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Valorization of desalination brines by electrodialysis with bipolar membranes using nanocomposite anion exchange membranes

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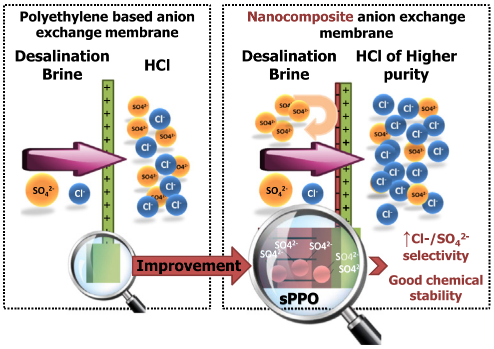
HIGHLIGHTS

- HCl and NaOH were produced from synthetic desalination brines by EDBM.
- Nanocomposite anion exchange membranes increased Cl^-/SO_4^{2-} permselectivity.
- Nanocomposite membranes showed stability with time working with acids and bases.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrodialysis with bipolar membranes (EDBM) is a promising technology that simultaneously treats and valorizes desalination brines into acids and bases. An important techno-economic challenge of EDBM in this application is the purity of the products, related to the need for more selective ion exchange membranes with good stability working with acids and bases. This work presents the results of the treatment of model desalination brines by EDBM using nanocomposite anion exchange membranes in order to reduce the sulfate content as the main impurity in the acid stack. These membranes are composed by polyethylene, polypropylene, sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (sPPO) and different loads of Fe_2O_3-SO_4^{2-} nanoparticles. A reduction of the sulfate content in the acid stack was observed when using nanocomposite membranes. The stability of these membranes was evaluated measuring the Cl^-/SO_4^{2-} selectivity after 31 h, 62 h and 93 h of operation. FTIR spectra before and after 93 h of operation also confirmed the stability of the membranes. The evolution of the main impurities in the acid and the base stacks versus time when applying different current densities is included and related to current efficiency. An estimation of the proton and hydroxyl ions leakages at the different current densities is also presented.

1. Introduction

Desalination is a competitive alternative, worldwide implemented, for the freshwater supply of countries under water shortages. However, it is associated to both indirect and direct burdens that compromise its

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Table 1
Characteristics of the nanocomposite membranes used in this study.

Membrane	Water contact angle (°)$^{i)}$	Electrical resistance ($\Omega \cdot cm^2$)$^{ii)}$	Limiting J[a] ($mA \cdot cm^{-2}$)$^{iii)}$	Permselectivity SO_4^{2-}/Cl^-
Commercial AM-PP	100.1	6.3	22	1.079
AM-0.2NP	63.7	6.1	22	0.814
AM-0.4NP	61.6	6.1	20	0.805
AM-0.6NP	65.8	6.4	16	0.859

Analytical techniques used for membrane characterization: i) Water contact angle measurement, ii) Electrochemical impedance spectroscopy and iii) Chronopotentiometry.

[a] For a solution formed by NaCl 0.05 $mol \cdot L^{-1}$ and Na_2SO_4 0.05 $mol \cdot L^{-1}$.

sustainability [1]. Indirect environmental burdens are related to greenhouse gases emissions due to the high-energy requirements of desalination technologies. The integration of desalination technologies with renewable power devices is a promising option to overcome this global burden [1–3]. Direct impacts of desalination are associated to the local disposal of desalination brines. The relatively low recovery of conventional desalination technologies (ranging from 50% to 85% [4]) causes the generation of high amounts of brines, which content varies depending on the feed water quality, feed water pretreatment, produced water quality and cleaning procedures [5]. This means that per 1 m^3 of produced freshwater, a range which goes from 0.3 m^3 to 1 m^3 of brines are generated. Taking into account the desalination capacity projected for 2015 ($97.5 \cdot 10^6$ $m^3 \cdot day^{-1}$ [6]), the worldwide production of brines could be somewhere between $29.3 \cdot 10^6$ $m^3 \cdot day^{-1}$ to $97.5 \cdot 10^6$ $m^3 \cdot day^{-1}$. The most common conventional method for the disposal of brines is seawater discharge, followed by sewer discharge, deep well injections and solar ponds. According to [7] the distribution of these methods for brine disposal is 41%, 31%, 17% and 2% respectively. However, all of these methods present limitations and environmental issues such as high land requirement (evaporation ponds), risk of salt leakages to groundwater (deep well injections and evaporation ponds) and modifications of the receiving media (seawater and sewer discharge). Additionally, it should be taken into account that the disposal of brines into the sewer is only possible for low volumes of brines due to the fact that high quantities affects the performance of the biological treatment at wastewater treatment plants [8]. Thus in the case of high capacity inland desalination plants, the lack of a suitable disposal method can compromise the economic viability of the plant. There is still a need for an innovative solution to avoid the direct environmental impacts associated to the disposal of brines.

Electrodialysis (ED) is a well-known technology for desalination of water [1] that has been reported as an effective approach for the treatment of desalination brines [9–11]. ED allows the concentration of brines with the consequent volume reduction and freshwater generation. Electrodialysis with bipolar membranes (EDBM) is a promising alternative that allows the simultaneous treatment and valorization of desalination brines into acids and bases. The main components of EDBM are anion exchange membranes (AEM), cation exchange membranes (CEM), bipolar membranes (BM) and two electrodes. The electric field generated between the electrodes is the driving force that separates sodium (Na^+) from chloride (Cl^-) through the corresponding CEM and AEM. At the same time this electric field allows the dissociation of water into protons (H^+) and hydroxyl ions (OH^-) in the bipolar membranes. Thus, EDBM simultaneously deals with desalination brines, lowering its salt content, and does valorize this salt into hydrochloric acid and sodium hydroxide. Several works in the literature deal with the modeling [12,13] and laboratory experimental work [14–20] of EDBM for treatment and valorization of brines, mainly focusing on the feasibility and optimization of operation conditions for the treatment. However, there are still some technical and economic challenges to overcome before this approach can develop its full potential.

A comprehensive summary and discussion of these challenges can be found in our previous work [21]. One of the main techno-economic barriers that we have identified so far is related to the low purity of the products and the need for more selective ion exchange membranes with good stability working with acids and bases. In particular, this barrier is addressed in this work by the use of novel nanocomposite AEM to reduce the content of sulfate (SO_4^{2-}) in the acid, which is its main impurity [21].

Thus, this work presents the performance of a new nanocomposite commercial based polyethylene AEM in the valorization of desalination brines by EDBM. These membranes, composed mainly by polyethylene, polypropylene, sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (sPPO) and different loads of Fe_2O_3-SO_4^{2-} nanoparticles (0.2% $g \cdot g^{-1}$ to 0.6% $g \cdot g^{-1}$) have a very promising performance in terms of Cl^-/SO_4^{2-} selectivity for the treatment of brines from seawater desalination. In the present work, we state two different hypothesis: i) the developed nanocomposite membranes are suitable for valorization of model desalination brines by EDBM, and ii) its use can improve the quality of the obtained acid. For this purpose, this work presents the results of acid and base generation by EDBM using commercial and nanocomposite AEM as well as commercial cation exchange membranes and bipolar membranes. The influence of current density (80 $A \cdot m^{-2}$–750 $A \cdot m^{-2}$)

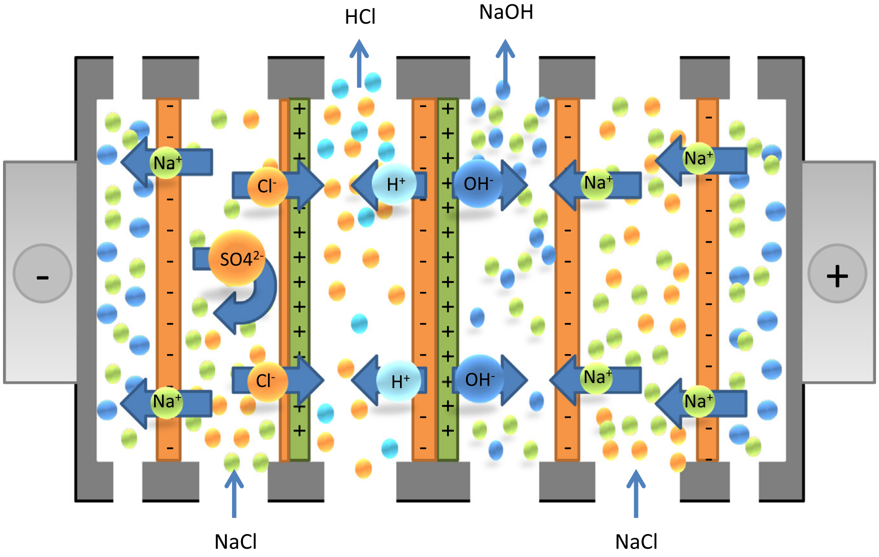

Fig. 1. Stack configuration used for EDBM experiments (CEM-AEM-BP-CEM-CEM).

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