

## Desalination and Treatment of Oilfield Produced Waters

Giovanni Campisi, Alice Sorrenti, Paulo B. Mofatto, Alessandro Cosenza, Serena Randazzo\*, Santo F. Corsino, Marco Capodici, Michele Torregrossa, Alessandro Tamburini, Giorgio Micale

Dipartimento di Ingegneria, Università degli Studi di Palermo (UNIPA), Palermo, Italy, Viale delle Scienze Ed.6. 90128.  
 Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Firenze, Italy, Via Giusti 9, 50121  
[serena.randazzo@unipa.it](mailto:serena.randazzo@unipa.it)

Produced water is a salty and organic-polluted byproduct drilled out during the oil extraction. An annual production of 11.2 million of m<sup>3</sup> is estimated, based on the production of at least 3 barrels of PW for every barrel of oil extracted. The composition changes according to the well characteristics and to the addition of chemicals during the extraction process. Generally, a high salinity (up to 300 g L<sup>-1</sup>), due to the contact with subsurface rocks, is observed together with a large amount of dissolved hydrocarbon compound contaminants. Thus, their treatment could be designed on case-by-case basis through tailored studies and experimental investigations as it is not possible to standardize the characteristics of PW.

In this work, an innovative PWs treatment scheme is proposed where an Assisted Reverse Electrodialysis (ARED) unit and a Sequencing Batch Moving Bed Biofilm Reactor (SBMBBR) were coupled: ARED is used to reduce the PWs salinity to values lower than 20 g L<sup>-1</sup> of NaCl to let the stream compatible with the downstream biologic treatment, where the organic content is reduced ensuring compliance with legislative disposal limits. The desalination was performed under current-control mode and the ARED required less than 2 kWh·m<sup>-3</sup>PW for reaching the target outlet concentration. The organic content in SBMBBR successfully decreased, showing a Total Organic Carbon (TOC) abatement of about 80%.

### 1. Introduction

During the operation of extraction of oil, due to the depth of the reservoir, the fluid pressure of the oil certainly helps the drilling techniques. However, over time this pressure difference decreases, and water is used to enhance the oil recovery, according to the so-called waterflooding method. As a result, downstream separation processes are necessary to separate the water from the organic component.

The water, referred to as produced water (PW), is characterised by high salinity, due to the contact with subsurface rocks and by the presence of hydrocarbon compound contaminants (Jiménez et al., 2018). Overall, PWs present a complex and variable composition depending on oil maturity, extraction methods, well depth and site morphology (Ji et al., 2024). Considering all these variables, PWs do not show specific characteristics, i.e. they do not have all the same composition, and thus, it is not possible to standardise the procedure for the treatment of PWs. Indeed, their treatment could be defined for each specific case, depending on the composition of the PW, carrying out ad-hoc studies and experimental investigations.

Moreover, large volumes of PWs are produced. Al-Ghouti et al. report an annual generation of 11.2 million of m<sup>3</sup> of PW, specifying that the production could increase with the well age, generating at least 3 barrels of PWs for every barrel of oil produced (Al-Ghouti et al., 2019).

The management of PWs usually consists of re-injection into the well. Environmental awareness has increased in recent years, and also the legislative attention to environment protection, thus this current procedure might not be longer possible. It is required to treat PWs appropriately, with the aim of leading to (i) the Minimum Liquid Discharge (MLD) target and to (ii) the reuse for potable or irrigation purpose (Duarte Cesar et al., 2024).

Typically, five main process categories are employed to treat PWs: membrane technologies, biological treatment processes, electro-chemical coagulation, physical/chemical treatment processes and chemical catalytic oxidation. They are often implemented in sequence and/or in combination and the overall efficiency of each

treatment system depends on the type of contaminants to be removed and their concentration oxidants (Mansour et al., 2024). However, using of efficient and innovative treatment chains could be crucial for the effective treatment of PWs. Indeed, the scientific community shows even more interest and efforts to propose new technologies and treatment chains capable of handling PWs. As an example, Wenzlick and Siefert proposed to recover valuable products such as ten-pound brine and fresh water from PWs by using nanofiltration (NF) and reverse osmosis (RO) (Wenzlick and Siefert, 2020); while others focused on integrating oxidation and membrane processes, specifically advanced oxidation methods by using ozone, chlorine or Fenton based oxidants (Ji et al., 2024).

Although physical and chemical treatments are the most efficient, they are also the most expensive. Conversely, biological treatments are among the most cost-effect and efficient technologies to deal with wastewaters. However, the biological remediation, usually used or the treatment of urban wastewaters, shows the main limit of the high salinity, i.e., PWs high salinity is detrimental for conventional bio-remediation treatment processes (Nie et al., 2009) and a maximum value could be not exceeded. In addition, direct dilution of wastewater is not allowed as regulated by D.Lgs 152/06 (Italian law).

In the present work, an innovative treatment chain is proposed for the treatment of PWs by coupling two main technologies: (i) the Assisted Reverse Electrodialysis (ARED), already described in other papers of some of co-authors (Campisi et al., 2023) and tested not only in the field of PWs treatment but also for brine valorization (Filingeri et al., 2024) and hydrogen production (Pellegrino et al., 2024); (ii) the biological treatment, by using a Sequencing Batch Moving Bed Biofilm Reactor (SBMBBR), already tested by some of co-authors for saline wastewaters containing hydrocarbons (Campo et al., 2016), which combines the advantages of attached growth, suspended growth and SBR systems, to provide high tolerance to shock loads and recalcitrant compounds degradation.

The ARED process was selected as the low-cost pre-treatment for the salinity reduction, necessary for the subsequent biological step. These technologies were tested and the results are here presented.

## 2. Treatment chain

The innovative treatment chain proposed in this work consisted of two main apparatuses: the ARED and the SBMBBR. The scheme is reported in Figure 1.

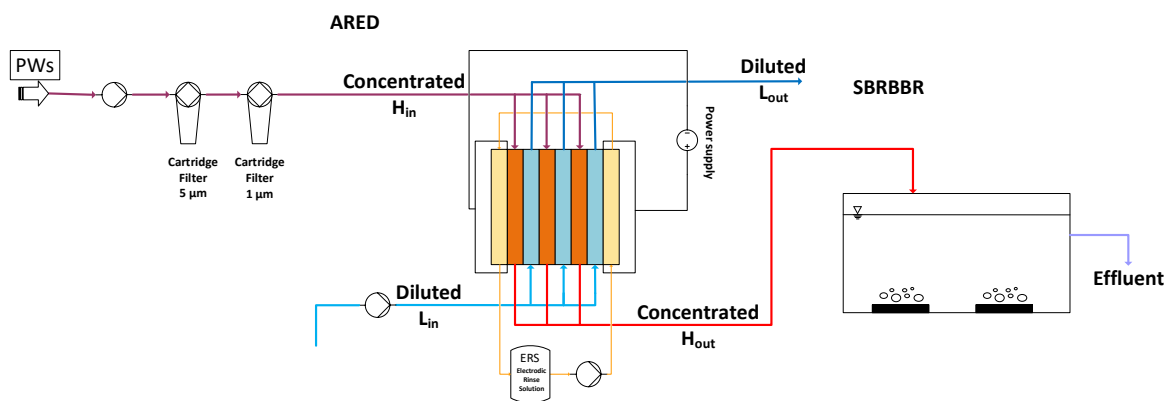


Figure 1: Scheme of the proposed treatment chain

PWs are fed to a filtration system constituted of 2 cartridge filters in series (5 and 1  $\mu\text{m}$ ) to avoid clogging phenomena. Then, they enter 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). Between the membranes, the spacers were placed to create the channels. Here, a concentrated solution (H) and a low-concentrated solution (L) are alternately fed. Electrode compartments, where an Electrode Rinse Solution (ERS) continuously circulates are positioned at both ends of the stack. In these compartments, ERS contains redox couples ( $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) allowing the conversion of electric current into ionic current. After the dilution up to an equivalent NaCl concentration target of  $20 \text{ g L}^{-1}$  the PWs are sent to the biological section (see Figure 1). It consisted of a biological reactor with Integrated Fixed Film Activated Sludge (IFAS) technology operating in a batch cycle, named SBMBBR (Sequencing Batch Moving

Bed Biofilm Reactor). The purpose is to reduce the organic content of PWs and make them respectful of the legislative limit for disposal.

### 3. Experimentals

The experimental tests were performed with real PW solutions with an initial conductivity of  $95 \text{ mS cm}^{-1}$ , corresponding to a concentration of  $66 \text{ g L}^{-1}$  of NaCl, assuming that the salinity of PW is mainly due to the presence of this salt.

The ARED unit had a  $10 \times 10 \text{ cm}^2$  active area constituted by 10 cell pairs, assembled with Fujifilm membranes Type 10 and separated by  $300 \text{ }\mu\text{m}$  woven spacers. Once completed the assembling, the unit was closed, tested and then opened after several and several cycles. Then, membranes were disposed as solid waste.

The solution was recirculated in the stack to achieve the result of salinity reduction to a NaCl concentration of  $20 \text{ g L}^{-1}$  (corresponding to a conductivity of  $33 \text{ mS cm}^{-1}$ ) Each load of PW had a volume of approximately 4 L. The diluted solution was also recirculated in a separated tank and it had a volume of 50 L. The test lasted approximately 24 h. The treated PW was then collected in a buffer reservoir and transferred to the biological reactor once the previous cycle was completed.

The bioreactor had a capacity of 20 L and 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  $5,500 \text{ m}^2/\text{m}^3$ ) with a total volume of 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  $5 \text{ L min}^{-1}$ ) to allow the aeration, as represented in Figure 2 and two peristaltic pumps for the PW feeding and effluent discharging. All the equipment were connected to a PLC for cycle phase management.

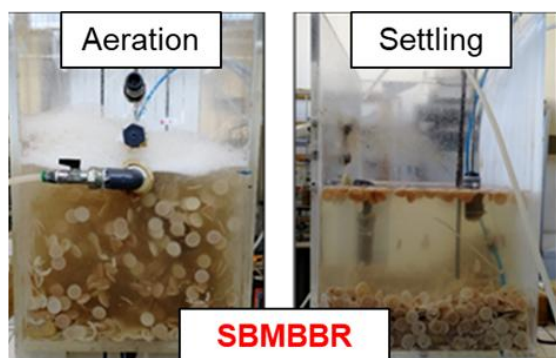


Figure 2: Steps of aeration and subsequent settling during the operation of the SBMBBR

The biological reactor SBMBBR operated in continuous mode, by alternating cycles with a duration of 6 h. The volumetric exchange ratio was set to 5 % to avoid organic overloading. Consequently, the treatment capacity of the plant was  $4 \text{ L day}^{-1}$ . Each cycle was divided into the following phases: a feeding phase lasting 1 h; a reaction phase lasting 3 h (see Figure 2a); a settling phase lasting 2 h (see Figure 2b); and a discharge phase lasting 30 min.

Biological performances were evaluated by measuring the total organic carbon (TOC) and total petroleum hydrocarbons (TPH) removal efficiencies. Thus, samples were withdrawn from surface water at the inlet and outlet of the ARED and of the biological reactor and TOC and TPH were measured.

TOC was evaluated by using a Shimadzu TOC-V analyser. Before, samples were filtered by using membranes with a pore diameter of  $0.45 \text{ }\mu\text{m}$ .

TPH was detected by using a GC-FID (Gas Chromatography-Flame Ionization Detector) equipped with a HP-5 capillary column ( $30 \text{ m} \times 0.320 \text{ mm} \times 0.25 \text{ }\mu\text{m}$ ) and a FID detector. An alkane analytical standard mixture, C10 - C40 (all even),  $50 \text{ mg L}^{-1}$  each, from Sigma Aldrich, was used for performance tests of GC-systems and to prepare the calibration curve in the range of 4-200 ppm of the standard in hexane. Before the analysis, samples were prepared by performing a liquid/liquid extraction with a solution of 20 ppm of n-decane ( $\text{C}_{10}\text{H}_{22}$ ) e 20 ppm of n-tetracontane ( $\text{C}_{40}\text{H}_{82}$ ) in hexane. Then, samples were anhydriified by using  $\text{Na}_2\text{SO}_4$  and subsequently purified by using Supelclean™ ENVI-Florisil tubes of 500 mg.

At the end, TPH was calculated by evaluating the total area included between the end of the peak of n-decane ( $\text{C}_{10}\text{H}_{22}$ ) and the beginning of the peak of the n-tetracontane ( $\text{C}_{40}\text{H}_{82}$ ).

#### 4. Results and Discussion

The main parameters evaluated for each 4 L-charge of PW at both units of ARED and SBMBBR were the conductivity, TOC and TPH. The trend for one treatment cycle is described in Figure 3, where it is possible to observe the values of these parameters at the inlet and the outlet of each unit (highlighted red for ARED and blue for SBMBBR). As stated before, the PW entered in the ARED unit with a conductivity of about  $95 \text{ mS cm}^{-1}$ , and after 24 h of treatment, the outlet conductivity was always lower than  $33 \text{ mS cm}^{-1}$ , corresponding to a salinity concentration lower than  $20 \text{ g L}^{-1}$  (see Figure 3a). The total applied energy for the salinity reduction in the ARED unit until the goal conductivity was of about  $7.4 \text{ Wh}$  (i.e.,  $1.84 \text{ kWh m}^{-3}$ ). Conversely, the conductivity in the SBMBBR remains constant at the value from the outlet ARED.

Along the ARED unit the TOC concentration remained constant at the initial value of about  $95 \text{ mg L}^{-1}$  and when the PW enters the SBMBBR for the biological treatment, a TOC abatement of 80% was achieved (from 95 to  $19 \text{ mg L}^{-1}$ ) (see Figure 3b). 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.

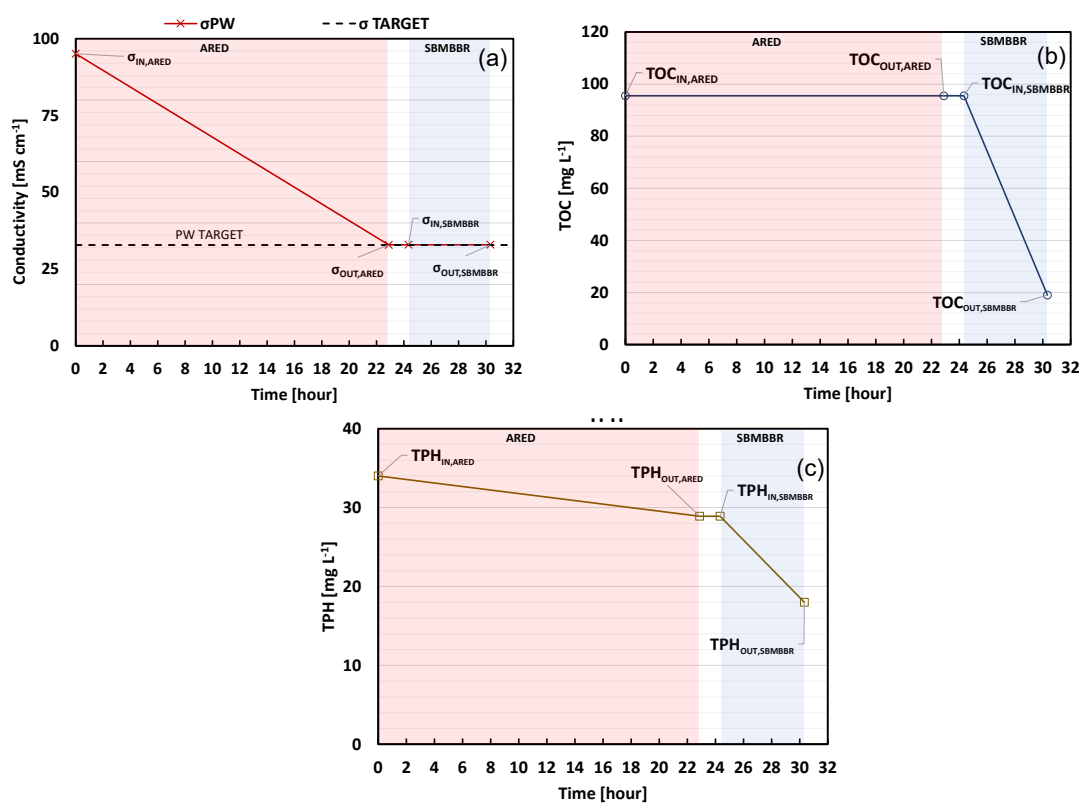


Figure 3: Conductivity ( $\sigma$ ) (a), Total Organic Carbon (TOC) (b) and Total Petroleum Hydrocarbons (TPH) (c) trends of a single PW load (4 L) in the A-RED unit and the SBMBBR reactor.

For what concern the TPH concentration, in Figure 3c is shown a slight decreased by about 15 %, as the initial value at the inlet of the integrated system was  $34 \text{ mg L}^{-1}$  and it was reduced to an average value of  $29 \text{ mg L}^{-1}$ ). This fact can be ascribed to the adhesion of hydrocarbons on the ARED components due to continuous recirculation of PW, considering that no reduction of organics can be taken in account in this unit. On the other hand, in the biological unit, the TPH concentration was reduced to an average of  $18 \text{ mg L}^{-1}$ , which corresponds to an abatement 30 %. This result, in addition to the reduction in the ARED, leads to a total TPH decrease of about 45 %. As an example, in Figure 4 is reported a representation of the peaks relieved from the chromatogram obtained for the evaluation of TPH at the inlet and outlet of the SBMBBR. It is possible to observe that hydrocarbons from C14 to C18 seem to be more susceptible to the treatment as their concentration dramatically decrease. On the contrary, heavier compounds show the same value after the treatment demonstrating a poor effectiveness of the biological process for them. As further evidence of the efficiency of the bioreactor, the gradual development of the biofilm on the carriers is shown in Figure 5.

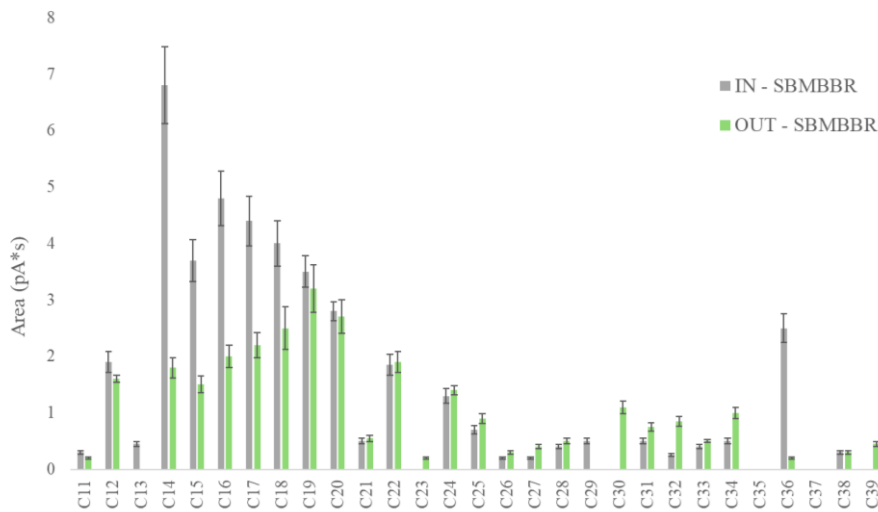


Figure 4: Representation of the peaks relieved from a chromatogram including C11-C39 hydrocarbons

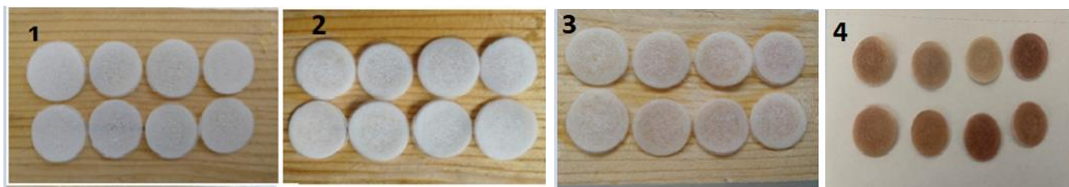


Figure 5: MutagBioChips carriers modification in the time: 1) new carriers at t=0, 2) at 37<sup>th</sup> day, 3) at 100<sup>th</sup> day and at 4) 184<sup>th</sup> day

Overall, the bacterial mass per unit surface area was 38.17 g m<sup>-2</sup>, 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<sub>2</sub> L<sup>-1</sup>.h<sup>-1</sup>. In contrast, the concentration of suspended biomass was quite modest, averaging around 400-500 mgTSS L<sup>-1</sup>.

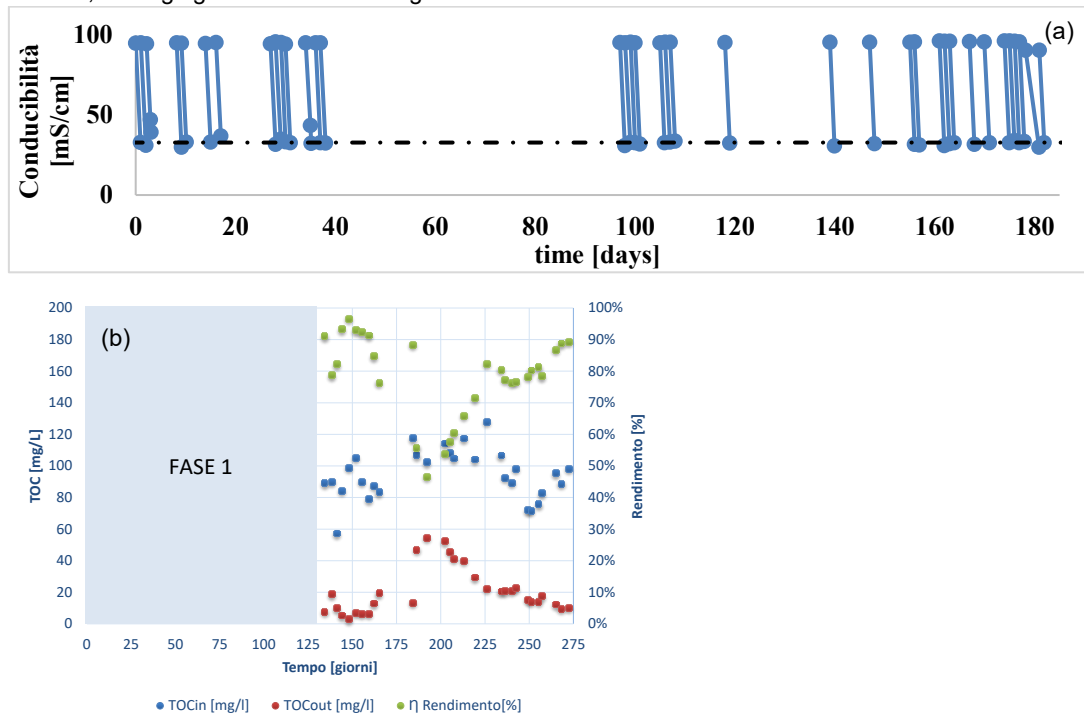


Figure 6: Stability of the operating units: ARED (a) and SBMBBR (b)

Several tests were performed and the main parameters were monitored to assess the stability of the operating units. In particular, ARED was tested for 180 days and, as shown in Figure 6a, the result of salinity reduction to  $20 \text{ g L}^{-1}$  was almost always reached in 24 h.

For what concerns the biological step, the SBMBR operated for more than 275 days, maintaining an average performance related to a TOC abatement of 70 % (see Figure 6b).

## 5. Conclusions

A novel treatment chain was developed and tested with real PWs, by coupling ARED and biological treatment. Due to the requirement of low salinity for biological remediation, a preliminary desalination of the stream is necessary and this role was effectively addressed using an ARED unit. Indeed, it was able to reduce the salinity down to the concentration target of  $20 \text{ g L}^{-1}$ , established as a minimum requirement for the bacteria growth in the next step.

For what concerns the biological step, the use of a SBMBR 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. The biological system stably operated for more than 275 days, maintaining an average performance related to a TOC abatement of 70 %.

These preliminary results on the coupling of ARED with SBMBRR show that the integrated proposed treatment is effective and efficient and it could be a promising option for the future. More specifically, the ARED could represent an appealing way to economically manage this kind of wastewaters.

Of notes, even if the outgoing effluent is currently proposed to be disposed, in the view of a circular economy approach, an additional valorisation section was proposed by some of co-authors elsewhere for a subsequent recovery of the high-value minerals present in the PWs, while for the diluted stream it was proposed a recirculation to the ARED unit after regeneration by RO (Campisi et al., 2023).

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