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Assisted Reverse Electrodialysis for salinity reduction of produced waters

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Produced Waters (PWs) are wastewaters that come from the oil industry and are particularly salty and polluted with hydrocarbons. Recently, membrane processes have been proposed for their treatment within the framework of a circular economy approach: the treatment and reuse of these waters requires a thorough understanding of the processes, particularly regarding the fate of valuable ions. Desalinating PW can be beneficial upstream of cheap and effective biological treatment processes. With this respect, an experimental study about ions flux through the Ions Exchange Membranes (IEMs) of a laboratory scale Assisted Reverse Electrodialysis (A-RED) unit was conducted aiming at a downstream mineral recovery. The passage of several cations, such as Na+, Ca2+, Mg2+, Li+, Rb+ and B3+, was measured in a synthetic solution mimicking the real PW composition. Tests were carried out either in once-through mode or recirculating the feed solutions always applying an external voltage of 3.6 V. The solutions were sampled at regular intervals and analysed. As a result, data on the passage of each of them through the membranes was evaluated. As expected, Na+ and Li+ ions were found to exhibit the largest flux. A slight less value was found for B3+ due to its high concentration in PW. Much lower values were measured for Ca2+, Mg2+ and Rb+. The present work poses the basis for a more in-depth analysis of ion transfer in desalination membrane processes for PW, which would allow an easier design of treatment equipment while considering a possible recovery of valuable ions.

* 1. Introduction

Industries such as leather production, pharmaceuticals, and food processing generate hypersaline and organic-polluted effluents. However, the largest volumes come from crude oil and natural gas extraction, where the wastewater is known as Produced Water (PW). With a typical water-to-oil ratio ranging from 3:1 to 9:1—depending on the age and condition of the wells—global produced water (PW) generation exceeds 320 million barrels per day and accounts for 5–19% of oil well management costs (Fakhru’l-Razi et al., 2009). Given that crude oil production can vary from approximately 500 barrels per day in tight oil wells to as much as 5,000–30,000 barrels per day in highly productive wells (Santos et al., 2010; Wachtmeister et al., 2017), it becomes evident that the volume of produced water involved is huge. The composition and quantity of PW vary significantly depending on geological conditions, extraction methods, and the chemicals used in processing (Fakhru’l-Razi et al., 2009). Total dissolved solids (TDS) levels can reach up to 300 g/L (Al-ghouti et al., 2019), and besides sodium, other cations are present in a concentration higher than that in seawater, such as magnesium, rubidium, lithium and boron, which are among the Critical Raw Materials (CRMs), crucial to Europe’s economy (European Union, 2025). Thus, their recovery could be an important process to secure EU supply. Some studies demonstrated how it is possible to recover some CRMs (Sr(II), Co(II), Ga(III), Ge(IV) and B(III)) by ion exchange processes, such as batch crystallisation and reactive precipitation solutions (Vallès et al., 2023).

For what concerns the disposal of PWs, they are currently reinjected into the wells or discharged into the sea. These strategies remain economically preferred, even if they are increasingly challenged by regulatory restrictions and public concerns. Various methods have been employed to reduce PW salinity, with thermal technologies being the most widely adopted, although expensive. Multistage flash (MSF) distillation, multi-effect distillation (MED) and vapor compression distillation (VCD) are some of these (Jiménez et al., 2018).

Considering the extreme variability in composition, treatment methods for PW require a customized analysis. In addition to high salinity, PW typically contains dissolved metals and hydrocarbons derived from crude oil, which further complicate its treatment. Therefore, innovative and safer treatment methods are necessary. Furthermore, the simultaneous recovery of critical raw materials (CRMs) before disposal may be of great interest.

In recent years, there has been an increasing interest from the scientific world on the use of membrane processes also for the treatment of industrial effluents. For example, Luque et al. (Luque et al. 2017) proposed the use of Reverse Electrodialysis (RED) for the treatment of wastewater from fish canning factory waste streams. Later, the same unit was proposed for PW treatment by Cosenza et al. (2022). In detail, RED is a membrane process taking advantage of the use of Ionic Exchange Membranes (IEMs) and designed to obtain electrical energy by mixing two solutions at different salinity. More precisely, a RED unit consists of multiple pairs of cation exchange membranes (CEMs) and anion exchange membranes (AEMs), which are alternately stacked to create spacer-filled channels for a concentrated solution and a diluted one. The single repetition of a CEM, an AEM, the diluted and concentrated compartment is named cell-pair. Although the process is typically adopted for energy production, the ion migration from the concentrated feed towards the diluted one can be boosted by working in assisted condition, i.e., Assisted-Reverse Electrodialysis (Vanoppen et al. 2016). Hence, a voltage difference is applied across the unit to enhance the natural movement of ions through the membranes.

With this respect, Campisi et al. (Campisi et al. 2023) proposed a treatment scheme for PWs, where the salinity was firstly reduced into an A-RED unit and then wastewater was treated in a biological system. Downstream, once the hydrocarbon content has been sufficiently reduced, the stream can be valorised before the disposal by recovering some valuable species such as CRMs.

Thus, it could be important to study the effective fluxes of the dissolved ions of interest through IEMs. In fact, beside the commonly studied Na+ and Cl-, potentially, all dissolved ions can permeate through membranes, and in the case of valorisation of CRMs, it is important to know their fate in the treatment chain to avoid any potential loss.

In this work, an experimental campaign was conducted to study the passage of PW ions through the IEMs of a lab-scale RED unit operated under assisted conditions (i.e., A-RED). The aim is to estimate the amount of high-value salts that potentially do not permeate the membranes by remaining in appreciable concentrations in the concentrate solution. On the other hand, in the case of elements potentially detrimental to the environment (such as boron), it is possible to define the suitability of the process for dealing with these wastewaters.

* 1. Experimental section

The A-RED unit had an active area of 10x10 cm2. It was equipped with 10 cell-pairs, with Fujifilm type 10 membrane, and with woven spacers 300 μm thick creating the compartments where the solutions are forced to flow. At both ends of the stack, two electrodes sandwiched the cell package. In the electrodic compartments, an electrode rinse solution (ERS) was recirculated: it was prepared with K3[Fe(CN)6] and K4[Fe(CN)6]·3H2O salts (Sigma Aldrich, >99%) in a 0.1 M concentration. The reversible redox couple allowed the conversion of the electric current into an ionic flux. End-membranes (Fumasep, FKS-50) were positioned between the electrode compartments and the cell packages to close the system, ensuring the ERS isolation.

The feed streams were synthetic solutions: the high concentrated solution (H) was prepared with the aim of mimicking the ionic composition of a real PW, provided by a European company. On the contrary, the low concentrated solution (L) was prepared by dissolving 0.73 g/L of NaCl in water to reproduce the composition of common industry process water. The composition of the synthetic PW is reported in Table 1, where the indicated standard deviation refers to the variations among the different solutions prepared for the various tests conducted. The chemicals used for realizing the solutions were NaCl (≥99.99%), MgCl2∙6H2O (99.9%), CaCl2 (≥99.9%), LiCl (≥99.98%), RbCl (99.95%) and H3BO3 (≥99.5%), all provided by Sigma Aldrich.

Table 1. Ionic composition of the synthetic PW used in the experimental campaign.

|  |  |
| --- | --- |
| *Ion* | *Concentration [mg/L]* |
| *Na+* | 22168 ± 43 |
| *Mg2+* | 612.88 ± .063 |
| *Ca2+* | 2257.38 ± 25.13 |
| *Li+* | 9.80 ± 0.2 |
| *Rb+* | 2.85 ± 0.02 |
| *B3+* | 110 ± 1.8 |

Regarding the procedure, the membranes were conditioned in a solution of about 30 g/L of NaCl for 24 h. The feed solutions were pumped into the unit with a velocity of 0.3 cm/s inside the channels, in a co-current configuration using two peristaltic pumps (Leadfluid WT/600/S). Another peristaltic pump (Seko Kronos 50, Rieti, Italy) was used to recirculate the ERS.

Two different types of tests were carried out: 'once-through test' and 'recirculation test' depending on whether the outlet streams of the unit were sent to a separate reservoir or recirculated into the same accumulation tank (see Figure 1). The once-through test had a duration of 3 hours to allow the membranes enough time for conditioning and samples were taken at the end of the test. On the contrary, the recirculation test lasted 9 hours, duration determined by the need to reduce the salinity of 3 litres of PWs to 20 g/l to make them suitable for a subsequent biological step. Samples from the concentrated and dilute solutions were withdrawn each hour. Moreover, laboratory scales (Kern Kbj) were used to constantly monitor the tanks weight and calculate the water passage during the test.



Figure 1. Diagram of the experimental set-up. The dashed blue and orange lines (Recirculation Test) refer to the recycle of the concentrated outlet and of the diluted outlet in the H and L tank, respectively. The broken grey lines indicate the electrical connections.

Tests were carried out applying an external voltage equal to 3.6 V, corresponding to a current being twice the measured short circuit current, i.e., 0.63 A. This voltage value was applied by using a power supply (BK Precision BK1900B). Two multi-meters (Fluke 175 True RMS) were connected to the electric circuit and used to measure voltage and current.

All the samples collected were properly analysed with specific methods. Lithium and Rubidium were analysed by Flame Atomic Emission Spectrophotometry (F-AES, PerkinElmer AAnalyst 200 spectrophotometer). Calibration curves were constructed by adding NaCl 1000 mg/L, to minimize/suppress the metals ionization increasing the method sensitivity (Fujinaga et al., 1980)(Fujinaga et al., 1980). To this purpose, Riedel-de Haën ≥ 99.8% NaCl was used, after drying at 383.15 K in an oven for 2 h. Li and Rb standard solutions 1000 mg/L in 2 % HNO3 (CPAchem) were used for calibration curves. Boron concentration was measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Perkin Elmer Optima 2100, equipped with an autosampler model AS-90). 1000 mg/L boron standard solution (CPAchem) was used for calibration curves. All samples were previously filtered with 0.45 µm syringe filters, acidified with HNO3 (Sigma-Aldrich, ≥ 65%) to avoid the formation of slightly soluble hydrolytic species and diluted. Each solution was prepared using freshly, CO2-free ultrapure water (ρ ≥ 18 MΩ cm−1) and grade A glassware. Na+, Ca2+ Mg2+ and Cl- concentration was measured using ion chromatography (IC) analysis, performed with a Metrohm 822 Compact Plus IC system, equipped with a Metrosep C4 cation-exchange column and a Metrosep A Supp 5 anion-exchange column.

* 1. Results and Discussion

In the once-through test, the ionic passage was constant for the entire duration of the test, demonstrating that membranes were quickly conditioned and achieved their steady state condition in few times.

The results of the chemical analysis for the H solution are shown in Figure 2 and reported in g/L for the Na+, Mg2+, Ca2+ (Figure 2 a-b) being the most present ions in solution, while the Li+, Rb+ and B3+ (Figure 2 c-d) are shown in mg/L. A little variation is observable per each passage through the A-RED unit: more precisely, it was about 7%, 5% and 10% for Na+, Ca2+ and Mg2+ respectively, and 5%, 4% and 14% for Li+, Rb+ and B3+ respectively. Notwithstanding the 14% loss observed for boron, its concentration in the dilute stream is 2.43±0.06 ppm, which still complies with the limits of Italian law (D.Lgs 152/06).

Each test was repeated twice, and relevant error bars are reported in the figures. Notably, the difference observed was always below 4%, thus proving the reliability and the reproducibility of the tests carried out.



(a)

(b)

 

(d)

(c)

Figure 2. Ionic concentration in the H inlet (a-c) and in the H outlet (b-d) solutions in once through test. The H outlet concentrations refer to the value at 3 hours.

It is important to note that ion fluxes remain constant throughout the test, with no significant variations over the 3-hour duration. Considering the entire membrane surface and the duration of the test, it is possible to calculate the ion fluxes crossing the membranes (reported in Table 2). These results represent a very important information in case of salinity reduction with A-RED technology of wastewater containing a wide variety of dissolved ionic compounds. As expected, the fluxes of Na+ and Li+ show the higher values, mainly due to the high capacity of this small ions to permeate the membranes, whereas the values for the others are lower.

For what concerns the recirculation tests, they were useful to propose an ion passage model hypothesis. In fact, by plotting the concentration of each cation vs. time (see Figure 3), it was possible to devise an equation for the time-decreasing concentration. These mathematical equations are reported in Table 3.

In particular, Na+, Mg2+, Ca2+ and Li+ concentrations in the H stream were found to linearly decrease while the Rb+ ions decrease following an exponential function. Conversely, for B3+ a reasonably acceptable fit was found with and exponential law. This piece of information is useful to understand the fate of valuable ions when large scale units are to be designed and operated. In other words, once the A-RED unit has been designed and the residence time is known, the equations can be used to have an estimate of the amount of ions shifting from the PW to the dilute side. As it can be seen in the Figure 3, valuable ions as Li and Rb rapidly decrease, thus requiring great attention during the design and operation of the industrial A-RED unit to make their recovery still feasible and, more important, profitable. However, it is worth noting that the experiment was conducted for 9 hours under recirculation mode, which inherently accentuates ion migration and diffusion. In contrast, with reference to the once-through mode, the latter is much more representative of an industrial-scale system for which the fluid enters and is diluted in a single passage and for which residence times are quite limited. Last but not least, special attention should be paid to boron whose concentration cannot exceed 4 mg/L when discharged to marine environment, according to Italian legislation.

Table 2. Ion fluxes across the membranes.

|  |  |
| --- | --- |
| *Ion* | *Flux [mol/(m2s)]* |
| Na+ | 6.4E-05 |
| Mg2+ | 1.1E-06 |
| Ca2+ | 5.3E-06 |
| Li+ |

|  |
| --- |
| 5.4E-05 |

 |
| Rb+ | 4.4E-07 |
| B3+ | 1.2E-05 |



(a)



(b)

Figure 3. Ion concentration trends versus the time in recirculation mode. Na+, Mg2+ and Ca2+ are reported in (a) and Li+, Rb+ and B3+ in (b).

This preliminary study proposed for the first time equations allowing the estimation of the ion passage during a saline abatement process with an electro-membrane technology such as the A-RED (Table 3).

Table 3. Concentration equation in function of time for the studied ions in the concentrated solution. t is expressed in seconds. [Na+], [Mg2+], [Ca2+] are expressed in g/L. [Li+], [Rb+], [B3+] are expressed in mg/L.

|  |
| --- |
| [Na+] = $-1.72 t+22.21$ |
| [Mg2+] = $-0.04 t +0.63$ |
| [Ca2+] = $-0.21 t+2.23$ |
| [Li+] = $-0.47 t+9.67$ |
| [Rb+] = $3.55e^{-0.25 t}$ |
| [B3+] = $112.97e^{-0.022t}$ |

* 1. Conclusions

In this study, A-RED was studied as a novel process for salinity reduction: it leverages the salinity gradient between two solutions while boosting the ion transport by applying an external voltage. This approach accelerates the natural movement of ions, making the desalination process more convenient. A synthetic produced water was prepared in the laboratory, replicating the main ionic composition of a real PW, including Na+, Mg2+, Ca2+, Li+, Rb+ and B3+ ions. The ionic fluxes were studied using a lab-scale A-RED unit, and the average flux for each ion was determined. Additionally, a 9-hour recirculation test was conducted to establish the time-dependent behaviour of ion transport. These findings are strategically important when PW is intended for further treatment, as understanding ion passage is crucial for a possible downstream recovery. For instance, certain ions, such as lithium and rubidium, have a high economic value and understanding their fate in the treatment chain is crucial for designing a profitable recovery step. In addition, borate compounds are harmful to the environment, and their discharge into groundwater or seawater is strictly regulated. For this reason, in the case of final disposal of PW into the natural environment after treatment, the ability to estimate the concentration of dissolved boron using a simple equation represents a preliminary yet powerful tool for adjusting process parameters appropriately. Concerning results, bivalent cations exhibited the lower fluxes and are expected to remain mainly in the PW while passing the A-RED unit. Conversely, a meaningful concentration reduction was found for Li+ and Rb+, thus posing a question mark on how devising a possible downstream recovery.

Further analysis is needed to refine the ion transport model, for instance by adopting real PWs. This research can contribute to the design of an overall treatment chain for PW including a remunerative ion recovery step.

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