Salinity Reduction of Real Produced Waters via Assisted Reverse Electrodialysis

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Produced waters (PWs) are waste streams generated during the crude oil extraction processes. The management of these wastewaters is complicated by the large volumes extracted during the oil recovery operations: these depends on the life of the oil-well: typically, 3 barrels of PWs on average are produced for each barrel of oil extracted. After oil separation, PWs are usually re-injected into the well, but this approach is not always possible without a preliminary and suitable treatment. Bioremediation techniques might be a good option, but they fail due to the PWs high salinity, which inhibit bacteria growth and metabolism. Thus, reducing their salinity upstream a bioremediation unit is a matter of crucial importance. To this aim, Assisted Reverse electrodialysis (ARED) along with the use of a dilute stream typically available on site is here proposed as a novel solution. In ARED an additional voltage is applied in the same direction of the salinity gradient through the membranes in order to enhance the passage of ions from the PW to the diluted solution, thus significantly reducing the required membrane area. An experimental campaign was carried out in order to assess the process feasibility. A fixed volume of real PWs was fed to a laboratory scale ARED unit. Each experimental test lasted for three days to reduce the salinity down to about 20 g l^{-1}, a value compatible with the biomass metabolism for a downstream bioremediation step. Two different types of commercial membranes were tested and relevant energy consumptions were calculated. The long-runs performed did not show a significant loss of efficiency due to fouling, thus suggesting that ARED might a suitable technology for a pre-dilution of produced waters.

1. Introduction

The main oil-drilling techniques exploit the fluid pressure due to the depth of the reservoir, which can vary from hundreds of metres to several kilometres. Due to the high pressures, the crude also drags water with it. This is why separation processes are downstream carried out to separate the organic part from water (Pereira et al., 2019). These waters are generally (i) rich in salt for their prolonged contact with the underground rocks, and (ii) polluted by hydrocarbon compounds (Jiménez et al., 2018). Generally, they are called Produced Waters (PWs) and have complex and variable compositions depending on the morphology of the site, the maturity of the oil, the method used for extraction, the depth of the well and the separation and oil production processes (Nasiri and Jafari, 2016). Due to all these variables, it is not possible to standardise PW features, rather, these have to be defined on a case-by-case basis with ad hoc studies, based on the source and process involved.

The largest PWs daily production volumes (60%) are those related to crude oil extraction (Igunnu and Chen, 2014), for which there are medium production volumes when the plant is at the beginning of its life. Such volumes increase with the well age: typically, it is estimated that for each oil barrel, 3 barrels of PWs come out on average (Al-Ghouti et al., 2019). Unfortunately, often these wastewaters are discharged into the ocean: in 2003 almost 800 million of m^3 of PWs were discharged around the world by offshore sites (Neff et al., 2011) and in 2017 only in the OSPAR area there was a discharge of 4000 tons of PWs (Beyer et al. 2020). In on-shore plants, PWs are typically re-injected into the extraction well after a rough hydrocarbon separation, because their treatment is too expensive.

Attention on environmental issues has been increasing in the last years, thus attracting the interest and the efforts of the scientific community towards the proposal of new technologies and treatment chains able to deal with PWs. According to the circular economy principles, if safety and health requirements are complied with, the treatment of effluents could be a reasonable chance for the reuse of water in arid areas for irrigation purposes, drinking water for livestock, etc. (Ruiz-Aguirre et al., 2021). Three main process categories are typically adopted in order to treat PWs: the physical treatment (e.g. evaporation, filtration), chemical processes (e.g. oxidants, electrochemistry), and biological remediation (Liu et al., 2021). Physical and chemical treatments are the most efficient methods, but they are also the most expensive. Conversely, biological treatments might be intrinsically cheaper but hindered by the high salinity of the PWs. With this respect, pre-dilution of PWs is a crucial point for the development of treatment chains based on bioremediation techniques (Lay et al., 2010). Reverse Electrodialysis (RED) and Assisted Reverse Electrodialysis (ARED) may guarantee a suitable PWs dilution via the transfer of its ions towards dilute process-waters available on site.

A RED (or ARED) stack is constituted by two plates where the electrodes are allocated, and by a repetition of ionic exchange membranes (IEMs) between them. The repetition of one cationic and one anionic exchange membrane (respectively CEM and AEM), separated by two spacer-filled channels constitutes the cell pair, i.e. the repetitive unit of the stack (Tian et al., 2020). Two different salty solutions are fed into the unit, one rich in salts (H, high salt concentration) and one with a minor content (L, low salt concentration). The presence of the IEMs allows a controlled migration of ions according to the salinity gradient: ionic fluxes in the stack and electrical current in the external circuit are linked via suitable red-ox reactions occurring in the electrodic compartments. In RED, electric energy is generated by the salinity gradient and a resistor (i.e. a load) is inserted into the electrical circuit to simulate an external user (Veerman and Vermaas, 2016). In ARED, electrical energy is consumed in order to enhance the ion migration (also in this case according to the salinity gradient direction) and therefore a power supply is needed. ARED has been firstly proposed in literature as a novel technique to decrease the energetic demand of a reverse osmosis (RO) unit for seawater desalination (Vanoppen et al., 2018). Recently, it has been proposed as post-treatment methods for RO in order to re-mineralize its permeate (Filingeri et al., 2022; Philibert et al., 2022).

Cosenza et al. (2022) have already shown the feasibility of dealing with PWs in a RED unit. ARED has also been found to be an option more economically convenient than a corresponding RED unit with a cost of 1.32 € per m^3 of PWs treated (Campisi et al., 2023). The latter was demonstrated via a techno-economic model, but no experimental tests have been carried out with real PWs so far. In this work, an experimental investigation with a laboratory-scale ARED unit is presented here to desalinate real PWs for the first time. The tests were performed with two different type of membranes and a long-run lasting more than 72 hours was performed. The aim of this work is to show the behaviour of an ARED unit dealing with real PWs in order to evaluate the performance of the system and its efficiency. The desalination of PWs has been carried out down to the concentration of 20 g l^{-1}, corresponding to a salinity value compatible with downstream biological treatments (Lay, Liu, and Fane 2010; Mannina et al. 2016).

2. Materials and methods

2.1 Stack features and feed solutions

The lab-scale stack of reverse electrodialysis 0.1 x 0.1 m^2 was assembled with 10 cell pairs (N_{cp}). Channels were provided with woven spacers with a thickness of 270 µm (Redstack, Sneek, The Netherlands). Solution velocity in the channels was set at 0.5 cm s^{-1} corresponding to a total volumetric flow rate of 81 ml min^{-1}. The tests were carried out with two different membranes:

- Fujifilm Type 10 AEM and Fujifilm Type 10 CEM (Fujifilm Manufacturing Europe, Tilburg, The Netherlands);
- Fumasep FAS-50 AEM and Fumasep FKS-50 CEM (Fumatech, Bietigheim-Bissingen, Germany).

The cell package is assembled with an additional cationic membrane (known as end membrane) that is used to separate the electrode from the feed: a FKS-50 CEM was used for both cases.

Concerning the feed, the concentrated solution employed is a real PW extracted from an oil industrial well located in southern Europe. The composition and main features of this wastewater are reported in Table 1 and in Table 2.

All tests were performed by considering as low-concentration (L) feed solution, a synthetic solution of pure NaCl, with a concentration of 0.7 g l^{-1} and a conductivity of 1.49 mS cm^{-1}. This concentration value was selected to mimic the typical concentration of process-water often available in the relevant oil extraction industries. Recrystallized NaCl solid from Volterra (Italy) with a purity of 99.8% and demineralized water with a conductivity lower than 10 µS cm^{-1} were used to prepare the artificial solutions.

$K_3Fe(CN)_6/K_4Fe(CN)_6\cdot 3H_2O$ (0.1 M) was adopted as electrode rinse solution. NaCl was added (concentration of 0.6 M) as a supporting electrolyte in order to reduce the osmotic fluxes with the adjacent channels. Two DSA were employed as electrodes.

Table 1 Composition of main ions in PWs.

Ions	[ppm]	error
Na^+	21,940.75	± 39.00
K^+	1,178.00	± 3.75
Ca^{2+}	4,195.00	± 20.25
Mg^{2+}	613.75	± 2.25
Cl^-	38,205.00	±648.50
SO_4^{2-}	212.75	± 4.25

Table 2 Main properties of PWs.

Properties		
pH	7.15	-
Total Organic Carbon (TOC)	368.00±3.60	mg l^{-1}
Conductivity	104.20	mS cm^{-1}
Equivalent NaCl concentration	74.20	g l^{-1}

2.2 RED/ARED fundamentals, performance parameters and experimental details

Polarization and power curves are the typical graphs concerning the evaluation of a RED or an ARED unit. A qualitative representation of them is provided in Figure 1. When no current is flowing into the system, the voltage measured by the instrument is the maximum one and corresponds to the open circuit voltage condition (E_{OCV}). When the external circuit is closed (i.e. an external load is connected) and ions start moving naturally from the concentrate to the dilute (RED), the current starts to flow (I_{EXT}) and the electric voltage (E_{STACK}) decreases. When the external load resistance is somehow equal to the internal resistance of the unit (R_{STACK}), the power curve exhibits a maximum (P_{MAX}). Finally, when the salinity gradient energy is totally dissipated by the internal stack resistance, no power is produced by the system notwithstanding the ionic current in the stack is the maximum allowed in RED conditions (i.e. short-circuit current, I_{SC}). In order to have a current higher than I_{SC} in the stack (ARED conditions), a power supply (instead of a load) is needed in the external circuit and energy has to be spent as a consequence. Clearly, the higher the electrical current flowing, the quicker the PW dilution. ARED experiments were carried out in the present work.
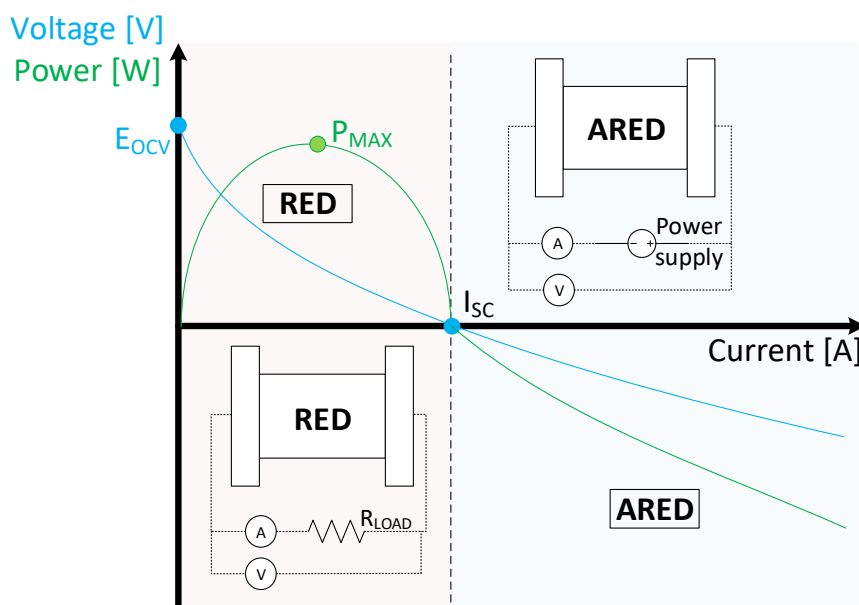

Figure 1 Qualitative trend of polarization curve (in blue) and power curve (in green) versus the current flowing in the system. Schematic representations of the external circuit in the RED or ARED configuration.

In order to evaluate the performance of the unit, it is important to know the power drawn by the system. The gross power density PD collected during the experiments is defined as follows:

$$PD = \frac{E_{STACK} \cdot I_{EXT}}{N_{cp} \cdot A_m}$$

(1)

where N_{cp} is the number of cell pairs and A_m is the active membrane area.

Power is measured during ARED experiments to monitor the energy requirements of the process. More precisely, the specific energy consumption needed to desalinate one cubic meter of PW down to 20 g l⁻¹ was calculated. In formula:

$$SEC = \frac{1}{V_{PW}} \int_{t=0}^{t_d} E_{stack} \cdot I_{EXT} \, dt \tag{2}$$

where V_{PW} is the volume of PW treated during the time t_d needed to achieve the target dilution concentration (i.e. 20 g l⁻¹). Furthermore, spot measurements of current, voltage, conductivity and pressure drop were collected during the long-run tests. Recording the pressure drops (ΔP_H) in the spacer-filled channels during the long-run is important to assess the impact of fouling on the performance. The tests involved the use of auxiliary equipment, such as pumps for the fluid handling, cartridge filters (5 µm) to remove suspended solids and UV lamps to prevent bacterial growth in the diluted tank. The treated volume for both tests was 25 l, and the concentrated solution was put in recirculation-mode for the dilution purpose. A feed and bleed system was adopted for the dilute solution in order to guarantee a constant inlet concentration of 0.7 g l⁻¹. To this aim, the tank hosting the dilute solution was filled daily with demineralised water and the stoichiometric amount of a more concentrated NaCl solution. In order to carry out the test, a power supply provided a current of 0.92 A to the system: it corresponds to three times the short-circuit current (I_{SC}) of the stack equipped with Fumasep membranes. For the sake of comparison, the same current was also applied for the test with Fujifilm membranes. Both tests lasted for about 3 days, a time compatible to both the operating conditions (boosted by the power supply) and the small PW volume to be processed. Clearly, desalination via ARED at industrial scale is expected to be operated in once through mode without any recirculation.

3. Results

During the long-run ARED test, different variables were monitored over time. Results are reported in Figure 2.
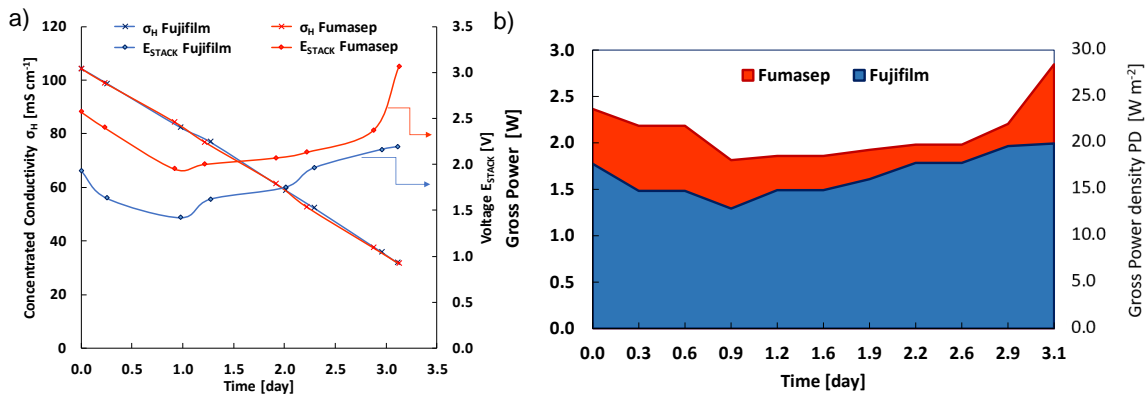

Figure 2 a) Conductivity of the PW and voltage applied by the power supply versus time. b) Corresponding power and power density consumed during the ARED test. The blue curves referred to the Fujifilm membrane set-up and the red ones to the Fumasep membrane set-up.

Figure 2.a shows the time variation of the conductivity σ_H of the PW for the two different membrane set-ups. This information is used to evaluate the reduction of the PW concentration during the experiment. As it can be seen, the trend is almost linear with time due to the fixed current apply to the stack, determining an average dilution velocity of about 0.97 mS cm⁻¹ per hour. On the second vertical axis of Figure 2.a, the potential difference the power supply has to provide to keep the current constant is shown. During the first day, the stack voltage decreases notwithstanding the electrical resistance of the concentrated solution is increasing. This is counterintuitive and is due to the conditioning of the ionic exchange membranes with the real PWs: at the beginning of the test (i.e. first days) they exhibit an electrical resistance decreasing over time. In fact, the stack resistance falls from 5.75 to 4.64 Ω for the Fujifilm between the first 30 hours and from 6.89 to 6.18 Ω for the Fumasep. After 1-1.5 days the stack voltage starts increasing as expected to guarantee the external current to be constant while the electrical resistance of the concentrate stream is increasing. The tests were stopped on day 3 when the target conductivity of 32.8 mS cm⁻¹ (corresponding to a salinity of 20 g l⁻¹) was reached. Figure 2.b shows the corresponding gross power consumed by the ARED unit: being the current constant, of course, the trend mimics the voltage one reported in Figure 2.a. More important, Figure 2.b indicates that the ARED unit equipped with the Fumasep membranes is more energy demanding than the Fujifilm membranes one. With

reference to Figure 2.b, the SEC to desalinate 1 m^3 of treated PWs was found equal to 4.8 kWh m^{-3} for the Fujifilm unit and 6.1 kWh m^{-3} for the Fumasep one. These energy consumptions are needed only to desalinate the PW streams and represent a portion of the energy required by a PW overall treatment plant. On the other hand, these are lower than the typical sea-water desalination consumptions currently adopted (e.g. 40-50 kWh m^{-3} for Multi-Effect Distillation (Tamburini et al., 2017) or 2.9-4.2 kWh m^{-3} for Reverse Osmosis (Igunnu and Chen 2014)). As consequence the energy for more concentrated brines as the PW is expected to be higher. Figure 3 reports the pressure losses recorded during the long-run in the concentrate (Figure 3.a) and in the dilute channel (Figure 3.b).
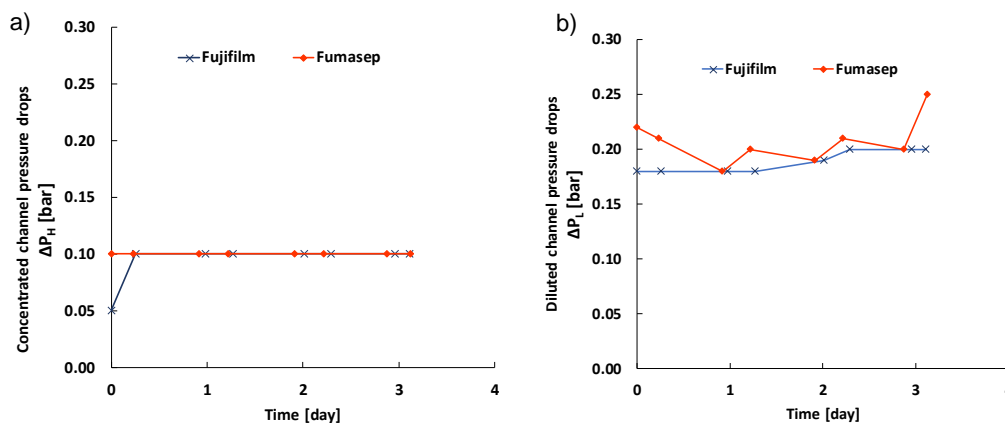

Figure 3 Pressure drops a) in the concentrate and b) in the dilute channel as a function of time.

As it can be observed, during the tests there was no significant change in the pressure drops, which remained approximately constant at a value of 0.2 bar for the dilute solution channel and 0.1 bar for the concentrate channel. Pressure drops are a bit larger in the dilute channel notwithstanding PW are fed to the concentrate channel. This is not surprising because bio-fouling is expected to be inhibited or at least hindered at high salinity conditions. It is an important piece of information because it suggests that fouling might not be an issue. Of course, several and longer tests have to be carried out in order to evaluate whether fouling may have an impact on the process performance.

Conclusions

Nowadays, PWs are attracting an increasing interest in the academic and industrial world due to their disposal issues. Among the treatment methods, biological processes are the most interesting and economically viable, but the high salinity of PWs has to be significantly reduced in order to allow their use. RED and ARED have been proposed as desalination step for these waters. In this work the behavior of an ARED unit operated with real PWs was studied. PWs were diluted to a salinity of 20 g l^{-1}, a value that makes a downstream biological step feasible and effective. To this purpose, a laboratory ARED stack was used and, for the first time, two long-runs were carried out to test two different membranes. PWs were recirculated and the long-runs lasted approximately 3 continuous days. The results show that, at a fixed current of 0.92 A, a specific energy consumption of 4.8 and 6.1 kWh m^{-3} for Fujifilm and Fumasep membranes, respectively, is needed for the PW dilution. Interestingly, pressure drops were found somehow constant during the long-runs although real PW were adopted. These preliminary results suggest that ARED is able to operate with real dirty waters while maintaining good performances and efficiencies. Longer experiments are needed in order to better evaluate the impact of fouling on the system performance.

Nomenclature

A_m – Membrane area, m
AEM – Anionic exchange membrane
ARED – Assisted reverse electrodialysis
CEM – Cationic exchange membrane
IEM – Ionic exchange membrane
E – Voltage, V
H – High concentrated solution/compartment
I – Current, A
L – Low diluted solution/compartment
N_{cp} – Number of cell pairs

PD – Power density, W m^{-2}
PW – Produced water
RED – Reverse electrodialysis
RO – Reverse osmosis
SEC – Specific energy consumption, kWh m^{-3}
t_d – time of test, h
V_{PW} – Volume treated of produced water, m^3
ΔP – Pressure drops, Pa
σ – Conductivity, mS cm^{-1}

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