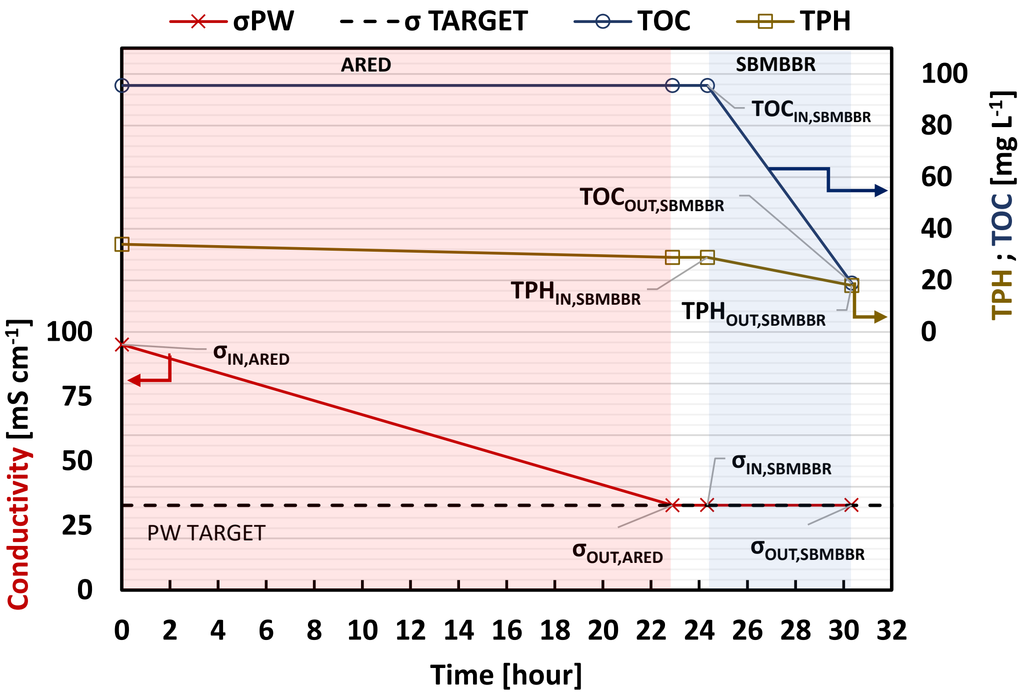

Figure 2. a) Conductivity (σ), Total Organic Carbon (TOC) and Total Petroleum Hydrocarbons (TPH) trends of a single PW load (4 L) in the A-RED unit and the SBMBBR reactor.

Conclusions

A novel treatment chain was developed and tested with real PW. The need for a preliminary desalination was effectively addressed using an ARED unit, able to reduce the salinity down to the concentration target of 20 g L^{-1}, established as a minimum requirement for the bacteria growth. The SBMBBR was identified as one of the most promising biological treatment for dealing with PWs, for which a TOC reduction of 80 % was observed. At the same time, also a reduction up to the 40 % of the TPH concentration was detected. These preliminary results on the coupling of ARED with SBMBRR show that the integrated proposed treatment is effective and efficient and a promising option for the future.

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