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"Nuevas membranas *nanocomposite* para una desalación sostenible"

"Novel nanocomposite membranes for a sustainable desalination"

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Esta tesis doctoral se presenta como un resumen de trabajos previamente publicados o enviados para su publicación en revistas científicas incluidas en el *Journal of Citation Reports-Science Edition* (JCR), cumpliendo con la normativa existente en la Universidad de Cantabria y en el Departamento de Ingenierías Química y Biomolecular referente a la elaboración de tesis doctorales por compendio de artículos previamente publicados. Esta tesis se ha desarrollado en el grupo de investigación Ingeniería de Procesos Sostenibles del Departamento de Ingenierías Química y Biomolecular de la Universidad de Cantabria, bajo la supervisión de la Dra. Raquel Ibáñez Mendizábal y el Dr. Antonio Domínguez Ramos, en el marco de una beca de Formación de España. Durante la elaboración de la tesis doctoral se han realizado tres estancias predoctorales: dos estancias de cuatro meses de duración (marzo-junio 2015) y tres meses de duración (febrero-abril 2016) en la Escuela de Ingenería Civil y Medioambiental del *Georgía Institute of Technology* (EE.UU.) bajo la supervisión del Prof. Yongsheng Chen y una estancia de dos meses de duración (junio-julio 2016) en el Departamento de Ingenierías Química y Biomolecular de la *University of Sydney* (Australia) bajo la supervisión del Prof. Hans Coster.

A continuación se listan las contribuciones científicas publicadas (1-4) y en proceso de revisión (5), así como las contribuciones a congresos publicadas en libros con ISBN:

- a) Artículos en revistas científicas, indicando lista de autores por orden de firma, título del artículo, título de la revista, número de la revista, año de publicación, números de la primera y última página, denominación del área temática de la revista, cuartil en el área temática, y posición relativa en el área temática:
- <u>C. Fernandez-Gonzalez</u>, A. Dominguez-Ramos, R. Ibañez, A. Irabien. Sustainability assessment of electrodialysis powered by photovoltaic solar energy for freshwater production. Renewable and Sustainable Energy Reviews, 47 (2015) 604-615. Energía y combustibles, Q1, 6/88.



SEPARATION

& PURIFICATION Reviews

- <u>C. Fernandez-Gonzalez</u>, A. Dominguez-Ramos, R. Ibañez, A. Irabien. Electrodialysis with bipolar membranes for valorization of brines. Separation and Purification Reviews, 45 (2016) 275-287. Ingeniería Química, Q1, 5/135.
- <u>C. Fernandez-Gonzalez</u>, A. Dominguez-Ramos, R. Ibañez, Y. Chen, A. Irabien. Valorization of desalination brines by electrodialysis with bipolar membranes using nanocomposite anion exchange membranes. Desalination, 406 (2017) 16-24. Ingeniería Química, Q1, 12/135.



- <u>C. Fernandez-Gonzalez</u>, B. Zhang, A. Dominguez-Ramos, R. Ibañez, A. Irabien, Y. Chen. Enhancing fouling resistance of polyethylene anion exchange membranes using carbon nanotubes and iron oxide nanoparticles. Desalination, 411 (2017) 19-27. Ingeniería Química, Q1, 12/135.
- <u>C. Fernandez-Gonzalez</u>, J. Kavanagh, A. Dominguez-Ramos, R. Ibañez, A. Irabien, Y. Chen, H. Coster. Electrochemical impedance spectroscopy of enhanced layered nanocomposite anion exchange membranes containing iron oxide nanoparticles and carbon nanotubes. Journal of Membrane Science, (En revisión). Ingeniería Química, Q1, 7/135.



Adama Menadisat Terretaria Internet

DESALINATION

- b) Contribuciones a congresos publicadas en libros (*Proceedings*) con <u>ISBN</u>, indicando lista de autores por orden de firma, título de la contribución, congreso, fecha de celebración, lugar de celebración, ISBN y tipo de comunicación:
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- <u>C. Fernandez-Gonzalez</u>, A. Dominguez-Ramos, R. Ibañez, A. Irabien. About the sustainability of the electrodialysis powered by photovoltaic solar energy. IX Iberoamerican congress on membrane science and technology. 25-28 mayo 2014, Santander (España). <u>ISBN</u>: 978-84-697-0397-7. Comunicación poster y presentación flash.

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"Una meta sin un plan es solo un deseo"

"A goal without a plan is only a desire"

Larry Elder (1952-)

Abogado y escritor/ Lawyer and Writer

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Resumen

Abstract

"La ciencia es como la tierra, solo se puede poseer un poco"



"Science is like the land, you can only have a little"

Voltaire (1694-1778)

Filósofo/ Philosopher

Resumen/Abstract

Las tecnologías de desalación, con una capacidad instalada de 100 millones de metros cúbicos en 2016 y una proyección de 140 millones de metros cúbicos en 2030, juegan un papel fundamental en el abastecimiento de agua dulce a nivel global. Sin embargo, la desalación de agua está así mismo asociada con impactos directos e indirectos que comprometen su sostenibilidad ambiental. El principal impacto global indirecto procede del alto consumo energético por unidad de producto deseado. El impacto directo local, en el entorno de la instalación de la planta de desalación, se debe fundamentalmente al vertido de cantidades significativas de concentrados de desalación como subproducto.

El objetivo general de la tesis doctoral es el desarrollo de estrategias innovadoras para mejorar la sostenibilidad ambiental de la desalación mediante electrodiálisis (ED), una de las tecnologías de desalación con membranas más importantes a nivel global para la desalación de agua salobre, incidiendo sobre sus principales impactos ambientales asociados a su consumo energético y a la generación de concentrados de desalación.

En relación al consumo energético se han abordado dos acciones estratégicas. La primera consistió en el estudio de la sostenibilidad de la integración de la ED con energías provenientes de fuentes renovables, analizando el efecto de reducir la carga ambiental asociada a la electricidad de red mediante su sustitución por una fuente primaria baja en carbono como la energía solar fotovoltaica (PV). Se evaluaron los aspectos ambientales, económicos y sociales de la integración ED-PV, se identificaron las principales barreras técnicas y económicas de este acoplamiento, y se presentó una previsión económica a medio-largo plazo de la combinación ED-PV, tomando como caso de estudio una planta de 39 m³·día⁻¹ de capacidad operada en las Islas Canarias.

La segunda acción estratégica consistió en el desarrollo de nuevas membranas de intercambio aniónico *nanocomposite* con el objetivo de mejorar la eficiencia del proceso de desalación y reducir el consumo energético por unidad de producto. Estas membranas *nanocomposite* están formadas por una membrana de intercambio aniónico comercial de polietileno y una película cargada negativamente formada por polióxido de (2,6-dimetil-1,4-fenileno) sulfonado y un nanomaterial: nanopartículas de óxido de hierro sulfonadas Fe₂O₃-SO₄²⁻ o nanotubos de carbono multipared oxidados CNTs-COO⁻.

La introducción de esta película *nanocomposite* en la membrana comercial de polietileno causó un cambio significativo en las características físico-químicas de la superficie de la membrana como su composición, hidrofilicidad, rugosidad y carga, dando como resultado una mejora de su resistencia frente al *fouling* orgánico, su selectividad hacia iones monovalentes y su flujo de aniones CI⁻. Las dos películas *nanocomposite* presentaron un comportamiento muy similar tanto en la caracterización de propiedades superficiales de la membrana como en la evaluación de su comportamiento frente a fenómenos de *fouling* orgánico y transporte de iones. Además, en este trabajo se presenta un modelado del comportamiento eléctrico, tanto de membranas de intercambio iónico comerciales como de membranas *nanocomposite*. Para ello se ha realizado el ajuste de datos de impedancia a un modelo matemático tipo Maxwell-Wagner, con el que se ha propuesto un circuito eléctrico equivalente para cada membrana, el cual permite relacionar cambios en propiedades eléctricas con cambios estructurales y avanzar en el conocimiento del comportamiento eléctrico de membranas avanzadas multicapa.

En relación a la problemática local asociada a la generación de notables cantidades de concentrados de desalación, se ha propuesto como acción estratégica la utilización de la tecnología de ED con membranas bipolares (EDBM) para el tratamiento y valoración de los concentrados de desalación en forma de HCl y NaOH. Para ello, se han identificado las principales barreras de esta tecnología en la valorización de concentrados de desalación, entre las que destaca la baja pureza de los productos obtenidos en relación con los grados comerciales, y se ha estudiado la influencia de la densidad de corriente sobre la evolución de las principales impurezas del ácido $(SO_4^{2^-})$ y la base (K^+) . Así mismo, se ha comparado la mejora en la pureza del ácido obtenido utilizando membranas comerciales y membranas *nanocomposite* y se ha evaluado la estabilidad de las membranas *nanocomposite* al trabajar con ácidos y bases en EDBM.

Resumen/Abstract

Desalination technologies, with an installed capacity of 100 millions of cubic meters per day in 2016 and a projected capacity of 140 millions of cubic meters per day in 2030, play a key role in global freshwater supply. However, water desalination is associated with direct and indirect impacts that compromise its environmental sustainability. The main global indirect environmental impact derives from the high-energy consumption per unit of desired product. The direct local impact, in the vicinities of the desalination plant, is mainly due to the discharge of significant amounts of desalination concentrates as subproducts.

The main objective of this doctoral thesis is the development of innovative strategies to improve the environmental sustainability of desalination by electrodialysis (ED), one of the most important membrane desalination technologies globally for desalination of brackish water, focusing on its main environmental impacts associated to its energy consumption and the generation of desalination brines.

Regarding the energy consumption, two strategic actions have been addressed. The first one consisted in studying the sustainability of the integration of ED with energies from renewable sources, analyzing the effect of reducing the environmental burden associated to the grid-mix by its substitution for a low-carbon primary source such as photovoltaic solar (PV) energy. Environmental, economic and social issues regarding the integration of ED-PV were evaluated. The main technical and economic barriers for this coupling were identified and a medium-long term economic forecast for the combination ED-PV, taking as a case of study a desalination

plant of 39 m³ per day of desalination capacity operated in the Canary Islands has been presented.

The second strategic action consisted in developing new nanocomposite anion exchange membranes targeting the enhancement of the desalination process and reducing the energy consumption by unit of product. These nanocomposite membranes are composed of a commercial polyethylene anion exchange membrane and a negatively charged nanocomposite film made of sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) and a nanomaterial: sulfonated iron oxide nanoparticles $Fe_2O_3-SO_4^{2^2}$ or oxidized multiwalled carbon nanotubes CNTs-COO⁻.

The addition of this nanocomposite film in the surface of the commercial polyethylene membranes caused a significant change in the physico-chemical properties of the membrane surface such as composition, hydrophilicity, roughness and charge, resulting in an enhancement in their resistance against organic fouling, their selectivity for monovalent ions and their flux of Cl⁻ anions. The two nanocomposite films showed a very similar performance during the characterization of the membrane surface and the evaluation of their performance regarding fouling phenomena and ion transport.

Besides, this thesis includes a modeling of the electrical performance of commercial and nanocomposite membranes by the fitting of impedance data to the Maxwell-Wagner mathematical model. From this modeling, an equivalent electric circuit was proposed for each membrane, which allows relating in electrical properties with structural modifications in membranes as well as advancing in the knowledge of the electrical performance of advanced multilayered membranes.

Regarding local issues associated with the generation of huge amounts of desalination brines, the use of ED with bipolar membranes (EDBM) for the treatment and valorization of desalination brines into HCl and NaOH was proposed as strategic action. The main technical and economic barriers of this technology for the valorization of desalination brines were identified, being the low purity of the obtained products highlighted in relation to commercial grades. In this thesis, the influence of the current density over the evolution of the main impurities of the acid (SO_4^{2-}) and the base (K^+) has been studied. A comparison of the purity of the acid using commercial and nanocomposite membranes was performed, as well as an evaluation of the stability of nanocomposite membranes working with acids and bases in EDBM.



"Todos los triunfos nacen cuando nos atrevemos a comenzar"



"All the triumphs are born when we dare to start"

Eugene Fitch (1841-1911)

Soldado, abogado, político y escritor/*Soldier, lawyer, politician and writer*.

CAPÍTULO 1: PLANTEAMIENTO

1.1. Marco de la tesis

Los datos de la Asociación Internacional de Desalación [1] muestran que, a fecha de 30 de junio del 2015, y con una capacidad de desalación instalada de 86,6 millones de metros cúbicos al día, la desalación de agua afectó de forma directa a 300 millones de personas, que consumieron agua desalada para satisfacer parte o la totalidad de sus necesidades diarias de agua dulce. La capacidad de desalación instalada en 2016 se estima en 100 millones de metros cúbicos al día, distribuídos en 18.000 plantas de desalación instaladas en 150 países, con una proyección de 140 millones de metros cúbicos al día para el 2030 [2]. Dentro de las tecnologías de desalación, divididas en procesos térmicos y procesos de membranas, la desalación con membranas juega un papel fundamental con un 67% de la capacidad instalada a nivel mundial [2,3]. De ese 67%, un 63,4% de la capacidad mudial (o 94,6% de la capacidad mundial de desalación con membranas) se corresponde con la tecnología de ósmosis inversa y un 3,3% de la capacidad mundial (equivalente a un 4,9% de la capacidad mundial de desalación con membranas) con la electrodiálisis [3].

La desalación es un tratamiento de agua intensivo energéticamente, siendo el trataminto de agua con mayor requerimiento de energía. Al mismo tiempo, se requieren grandes cantidades de agua para generar energía. Esto provoca que agua y energía, y por tanto la industria de la producción de agua y la generación de electricidad, estén íntimamente ligadas. Para la industria de la generación de energía, el nexo más importante con el agua radica en el proceso de producción de electricidad [4]. En el 2010, el 15% del agua dulce producida a nivel global mediante tecnologías de desalación fue destinada a la generación de energía [2]. Para la producción de este agua se requirieron 7,4 TWh de electricidad con unas emisiones de CO₂ por valor de 76 millones de toneladas [2]. En el caso de la industria del agua, los nexos relacionados con la energía no solo se limitan al proceso de producción y tratamiento de agua, sino también a su distribución por ser el agua un producto voluminoso y pesado [4]. Se estima que en 2010, el 7% de la energía generada a nivel global se destinó a la producción y distribución de agua dulce y el tratamiento de aguas residuales [5]. Entender el nexo agua-energía, gestionando estos dos recursos de manera conjunta, puede ayudar a minimizar sus consumos y reducir los impactos al medio ambiente [6,7].

La desalación está asociada a cargas ambientales directas e indirectas. Los impactos indirectos en forma de emisiones de gases de efecto invernadero se derivan del gran consumo de energía, ya mencionado anteriormente, especialmente durante el proceso de desalación de agua. En términos generales, los procesos de desalación térmicos tienen un consumo de energía específico mayor que las tecnologías de desalación con membranas (7 kW·h·m⁻³ a 27 kW·h·m⁻³ frente a 1 kW·h·m⁻³ 6 kW·h·m⁻³) [8]. Estos consumos enérgicos se pueden traducir, teniendo en cuenta el mix energético español, en unas emisiones de CO₂ equivalentes de 3,6 kg CO₂ eq. m⁻³

a 13,8 kg CO_2 eq. m⁻³ para la desalación térmica y de 0,5 kg CO_2 eq. m⁻³ a 3,0 kg CO_2 eq. m⁻³ con tecnologías de membranas, teniendo en cuenta un factor de emisión de 0,511 kg CO_2 eq. \cdot kW·h⁻¹ [9].

Las cargas ambientales directas más importantes provienen de la generación de grandes cantidades de concentrados de desalación, cuya principal forma de gestión es el vertido. Las tecnologías convencionales de desalación como la ósmosis inversa y la electrodiálisis operan con unas recuperaciones de entre el 50% y el 80% [10]. Esto se traduce en que por cada 1 m³ de agua dulce producida genera entre 0,25 m³ y 1 m³ de concentrados de desalación. Teniendo en cuanta la capacidad de desalación de 2016, la producción mundial de concentrados de desalación se puede estimar en un rango de entre 25 millones de metros cúbicos al día y 100 millones de metros cúbicos al día. La composición de estos concentrados depende de la calidad del agua de alimentación, su pretratamiento, la calidad del agua producida y los procesos de limpieza utilizados [11].

Los métodos más comunes para la gestión de concentrados de desalación son el vertido en estangues de evaporación [12], la descarga en minas abandonas o pozos profundos [13], el vertido costero [14], el mezclado [15] y el vertido al alcantarillado [16]. Sin embargo, a pesar de que hay una gran cantidad de opciones disponibles, todas ellas presentan limitaciones relacionadas con problemas medioambientales, como la necesidad de grandes cantidades de terreno en el caso de los estanques de evaporación [17,18], el riesgo de fugas de sal a aguas subterráneas [18-20] y modificación de las características físico-químicas del medio receptor [20-22]. De acuerdo a la referencia [23] la distribución de estrategias de gestión para estos concentrados es 41% para el vertido en el mar, 31% para la descarga al alcantarillado, 17% para la descarga en pozos profundos y 2% para el vertido a estangues de evaporación. Dado que la opción mayoritaria de gestión de concentrados de desalación es el vertido en el mar, la principal carga ambiental de los concentrados es la modificación de las propiedades físicoquímicas del medio receptor, principalmente temperatura, salinidad e introducción de contaminantes. Las consecuencias de dichos vertidos costeros son los efectos de esta modificación del medio sobre la fauna silvestre en los alrededores del punto de descarga y el potencial daño irreparable sobre el medio marino [24].

Según el *World Water Council*, el mayor reto para en la gestión del agua es su integración en los ecosistemas y el consumo energético asociado [25]. Una estrategia utilizada en la actualidad para mejorar los procesos de desalación desde un punto de vista energético, la cual se espera ayude a aumentar la sostenibilidad des tecnologías de desalación [26], es la incorporación de nanomateriales en las tecnologías de membranas. La introducción de nanomateriales en las membranas de desalación ha demostrado tener numerosas ventajas en cuanto a productividad de agua, rendimiento de la separación y resistencia química, térmica y frente al *fouling* [26-31]. Se prevé que en los próximos 5 a 10 años el conocimiento fundamental y aplicado en

nanotecnología ayudará a producir soluciones para desarrollar y comercializar la siguiente generación de productos de membranas sostenibles y tecnologías de desalación [26,27]. De hecho, ya se encuentran en el mercado membranas comerciales de ósmosis inversa para la desalación de agua de mar y agua salobre que utilizan nanomateriales, como las membranas *NanoH2O* de *LGChem* [32].

La unidad SOSPROCAN del Departamento de Ingenierías Química y Biomolecular de la Universidad de Cantabria, formada por los grupos de investigación Procesos Avanzados de Separación, Desarrollo de Procesos Químicos y Control de Contaminantes, Ingeniería de Procesos Sostenibles y Tecnologías Medioambientales y Bioprocesos, tiene una amplia experiencia y trayectoria en el uso de tecnologías de membranas para separación de gases y tratamiento de aguas. Específicamente, dentro del uso de tecnologías de membranas destacan como principales antecedentes a este trabajo la tesis doctoral "Contribución a la investigación y desarrollo de la tecnología electrodiálisis con membranas bipolares" elaborada por la Dra. Pilar Mier López y dirigida por la Prof. Inmaculada Ortiz Uribe y la Dra. Raquel Ibáñez Mendizabal, en cuanto a la utilización de electrodiálisis con membranas bipolares, y la tesis "Tratamiento integrado y valorización de concentrados salobres de ósmosis inversa" elaborada por la Dra. Antía Pérez González y dirigida por la Prof. Inmaculada Ortiz Uribe y la Prof. Ane Urtiaga Mendía en lo referente al tratamiento de concentrados de desalación. Así mismo, la unidad SOSPROCAN también destaca por sus trabajos en la sostenibilidad de procesos y la integración de energías renovables con tecnologías electroquímicas de tratamiento de agua, entre los que destaca la tesis "Electrooxidación Solar Fotovoltaica (ESOF) de aguas residuales con carga orgánica" elaborada por el Dr. Antonio Domínguez Ramos, codirector de esta tesis doctoral y dirigida por el Prof. Ángel Irabien Gulías y el Dr. Rubén Aldaco García.

La presente tesis doctoral se enmarca en los objetivos de dos proyectos nacionales de investigación aprobados en convocatorias públicas competitivas del Ministerio de Economía y Competitividad del Gobierno de España: el proyecto CTM2011-23912 "Mejoras técnicas y energéticas en la tecnología EDBM. Recuperación de ácidos y bases de concentrados de OI como caso de estudio" y el proyecto CTM2014-57833-R "Estrategias de Recuperación de Salmueras", siendo la investigadora principal lider de ambos la Dra. Raquel Ibáñez Medizábal, responsable del citado grupo de investigación Ingeniería de Procesos Sostenibles.

1.2. Objetivos y estructura

Partiendo del marco descrito en el apartado 1.1., el objetivo general de la tesis doctoral es el desarrollo de estrategias innovadoras para mejorar la sostenibilidad ambiental de la desalación mediante electrodiálisis (ED). Para ello se ha incidido sobre dos aspectos de la ED, asociados a los principales impactos ambientales de esta tecnología sobre el medio ambiente. Por un lado, se encuentra su impacto global indirecto, fundamentalmente como promotor del cambio climático, derivado de la generación de la electricidad necesaria como consecuencia de su alto consumo energético por unidad de producto deseado. Por otro lado, está el impacto local en el entorno de la instalación de la desalación, debido al vertido de grandes cantidades de concentrados de desalación como subproducto.

Los objetivos específicos planteados en esta tesis y desarrollados en las publicaciones que forman esta tesis, se concretan en:

- Evaluación de la sostenibilidad de la integración de la tecnología de desalación mediante ED con energía solar fotovoltaica.
- Identificación de las principales barreras técnicas y económicas para la valorización de concentrados de desalación mediante ED con membranas bipolares.
- Síntesis y caracterización de membranas de intercambio aniónico *nanocomposite* para mejorar la eficiencia de desalación mediante ED.
 - Estudio de la mejora de membranas *nanocomposite* en términos de resistencia frente al *fouling* y transporte de aniones tomando como referencia membranas heterogéneas comerciales de polietileno.
 - Comparación del comportamiento de dos nanomateriales en las propiedades de la membrana *nanocomposite*.
 - Modelado matemático del comportamiento eléctrico de las membranas nanocomposite en comparación con membranas heterogéneas comerciales de polietileno.
- Uso de membranas *nanocomposite* para el tratamiento y valorización de concentrados de desalación mediante EDBM.

 Estudio de la influencia del tiempo de operación y la densidad de corriente sobre las principales impurezas generadas en HCI y NaOH producidos en el proceso de valorización de concentrados de desalación mediante EDBM.

De acuerdo con los objetivos específicos, y considerando la normativa vigente en la Universidad de Cantabria a través de su "Reglamento para la elaboraciónde tesis doctorales como compendio de artículos previamente publicados" [33], y la "Normativa de los estudios de doctorado de la Universidad de Cantabria" [34] para la elaboración de tesis con mención internacional, el presente trabajo se desarrolla en tres capítulos distribuidos de la siguiente forma:

El Capítulo 1: consiste en el planteamiento de la presente tesis, conteniendo el marco y los objetivos.

El Capítulo 2: supone el núcleo central de la tesis, incluyendo copia de los artículos que la sustentan. Estos artículos se integran en el ya mencionado objetivo general de la tesis, desarrollo de estrategias innovadoras para mejorar la sostenibilidad ambiental de la desalación mediante ED, incluyendo el estudio de la sostenibilidad de la integración de la ED con energías renovables en la publicación *"Sustainability assessment of electrodialysis powered by photovoltaic solar energy for freshwater production"*, el desarrollo de membranas nanocomposite para la mejora del proceso de desalación mediante ED en las publicaciones *"Enhancing fouling resistance of polyethylene anion exchange membranes using carbon nanotubes and iron oxide nanoparticles"* y *"Electrochemical impedance spectroscopy of enhanced layered nanocomposite anion exchange membranes containing iron oxide nanoparticles and carbon nanotubes"* y el tratamiento y valorización de los concentrados de desalación generados en los trabajos *"Electrodialysis with bipolar membranes for valorization of brines"* y *"Valorization of desalination brines by electrodialysis with bipolar membranes using nanocomposite anion exchange membranes"*.

El Capítulo 3: comprende un resumen global de los principales resultados junto con las conclusiones generales obtenidas así como las claves a las que se ha llega a través de la elaboración de esta tesis doctoral para seguir progresando hacia una desalación de agua mediante electrodiálisis más sostenible.

1.3. Referencias del Capítulo 1

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"Ciencia es todo aquello sobre lo cual siempre cabe discusión."

"Science is everything about which there is always discussion."



José Ortega y Gasset (1883-1955)

Filósofo/ Philosopher

CAPÍTULO 2: ARTÍCULOS CIENTÍFICOS

2.1 Artículo: "Sustainability assessment of electrodialysis powered by photovoltaic solar energy for freshwater production." (Carolina Fernández-González et al., Renewable and Sustainable Energy Reviews, 2015).

En este artículo se evalúa la sostenibilidad de la integración de la electrodiálisis (ED) con la energía solar fotovoltaica (PV) para la producción de agua, en comparación con el uso ED conectada a la red eléctrica, teniendo en cuenta aspectos ambientales, económicos y sociales. Los aspectos ambientales se han abordado desde el punto de vista de las emisiones de gases de efecto invernadero expresadas en forma de CO₂ equivalente; los elementos económicos se han presentado como el coste del agua obtenida por unidad de volumen; mientras que los aspectos sociales se han cuantificado como los puestos de trabajo temporales y permanentes generados.

En primer lugar, se introducen las tecnologías de ED y ósmosis inversa (RO) como principales tecnologías de desalación con membranas, centrando este estudio en el agua salobre, por ser el campo de aplicación en el cual la ED se usa a nivel industrial en la desalación de agua. Los datos globales de consumo de combustibles fósiles asociados a las tecnologías de desalación a nivel global permiten justificar la necesidad de integrar dichas tecnologías con energías renovables. Se presenta una visión del estado de arte de la integración de tecnologías de desalación con energías renovables donde se señala la integración de ED con PV como una de las combinaciones más prometedoras, para la cual se incluye un resumen de las plantas instaladas a nivel mundial. Posteriormente, se detallan los aspectos ambientales asociados al consumo energético de la ED y RO comparando las emisiones de CO₂ equivalentes correspondientes con el caso de estudio tratado. En este caso se considera una planta de desalación mediante ED con una capacidad de 39 m³·día⁻¹ para el tratamiento de agua salobre (desde 580 mg·L⁻¹ a 5.000 mg·L⁻¹ como salinidad) que integrase PV instalada en las Islas Canarias. En cuanto a los elementos ecómicos, en primer lugar se introduce una comparación de la economía de la desalación convencional (conectada a la red eléctrica) en comparación con la desalación renovable (conectada a energías renovables). Después se presenta un pronóstico económico a medio plazo de la evolución del precio del agua obtenida mediante una planta de ED conectada a la red eléctrica o a PV en las Islas Canarias suponiendo tres escenarios: optimista, intermedio y pesimista. En los tres escenarios se asume un descenso en los costes de inversión de las membranas y los módulos solares y una subida del precio de la electricidad. La diferencia entre los tres escenarios radica en los rangos de los valores que se asumen en cada uno. En el escenario más desfavorable para la integración ED-PV, tanto la subida del precio de la electricidad procedente de la red eléctrica como la bajada en los costes de inversión de los módulos solares toman el valor más bajo dentro del rango considerado. En el escenario más favorable para la integración ED-PV, los parámetros anteriores toman en este caso el valor más alto dentro del citado rango. En el escenario intermedio se utilizan valores dentro del rango. Los aspectos sociales se abordan desde el punto de vista de la generación de empleo temporal y permanente, primero para la desalación de agua y después aplicada al caso de estudio que integraría la PV. Por último, en este artículo se presentan las principales barreras técnicas, económicas y tecno-económicas que evitan una mayor penetración de la ED conectada con energías renovables en el mercado.

A continuación se resumen los principales resultados y conclusiones de este artículo.

En cuanto a los aspectos medioambientales, la integración ED-PV como alternativa a la conexión de ED a la red eléctrica provoca un descenso significativo de las emisiones de gases de efecto invernadero dando como resultado unas emisiones por valor de 0,02 kg $CO_2 \cdot m^{-3}$ a 0,03 kg $CO_2 \cdot m^{-3}$, un orden de magnitud inferiores a la conexión de ED a la red eléctrica, lo cual es directamente proporcional al ratio de cargas ambientales entre las posibles formas de alimentación eléctrica. La ED presenta unos consumos energéticos específicos menores que la RO para una concentración por debajo de 5.000 mg·L⁻¹ de sólidos totales disueltos. Por lo tanto, la integración ED-PV es una alternativa más sostenible ambientalmente que la integración RO-PV desde el punto de vista de la huella de carbono para ese rango de salinidad.

Economicante, en la actualidad, la integración de energías renovables con tecnologías de desalación en general y la ED-PV en particular, está asociada a zonas aisladas y remotas debido al alto coste del agua desalada. Sin embargo, la previsión a medio plazo presentada en este trabajo, apoyada sobre las hipótesis de un descenso en los costes de inversión en PV y membranas de intercambio iónico y un aumento del precio de la electricidad, todo ello considerando el caso de estudio de obtención de agua dulce en las Islas Canarias, ha mostrado la probable rentabilidad de la integración ED-PV antes del 2020 en el escenario más favorable y antes del 2050 en el más desfavorable. Se espera un rango de precios de agua producida mediante ED-PV entre 0,15 €·m⁻³ y 0,40 €·m⁻³ justo después del punto de rentabilidad.

Los beneficios sociales de las tecnologías de desalación referidas a la generación de empleo son claros. La desalación utilizando energías renovables genera más puestos de trabajo directos e indirectos, mejorando la percepción social de las nuevas plantas de desalación construidas gracias a la necesidad de construir el aporte fotovoltaico. Se puede asumir un amplio rango de generación de empleo de entre $1,03 \cdot 10^{-4}$ puestos permanentes por m³·día⁻¹ a 4·10⁻³ puestos permanentes por m³·día⁻¹ durante la operación de la planta.

Como principales barreras que evitan una mayor penetración de la integración de la ED con energías renovables destacan entre otras: el ajuste del suministro de energía intermitente de las energías renovables con la demanda de agua, la eficiencia de los módulos solares, y el alto coste de producción del agua dulce en comparación con su bajo coste en el mercado como *commodity*.

Por lo tanto, para conseguir una desalación más sostenible, el desarrollo de la desalación debe producirse en paralelo a un aumento en el uso de energías renovables. La justificada sosteniblidad de las energías renovables, y en particular la PV, junto con una disminución esperada en los costes de inversión de la PV, pone de manifiesto que la integración de tecnologías de desalación con energías renovables será provable en un futuro cercano. Las tecnologías de desalación son la solución más probable en un escenario global de aumento de la escasez de agua. Debido a que la ED tiene un menor consumo energético que la RO para el tratamiento de aquas con bajo contenido en sólidos en suspensión, el uso de ED debería aumentar a corto-medio plazo. En este contexto, a pesar de las barreras mencionadas en este trabajo, la combinación ED-PV se espera que juegue un papel relevante como una alternativa sostenible para la desalación de agua salobre. De acuerdo a los resultados de este trabajo, el uso extendido de ED-PV debería tener lugar entre los años 2020 y 2050, una vez que la desalación renovable sea más económica que la desalación convencional. Las cifras anteriores deberían ser de utilidad para los responsables de la toma de decisiones a la hora de seleccionar la opción mas adecuada para la obtención de agua dulce considerando la naturaleza multiobjetivo y multi-variable de la sostenibilidad.
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Sustainability assessment of electrodialysis powered by photovoltaic solar energy for freshwater production



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ABSTRACT

Membrane desalination does help at procuring an increasing freshwater (FW) global demand. Energy requirements of desalination technologies compromise the environmental sustainability of desalination. The integration of renewable energies with desalination technologies might improve the sustainability of desalinated water over other alternative FW sources.

This paper discusses the sustainability of Electrodialysis (ED) powered by photovoltaic solar (PV) energy as one of the most promising configurations for the desalination of brackish water. Environmental, with special focus on energy consumption as a function of salinity, economic, and social issues have been considered and main figures for an ED–PV case study in the Canary Islands focused in FW production are given. Energetic considerations have also been deeply discussed in the section of environmental issues. Reverse Osmosis has been taken as the reference technology. The reference energy consumption for ED of brackish water (2500–5000 mg L⁻¹) includes a range of 0.49–0.91 kW h m⁻³. Due to this range and regarding to the environment, the use of ED–PV is in the range of 0.02–0.03 kgCO₂ m⁻³ (only due to energy supply), which is a decrease of one order of magnitude compared to grid mix supply.

A medium-term forecast for ED–PV is presented in which might be economical over conventional grid mix supplied ED before 2020 under the most optimistic scenario, leading to a production costs around $0.15-0.4 \in m^{-3}$. With respect to social issues, renewable desalination contributes to a significant increase of local direct and indirect employment but under a wide range of 0.1–4 permanent positions per 1000 m³ day⁻¹.

Finally, the main identified barriers for ED–PV preventing a larger market penetration are the matching of the intermittent output of renewable energies with water demand, lifetime of membranes, efficiency of solar panels and the high production cost of freshwater compared to its low market price as commodity.

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1. Introduction

Desalination technologies (DES) are being extending all over the world in order to satisfy freshwater (FW) demand in countries under water shortages. Electrodialysis (ED) and Reverse Osmosis (RO) are two of the most important membrane DES technologies for the treatment of brackish water (BW), a water resource preferable than seawater (when available) due to economic reasons for FW production. Indeed, BW utilization has growth at a rate of 12% in the last decade [1]. The treatment of BW is a well-known application of ED [2]. A recent study has pointed out that DES of BW by means of ED is one of the applications where this technology is cost-effective [3]. This application is applied at industrial scale and several plants using ED (equipped with reversal polarity units) can be found all over the world. Some examples of DES plants under operation in the Canary Islands (Spain) are located in *Tamaimo* (capacity: 2100 m³ day⁻¹), *Valle de San Lorenzo* (capacity: 12,000 m³ day⁻¹), *Aripe* (capacity: $12,000 \text{ m}^3 \text{ day}^{-1}$) and *Icod II* (capacity: $4000 \text{ m}^3 \text{ day}^{-1}$).

No matter what the technology for DES is chosen, it is an intensiveenergy option. It is reported that, in general terms, to produce 1 m³ of FW by means of DES is necessary about 25 kg of oil [4]. The installed DES capacity in 2008, which was 7.5% of total world FW demand, would require 1.42 million tons of oil day^{-1} [5]. Thus, if the energy dependence of fossil fuels does not change, the increase of DES will create new energy and environmental problems. According to the World Water Council, the greatest challenges for the management of water are its integration with ecosystems and energy consumption [6]. In this sense, the sustainability of the production of FW is compromised. Sustainability must be understood as a multi-objective function with multiple input variables, being those variables grouped in environmental, economic and social objectives [7]. These 3 objectives usually present opposite trends and the most adequate trade-off must be pursued. Regarding production of FW, negative direct (from brines) and indirect (from the energy consumption) consequences for the environment can be considered, coupled to different levels of sectorial employment and final cost for each unit of volume produced. Consequently the integration of renewable energies in the production of FW must be an essential component of its future development. Whereas studies regarding the sustainability or at least the environmental component of FW production by different DES technologies are available in the literature ([8,9]), within that context, we have focused on the update of the current state-of-the-art of ED and its integration with renewable energy (RE) as photovoltaic solar (PV) energy from the three pillars of sustainability using a process engineering perspective. In this work, a case study used as example will consider an small capacity ($< 1000 \text{ m}^3 \text{ day}^{-1}$ as defined in [5]) ED plant located in the Canary Islands using BW from TDS 2000 to 5000 mg L^{-1} (such as those from low salinity BW aquifers) in order to provide FW for drinking purposes at TDS 200 mg L⁻¹ and powered by PV solar energy. Reverse Osmosis (RO) is the reference technology for comparison. All numbers will be expressed in terms of treated m³ thus no numbers of FW supplied population are reported. Thermal based technologies are also included in the context of the study. As a result, the work is divided in 6 sections: (i) a brief introduction to describe the intended aim of the work; (ii) the state-of-the-art of the integration of ED with renewable energies; (iii) environmental issues, especially those regarding indirect burdens from energy consumption; (iv) economic issues, focused on cost structure and time trend production costs; (v) social issues as level of employment and finally (vi) a summary of the current technical and economic barriers for a larger market penetration of the ED powered by PV. Elements discussed in the different sections can be considered for supporting and helping decision-makers in water management plans, especially in locations plenty of solar irradiation and BW resources.

2. The state-of-the-art of renewable ED

Many reviews are available in the literature discussing the integration of desalination with renewable energies ([4,5,10–20]). Among them, it can be found specific reviews that deal with solar DES ([17–19]) and even exclusively with PV–DES ([20]). Given this significant amount of available information, the present study includes a general summary of the state-of-the-art. Then the subject is focused in the integration of RE with ED as proposed technology in the present work.

Lots of possible combinations between RE and DES technologies are described. Table 1 includes a summary of these alternatives (black dots and ticks). Among them, it can be found thermal DES alternatives such as solar distillation (SD), multieffect humidification (MEH), membrane distillation (MD), thermal vapor compression (TVC), multistage flash distillation (MSF), multi-effect distillation (MED) and mechanical vapor compression (MVC). On the other hand, membrane DES options are ED and RO. Additionally, taking into account the different maturity stages of the RE and the availability of the renewable resources, the options with more potential have been highlighted.

Regarding the most tested technologies, the distribution of 131 representative renewable DES plants was reviewed in the project PRODES ([21,23]). In this project, it was reported that 85% of the RE–DES plants were powered by solar energy. Among the solar DES plants, 46% were membrane-based while 39% were thermal-based. The most used technology was RO with a 31% of the total installed capacity. Additionally, it should be emphasized the importance of PV energy with 34% of the RE–DES plants. This percentage is even higher, 43% of the installed capacity according to [5,24]. Moreover, the contribution of ED–PV in the former study of PRODES was of 3%, although in another recent reference a 9% was mentioned [11].

Table 1

Combinations of desalination technologies with RE according to [5,12,14,21,22]. The most promising alternatives according to [12] are highlighted with a tick. T=Thermal energy, E=Electric energy and M=Mechanical energy.

	Sola	r	Win	d	Geoth	ermal	Oce	an	
	Т	E	М	E	Т	E	E	М	Т
SD	•								
MEH	•				•				•
MD	•				•				•
TVC	•				•				•
MSF	\checkmark				•				
MED	\checkmark	•		•	•	•	•		•
ED		\checkmark	•	•		•	•	•	
MVC		•	•	•		•	•	•	
RO		\checkmark	٠	~		•	٠		

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Nomenclature	PPV price of PV [\in Wp ⁻¹]
	RF _{Elect} replacement factor of electrodes [°/1]
$A_{\rm AM}$ area of anionic membranes $[m^2]$	RF _{Memb} replacement factor of membranes [°/1]
$A_{\rm CM}$ area of cationic membranes $[m^2]$	RFPM ratio full plant membrane [°/1]
A_{Flect} area of electrode [m ²]	RFPPV ratio full plant PV [°/1]
AF amortization factor $\left[\text{vear}^{-1}\right]$	SEC_V specific energy consumption per unit of volume trea-
AP _{PV} available power of PV [Wp]	ted [kW h m ^{-3}]
ATV annual treated volume $[m^3 \text{ vear}^{-1}]$	TAC _{ED} total annualized cost of ED [€ m ⁻³]
C_{Chem} cost of chemicals [$\in \text{m}^{-3}$]	TAC _{PV} total annualized cost of PV [€ m ⁻³]
C_{Disp} cost of disposal [$\in m^{-3}$]	TCC _{ED} total capital cost of ED [\in]
$C_{\rm FD}$ cost of ED without membranes [€]	TCC _{PV} total capital cost of PV [€]
C_{ED} cost of water obtained in a ED/Grid plant [\notin m ⁻³]	TC _{Oper} total operation cost $[\in m^{-3}]$
C_{FloctB} cost of electrode replacement $[\notin m^{-3}]$	TC _{O&M} total operation and maintenance cost (without elec-
C_{Energ} cost of energy $[\in m^{-3}]$	tricity) [$\in m^{-3}$]
$C_{\rm Ib}$ cost of labor $[\in m^{-3}]$	
C_{Memb} cost of membranes $[\in]$	Abbreviations
C_{MembR} cost of membrane replacement [$\in m^{-3}$]	
$C_{\text{ED, PV}}$ cost of water obtained in a ED–PV plant [$\in \text{m}^{-3}$]	BW brackish water
C _{PVI} cost of PV infrastructure [€]	DES desalination
C_{PVM} cost of PV modules [€]	ED electrodialysis
C_{Sp} cost of spares $[\in m^{-3}]$	EDR electrodialysis reversal
D_{AS} dosage of anti-scalants [kg m ⁻³]	FW freshwater
DC_{ED} direct cost of ED [€]	IEx ion-exchange
DC_F fraction of direct cost [°/1]	MD membrane distillation
DC_{PV} direct cost of PV [€]	MED multi-effect distillation
DP depreciation period [y]	MEH multi-effect humidification
FR flow rate $[m^3 day^{-1}]$	MSF multistage flash distillation
IC_{ED} indirect cost of ED [€]	MVC mechanical vapor compression
IC_{PV} indirect cost of PV [\in]	PV photovoltaic
IR interest rate [°/1]	RE renewable energies
NEH number of equivalent hours at a solar irradiation of	RO reverse osmosis
$1000 \text{ W m}^{-2}[\text{h day}^{-1}]$	SD solar distillation
P_{AM} price of anionic membranes $[\in m^{-2}]$	SEC specific energy consumption
P_{AS} price of anti-scalants [$\in kg^{-1}$]	SW seawater
$P_{\rm CM}$ price of cationic membranes [$\in m^{-2}$]	TDS total dissolved solids
P_E price of electricity [$\in kW h^{-1}$]	TVC thermal vapor compression
P_{Elect} price of electrodes [$\in m^{-2}$]	
PR_{PV} performance ratio of PV [°/1]	

In spite of being a considerable number of RE–DES plants, it is worthy to mention that most of these plants were of small capacity and they have been developed in the context of international cooperation research projects, with no further expectations of long-term operation ([12,25]). The main reason for the lack of commercial high scale RE–DES plants is the economic constraint associated to water production cost.

Considering the economics of DES technology, it is reported that membrane desalination by means of ED or RO are currently the most cost-competitive solar options [11]. Additionally, in Table 1 it was shown that among the most promising renewable desalination configurations are both ED-PV and RO-PV. Nevertheless, there are several PV options that can be considered in order to be coupled with membrane processes: PV energy with batteries, PV alone (without storage), PV as an auxiliary energy source and a hybrid PV system (PV and an auxiliary component to supplement the local source, usually, fossil fuels or wind generators). A qualitative comparison for all of these alternatives individually and for membrane DES technologies powered by PV can be found in [26], as a function of technical, economic and human resource criteria. In this work, it can be seen that the PV alone is considered superior than the others alternatives both in technical and economic terms. In case of human resources, certain variability of the PV alone makes the PV with batteries a better option. Should the specific application introduced (BW or SW–DES by means of ED or RO), it was showed that DES by means of PV without storage is the best option both for ED and RO. Additionally, DES with PV performances better for BW than for SW. Besides the better option for PV–DES is the desalination of BW by small scale ED plant (below 2 m³ day⁻¹). On the subject of comparison between RO and ED, it can be also added that, regarding to the installation in remote areas, ED is more suitable for BW–DES due to its robustness and simpler operation and maintenance than RO [4,15]. Besides, ED has a better adaptation to intermittent energy input [15] and according to [20] ED–PV is an alternative more cost-competitive for small scale systems than others.

Regarding to the combination ED–PV, it can be mentioned that there are several installations of ED–PV worldwide. All of the plants summarized in Table 2 are stand alone. In this Table 2, it is recorded some of the technical characteristics of the installation (location, capacity, year, feed salinity and number of cell pairs), the economics (water cost) and the energy related issues of the process (specific energy consumption (SEC) and PV system features). The existence of subsidies for desalination in the country of origin of the ED–PV installation has also been included. From the data of Table 2, it can be concluded that despite of the wide range of plant capacities (1–200 m³ day⁻¹), most of the installations were of small size and desalinated BW all over the world. The SEC is between 0.4 and

Table 2

ED–PV powered desalination plants installed worldwide. All original \$ references were converted to \in by a ratio of 1.3417 \$ \in^{-1} , while the figures in INR were converted to \in by a ratio of 64.7153 INR \in^{-1} .

Location	National subsidies	Capacity $(m^3 d^{-1})$	Year	Feed TDS $(mg L^{-1})$	Cell Pairs (number)	Water cost (€ m ⁻³)	SEC (kW h m ⁻³)	PV system (kW _p)	Ref.
Spencer Valley, Mexico	Yes	2.8	1986	1,000	-	11.9	0.82	1 (tracking)+2.3 (stationary)	[11]
Thar Desert, India	Yes	1	1986	5,000	42	-	1 ^b	0.45	[11]
Ohsima Island, Japan	Yes	10	1986	a	250	4.3	-	25	[11]
Fukue, Japan	Yes	200	1990	700	-	-	0.6-1	65+Batteries	[11]
New Mexico, Mexico	Yes	18	1996	900	-	-	0.8	2.3 + Batteries	[11]
Isa, Bahrain		1.14	2002	3,300	24	-	-	0.132	[11]
Alicante, Spain	Yes	1.32	2006	2,000	80	-	-	0.272	[11]
Alicante, Spain	Yes	13.7	2008	4,473	-	0.14-0.32	1.33-1.47	38.45	[33]
-		< 100	-	< 5,000	-	7.6-8.7	1.5-4	-	[34]
-		-	-	1,500 3,500	-	4.3-11.9	1.5 4	-	[20] [20]
-		< 100	-	-	-	8-9	3-4		[21]
La luz, Mexico	Yes	15	1979	-	-	-	-	5	[35]
Colorado, USA	Yes	2.8	1995	-	-	-	-	2.3	[35]
Canary Islands, Spain	Yes	4	2013	2,240-3,392	340	-	0.618	3.69	[36]
Zaragoza, Spain	Yes	4.3	2013	580-10,000	10	-	0.4-0.6	0.103-0.308	[37]
Range	-	1–200	1986- 2013	580-5,000	10-340	0.14–11.9	0.4-4	0.103-65	Ī

^a Seawater sources.

^b kW kg⁻¹ removed salt.

4 kW h m⁻³ and most of the plants used PV alone, without any storage. SEC values will be discussed in detail later. It is worth mentioning that all the countries present in Table 2 have desalination subsidies. Some examples of these subsidies can be found in [27] for Mexico, [28] for India, [29] for Japan, [30] for Spain and [31] for USA. Spain is an example of country with subsidies for desalination of water [32]. In the specific case of Canary Islands, a recent Spanish for Official State Bulletin ([30]) has approved subsidies accounting for a total amount of 4 million of euros for several desalination plants.

3. Environmental issues of ED associated to energy consumption

Technological advance has caused the reduction of the energy consumption of DES. However, it can be found a great difference between the energy requirements of the available DES technologies. Consequently, these different requirements lead to different environmental burdens due to the different final energy sources (such as electricity) that can be used as will be discussed next. Because the final energy sources are based on primary energy sources (from coal to sun), the associated environmental burdens will be also different. Thus, the indirect burdens of DES plants comes from its SEC in the form of different amounts of greenhouse gases, sulphur dioxide, nitrogen oxides [38] among others due to the source used to power the facility as the released in-situ air pollution of DES is meaningless. Consequently, not only it is relevant the SEC value but the chosen source, because it determines the actual burden and compromises the environmental sustainability assessment.

In general terms, thermal processes (both BW and SW) have higher SEC per unit of volume than membrane processes (SEC of thermal processes is in the range of 7–27 kW h m⁻³ while in membrane based technologies decreases up to 1–6 kW h m⁻³ [13,34]). Regarding our target water source, within membrane processes, ED and RO presents similar SEC for BW–DES (SEC of BW–RO is 1.5–2.5 kW h m⁻³ while SEC of BW–ED has a lower

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bound at 0.7–2.5 kW h m⁻³ [24]). Therefore, according to the previous reference, from a strictly cost-effective point of view, the break-point as a function of salinity favors ED at TDS below 5000 mg L⁻¹, and from an SEC point of view, the break-point is at 2500 mg L⁻¹. In this sense, it was recently highlighted that the most cost-effective operation point in ED is strongly dependent of energy consumption because of the input and output concentration relationship and only a narrow combination of those values can provide the lowest cost [3].

For example, in [39] EDR presents a SEC around 10% lower than RO in the treatment of a BW with a TDS of 1015 mg L⁻¹. In the case of SW, the increase in ED energy consumption makes of the RO the chosen technology [17]. Typically, EDR is selected over RO for systems that have particular water chemistry such as a high sulfate to chloride ratio [9]. Due to thermodynamic limitations in the SEC of DES, it is concluded in [40] that further improvements in the energy efficiency of DES must be focused on the reduction of pre and post treatments stages, by improving membrane resistance against biofouling and the mixing in the modules. Moreover, eliminating the pretreatment would substantially reduce the SEC, capital cost and environmental impact of DES [40]. However, DES requires a feed water free of pollutants in order to avoid operational problems [41] being the need of pretreatment more significant for RO than for ED [14].

Additionally, due to the energy required, the installation of new DES plants has affected the energy and the environmental footprint of a country [42]. Thus, it is proposed that any new DES plant should only be constructed if it does not affect the greenhouse gas balance and therefore, the ratio between renewable energy and burning fossil fuel energy is preserved over time [43]. The direct integration of membrane process with renewable energies (such as RO–PV) is reported to be more sustainable than other conventional alternatives when the consumption of fossil fuels is prioritized over other sustainability criteria [8]. ED–PV for BW–DES was reported to be a sustainable DES alternative with a saving of up to 0.724 kgCO₂-eq. m⁻³ (originally 1.81 gCO₂ batch⁻¹) in relation to the electrical grid connection in Spain using an emission factor of 0.223 kgCO₂ kW h⁻¹ [37].

Table 3

Summary of electricity requirements for RO [28] according to Table 2 for ED–PV, the case study in the Canary Islands and associated life cycle CO_2 -eq. emissions (LC) for each option. Values expressed as kg CO_2 -eq.(capita day)⁻¹) can be obtained by multiplying by 0.15 m³(capita day)⁻¹ for the Canary Islands region [48].

Technology	Salinity range (mg L ⁻¹)	SEC (kW h m ⁻³)	LC CO ₂ -eq. (grid mix option, emission factor 0.511 kg CO ₂ -eq. kW h^{-1})*** (kg CO ₂ -eq. m ⁻³)	LC CO ₂ -eq. (PV option, emission factor 0.033 kg CO ₂ - eq. kW h^{-1}) *** (kg CO ₂ -eq. m ⁻³)
RO ED-PV Case study ED-PV	BW 580– 5000 2500– 5000	1.5–2.5 0.4–4 0.49–0.91	0.8–1.3	0.05–0.08 0.01–0.13 0.02–0.03

* A range of 0.2–2.0 kg CO $_2$ -eq. m^{-3} would be obtained in case of a connection to the grid mix

** A range of 0.3–0.5 kg CO₂-eq. m^{-3} would be obtained in case of a connection to the grid mix

**** Emission factors were taken from [47].

In order to compare the environmental sustainability of both membrane DES options, Table 3 presents the Global Warming burdens for a case study of a ED-PV plant located in Puerto de la Cruz, Santa Cruz de Tenerife, Canary Islands (solar irradiation at an inclined plane of 25° of 5.26 kW h m⁻² day⁻¹ according to [44]). The water source is BW from an aquifer at an inlet concentration of TDS 2500, 3000 and 5000 mg L⁻¹. Final FW product is at TDS 200 mg L⁻¹. The energy consumption for this specific case study was obtained from simulations using an online simulator [45]. Data for the membrane stack appears in Table 5. The irradiation for the model at the selected angle was of 0.692 kW m^{-2} and was calculated as the annual average of maximum daily irradiation for each month at the 25° angle [44]. This simulator provides a base case of an ED plant of $48 \text{ m}^3 \text{ day}^{-1}$ for a BW-DES plant coupled with PV (model originally named as "BWED 48 FB PV"). The simulator was developed by The Middle East Desalination Research Centre ([46]). Energy consumption values are available in Tables 3 and 5.

Because of the linear relationship between SEC and LC emissions, operation in the low range of conductivity directly favors the ED–PV versus RO. According to Table 3, a wide variability is shown regarding the pair salinity-energy consumption because of the different sources. However, in Table 2, different sources provide similar SEC values at salinity around 5000 mg L⁻¹, which demonstrate the validity of the simulation tool used. Different studies considering the life cycle thinking have been published. The energy assessment of the distribution of water in Sicily shows that DES supposes a 74% of the total impact and represents the higher contribution to all the impact categories considered, being the most relevant impact categories global warming potential, non-renewable energy resources and water consumption [49]. However, it is worth to keep in mind that DES is not the only alternative for obtaining FW. The life cycle assessment of recycled, desalinated and imported water in California showed that the emissions of DES were 2-18 times higher than the other alternatives and 85% of the energy required in DES belongs to the treatment that takes place in the DES plant [50]. Life cycle assessment of desalination in comparison with the transfer of water from a river was performed in Spain [51], concluding that the more relevant stage in terms of environmental load of both alternatives was the operation. The environmental load of the transference of water was slightly lower than the corresponding to DES. However, DES was presented as an alternative with more room for improvement.

Apart from the indirect emissions of greenhouse gases due to the production of the PV modules, land is one natural resource affected by the installation. According to the NREL of the U.S. Department of Energy [52], for small PV plants (between 1 MW and 20 MW) a value of 61 GW h(yr km²)⁻¹ (equivalent to 30 MW km⁻²) is expected to be used, including roads and other facilities. A range of 72–203 GW h(yr km²)⁻¹ is suggested in [53] for an irradiation of 1800 kW h m⁻² yr⁻¹. For sustainability purposes, land use should be also taken into account.

It has been widely proven that the environmental sustainability of DES is strongly related to a decrease in the emissions of greenhouse gases (indirect burdens) whereas impacts from brines are specific to an individual site (direct burden). The integration of ED–PV for the DES of BW is the most sustainable membrane DES technology due to its lower SEC especially in the low range of conductivity. The use of PV supposes a reduction of one order of magnitude in the greenhouse gases emissions in the stage of DES life cycle in the suggested highest burden step, the operation. This improvement might make of DES a more environmentally sustainable alternative than other FW resources such as transfer of water. Thus, in order to achieve a more sustainable DES, the development of DES should be done in parallel to an increase of the use of renewable energies.

4. Economic issues of ED

4.1. The economy of renewable vs conventional desalination

Regarding the economic assessment of ED, Table 4 presents the specific water cost for FW production by means of conventional and renewable DES considering BW or SW including specific data for membrane DES. From this Table 4, it can be observed that in general terms, renewable DES for both BW and SW is more expensive than conventional DES (BW–DES: conventional 0.19– $9.68 \in m^{-3}$ and renewable 2–18.63 $\in m^{-3}$; SW–DES: conventional 0.34–2.7 $\in m^{-3}$ and renewable 0.71–21.61 $\in m^{-3}$).

The origin of the different costs between renewable and conventional DES is that the introduction of RE in DES technologies involves a decrease in operation costs but at the same time, a considerable increase of investment costs [18,56]. This leads to more expensive water from renewable DES, because even if wind or solar resources are for free, the obvious capital cost needed to generate the renewable energy must be effectively balanced by the produced FW.

Additionally, it must be taken into account that the difference of scale between conventional and renewable DES, also contributes to the pronounced difference of water production cost

Table 4

Summary of cost of water produced by renewable energy desalination and conventional desalination. All original \$ references were converted to \in by a ratio of 1.3417 \$ \in^{-1} . Data from original sources.

Energy	BW		SW		
supply	Water cost (€ m ⁻³)	Ref.	Water cost (€ m ⁻³)	Ref.	
Generic conv.	0.19–9.68	[18,34,54]	0.34–2.7	[18,28,54,55]	
RO _{Large Scale}	0.19-0.40	[34]	0.34-0.49	[34]	
RO _{Small Scale}	0.42-9.68	[34]	0.52-1.28	[34]	
ED _{Large Scale}	0.45	[34]	-	-	
ED _{Small Scale}	0.78	[34]	-	-	
Generic RE	2-18.63	[11,18,34]	0.71-21.61	[11,18,34,55]	
RO-PV	4.84-6.78	[34]	5.93-21.61	[34]	
ED-PV	6.34-11.93	[34]	4.23	[11]	
RO-Geo	-	-	0.85-2.14	[55]	
RO-Wind	-	-	0.71-1.76	[55]	
RO-ST	-	-	1.50-1.86	[55]	

[12,18]. From Table 4, it can be observed that the difference between renewable and conventional DES depends on the capacity of the DES plant. If the ratio of production cost is done between a renewable plant (usually of small capacity), and a conventional plant of large capacity, it will result in a great difference. Some examples of this ratio, taking into account grid and PV energy supplies, are 12–36 for BW–RO, 12–55 for SW–RO and 14–27 for BW–ED. Nevertheless, if the water cost of small conventional DES plants is considered, the ratio between the cost of renewable and conventional DES decrease to 5–42 for SW–RO and 8–15 for BW–ED. In the case of the BW-RO, the combination PV–RO can be even cheaper than the conventional BW–RO plant (ratio renewable/conventional=0.5–16.2). SW–RO coupled with other RE such as geothermal and wind, in some cases, can be also a cheaper option than small conventional DES plants.

Therefore, nowadays, the profitability of renewable DES is associated to isolated locations or areas with very limited access to grid power, where small stand-alone plants are the only techno-economic solution. The selection of the suitable renewable sources for these plants depends on several factors such as plant size, salinity of the raw water resource, remoteness, technical infrastructure and type of local resources [12]. Among the possible combinations of DES with RE, solar and wind energy are the most promising in terms of economic and technological feasibility [5]. Actually, in practice, the suitable RE for stand-alone power generation are wind turbines and PV modules [16], being PV the technology recommended for small capacity plants [14,25,57]. However, it must be taken into account that DES systems powered by PV use complex, capital intensive, high-tech equipment; water is produced with extremely high quality but also is relatively expensive [26]. Although some other advantages of PV such as feasibility of developing small DES plants, limited maintenance cost, environmentally friendly, not noise or direct pollution, easy transportation and installation ([12,20,57]), might balance the PV economics [12].

4.2. Economic issues in the case of study: ED-PV in the Canary Islands

It has been mentioned that ED is the chosen membrane technology for the treatment of BW due to its advantages over RO especially at the low range of conductivity. In this sense, the difference of production costs between conventional and renewable BW–DES is still preventing the full expansion of ED–PV in the market. Nevertheless it is said that the profitability of renewable DES will be achieved in a near future due to the expected increase in the electricity cost as utility. Additionally, in the particular case of ED–PV, the investment cost of PV and ion exchange (IEx) membranes is also expected to decrease. Despite of mentioning this likely scenario, to the best of our knowledge, no reference has previously estimated a period of time in which renewable DES could potentially become an economically attractive option. Thus, in this study, a first attempt to give a preliminary temporal range in which the integration of ED with PV will be economically viable is presented next.

In Fig. 1, it is shown the prediction for the evolution of the production cost of FW obtained by means of ED-Grid and ED-PV in the case study of the Canary Islands. This prediction has been developed under three different scenarios: ED-PV or ED-Grid high, which are the scenarios with the most adverse values of the variables: ED-PV or ED-Grid medium, which are representative of mean values: and ED-PV or ED-Grid low, which are the scenarios with the most favorable values of the variables. These estimations suppose the continuity of the trend of increasing electricity cost and decreasing PV and membrane investment costs. In order to quantify these trends, two different strategies have been followed. In the case of the electricity cost, historical data of the energy price for industrial consumers in Spain has been collected from the statistical office of the European Union (Eurostat, [58]). The medium annual increase of the electricity price has been calculated for a period of 12 years (from 2000 to 2012) and it has been supposed to be maintained at the same rate in the period of 2012 to 2050. Of course this can be considered as a rough assumption but it is out of the scope of this paper to complete predictions on utility cost in Europe or Spain.

Three different initial membrane investment costs were assumed (see Table 7). Regarding to the decrease of the investment cost in membranes, the predictions of a decrease of one order of magnitude in 10 years was taken from [59]. Afterwards, the price of membranes has been considered constant. In the case of PV, the forecast provided by [60], ranging from 4.25 \in W_p⁻¹ to $0.75 \in W_p^{-1}$, together with the two possible predictions proposed in [61] (2050 prices: $1.52 \in W_p^{-1}$ or $0.28 \in W_p^{-1}$) have been used. These range cover other proposals such those pursued by the SunShot Intitiative of the U.S. Department of Energy, targeting 0.5 W_{p}^{-1} by 2020 [62]. The decrease of the membrane and PV prices was supposed to be lineal regarding time, with a constant annual decrease rate. The model used in order to estimate the cost of DES can be found in the Appendix 1. For a better understanding of this model, Fig. 2 includes a graphical explanation of the relationship between the different data and variables used. Additionally, this Fig. 2 includes a clear differentiation between the variables and data used for the cost estimation of ED-PV and ED-GRID. For the sizing of the installation in the Canary Islands, that is, membrane area and PV installed power, the same simulations as in the environmental assessment were considered. The list of technical variables obtained from these simulations is shown in Table 5 as a



Fig. 1. Desalination cost projection for ED-Grid and ED-PV.



Fig. 2. Flow chart of the relationship between variables and constants used in the model for cost estimation.

Table 5

Values for the technical variables obtained from the simulator [45] for a feed salinity of 2500, 3000 and 5000 ppm and a product salinity of 200 mg L^{-1} .

		Low value	Medium value	High value
Salinity of the feed SEC Specific flow rate Number of cell pairs per stack	$\begin{array}{l} (mgL^{-1}) \\ (kWhm^{-3}) \\ (m^3h^{-1}m^{-2}) \end{array}$	2500 0.49 0.09 50	3000 0.57 0.10 50	5000 0.91 0.11 50
Active area of membranes Number of stacks	(m ²)	0.3 4	0.3 4	0.3 4

function of each of the three assumed scenarios (low, medium or high). Additional technical and economic assumptions are displayed in Tables 6 and 7, respectively.

Fig. 1 corresponds to the FW production cost by means of conventional DES of BW by ED in the three scenarios (ED-Grid High, ED-Grid Medium and ED-Grid Low). It can be observed two different evolutions in the cost of the water with time. In the case of ED-Grid High, the cost of the water product decreases with time during the first 10 years and then increases up to 2050. In contrast, in the case of ED-Grid Medium and ED-Grid Low water cost always grows. This difference is due to the strong influence of the membrane investment cost in ED-Grid High. At the beginning of the period, the fall in the annualized cost from membrane investment is higher than the rise in the price of electricity. However, after 10 years, when the price of membranes becomes constant, the increase in the price of electricity cause the same in the price of the water in the scenario ED-Grid High, even more pronounced than in scenarios ED-Grid Medium and ED-Grid Low, since in the former scenario larger energy consumption is needed for the desalination of water (see Table 5). Regarding to the results of Fig. 1, the initial values of water cost in two of three estimations

Table 6

Values for the technical parameters assumed in the estimation. NEH was calculated as an annual average irradiation for an inclination angle of 25° (optimum angle) for the selected location.

		Value	Reference
Daily working hours	(h)	22	[65]
Dosage of anti-scalants	(kg m ⁻³)	0.0002	[65]
NEH	(h day ⁻¹)	5.26	[44]
PR _{PV}	(%)	75	[61]

Table 7

Values for the economic parameters assumed in the estimation.

		Value	Reference
Annual increase in electricity price	(%)	5.95	[58]
Annual decrease in membrane price	(%)	20	[59]
Annualized increase in water price	(%)	1.7	[48]
Depreciation period	(year)	20	[66]
Interest rate	(%)	5	[67,68]
Initial membrane prices _{Low}	(€m ⁻²)	74.5	[69]
Initial membrane prices _{Medium}	(€m ⁻²)	100.2	[70]
Initial membrane prices _{High}	(€m ⁻²)	842	[71]
Price of electrodes	(€ m ⁻²)	1000	[65]
Ratio full plant/membrane		0.71	[65]
Ratio full plant/PV		0.5	[72]
Replacement factor of membranes	$(\% year^{-1})$	15	[73]
Replacement factor of electrodes	(% year ⁻¹)	100	[74]
Fraction of direct cost	(%)	10	[73]
Price of anti-scalants	(€ kg ⁻¹)	3	[65]
Cost of spares	(€ m ⁻³)	0.25	[73]
Cost of labor _{Low and Medium}	(€m ⁻³)	0.022	[73]
Cost of labor _{High}	(€m ⁻³)	0.184	[74]
Cost of brine disposal	(€ m ⁻³)	0.0011	[73]
Conversion rate	(€\$ ⁻¹)	1.3417	[75]

(0.30, 0.28 and 0.84 \in m⁻³, respectively) are similar to the figures reported in the literature for the conventional BW-ED (see Table 4, $0.45-0.78 \in m^{-3}$) for 2005 as reference. The lower values of the Low and Medium scenarios, in relation to the minimum previously reported water cost range, are probably due to the strong influence of several hypotheses such as cost of labor or price of chemicals. These values affect the final water cost, but they do not affect the difference of costs between renewable and conventional desalination because they belongs to the operation and maintenance cost. Regarding to the curves corresponding to ED-PV it can be seen that the initial estimated water cost (0.30, 0.28 and 0.84 \in m⁻³) is remarkably lower than the values reported for generic renewable BW-DES (see Table 4. 2.00–18.63 \in m⁻³) and for BW-ED-PV in particular (see Table 4, 6.34–11.93 € m^{-3}). However, in Table 2 corresponding to ED–PV plants, a different range of 0.14–11.9 $\in m^{-3}$ was reported. This is possibly due to different references included in than compared to the reference chosen previously [34]. The difference between the estimated values and those reported in the literature might be explained by the high variability of the investment costs for PV, and also, due to the influence of local parameters such as solar irradiation and temperature of operation over the performance of PV. Moreover, the ED-PV cost estimated in this work for the Canary Islands in Spain is very similar to the one reported for a ED-PV installation in Alicante (Spain) (0.14–0.32 \in m⁻³ [33]). Additionally, the distribution of the annualized cost of ED and PV obtained in the present work (48.3% ED and 51.7% PV for ED-PV High) is comparable to that reported in [17] for the specific integration of RO-PV (41-69% RO, 31-59% PV), the most similar renewable DES cost distribution to ED-PV reported in the former reference. As a benchmark, Fig. 1 also includes the historical evolution price of water for the consumers in the Canary Islands and a prediction of its evolution (pink and green lines, respectively). This price $(1.15-1.97 \in m^{-3})$ is higher than the water cost estimation of this work (0.12–1.25 \in m⁻³) because the former not only includes the production cost of the FW, but also includes other costs such as distribution and later treatment of the water. Values expressed as kg CO_2 -eq.(capita d)⁻¹) can be obtained by multiplying by 0.15 m³(capita d)⁻¹ for the Canary Islands region [48].

According to the estimations presented in this Fig. 1, under the most favorable conditions, the combination ED–PV could be potentially profitable before 2020 (intersection between ED–PV Low and ED–Grid Low curves), while under the worst conditions, 20 to 30 additional years would be necessary (intersection between ED–PV High and ED–Grid High curves). In the other hand, in Fig. 3 it is presented the ratio between the production cost of ED–PV and ED–Grid in the three chosen scenarios. This representation allows a clear comparison of the two DES options regardless of the values of the economic assumptions that equally affect ED–Grid and ED–PV cost. The initial values of these ratios are 2.45, 2.08 and 1.38 for the Low, Medium and High scenarios, respectively. These values are very far away from those which can be calculated from data in



Fig. 3. Ratio of the cost of the water produced by an ED plant directly connected to PV energy and connected to the grid.

Table 4 (8.13–15.3 for BW-ED). However, the ratios calculated in this work fit better the relationship of 1.29 reported in [63], for the specific case of the comparison of ED-PV and ED powered by means of a diesel generator. This could be due to the fact that in [63], both ED-PV and ED-conventional data are calculated using the same economic assumptions. As opposite, as the data from Table 4 is provided by individual references of conventional and renewable DES plants, the variability of the completed economic assumptions lead to very different figures than those reported in this work. According to Fig. 3, in 2017 the cost of renewable and conventional ED would be equal under the most favorable scenario. However, under the other two scenarios the economics of both desalination technologies would not be equal until 2024. Obviously, there is no question about the potential influence of the location in the case study. For electro-powered processes, in Spain, the effect of location could lead up to differences as high as 170% in the requested PV power for a defined efficiency [64]. This has a direct effect on the economics of the water. A reduction of 25% in the solar global irradiation (0.519 kW m⁻² of maximum daily irradiation instead of 0.692 kW m⁻²) would lead to a price of 0.12–0.33 \in m⁻³ in the EP– PV medium (instead of 0.11–0.28 \in m⁻³) and consequently, a delay in the potential profitability of ED-PV (after 2020 in the most optimistic scenario and before 2050 in the most pessimistic one).

Nowadays, renewable DES is still more expensive than conventional DES and thus, renewable DES profitability is associated to isolated areas with no or difficult access to grid electricity. The reported costs for both RO–PV and ED–PV are much higher than the cost of conventional membrane DES of BW. The preliminary forecast presented in the present work for the integration ED–PV, based on a potential increase in electricity price and decreases in membrane and PV investment cost, has confirmed the likely profitability of renewable DES in the near future, making of renewable DES not only a more environmentally sustainable alternative, but also more economically sustainable.

5. Social issues as employment generation

The construction and operation of new DES plants implies not only economic considerations but also social issues. The social acceptability of new DES plants can be improved by the generation of job opportunities [38]. Although modern DES plants can operate largely unattended because of automation [76], the construction of new DES plants is associated with the creation of local employment [77]. However, this staff must be qualified, since qualified employees are an essential requisite for a well-established DES industry [78]. Tasks as operation monitoring, analyzing the trends of information, anticipation of problems and maintenance of equipment must be done by trained staff [79]. This is indispensable for the sustainable operation and maintenance of RO [80], with a more complex maintenance than ED and some thermal DES technologies [8].

5.1. Temporary and permanent work

Regarding to the construction of DES installations, it is estimated that a DES plant of 189,000 m³ day⁻¹ and 25 km of pipelines could potentially require up to 280 temporary workers (80 for the plant and 200 for the pipelines [81]) not matter the selected technology. It is worth to mention that the employment generated during the construction of a DES plant is temporary, but also significant during the years of construction.

In the case of the operation of the plant and thus, permanent employment, according to [83], workers in a DES plant can be divided in 5 groups, management, administration, operation, maintenance and training-safety-lab. The reported figures of employees needed in operation and maintenance are 2 workers at full-time supposing 8 h day⁻¹ and 176 h month⁻¹ for a capacity of 3 MGD $(11,364 \text{ m}^3 \text{ day}^{-1})$ in EDR [39], 5 employees for a RO plant of 1250 m³ day⁻¹ [83], 75 employees for 50,000 m³ day⁻¹ (DES technology not specified) [82], 12 workers for a in RO plant of $50.000 \text{ m}^3 \text{dav}^{-1}$ [84] and 31 workers for a in RO plant of 300,000 m³ day⁻¹ [85]. These data suppose a wide range of employment intensity: $1.03 \times 10^{-4} - 4 \times 10^{-3}$ permanent positions $(m^3 day^{-1})^{-1}$, probably, due to the scarcity of references that provide this type of data and the variability in the DES plant capacity. It must be taken into account that changes of scale in the capacity of a DES plant influence the number of workers. Thus, for instance, a plant with a capacity of 100 MGD $(378.800 \text{ m}^3 \text{ dav}^{-1})$ (DES technology not specified) employs only 4 times the workers than a facility with a capacity of 3 MGD $(11,364 \text{ m}^3 \text{ d})$ [86]. Additionally, technological development of the country and labor cost should also be taken into account. Thus, while a RO plant located in Adelaida (Australia), with a capacity of 300,000 m³ day⁻¹, has a ratio of 4×10^{-3} permanent worker $(m^3 day^{-1})^{-1}$, the lower labor cost in Argelia causes a fall of this ratio down to 5×10^{-4} permanent worker $(m^3 day^{-1})^{-1}$ [85]. In relation to the comparison between RO and ED, in [39] it is reported that for the treatment of the same BW and the same plant capacity, EDR requires around an 18% more hours of staff than RO. However, insufficient data to claim a larger employment intensity in RO compared to ED or viceversa is at least questionable.

5.2. Social issues in the case of study: ED-PV in the Canary Islands

Taking into account direct and indirect jobs in the 5 groups previously mentioned, up to 207 employees can be involved in the daily activities in a desalination plant (DES technology not specified) with a capacity above 50,000 m³ day⁻¹ [83]. Additionally, if ED is supplied by PV, each installed MW_p could create around 30–60 direct and indirect jobs [87]. As the employment intensity is expressed considering flow rate capacity, the same rate of 1.03×10^{-4} – 4×10^{-3} permanent positions \cdot (m³ day⁻¹)⁻¹ during the operation (plus corresponding from PV), 4.2×10^{-4} temporary positions \cdot (m³ day⁻¹)⁻¹ and 8 temporary positions \cdot km pipeline⁻¹ during the construction phase, can be applied to the described case study corresponding to the Canary Islands.

This section makes clear that DES can contribute to a significant increase in the local employment of certain area in the construction phase. The employment intensity of EDR was reported to be similar to RO. The combination ED–PV generates more direct and indirect employment than conventional membrane DES because of the benefits of the PV installation. The new employment generated might improve the social acceptance of new DES plants making DES a more sustainable alternative for the production of FW.

6. Technical and economic barriers for the integration of ED with renewable energies

The environmental benefits of ED have been shown in a previous section; nevertheless there are some barriers that should be overcome before developing the full potential of ED. For this section, three different kinds of barriers are defined: technical, techno-economic and economic. Technical barriers are related to unsolved scientific problems that limit the performance of the system. Techno-economic barriers are associated to process optimization so can be directly converted into economic limitations. The competitiveness of the technology in the market relates to the economic barriers.

The most challenging technical issue for the integration of ED with solar energy generation is the optimum matching between intermittent output of RE and water demand [13]. According to [88], there are two possible strategic solutions to solve this problem: systems oriented to satisfy DES needs (demand-side management) and systems oriented to supply energy for DES (power management). Demand-side management uses hybrid energy units capable of the production of a steady state energy output. Power management systems only operate when the available energy is appropriate for desalination.

A technical challenge related to demand-side management is to establish a suitable energy storage to smooth the output of renewable energy [13]. The most common example is the use of batteries which implies techno-economic problems such as premature battery failure and decrease in battery efficiency. The lifetime of the batteries can be reduced from 3-8 to 2-6 years due to internal corrosion at high temperatures [5]. Additionally, in the case of lead-acid batteries, battery efficiency must be also taken into account since this storage system has a significant energy loss in the cycle of charge and discharge [89]. Moreover, the efficiency of this kind of batteries is between 75% and 80%, thus about a 20–25% of additional energy is needed to palliate battery losses [90]. Furthermore, efficiency may be lower due to self-discharge when the ambient temperature is high [91], battery ages and inappropriate operation conditions [92]. Nevertheless, ED can be adapted to changes in inlet energy ([4,15]) since it can be easily start-up and shut-down [93]. This helps at the intermittent operation. Additionally ED shows a good behavior with fluctuating fluxes from RE, and it is reported to have a better performance than RO when an intermittent energy input is applied [14,19]. Some references of renewable energy powered without battery systems RO or ED set-ups are available in [89,91,94] and [33,93,95], respectively. Thus a simple power management system ED-PV without energy storage can be applied with a suitable power control device [26]. Although ED–PV requires high-tech equipment, relatively simple setup, compact design, robustness and long lifetime of the energy supply system components are technical and techno-economic advantages of this configuration [14]. However some other economic disadvantages like higher cost, possible electric problems and higher standby periods, with consequent increase in the risk of membrane fouling, make sizing of the energy system a critical issue [14]. The primary barrier for the integration of ED with RE is the high production cost of desalinated water when compared to water produced by means of conventional energy supply. Among RE, PV energy is the most utilized energy source due to its maturity and compatibility with ED. In the present work it has been demonstrated that, a likely reduction of membrane and PV investment cost, together with an increase in the cost of Grid energy might make ED-PV overcomes this barrier. Other ways to reduce PV-ED costs are (adapted from [20,5]): use of investment incentives to expand PV market, improvement of the performance of both PV devices and membrane technology, use of energy generation systems without batteries and investment in education on operation and maintenance. Investment incentives are necessary to reduce the high initial payment of PV systems [20]. In order to improve the performance of PV devices, further research must enhance efficiency, production cost and lifetime of solar cells [20]. In the case of the membrane system, it is recommended the use of direct current positive-displacement pumps and energy recovery devices for water pumping [5] as well as the improvement of membrane performances and lifetime [20]. The choice of battery-less system can reduce significantly investment cost since the batteries contribution to the cost life cycle of a PV system can be as high as 40% [96]. Additionally, systems without batteries require less maintenance [91]. However, in the medium term, the cost of conventional DES will maintain a continuous rise due to the exhaustion of supply of fossil fuels [18] and RE can potentially be economically



Fig. 4. Summary of the main barrier for the integration of ED with RE.

paired. Our preliminary forecast has shown a potential profitability of ED–PV before 2020 in the case of a more optimistic scenario and before 2050 in the case of a more pessimistic scenario. However, as previously mentioned, BW–ED–PV is a suitable option for isolated plants of small capacity. In the case of larger systems, ED–PV becomes less cost effective because of the high investment cost and land requirements of PV modules [13]. Besides, the number of competing power supply options is still growing [26]. On the other hand, land requirements can be significantly reduced by using high efficiency Si PV modules (22.9% for Si crystalline, 18.5% for Si multi-crystalline and 8.2% for Si thin-film poly-crystalline [97]).

The integration of ED with solar assisted processes is not so tested for SW–DES. The main reasons are the high energy consumption of ED related to high salt concentration ([4,14,26]) and the relative short lifetime of membranes when working at high current densities [17]. In Fig. 4, a summary of the main barriers for the integration of ED with RE is presented.

7. Conclusions

Since the high SEC of DES is recognized as the main cause of burdens to environment apart from the direct local impact from brines, the integration of DES technologies with RE has been proposed as a more sustainable alternative. In this work, it has been evaluated individually the three components of sustainability (environment, economy and society) applied to DES of BW by means of ED–PV. A case study considering FW production in the Canary Islands from BW has been used as example for the ED powered by PV and compared to the reference of RO.

Regarding to the environment, the use of ED–PV instead of ED connected to the grid mix supply supposes a significant reduction in the emissions of greenhouse gases up leading to 0.02-0.03 kg CO₂ m⁻³. ED presents lower SEC values than RO for BW in its low salinity range, that is, below TDS 5000 mg L⁻¹. Therefore ED–PV appears as a more sustainable alternative than RO–PV just because of the lower SEC in that salinity range.

Economically, nowadays, renewable DES in general and ED–PV in particular are associated to isolate locations due to the high cost of the desalinated water. However, the medium term forecast presented in this work for the hypothesis of a decrease in PV and membrane investment cost and an increase in electricity price (considering the case study of FW in the Canary Islands) has shown the likely profitability of ED–PV before 2020 in the case of an optimistic scenario and before 2050 in a pessimistic scenario.

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A range of 0.15–0.4 \in m $^{-3}$ is expected for ED–PV just after the profitability point.

The social benefits of DES referred to employment generation are clear, and renewable DES generates more direct and indirect jobs than conventional DES, improving the social perception of new plants. A wide range of $1.03 \times 10^{-4} - 4 \times 10^{-3}$ permanent positions (m³ day⁻¹)⁻¹ during the operation can be assumed.

Consequently, in order to achieve a more sustainable DES, the development of DES should advance in parallel to a growth in the use of renewable energies. The proven sustainability of renewable energies and in particular PV, together with the expected reduction in investment cost of PV equipment, makes clear that the integration of this renewable energy will be usual in the near future. The problem of water scarcity will be aggravated being DES technologies the most likely solution. As ED has lower energy consumption than RO for BW-DES of low content in TDS, the use of ED will increase in the short-medium term. In this context, despite of the previously mentioned barriers, the combination ED-PV is expected to play a relevant role as a sustainable alternative for the BW-DES. According to the results of this work, the widespread use of ED-PV will take place between 2020 and 2050, once renewable DES is cheaper than conventional DES. Previous figures should help decision-makers at selecting the most suitable option for FW production considering the multi-objective and multi-variable nature of Sustainability.

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Appendix 1. Mathematical model for cost estimation

Equations $C_{ED-GRID} = TAC_{ED} + TC_{Oper}$ (A.1) $TAC_{ED} = TCC_{ED} \cdot AF/ATV$ (A.2) (A.7)

 $AF = IR/(1 - (1 + IR)^{-DP})$ (A.3)

 $TCC_{ED} = IC_{ED} + DC_{ED} = (DC_F + 1) \cdot (C_{Memb} + C_{ED})$ (A.4)

 $C_{\text{Memb}} = A_{\text{AM}} \cdot P_{\text{AM}} + A_{\text{CM}} \cdot P_{\text{CM}} \tag{A.5}$

 $C_{\rm ED} = \rm RFPM \cdot C_{\rm Memb} \tag{A.6}$

 $TC_{Oper} = TC_{O\&M} + C_{Energ}$

 $TC_{0\&M} = C_{MembR} + C_{ElectrR} + C_{Chem} + C_{Sp} + C_{Lb} + C_{Disp}$ (A.8)

 $C_{\text{MembR}} = \text{RF}_{\text{Memb}} \cdot C_{\text{Memb}} \cdot \text{AF}/\text{ATV}$ (A.9)

 $C_{\text{FlectR}} = \text{RF}_{\text{Flect}} \cdot P_{\text{Flect}} \cdot A_{\text{Flect}} \cdot AF/\text{ATV}$ (A.10)

 $C_{\rm Chem} = D_{\rm AS} \cdot P_{\rm AS} \tag{A.11}$

 $C_{\text{Energ}} = P_E \cdot \text{SEC}_V \tag{A.12}$

 $C_{\text{ED PV}} = \text{TAC}_{\text{ED}} + \text{TAC}_{\text{PV}} + \text{TC}_{O\&M}$ (A.13)

 $TAC_{PV} = TCC_{PV} \cdot AF / ATV \tag{A.14}$

 $TCC_{PV} = IC_{PV} + DC_{PV} = (DC_F + 1) \cdot (C_{PVI} + C_{PVM})$ (A.15)

 $C_{\rm PVI} = C_{\rm PVM} \cdot \rm RFPPV \tag{A.16}$

 $C_{\rm PVM} = AP_{\rm PV} \cdot P_{\rm PV} \tag{A.17}$

 $AP_{PV} = SEC_V \cdot FR / (NEH \cdot PR_{PV})$ (A.18)

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2.2 Artículo: *"Electrodialysis with bipolar membranes for valorization of brines."* (Carolina Fernández-González et al., *Separation and Purification Reviews*, 2016).

En este artículo se evalúan las tecnologías de membranas basadas en un gradiente de potencial eléctrico, específicamente la electrodiálisis con membranas bipolares, para su aplicación en la valorización de salmueras.

Entre los distintos procesos industriales que generan grandes cantidades de salmueras destaca la industria de la desalación de agua debido a sus concentrados. Se presenta el vertido como principal método de gestión de estas corrientes salinas y se propone a la electrodiálisis con membranas bipolares (EDBM) como una alternativa innovadora, la cual permite el tratamiento y valorización de las salmueras en forma de HCI y NaOH. Entre los principales problemas medioambientales asociados al vertido de los concentrados de desalación, se señalan los efectos de este vertido sobre algunas características físico-químicas del medio receptor como la temperatura, la salinidad y la composición (introducción de contaminantes). Así mismo, se revisa el estado del arte de la generación de ácidos y bases a partir de salmueras de diferente origen, como desalación, minería o industria textil entre otros. Por último, se presentan las barreras técnicas, económicas y tecno-económicas que evitan una mayor penetración de la EDBM para la valorización de salmueras en el mercado. Las barreras técnicas son las relacionadas con dificultades no resueltas que limitan el comportamiento de la tecnología. Las barreras tecno-económicas son las asociadas a procesos de optimización, estando normalmente relacionadas con aspectos económicos. Las barreras económicas están ligadas a la competitivida de la tecnología en el mercado. En la identificación de estas barreras, se ha hecho especial énfasis en la comparación de concentraciones e impurezas del HCI y el NaOH comerciales con los obtenidos mediante EDBM a escala de laboratorio.

A continuación se resumen los principales resultados y conclusiones de este artículo.

La EDBM es una tecnología viable para la generación de HCl y NaOH a partir de salmueras de distintas aplicaciones a escala de laboratorio, la cual, con la I+D que ayude a superar las barreras técnicas identificadas en este artículo, estará lista para su escalado desde laboratorio a planta piloto y posterior implantación industrial. Aunque la calidad de estos productos obtenidos y su concentración dependen fuertemente del origen de las salmueras, son aceptables para auto-abastecimiento de las diferentes actividades industriales donde se producen. La pureza y concentración requeridas para alcanzar el grado comercial es aún un reto importante.

Con respecto al uso de los productos obtenidos, a pesar de que las plantas de desalación utilizan HCl para varias aplicaciones, las estimaciones indican que el tratamiento de un 1% de los concentrados de desalación generados sería suficiente para el autoabastecimiento de HCl. Por ello, se debe perseguir un aumento de calidad y concentración del HCl y NaOH obtenidos para llegar al grado comercial y poder dar salida a estos dos productos en el mercado. Por otra

parte, la incorporación de la EDBM en algunos procesos industriales que generan salmueras y son grandes consumidores de NaOH y HCl, como es el caso de la producción de glifosato, es una alternativa muy prometedora que permite la generación y consumo *in-situ* de los productos.

En cuanto a las barreras de esta tecnología para esta aplicación, este trabajo ha identificado los principales cuellos de botella, señalando las actuales áreas de interés. Dentro de estas barreras destacan la baja pureza de los productos, su alto consumo energético por unidad de producto y el coste de inversión de las membranas bipolares.

Un aumento significativo de la selectividad de las membranas de intercambio iónico junto con una limitación de los fenómenos de electro-ósmosis asociados a esta aplicación en concreto, llevarían a una mayor pureza de los productos obtenidos mejorando la eficiencia del proceso de recuperación. De esta forma se podrían obtener productos con grado comercial. La mejora de la pureza del HCI y NaOH, combinada con una definición de nuevos estándares de calidad para los productos obtenidos, directamente relacionados con los requerimientos de pureza para cada aplicación específica, llevaría a un aumento del número de aplicaciones y salidas comerciales para estos ácidos y bases producidos. Finalmente, el alto coste de inversión de las membranas bipolares (alrededor de $1.000 \in m^{-2}$) hace que los costes de inversión de la EDBM sean relativamente altos en comparación con otras tecnologías de membranas, obstaculizando su desarrollo. C. Fernandez-Gonzalez, A. Dominguez-Ramos, R. Ibañez, A. Irabien. *Electrodialysis with bipolar membranes for valorization of brines*. Separation and Purification Reviews, 45 (2016) 275-287.

Enlace a la publicación

2.3 Artículo: "Enhancing fouling resistance of polyethylene anion exchange membranes using carbon nanotubes and iron oxide nanoparticles." (Carolina Fernández-González et al., Desalination, 2017).



Figura 1. Resúmen gráfico del artículo *"Enhancing fouling resistance of polyethylene anion exchange membranes using carbon nanotubes and iron oxide nanoparticles".*

En este artículo se aborda la síntesis y caracterización de nuevas membranas *nanocomposite* como contribución al desarrollo de nuevas membranas para la mejora técnica y tecnoeconómica de los procesos de ED y EDBM y su aplicación a procesos de desalación y valorización de concentrados de desalación. Particularmente, este artículo se centra en la mejora del comportamiento frente al *fouling* de membranas de intercambio aniónico asociada a la introducción de una película que contiene nanotubos de carbono o nanopartículas de óxido de hierro.

La ED es una importante tecnología en la desalación de agua siendo el fenómeno del *fouling* una de las principales limitaciones que evita un mayor uso de esta tecnología de membranas. Junto a una definición de *fouling*, se presenta una clasificación de los tipos de *fouling* que afectan a membranas de intercambio iónico, entre los que se encuentra el *fouling* orgánico, el cual resulta objeto de este estudio. Se nombran diferentes estrategias para la prevención y mitigación del *fouling* en ED, para después centrar el trabajo en el desarrollo de membranas con mayor resistencia frente a los fenómenos de *fouling*. A continuación se describe la importancia de la incorporación de nanomateriales en estudios sobre desarrollo de membranas

para RO, apenas estudiada sobre membranas de intercambio iónico. Se describen las membranas nanocomposite sintetizadas de este estudio, membranas de intercambio aniónico basadas en una membrana de intercambio aniónico comercial de polietileno y una película nanocomposite. Esta película está formada por polióxido de (2,6-dimetil-1,4-fenileno) sulfonado (sPPO) y un nanomaterial que puede ser nanopartículas de óxido de hierro sulfonadas Fe₂O₃-SO4²⁻ (NPs) o bien nanotubos de carbono multipared oxidados CNTs-COO⁻ (CNTs), cada uno con una geometría completamente distinta. Para la determinación de cambios en las propiedades de la membrana asociados a la introducción de la película *nanocomposite* este trabajo ha utilizado: Espectroscopia Infrarroja por Transformada de Fourier para la determinación de su composición química, Microscopía Electrónica de Barrido para determinación de la morfología de su superficie y sección transversal, Microscopía de Absorcion Atómica para la determinación de su rugosidad, medida del ángulo de contacto del agua para la caracterización de su hidrofilicidad, y Espectroscopía de Impedancia Electroquímica (EIS) para la determinación de su resistencia electrica. La evaluación de la resistencia frente al *fouling* se llevó a cabo mediante cronopotenciometría, midiendo la evolución de la caída de voltaje a través de la membrana con el tiempo de operación. Los resultados se han presentado de forma sistemática, relacionando los cambios superficiales de las membranas con la mejora en el comportamiento frente al fouling observada, haciendo especial énfasis en la comparación del comportamiento de los dos nanomateriales.

A continuación se resumen los principales resultados y conclusiones de este artículo.

La introducción de la película nanocomposite en membranas de intercambio aniónico comerciales causó un cambio significativo en las características físico-químicas de la superficie de la membrana como su composición, hidrofilicidad y rugosidad, dando como resultado una mejora de su resistencia frente al fouling. Todas las membranas nanocomposite mostraron una superficie mas hidrofílica y homogénea que las membranas sin modificar. Los dos nanomateriales presentaron un comportamiento muy similar, observado durante el proceso de caracterización y confirmado en la posterior evaluación de su resistencia frente al fouling para dos cantidades de nanomaterial por unidad de masa de película muy similares (entre 0,2% g·g⁻¹ y 0,6% g·g⁻¹ para las NPs y entre 0,2% g·g⁻¹ y 0,8% g·g⁻¹ para los CNTs). Sin embargo, las membranas nanocomposite con CNTs presentaron un comportamiento ligeramente superior. Esto puede deberse a que los CNTs permitieron una mayor carga de nanomateriales antes de que se produjeran fenómenos de agregación. La capa cargada negativamente, con un espesor muy pequeño, alta hidrofilicidad y conductividad, no supuso cambios significativos en la resistencia eléctrica de las membranas. La mejor concentración de nanomateriales fue de 0,4% g·g⁻¹ para las NPs y 0,6% g·g⁻¹ para los CNTs mejorando la resistencia frente al *fouling* de las membranas en un 45% y 53% respectivamente. Estas membranas también presentaron las mayores hidrofilicidades. La mejora de la resistencia frente al fouling de las mejores membranas nanocomposite se mantuvo estable durante 12 horas de operación en contacto con el compuesto *foulant* modelo. Gracias a esta mejora, se consiguieron ahorros energéticos de entre el 49% y el 60% debido a la menor caída de voltaje a través de la membrana durante los test de ED a escala de laboratorio. Debido al similar comportamiento de ambos nanomateriales, una evaluación económica podría ser decisiva para la selección de la capa *nanocomposite*.

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Enhancing fouling resistance of polyethylene anion exchange membranes using carbon nanotubes and iron oxide nanoparticles



DESALINATION

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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Novel nanocomposite fouling resistant anion exchange membranes were synthetized.
- Polyethylene membranes were thin layered with nanoparticles or carbon nanotubes.
- Increase up to 53% in fouling resistance with optimal carbon nanotubes dosage
- Improved hydrophilicity and homogeneity of membrane surface led to energy savings.
- No significant performance changes were observed between the two nanomaterials.

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ABSTRACT

This work presents the enhancement of organic fouling resistance of nanocomposite anion exchange membranes made from a commercial polyethylene anion exchange membrane and a negative thin layer. This layer is composed of sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (sPPO) and two nanomaterials of different geometry and composition, oxidized multi-walled carbon nanotubes CNTs-COO⁻ (0.2% g g⁻¹ to 0.8% g g⁻¹) or sulfonated iron oxide nanoparticles Fe₂O₃-SO⁴₄⁻ (0.2% g g⁻¹ to 0.6% g g⁻¹). The novel nanocomposite membranes showed a relevant improvement in fouling resistance caused by the modification of some physicochemical characteristics of membrane surface such as charge, roughness and hydrophilicity. The nanocomposite layer did not show a change in the membrane resistance. No remarkable differences were detected when changing the nanomaterial during characterization of nanocomposite membranes. The optimized loading of iron oxide nanoparticles and carbon nanotubes at 0.4% and 0.6% improved membrane fouling resistance by 45% and 53%, respectively. The improved fouling resistance of the best nanocomposite membranes AM-0.6CNTs remained after 12 h of operation. Energy savings between 49% and 60% were also achieved.

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1. Introduction

Desalination is becoming essential for maintaining a supply of fresh water in countries under water shortages. Electrodialysis (ED) is a technology used in fresh water production from different sources, sharing

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3.6% of the total desalination capacity in 2014 with an installed capacity of 2.5 million m³ day⁻¹[1]. In ED, ionic components are selectively transported through ion exchange membranes (IEMs) in the presence of an electric field. When a potential is applied between two electrodes, anions are transported towards the anode through positively charged anion exchange membranes (AEMs), and cations are transported towards the cathode through negatively charged cation exchange membranes (CEMs) [2]. An advantage of ED over reverse osmosis (RO) is a higher water recovery as ED is not limited by brine osmotic pressure [3,4]. Additionally, ED is reported to be more economical than RO and thermal desalination technologies for the treatment of water with total dissolved solids (TDS) below 5000 mg L⁻¹[5].

Fouling is defined as one of the main limitations hindering a greater use of membrane processes [6]. Fouling consists in the undesired attachment of living organism or non-living substances to membrane surface or membrane structure [7]. This important issue affects membrane desalination technologies such as RO [8], membrane distillation [9,10] and ED [11,12]. Fouling affecting ion exchange membranes can be classified into colloidal fouling, organic fouling, scaling and biofouling [7]. The nature and state of the substance producing fouling or foulant determine the fouling classification. Colloidal fouling is generated by non-dissolved suspended solids or colloids. Organic dissolved substances cause organic fouling. Scaling is caused by dissolved salts and biofouling by live organisms. Regarding organic fouling and ED, the organic salts that usually produce fouling on IEMs are formed by a large anion that is a foulant for AEMs and a small cation that passes through the CEMs [13]. Thus, because most organic foulants are negatively charged, this phenomenon mainly affects AEMs [12], which makes the selection of AEMs with high fouling resistance essential [14]. AEMs are also reported to be more susceptible to fouling by natural organic matter than CEMs [15]. Some strategies for fouling prevention and mitigation of IEMs are the use of cleaning agents [16], pretreatment of solutions [17–19], mechanical removal [20], control of the hydrodynamic conditions [21], use of electrodialysis with reversal polarity [22,23] and pulsed electric field [24,25]. Fouling is a widely studied issue in membrane development for pressure driven desalination processes but they are only a few works about fouling resistant ion exchange membranes. One of the most important strategies for fouling prevention in membrane development is the modification of the membrane surface [7,26,27]. In the particular case of IEMs, the modification of surface physicochemical characteristics can include surface charge, hydrophobic/hydrophilic balance and roughness [7]. The modification of surface charge promotes electrostatic repulsion between charged foulants and membranes. The increase of membrane surface hydrophilicity avoids hydrophobic interactions of foulants and the membrane surface [26]. Smooth surfaces reduce the contact area for fouling attachment to the membrane surface [27]. Some examples of membrane surface modification techniques for fouling mitigation in IEMs involve the use of membrane sulfonating agents [26], layer by layer deposition [28] [29], immersion [30] or direct casting [31]. The use of nanomaterials plays a key role in membrane surface modification of pressure driven desalination processes for fouling and biofouling prevention and mitigation [6,32,33]. Carbon-based nanomaterials, in particular carbon nanotubes, are attracting special attention due to their flexibility, good mechanical properties, good electrical conductivity, easy scale-up, high purity and low production cost [6, 34-37]. However, only one work can be found in the literature regarding the use of nanomaterials for fouling resistant IEMs. Particularly, carbon nanotubes (CNTs) for fouling resistant cation exchange membranes were used in [38]. This previous study reports very promising fouling resistant membranes for power generation by reverse electrodialysis.

The authors of the present work support these previous findings in fouling resistant nanocomposite IEMs and supplement them by comparing the performance of two nanomaterials with a totally different geometry: 1) one-dimensional oxidized multi-walled carbon nanotubes CNTs-COO⁻ (CNTs) and 2) zero-dimensional sulfonated iron oxide nanoparticles $Fe_2O_3-SO_4^{2-}$ (NPs) in enhancing fouling resistance of AEMs. The

classification of nanomaterials into zero-dimensional and one-dimensional is based on the number of dimensions that do not belong to the nanoscale range. Nanoparticles are zero-dimensional nanomaterial as their only dimension, the diameter, belongs to the nanoscale range. On the other hand, carbon nanotubes are a typical example of one-dimensional nanomaterial as their diameters is usually in the nanoscale range, but not their length. A complete classification of nanomaterials according to their dimensions can be found elsewhere [39].

In our previous study [40] commercially available heterogeneous polyethylene AEMs were modified by direct casting of a solution that combines $Fe_2O_3-SO_4^{2-}$ nanoparticles with sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (sPPO). This coating introduced a very thin negatively charged layer on the surface of the AEMs providing them with monovalent selectivity. The most important findings of this previous work were: 1) The monovalent selectivity of nanocomposite membranes remained steady with long operation times in electrodialysis with bipolar membranes (up to 93 h of operation) and 2) the nanocomposite thin film was stable even when working with strong acids and bases. This stability is highly desired in electrodialysis when working with bipolar membranes [41].

The objective of this work is to evaluate the effects produced by the introduction of this negatively charged nanocomposite layer on the fouling resistance of polyethylene AEMs. Two different nanocomposite layers were used: 1) sPPO and $Fe_2O_3-SO_4^2$ (used as nanocomposite film in our previous work) and 2) sPPO and CNTs-COO⁻. Due to the nature of the sPPO film, the functionalized nanomaterials, and direct casting (as the chosen technique), the treatment provided the membrane surface with negative charges, high hydrophilicity and a smooth surface that significantly improved membrane fouling resistance. The hydrophilic character of sPPO, $Fe_2O_3-SO_4^2$ and CNTs-COO⁻ allowed a highly negative charge within a very thin layer. Thus, it improved conductivity and reduced the resistance of the negative layer that has been reported to contribute significantly to the total resistance of the membrane in other studies about membrane surface modification [30,46].

2. Experimental

2.1. Materials

Commercial heterogeneous polyethylene AEMs Ralex AM-PP (Mega, Czech Republic) were subjected to modification. Ralex AM-PP membranes are conventional membranes for ED widely used in different electrodialysis processes [47–49]. Some of the most attractive characteristics of AM-PP membranes are low price, longevity and long-term stability at pH 0-14 which made them good candidates [40]. Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) (analytical standard grade), chloroform (anhydrous, 99 wt%), methanol (anhydrous, 99.8 wt%), chlorosulfonic acid (99 wt%) and sulfuric acid (98 wt%) were purchased from Sigma Aldrich (St. Louis, USA). Dimethyl sulfoxide (DMSO) (ACS grade, 99.9 wt%) was obtained from VWR (Atlanta, USA). Iron (III) oxide nanoparticles (Ø50 nm, Sigma Aldrich, USA) were used as received for sulfonation. Oxidized multi-walled carbon nanotubes with an outer diameter lower than 8 nm, a length of 10 μ m -30μ m and a carboxyl group content of 3.86 wt% were purchased from Cheap Tubes (Cambridge, USA) (purity 95 wt%) and used as received. Sodium dodecyl sulfate (SDS, Sigma Aldrich) was used as a model organic foulant.

2.2. Surface modification of polyethylene anion exchange membranes

This work modifies the surface of a commercial polyethylene AEMs by a physical coating [50] using sPPO and $Fe_2O_3-SO_4^2$ or sPPO and CNTs-COO⁻. The modification of polyethylene membranes was performed only in the layer facing the dilute compartment, the one where the concentration of ions decreases. This was done for the following reasons: 1) lower current efficiencies in the desalination process

have been reported when the modified surface was facing the concentrate compartment [51] and 2) since negative charges of the membrane surface may attract Na⁺ cations, only the side that is in the opposite direction to the flux of cations in the cell (towards the cathode as shown in Fig. 1) was modified in order to avoid a loss of Cl^-/Na^+ permselectivity.

PPO and Fe₂O₃ sulfonation was carried out according to a procedure described in [42,43]. The sulfonation of PPO was performed by using chloroform and methanol as solvents and chlorosulfonic acid as the sulfonating agent. Fe₂O₃ powder nanoparticles were sulfonated by contact with a concentrated solution of sulfuric acid followed by calcination at 500 °C.

An exhaustive cleaning of the polyethylene membrane surface was done before surface modification. The membrane was submerged in a solution 0.1 mol L^{-1} HCl, rinsed with deionized water and submerged in a 0.1 mol L^{-1} NaOH solution. This procedure was repeated at least three times. After the pretreatment, the membrane was dried at room temperature. The modification of the membrane surface was done using a solvent-evaporation technique [52]. A PPO and DMSO solution of 19% g g^{-1} was mixed with different loadings of nanomaterials at 40 °C and continuously stirred for 24 h. The solution was then vibrated for 10 min for optimal dispersion of the nanomaterials. After that, the solution was cast onto the commercial membrane using the doctor blade method. The obtained nanocomposite membranes were dried in a vacuum oven at 60 °C for 24 h. The membranes were treated with 1 mol L⁻¹ HCl for 24 h, rinsed in deionized water and stored in a solution 0.5 mol L^{-1} NaCl. Table 1 includes a summary of the nanocomposite membranes obtained and the loading of nanomaterials used in this work. The loadings and compositions of NPs coated membranes, AM-0.2NP, AM-0.4NP and AM-0.6NP, are the same as the ones used in our previous work on valorization of desalination brines into acids and bases by electrodialysis with bipolar membranes [40].

2.3. Membrane characterization

2.3.1. FTIR spectra analysis

The chemical composition of unmodified and nanocomposite AEMs was determined by Digilab FTS7000 Fourier Transform Infrared



Fig. 1. Scheme of the experimental setup used to determine membrane resistance and fouling resistance.

Table	1
Sumn	าส

ummary of nanocomposite ion exchange membranes synthetized in this worl	rk.
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Name	Composition of the layer	Loading of nanomaterial (% g g^{-1a})
AM-0.2NP	SPPO, Fe_2O_3 -SO $_4^2$	0.2
AM-0.4NP	SPPO, Fe_2O_3 -S O_4^2	0.4
AM-0.6NP	SPPO, Fe_2O_3 -S O_4^2 ⁻	0.6
AM-0.2CNTs	SPPO, CNTs-COO ⁻	0.2
AM-0.4CNTs	SPPO, CNTs-COO ⁻	0.4
AM-0.6CNTs	SPPO, CNTs-COO ⁻	0.6
AM-0.8CNTs	SPPO, CNTs-COO ⁻	0.8

^a g nanomaterial g^{-1} layer.

Spectroscopy (FTIR) (Randolph, MA, USA) equipped with a Digilab UMA600 microscope. Spectra were scanned in a range of 700 cm⁻¹–4000 cm⁻¹ at a resolution of 4 cm⁻¹. For each sample, the scan was repeated 20 times. Results were corrected using a spectrum of ambient air as a background.

2.3.2. Scanning electron microscopy (SEM) analysis

Surface and cross-sectional morphology was studied using a Hitachi SU8230 cold field emission scanning electron microscope (CFE-SEM) (Tarrytown, NY, USA). Samples were dried at 60 °C for at least 24 h before testing.

2.3.3. AFM analysis

Keysight 5500 Molecular Imaging Atomic Force Microscope (AFM) (Keysight Technologies, USA) was used to analyze surface morphology. An area of 50 μ m by 50 μ m on each sample was scanned in the acoustic alternating current (AAC) mode using silicon cantilevers (Budget Sensors, Bulgaria). Picoview 1.12 software from Keysight Technologies (formerly Agilent) was used to process scanned images and generate morphological parameters.

2.3.4. Water contact angle

Dried samples were placed on a Ramé-Hart Model 250 goniometer (Succasunna, USA) for contact angle measurement using deionized water. At least three measurements were conducted for each sample.

2.3.5. Membrane resistance

Membrane resistance was measured using electrochemical impedance spectroscopy (EIS) in a two-compartment cell experimental setup shown in Fig. 1 with a 0.5 mol L⁻¹ NaCl solution. Oscillating voltages with an amplitude of 25 mV were applied by means of a Vertex potentiostat-galvanostat (Ivium Technologies, Eindhoven, Netherlands). Frequency of the impedance measurements ranged from 0.1 Hz to 1000 Hz. Membrane resistance was determined from the fitting of the response to the equivalent circuit for ion exchange membranes with solutions reported in [53]. Because of the fitting, a global parameter that includes membrane resistance and solution resistance (R_{M + S}) was obtained. This value was corrected by measuring the resistance of the solution in a blank experiment without the membrane.

2.4. Evaluation of fouling resistance

The evaluation of the fouling resistance of unmodified and nanocomposite membranes was performed by chronopotentiometry in the experimental setup shown in Fig. 1. The two-compartment cell was filled with a solution of 0.1 mol L⁻¹ NaCl and 0.0018 mol L⁻¹ SDS as the model foulant. Each compartment has a volume of approximately 0.2 L. The experiments were run for 100 min. The modified surface of the membrane was set facing the dilute compartment. The applied current density was 2 mA cm⁻² being the effective area of the membrane 4.8 cm². Fouling causes an increase in membrane resistance and thus an increase in the voltage drop through the membrane (ΔV). The fouling resistance of membranes was determined by measuring the evolution of ΔV with time using Luggin capillaries. Polyethylene membranes Ralex AM-PP and the best



Fig. 2. FTIR spectra of anion exchange membranes a) AM-0.8CNTs, b) AM-0.6CNTs, c) AM-0.4CNTs, d) AM-0.2CNTs, e) AM-0.6NP, f) AM-0.4NP, g) AM-0.2NP and h) Ralex AM-PP (unmodified membrane).

nanocomposite membrane were subjected to three 4-hour operation cycles with the model fouling solution. Membranes were rinsed with deionized water between cycles. The energy consumption during these cycles was calculated from the area of ΔV -t curves using the trapezoidal rule.

3. Results and discussion

3.1. Surface membrane composition

Fig. 2 shows the FTIR spectra of unmodified and nanocomposite AEMs. The characteristic peak of C—H stretch in —CH₂— and CH₃substitutes, corresponding to polyethylene and polypropylene of the AM-PP membranes, were observed at 2918 cm⁻¹ and 2850 cm⁻¹ respectively [54]. The transmittance band at 1170 cm⁻¹ was assigned to the C—O—C stretch of sPPO [54]. The presence of the —SO₃H substitute in the aromatic ring of PPO was confirmed by a peak at 1062 cm^{-1} [42]. FTIR spectra confirmed the success in coating the commercial membrane with the negatively charged thin film of sPPO and nanomaterials.

3.2. Membrane morphology

Scanning electron microscopy (SEM) was used to observe the morphology of unmodified and nanocomposite AEMs. Fig. 3a shows SEM images of surface and cross-section of Ralex AM-PP membranes, heterogeneous AEMs reinforced with polypropylene fibers. It can be clearly seen in these images that the fibers are distributed in the membrane matrix forming a uniform square grid parallel to its surface (Fig. 3a.1). From the cross-section images (Fig. 3a.3 and Fig. 3b.3), it can be



AM-0.2NP at 1 mm



Fig. 3. SEM images for unmodified membrane Ralex AM-PP a. 1-3 and nanocomposite membrane AM-0.2NP b. 1-3.

Table 2

Summary of morphological parameters of unmodified and nanocomposite membranes expressed in nm.

Membrane	Sq (nm)	Sp (nm)	Sv (nm)
AM-PP	702	2410	2090
AM-0.2NP	297	917	930
AM-0.4NP	160	773	448
AM-0.6NP	256	953	1060
AM-0.2CNTs	317	1180	949
AM-0.4CNTs	301	2090	1080
AM-0.6CNTs	506	1700	1240
AM-0.8CNTs	373	2290	824

concluded that there are two levels of fibers distributed homogeneously. This reinforcement provides the membrane with a very good mechanical stability and robustness but also a heterogeneous conductivity.

From the comparison of the SEM images for the unmodified membrane (Fig. 3a) and the nanocomposite membrane AM-0.2NP (Fig. 3b), an improvement can be seen in the surface homogeneity with membrane coating. This hypothesis was confirmed by atomic force microscopy (AFM), as will be discussed later. Cross-section images (Fig. 3a.3 and Fig. 3b.3) were used to determine the thickness of unmodified membranes (485 μ m), and the thin film of nanocomposite membranes (19 μ m). These results confirm the small contribution of the coating to the total thickness of the membrane (increase below 4%).

3.3. Membrane roughness

Modifications of membrane roughness with the coating, directly related to surface homogeneity, were determined by AFM. The membrane characterization was performed by means of three different morphological parameters displayed in Table 2 as 1) Sq (root mean square height), which is the standard deviation of the height distribution, also referred to as RMS surface roughness, 2) Sp (maximum peak height), which is the height between the highest peak and the mean plane of the surface, and 3) Sv (maximum pit height), which is defined as the depth between the mean plane of the surface and the deepest valley.

Membranes Ralex AM-PP presents a rough surface with a Sq of 702 nm. This roughness might be beneficial for the static adhesion between the commercial membrane and the nanocomposite thin film as rough surfaces result in a higher contact area [31]. The data presented in Table 2 and the 3D AFM images of Fig. 4 confirm the decrease of membrane surface roughness with the coating. Table 2 shows that all the morphological parameters that describe surface roughness are significantly lower for nanocomposite membranes than for the unmodified membrane, and thus, the membrane roughness decreased with the nanocomposite layer. Nanocomposite membranes modified with carbon nanotubes presented a surface slightly rougher than the ones modified with iron oxide nanoparticles. Sq decreased 36% to 77% in the case of NPs, and 28% to 58% when membranes are modified with CNTs. The incorporation of sPPO and nanomaterials made the surface of the membrane smoother because the coating might be accumulated in the valleys [31]. This is in agreement with the decreases in the height of the highest peak and the depth of the deepest valley (Sp and Sv, respectively) observed in the nanocomposite membranes. The apparent smoothness of the nanocomposite membranes was also observed in the SEM images of Section 3.2. Membrane morphology. A decrease of surface roughness was also reported when modifying a commercial AEMs by casting [31]. On the contrary, the use of layer by layer deposition [29] and immersion [55,46] has showed a significant increase of membrane roughness, making the surface rougher when increasing the number of layers [29] and the concentration of polymer [46].

3.4. Membrane hydrophilicity

One of the most important parameters regarding fouling phenomena and membrane resistance in desalination processes is membrane



Fig. 4. AFM 3D images of surface roughness for a) unmodified membranes AM-PP, b) nanocomposite membranes AM-0.2NP and c) nanocomposite membranes AM-0.6CNTs.

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 Table 3

 Summary of water contact angles of unmodified and nanocomposite anion exchange membranes.

	Contact angle (°)	Contact angle decrease (°)
AM-PP	100.1 ± 3.2	-
AM-0.2NP	63.7 ± 3.4	36
AM-0.4NP	61.6 ± 3.4	39
AM-0.6NP	65.8 ± 0.9	34
AM-0.2CNTs	59.7 ± 6.3	40
AM-0.4CNTs	62.9 ± 2.8	37
AM-0.6CNTs	57.9 ± 2.3	42
AM-0.8CNTs	60.7 ± 5.0	39

hydrophilicity [7,56] evaluated by WCA measurements. The introduction of nanomaterials on membranes can modify its physicochemical properties such as hydrophilicity [50]. Water contact angle measurements of Ralex AM-PP membranes and nanocomposite membranes are presented in Table 3. Fig. 5 illustrates how the modification of the membrane surface showed a significant increase in membrane hydrophilicity and thus, a decrease in the water contact angle. Ralex AM-PP membranes are very hydrophobic as they present a water contact angle of 100.1°. These high values have also been reported in other heterogeneous anion exchange membranes [29]. In the case of Ralex AM-PP membranes, based on polyethylene and polypropylene, the highwater contact angle might be due to the high presence of PP and PE on the surface, making the membrane water contact angle very close to the water contact angle of pure PE and PP, 94° and 97°, respectively [57]. A high content of polyethylene in the surface of heterogeneous membrane has also been reported in [58].

The introduction of sPPO and Fe_2O_3 - SO_4^2 nanoparticles on the membrane surface caused a decrease of 36°-39° in the water contact angle of nanocomposite membranes. This decrease in water contact angle is probably due to the high hydrophilicity and the large specific area of Fe_2O_3 - SO_4^2 nanoparticles [42] and to the increase of functional groups associated with the negative charge layer (sulfonic acid and sulfate groups) [31,44]. In the case of membranes modified with CNTs, the drop-in water contact angle is even higher, $37^{\circ}-42^{\circ}$ and due to the increase of negatively charged carboxyl groups on the surface of the CNTs [38] and sulfonic acid groups of sPPO. The WCA of the membranes modified with CNTs (57.9°-62.9°) is in agreement with WCA reported for nanocomposite cation exchange membranes made of sPPO and CNTs functionalized with COO⁻ for power generation by reverse electrodialysis (50.8°-75.9° for a loading between 0.1% g g⁻¹ and 0.8% g g⁻¹ CNTs [38]). The decrease of water contact angle in all of the nanocomposite membranes is translated into a higher fouling resistance to be discussed in Section 3.6. Membrane fouling resistance. The most hydrophilic nanocomposite membranes were AM-0.4NP for iron oxide nanoparticles and AM-0.6CNTs in the case of carbon nanotubes. These membranes also showed the best fouling resistance as later discussed.

3.5. Membrane electrical resistance

The energy consumption of an ED process is related to the resistance of the solutions and IEMs [59]. Thus, membranes with low electric resistance are preferable for operating with ED. Electric resistance of membranes depends on several factors such as membrane thickness [60] and water content [56]. From the results presented in Table 4, it can be concluded that the surface resistance of the modified AEMs in this work did not change after the coating. This could be due to the following reasons: 1) the thickness of the layer added to the membrane is very small (19 µm, from SEM images of Fig. 3b) when compared to the thickness of the unmodified membrane (485 µm, from SEM images of Fig. 3a); 2) the introduction of nanomaterials allows a high negative charge in a very thin layer. Although adding a new layer to the membrane surface would theoretically increase membrane resistance, the resistance of this layer is expected to decrease with increasing negative charge density and the resistance is not expected to increase drastically [61]. and 3) the negative layer is very hydrophilic. Water content and membrane hydrophilicity also have an important impact on membrane resistance. The ionic resistance of a membrane decreases dramatically when increasing water content [56]. Thus, the increase in surface hydrophilicity after coating the membrane (see Fig. 5 and Table 3) supports the hypothesis of high sPPO and functionalized nanomaterials' laver hydrophilicity, thereby achieving high water affinity of the layer and low electrical resistance. Additionally, the direct casting allows the modification of only one of the two sides of the membranes, reducing by half the potential resistance increase with the treatment (as only one layer is introduced on one of the sides of the membrane surface, instead of both sides).

A significant increase of membrane hydrophilicity when using iron oxide nanoparticles and carbon nanotubes has already been reported [38,42]. Thus, the contribution of the negative layer to the total resistance of the membrane is very low and does not affect the total ionic resistance of nanocomposite membranes. No significant changes regarding membrane resistance after modification by casting have been reported for heterogeneous AEMs [58].

Finally, some differences in membrane resistance have been reported when adding a negatively charged layer. The changes of membrane resistance ranged from slightly positive increments in the case of modification by direct casting (0.93 Ω cm² to 1.1 Ω cm² [31]) and layer by layer deposition (4.47 Ω cm² to 4.81 Ω cm² [29]) to relevant for immersion (from 2.5 Ω cm² to 5.0 Ω cm² [46]). Thus, the increase of membrane resistance might also be highly influenced by the selected modification method.

3.6. Membrane fouling resistance

Fouling is defined as one of the key problems for food processing and water treatment [7]. Membrane modification can lead to very promising advantages regarding fouling prevention such as less power



Fig. 5. Water contact angle of a) a membrane Ralex AM-PP and b) a nanocomposite membrane AM-0.6NP.

Table 4

Membrane resistance for unmodified and nanocomposite anion exchange membranes. A solution 0.5 mol L^{-1} NaCl was used as electrolyte.

Membrane	Surface resistance ($\Omega \ cm^2$)
AM-PP (as reported by supplier)	<8
AM-PP	6.3 ± 0.12
AM-0.2NP	6.1 ± 0.04
AM-0.4NP	6.1 ± 0.04
AM-0.6NP	6.4 ± 0.03
AM-0.2CNTs	6.2 ± 0.01
AM-0.4CNTs	6.4 ± 0.04
AM-0.6CNTs	6.8 ± 0.02
AM-0.8CNTs	6.3 ± 0.08

consumption and a lower pretreatment cost [7]. The most common method to estimate membrane stability against fouling is measuring the change in the voltage drop across the membrane [62]. Fig. 6 includes the evolution of ΔV for all nanocomposite membranes and the membrane Ralex AM-PP. From this figure it can be observed that all nanocomposite membranes have a better fouling resistance than the unmodified membrane. Nanocomposite membranes modified with CNTs showed a slightly better performance. To quantify the improvement in fouling resistance of nanocomposite membranes, Table 5 includes the evolution of the voltage drop with time as V min⁻¹. Fig. 7 shows the improvement of fouling resistance in % defined for each of the nanocomposite membranes *i* as Improvement_i in Eq. (1). $\Delta V_{\text{Nanocomposite}_i}$ is the slope of the different nanocomposites AEMs presented in Table 5 and $\Delta V_{\text{Unmodified}}$ is the slope of the unmodified Ralex AM-PP membrane of Table 5.

$$Improvement_{i} = \left(1 - \frac{\Delta V_{Nanocomposite_{i}}}{\Delta V_{Unmodified}}\right) \cdot 100 \tag{1}$$



Fig. 6. Evolution of voltage drop across the membrane (ΔV) for different AEMs: a) unmodified AM-PP, AM-0.2NP, AM-0.4NP and AM-0.6NP and b) unmodified AM-PP, AM-0.2CNTs, AM-0.4CNTs, AM-0.6CNTs, and AM-0.8CNTs. Current density was 2 mA cm⁻². Solution 0.1 mol L⁻¹ NaCl and 0.0018 mol L⁻¹ SDS.

Table 5

Slope of the evolution of the voltage drop with time for the different AEMs shown in Fig. 6.

Membrane	Slope (mV min^{-1})
AM-PP	1.04 ^a
AM-0.2NP	0.78
AM-0.4NP	0.58
AM-0.6NP	0.68
AM-0.2CNTs	0.69
AM-0.4CNTs	0.69
AM-0.6CNTs	0.49
AM-0.8CNTs	0.65

^a The slope was calculated using the data from 1000 s to 6000 s.

The introduction of the negatively charged hydrophilic layer supposed an improvement of fouling resistance that varied between 25% and 53% expressed as a decrease in the slope of ΔV vs time. The optimum loadings of nanocomposite membranes were 0.4% for Fe₂O₃-SO₄²⁻ nanoparticles and 0.6% for O-MWCNTs. These membranes also showed the highest hydrophilicity (see Table 3). The decrease in performance after the optimum dose of CNTs and NPs is probably due to the aggregation of nanomaterials in the thin layer. A homogeneous dispersion of nanomaterials in the polymer matrix is essential to transfer their properties to the nanocomposite layer [63].

Additional experiments were performed with the best nanocomposite membrane, AM-0.6CNTs being compared to the unmodified Ralex AM-PP membrane. In these experiments AM-PP and AM-0.6CNTs membranes were subjected to three 4-h cycles of operation. Fig. 8 includes the results of these experiments, which show that the difference in fouling resistance between the nanocomposite AM-0.6CNT membranes and the Ralex AM-PP membranes remained almost constant, even after 12 h of operation.

The main reason behind the improvement of this fouling resistance relies on the modification of three characteristics of membrane surfaces with significant influence over anti-fouling properties: membrane charge, surface roughness and hydrophilicity [32]. SEM and AFM images (Figs. 3 and 4, respectively) verify the improvement in the homogeneity of nanocomposite membranes. Nanocomposite membranes, with smoother surfaces than commercial membranes as previously presented had significantly lower fouling rates [64, 27]. The surface hydrophilicity of nanocomposite membranes was observed in the water contact angle measurements (as shown in Table 3 and Fig. 5). All of these modifications to membrane surface physicochemical characteristics provided nanocomposite membranes with enhanced antifouling properties in the presence of SDS as a model organic foulant. This fouling resistance was probed to be



Fig. 7. Improvement of the fouling resistance of nanocomposite membranes.



Fig. 8. Evolution of voltage drop across the membrane (ΔV) for polyethylene membranes AM-PP and nanocomposite membranes AM-0.6CNTs during three 4-hour cycles of operation. Current density was 2 mA cm⁻².

maintained with time. It is noteworthy that two nanomaterials, which are different in geometry and functionalization, can have such a similar performance and improvement in a very close loading $(0.2\% \text{ g g}^{-1} - 0.6\% \text{ g g}^{-1}$ for iron oxide nanoparticles and 0.2% g g⁻¹ - 0.8% g g⁻¹ for CNTs). These similarities were first observed during the characterization process and then confirmed in the evaluation of the fouling resistance. Nanocomposite membranes using CNTs performed slightly better in fouling resistance and surface hydrophilicity. This might be due to a slightly higher loading of nanomaterials before the aggregation processes.

The energy consumption using the unmodified Ralex AM-PP membrane and the best nanocomposite membranes AM-0.6CNTs was calculated from the area under the curves of Fig. 8. The energy consumption decreased by 59.7% in the first cycle, 57.5% in the second and 48.5% in the third cycle. These promising results give an idea of the potential energy savings of a process that uses nanocomposite membranes with fouling resistant properties.

4. Conclusions

This work presents the performance in terms of fouling resistance of novel nanocomposite anion exchange membranes based on a polyethylene commercial anion exchange membrane and a thin nanocomposite layer. This layer is composed of sPPO and one nanomaterial: onedimensional oxidized multi-walled carbon nanotubes CNTs-COO⁻ or zero-dimensional sulfonated iron oxide nanoparticles $Fe_2O_3-SO_4^{2-}$, each with a totally different geometry and composition. The introduction of this layer caused a significant change in some physicochemical characteristics of the membrane surface such as composition, hydrophilicity and roughness that led to an enhancement of their fouling resistance. All the nanocomposite membranes showed a more hydrophilic and homogeneous surface than the unmodified membranes. The two nanomaterials presented similar performance, observed during the characterization process and then confirmed in the evaluation of the fouling resistance when using similar loadings (0.2% g g^{-1} – 0.6% g g⁻¹ for NPs and 0.2% g g⁻¹ – 0.8% g g⁻¹ for CNTs). However a slightly better performance of nanocomposite membranes using CNTs was observed. It might be due to the fact that CNTs allowed a slightly higher dose of nanomaterials before aggregation. The modification of membrane surface properties was characterized by SEM, FTIR, AMF and water contact angle measurement. The negatively charged layer, with small thickness, high hydrophilicity and conductivity, did not present changes of membrane resistance. The best load of NPs and CNTs was respectively 0.4% g g^{-1} and 0.6% g g^{-1} improving fouling resistance by 45% and 53%. These membranes also presented the highest hydrophilicity. The improved fouling resistance of the best nanocomposite membrane AM-0.6CNT was stable during 12 h of operation in contact with the model foulant. Energy savings between 49% and 60% were achieved due to the lower voltage drop during electrodialysis laboratory scale test. As there is a very similar performance of both nanomaterials, an economic evaluation might be decisive for the selection of the nanocomposite thin film. Further work should explore and compare the effects of different nanomaterials on other transport properties of the membranes, such as flux of ions and permselectivity.

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2.4 Artículo: "Electrochemical impedance spectroscopy of enhanced layered nanocomposite anion exchange membranes containing iron oxide nanoparticles and carbon nanotubes". (Carolina Fernández-González et al., Journal of Membrane Science, en revisión).



Figura 2. Resúmen gráfico del artículo "*Electrochemical impedance spectroscopy of enhanced layered nanocomposite anion exchange membranes containing iron oxide nanoparticles and carbon nanotubes*".

En este artículo se estudia el transporte de iones a través de membranas *nanocomposite* así como su comportamiento eléctrico mediante EIS. El objetivo es relacionar los cambios estructurales ocasionados al sintetizar las membranas *nanocomposite* con los cambios eléctricos y de transporte de iones observados al comparar las membranas *nanocomposite* con membranas de intercambio aniónico comerciales.

Se introduce la modificación de la superficie de membranas de intercambio iónico como una de las aplicaciones más prometedoras de los sistemas multicapa y se muestra como la modificación de las propiedades superficiales de estas membranas puede tener una influencia significativa sobre su comportamiento en términos de selectividad y resistencia al *fouling*. Se introduce la

monoselectividad como una característica deseable en membranas de intercambio aniónico para evitar fenómenos de scaling y obtener productos de mayor pureza. Se señalan los procedimientos convencionales para conseguir esta monoselectividad y se introduce como nueva tendencia la introducción de una película cargada negativamente para conseguir una mejora simultánea de la monoselectividad y de la resistencia frente al fouling. A continuación se introduce la técnica EIS, la cuál permite identificar capas de diferente comportamiento eléctrico en membranas para, en este caso particular, disponer de un análisis más exhaustivo de los fenómenos de intercambio iónico. Se presentan los escasos estudios recientes que utilizan la EIS para caracterizar membranas de intercambio iónico formadas por varias capas así como la necesidad de que se avance hacia una nueva aproximación e interpretación de los resultados obtenidos teniendo en cuenta las nuevas interfases que se generan en las membranas multicapa. En el objetivo de este artículo se presenta la necesidad de estudiar las mejoras de monoselectividad de membranas multi-capa nanocomposite sobre las que se ha modificado la carga superficial y el mecanismo que explica dicha mejora. Se presentan las técnicas utilizadas para caracterizar las membranas y obtener evidencias cuantitativas y cualitativas de este cambio de carga superficial, medidas de potencial zeta y medidas de EIS. Se señala como los datos recogidos mediante EIS se ajustaron a un modelo matemático tipo Maxwel-Wagner, con el que se dividió a las membranas estudiadas en diferentes capas de distinto comportamiento eléctrico, proponiendo un circuito eléctrico equivalente. El análisis mediante EIS permitió obtener un significado físico a cada una de las capas ajustadas, tanto para membranas nanocomposite como para membranas comerciales, haciendo especial énfasis en la identificación de las diferencias estructurales de las membranas con sus diferentes comportamientos eléctricos. Por último, se estudia la influencia de la concentración de la disolución sobre los componentes eléctricos equivalentes de dicho ajuste.

A continuación se resumen los principales resultados y conclusiones de este artículo.

La introducción de la película *nanocomposite* sobre la superficie de las membranas comerciales provoca un cambio en la carga de la superficie de la membrana, dotando a la misma de cierta monoselectividad. La mejora de la monoselectividad fue de entre un 26% y un 34%, obteniéndose la máxima mejora para las membranas denominadas AM-0.4NP y AM-0.6CNT, en referencia a la dosificación de nanomateriales NPs o CNTs. Adicionalmente, este recubrimiento mejoró el flujo de ión Cl⁻ hasta un 17% sin observar descenso en la selectividad Na⁺/Cl⁻.

Los autores, en base a su conocimiento, consideran que es la primera vez que se publica una mejora simultánea de monoselectividad y flujo de Cl⁻ en este tipo de membranas, probablemente debido a la buena conductividad iónica de las películas *nanocomposite* utilizadas en este trabajo. El recubrimiento de las membranas comerciales provocó una modificación en las medidas de potencial zeta de la superficie de la membrana de intercambio aniónico de valores positivos a negativos (de 10 mV para la membrana comercial AM-PP a -10 mV para las

membranas nanocomposite AM-0.4NP y AM-0.6CNTs). Además, las medidas mediante EIS mostraron que, mientras que las membranas sin modificar se comportaron como una conductancia pura en presencia de corrientes alternas, las membranas nanocomposite presentaron un comportamiento conductivo y capacitivo. Esto implica que las membranas son capaces de almacenar carga debido a la coexistencia de una región positiva (membrana original AM-PP) y una región negativa (capa nanocomposite). Los ajustes de los datos de EIS a un modelo tipo Maxwel-Wagner mostraron que las membranas sin modificar se pueden describir con una sola capa formada por una única conductancia en las condiciones experimentales estudiadas. Sin embargo, las membranas nanocomposite deben ser descritas mediante 3 capas. Una capa se corresponde con una conductancia pura asociada a la membrana *nanocomposite*. Las dos capas restantes se describen como una combinación de una conductancia y una capacitancia identificadas como las dos partes de la capa de agotamiento (depletion layer) formada en la interfase de la capa positiva y la negativa de las membranas nanocomposite. Esta capa de agotamiento se divide a su vez en dos capas debido a la gran diferencia de constante dieléctrica de las dos regiones que forman la membrana nanocomposite ocasionada por la existencia de nanomateriales. La región de la membrana con nanomateriales tiene una constante dieléctrica mucho mayor, traducida en un mayor espesor de la capa de agotamiento y una menor capacitancia. Por el contrario, la región positiva de las membranas nanocomposite, con una constate dieléctrica significativamente menor, presentó una capa de agotamiento mucho más estrecha siendo responsable de la mayor parte del carácter capacitivo de las membranas nanocomposite. El estudio de la concentración de iones en disolución sobre los resultados de EIS mostró que tanto la conductancia como la capacitancia de las membranas aumentaron con el incremento de la concentración de la disolución de una forma lineal.

Todas estas evidencias mostraron de forma contundente que debido al tratamiento de las membranas comerciales de PE se produce un cambio en la carga de la superficie de la membrana de intercambio iónico, lo que causa una mejora en la selectividad monovalente de las membranas *nanocomposite*. Al mismo tiempo, este estudio muestra la importancia de las nuevas interfases creadas en la unión de la capa *nanocomposite* y la membrana de intercambio aniónico desde un punto de vista eléctrico. Esta es la primera vez que se identifican capas de agotamiento en membranas de intercambio iónico avanzadas multicapa. Esta identificación ayuda significativamente a entender mejor la naturaleza eléctrica de membranas avanzadas multicapa donde capas negativas y capas positivas generan nuevas interfases.

Adicionalmente, debido al comportamiento capacitivo de las membranas *nanocomposite* cuando son caracterizadas mediante EIS, dicha técnica se puede considerar una herramienta útil para monitorizar daños y estabilidad de membranas *nanocomposite*, ya que el carácter capacitivo de estas membranas se espera que desaparezca a medida que la capa *nanocomposite* se dañe. Esto se puede aplicar no solo a las membranas *nanocomposite* de este trabajo sino a todas las

membranas multicapa donde regiones positivas coexisten con regiones negativas generando interfases donde se forman capas de agotamiento en presencia de corrientes alternas.

C. Fernandez-Gonzalez, J. Kavanagh, A. Dominguez-Ramos, R. Ibañez, A. Irabien, Y. Chen, H. Coster. *Electrochemical impedance spectroscopy of enhanced layered nanocomposite ion exchange membranes. Journal of Membrane*. Available online 22 July 2017

Enlace a la publicación
2.5 Artículo: *"Valorization of desalination brines by electrodialysis with bipolar membranes using nanocomposite anion exchange membranes"*. (Carolina Fernández-González et al., *Desalination*, 2017).



Figura 3. Resúmen gráfico del artículo *"Valorization of desalination brines by electrodialysis with bipolar membranes using nanocomposite anion exchange membranes".*

En este artículo se estudia la aplicación de membranas *nanocomposite* con nanopartículas funcionalizadas de óxido de hierro (Fe₂O₃-SO₄²⁻) en la valorización de salmueras de desalación mediante la tecnología electrodiálisis con membranas bipolares (EDBM).

Se presenta la desalación como una alternativa para la producción de agua potable, considerando el hecho de que sus impactos directos e indirectos comprometen su sostenibilidad ambiental. Los impactos directos están asociados a la gran cantidad de concentrados de desalación que deben ser vertidos en el entorno de la instalación. Se muestran los métodos convencionales de gestión de los concentrados de desalación y se presenta a la EDBM como una alternativa prometedora capaz de rebajar la concentración salina de dichos concentrados y, al mismo tiempo, valorizarlos en forma de dos productos, HCI y NaOH. A continuación se muestra la baja pureza de los productos obtenidos como una de las principales barreras tecnoeconómicas de esta tecnología en esta aplicación y se presenta el uso de membranas de intercambio aniónico nanocomposite con nanopartículas de óxido de hierro como candidatas para mejorar la pureza del HCl obtenido. Estas membranas fueron sintetizadas mediante el recubrimiento de membranas de intercambio aniónico de polietileno con una película cargada negativamente de sPPO y diferentes cargas de nanopartículas de óxido de hierro funcionalizadas (0,2% g_1g^{-1} , 0,4% g_1g^{-1} o 0,6% g_1g^{-1}). Se presenta una comparación de la concentración final de la principal impureza del HCl, el SO₄²⁻, utilizando membranas comerciales y membranas nanocomposite con una concentración de nanopartículas de óxido de hierro

 $(Fe_2O_3-SO_4^{2^-})$ de 0,2% g·g⁻¹, 0,4% g·g⁻¹ o 0,6% g·g⁻¹. Además se presenta un estudio de la influencia de la densidad de corriente sobre la evolución de la eficiencia de corriente y la concentración de las principales impurezas, tanto del ácido $(SO_4^{2^-})$ como de la base (K^+) . La evolución de la concentración de Cl⁻, $SO_4^{2^-}$, Na⁺ y K⁺ fue medida mediante Cromatografía lónica. Por último, se presenta un estudio de estabilidad de la membrana nanocomposite AM-0.4NP al trabajar con ácidos y bases fuertes. Esta estabilidad se estudió mediante medidas de permselectividad $SO_4^{2^-}/Cl^-$ y Espectroscopia Infrarroja por Transformada de Fourier (FTIR).

A continuación se resumen los principales resultados y conclusiones de este artículo.

En este trabajo se ha conseguido una reducción del 10% en la principal impureza del HCl obtenido, el SO₄²⁻, utilizando membranas *nanocomposite*. Se llevó a cabo un estudio exahustivo de la evolución de las principales componentes y impurezas en los compartimentos de ácido y base. La evolución de Cl⁻, SO₄²⁻ y H⁺ en el compartimento del ácido fue lineal con el tiempo. Los flujos de Cl⁻ y SO₄²⁻ aumentaron de forma lineal con la densidad de corriente. En el caso del Cl⁻, la relación es lineal sin interceptar el origen. En el compartimento de la base se observaron tendencias similares para Na⁺, K⁺ y OH⁻. El compartimento de la base presentó una eficiencia de corriente ligeramente superior al del ácido, con unos valores entre 66% y 90% y entre 56% y 85% respectivamente. Los dos compartimentos presentaron una bajada en la eficiencia de corriente similar debido a fugas de H⁺ y OH⁻. La corriente asociada a estas fugas estuvo entre el 8% y el 35% en el ácido y entre el 4% y el 30% en la base. Las membranas *nanocomposite* mostraron una buena estabilidad trabajando con ácidos y bases, ya que su selectividad monovalente se mantuvo inalterada después de 93 horas de operación en EDBM. La estabilidad te las membranas AM-0.4NP, seleccionadas como óptimas, también fue confirmada mediante FTIR.

Por lo tanto estas membranas, que permiten una mejor calidad en el HCl obtenido, aunque todavía lejos de la concentración comercial, son adecuadas para la operación en EDBM y la valorización de concentrados de desalación en ácidos y bases. La estabilidad de estas membranas en largos tiempos de operación así como un análisis tecno-económico que tenga en cuenta la sostenibilidad de su uso en EDBM debe llevarse a cabo.

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



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HIGHLIGHTS

branes

and bases.

permselectivity.

· HCl and NaOH were produced from

synthetic desalination brines by EDBM.

· Nanocomposite anion exchange mem-

 Nanocomposite membranes showed stability with time working with acids

 Cl^{-}/SO_{4}^{2}

increased

GRAPHICAL ABSTRACT

A R T I C L E I N F O

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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 Fe₂O₃-SO₄²⁻ 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 CI^{-}/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.

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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



DESALINATION

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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·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·L⁻¹ and Na₂SO₄ 0.05 mol·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 m³ of produced freshwater, a range which goes from 0.3 m³ to 1 m³ of brines are generated. Taking into account the desalination capacity projected for 2015 (97.5 \cdot 10⁶ m³·day⁻¹ [6]), the worldwide production of brines could be somewhere between 29.3 \cdot 10⁶ m³·day⁻¹ to $97.5 \cdot 10^6 \text{ m}^3 \cdot \text{day}^{-1}$. 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 Fe₂O₃-SO₄²⁻ nanoparticles ($0.2\% g \cdot g^{-1}$ to $0.6\% g \cdot g^{-1}$) have a very promising performance in terms of Cl⁻/SO₄²⁻ 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·m⁻²)



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



Fig. 2. Stack configuration used for permselectivity experiments (CEM-AEM-CEM).

over acid and base production using nanocomposite membranes is presented. Additionally, a discussion of the influence of the current density (J) over the evolution of the concentration of the main impurities of the acid (SO₄⁻²) and the base (K⁺) is also included and related to the current efficiency (η). This is an advance regarding the already published data in the literature that only report the final value of the concentration of impurities [16,19] or just the evolution of one impurity in a compartment [18]. Finally, the stability of nanocomposite membranes working with acids and bases is evaluated by comparison of the Fourier transform infrared spectrum of the nanocomposite membranes before and after 93 h of operation in EDBM. The evolution of the monovalent selectivity of these membranes before and after three cycles of 31 h of operation in an EDBM stack is also presented.

2. Experimental methodology

2.1. Membranes

Nanocomposite membranes synthesized from direct coating of a commercial heterogeneous polyethylene based AEM (AM-PP, Mega,



Fig. 3. Final SO_4^{2-} concentration in the acid stack using commercial and nanocomposite AEM. J=120 A \cdot m^{-2}.

Czech Republic) were used in EDBM experiments for acid and base generation from desalination brines. The coating of the membranes is composed by sulfonated poly (2,6-dimethyl-1,4phenylene oxide) and functionalized iron oxide nanoparticles. These nanoparticles are commercial iron (III) oxide nanoparticles (Sigma Aldrich, Ø50 nm) that were sulfonated using sulfuric acid obtaining Fe_2O_3 -S O_4^{2-} . A precise description of the mentioned nanoparticles as well as their sulfonation process can be found elsewhere [22,23]. Three different loading of nanoparticles were studied 0.2% $g \cdot g^{-1}$, 0.4% $g \cdot g^{-1}$ and 0.6% $g \cdot g^{-1}$ which were named as AM-0.2NP, AM-0.4NP and AM-0.6NP, respectively. Some characteristics of the nanocomposite membranes and the commercial AEM AM-PP are shown in Table 1. Commercial heterogeneous polyethylene based CEM RALEX CM-PP (Mega, Czech Republic) were used for permselectivity and EDBM experiments. Bipolar membranes Fumasep FBM (Fumatech, Germany) were used for EDBM experiments.

2.2. Acid and base generation by EDMB

EDBM experiments were performed in a bench scale laboratory electrodialysis system (PCCell, Germany). A commercial electrodialysis cell with two electrodes of 100 cm^2 of effective area each, made of titanium and coated with ruthenium oxide were used. Anion and cation exchange membranes were stacked according to Fig. 1 (CEM, AEM, BP, CEM, CEM). Nanocomposite AEM were set with the negative layer facing the brine compartment. J was applied at different levels: 80 A·m⁻², 120 A·m⁻², 250 A·m⁻², 500 A·m⁻² and 750 $A \cdot m^{-2}$ by means of a power supply in order to cover the range commonly used in the literature. The temperature was set to approximately 20 °C using a refrigeration bath. The flow rate was $60 L \cdot h^{-1}$ for each compartment. Synthetic brines that simulate the composition of a brine from a reverse osmosis desalination plant in operation in Las Aguilas (Spain) (except for calcium and magnesium) were used in EDBM experiments. A brine with the same composition has already been used in a recent study [18], which was: Na⁺ 22.9 g·L⁻¹; K⁺ 0.730 g·L⁻¹; Cl⁻ 32 g·L⁻¹; $SO_4^2 = 5.27 \text{ g} \cdot \text{L}^{-1}$; $CO_3^2 = 0.120 \text{ g} \cdot \text{L}^{-1}$, and $HCO_3^2 = 0.170 \text{ g} \cdot \text{L}^{-1}$. Initial solutions for HCl as acid and NaOH as base in the corresponding compartments were 0.1 mol· L^{-1} in both cases. A solution of NaOH 0.5 mol· L^{-1} was used in the electrode compartment. Samples were withdrawn on an hourly basis for measurements of pH and concentration of Cl⁻, SO₄²⁻, Na⁺ and K⁺. Acid and base titration was also performed.

2.3. Permselectivity experiments and stability of nanocomposite membranes

Permselectivity experiments were performed in the laboratory scale experimental setup and experimental conditions described in the previous section for EDBM experiments, only modifying membrane configuration, solutions and J. The new membrane configuration for permselectivity experiments is shown in Fig. 2 (CEM, AEM, CEM). The modified surface of the anion exchange membrane was set facing the dilute compartment in order to act as a barrier to SO_4^{2-} ions. Solutions prepared with NaCl 0.05 mol·L⁻¹ and Na₂SO₄ 0.05 mol·L⁻¹ were fed to the dilute and concentrate compartment. A solution of Na₂SO₄ 0.5 mol·L⁻¹ was used as electrolyte in the electrode compartment. In this case, the J value was set to 120 A·m⁻², which is the same J value used for the characterization of the membranes. This value corresponds to the 75% of the limiting J of the nanocomposite membrane with lower limiting J (see Table 1).

The evaluation of the anion monoselectivity of the membranes was performed using the transport numbers for SO_4^{-2} and Cl^- in the dilute compartment. The transport number for a specific ion (t_A) can be

Table 2

Summary of the SO₄²⁻ flux in the acid stack using commercial and nanocomposite AEM.

Membrane	$(SO_4^{-2} \text{ flux}) \cdot 10^2 (\text{mol} \cdot \text{h}^{-1} \cdot \text{m}^{-2})$	\mathbb{R}^2	Decrease (%)
Commercial AM-PP	7.36	0.993	-
AM-0.2NP	6.52	0.990	12
AM-0.4NP	6.73	0.988	9
AM-0.6NP	6.24	0.992	15



Fig. 4. Evolution of Cl $^-$ concentration in the acid stack using commercial and nanocomposite AEM. J = 120 A \cdot m $^{-2}.$

defined as the ratio between the flux of that ion (J_{A1}) and the total flux of ions (J_T) :

$$t_A = \frac{J_{A1}}{J_T} \tag{1}$$

To evaluate the relative permselectivity of the membranes between different ions and avoid the mole fraction effect [24] the transport number ratio is defined in [25] as:

$$P_{A2/A1} = \frac{t_{A2}/t_{A1}}{C_{A2}/C_{A1}} = \frac{J_{A2}/J_{A1}}{C_{A2}/C_{A1}}$$
(2)

where t_{A2} and t_{A1} are the transport numbers of ions A2 and A1. C_{A2} and C_{A1} are the average concentration of ions A2 and A1 during the ED experiment in the dilute compartment. In this work, A1 corresponds to Cl^- and A2 to SO_4^{2-} , thus the lower the $P_{A2/A1}$, the higher the monovalent selectivity of the membrane. Fluxes of Cl^- , SO_4^{2-} and Na^+ were calculated from the evolution of the concentration of the different ions in the dilute compartment.

To evaluate the stability of the negatively charged layer on the surface of the anion exchange membrane, permselectivity tests were performed just to one of the three modified membranes. The selection of the membrane AM-0.4NP over the two other membranes was done because AM-0.4NP has the best set of properties from Table 1: lowest water angle contact, tied for lowest electrical resistance and highest monovalent permselectivity. Consequently, the membrane AM-0.4NP was tested after 3 cycles of EDBM experiments. Each cycle of experiments corresponds to one experiment at the five different current

2.4. Analytical methods

2.4.1. Ion chromatography

Concentrations of Cl⁻, SO²₄⁻, Na⁺ and K⁺ were measured by ion chromatography (Dionex ICIS-1100 for anions and Dionex DX-120 for cations, Dionex Corp., USA). Acid and base concentrations were determined by acid-base titration using analytical grade reagents.

2.4.2. FTIR spectra analysis

The chemical composition of the membranes before and after 93 h of operation in EDBM was determined by Fourier transform infrared spectroscopy (FTIR) (Spectrum 65, Perkin Elmer, Waltham, MA, US). Spectra were scanned in a range of 650 cm⁻¹–4000 cm⁻¹. For each sample, the scan was repeated 10 times. Results were corrected using a spectrum of ambient air as a background.

2.5. Data analysis

Current efficiency (η) for a specific product is a critical important parameter to evaluate EDBM viability as it determines the fraction of the applied current that is effectively converted [18]. Therefore η was calculated according to Eq. (3):

$$\eta = \frac{(C_t - C_0) \cdot \mathbf{V} \cdot \mathbf{F}}{\mathbf{N} \cdot \mathbf{I} \cdot t} \tag{3}$$

where C_0 and C_t are the initial concentration and the concentration of the acid and base at any time operation time t, V is the volume circulated in each compartment, F is the Faraday constant, N is the number of cell triplets, and I is the total applied current in the cell. Eq. (3) was also used to determine the amount of electric current used for transport of impurities to the acid and the base stack.

3. Results and discussion

3.1. Acid generation using commercial and nanocomposite membranes

EDBM experiments were performed using commercial and nanocomposite AEM to evaluate the increase in the purity of the products by using nanocomposite membranes. A J value of $120 \text{ A} \cdot \text{m}^{-2}$ was selected for these experiments as it was also used for the characterization of the monovalent selectivity of the AEM. According to the characteristics of the AEM used in this work (see Table 1), all the nanocomposite membranes (AM-0.2NP, AM-0.4NP and AM-0.6NP) are less selective to SO_4^2 – than the commercial membrane, being the best membrane. AM-0.4NP with a 34% lower $P_{A2/A1}$ than the commercial membrane. The reason behind the monovalent selectivity of the nanocomposite membranes is that the layer of sPPO and Fe₂O₃-SO₄² – nanoparticles confers a negative charge to the surface of AEM. This negative charge causes

Table 3

Cl⁻ flux in the acid stack for the different current densities and nanocomposite membranes used in this study.

	$J(A \cdot m^{-2})$									
	80		120		250		500		750	
Membrane	$\frac{F_{Cl^{-}}}{(mol \cdot h^{-1} \cdot m^{-2})}$	R ²	F_{Cl^-} (mol · h ⁻¹ ·m ⁻²)	R ²	$\frac{F_{Cl^{-}}}{(mol \cdot h^{-1} \cdot m^{-2})}$	R ²	F_{Cl^-} (mol · h ⁻¹ ·m ⁻²)	R ²	F_{Cl^-} (mol · h ⁻¹ ·m ⁻²)	R ²
AM-0.2 NP AM-0.4 NP AM-0.6 NP	2.2 2.5 2.5	0.998 0.997 0.996	3.3 3.1 3.0	0.996 0.995 0.996	5.8 5.7 5.3	0.993 0.992 0.997	12.1 11.9 11.3	0.995 0.993 0.996	16.5 15.7 16.0	0.993 0.996 0.992

Table 4	4
$s \cap 2 - f$	1

	$J(A \cdot m^{-2})$									
80		120 250			500		750			
Membrane	$F_{SO_4^{2^-}}$ (mol·h ⁻¹ ·m ⁻²)	R ²	$F_{SO_4^{2-}}$ (mol·h ⁻¹ ·m ⁻²)	R ²	$\begin{array}{c} F_{SO_4^{2-}} \\ (mol \cdot h^{-1} \cdot m^{-2}) \end{array}$	R ²	$F_{SO_4^{2^-}}$ (mol·h ⁻¹ ·m ⁻²)	R ²	$F_{SO_4^{2^-}}$ (mol·h ⁻¹ ·m ⁻²)	R ²
AM-0.2 NP AM-0.4 NP AM-0.6 NP	0.033 0.040 0.042	0.992 0.990 0.994	0.065 0.067 0.062	0.989 0.988 0.991	0.178 0.187 0.162	0.997 0.997 0.994	0.403 0.399 0.406	0.987 0.996 0.998	0.607 0.601 0.610	0.995 0.996 0.998

electrostatic repulsions between anions and the negative surface of the AEM. These repulsions are larger for multivalent ions such as SO_4^2 than for monovalent ions such as Cl⁻ [26], so the layer confers monovalent selectivity to the AEM. Nanocomposite membranes are expected to lead to a lower SO_4^{2-} content in the acid stack. From Fig. 3 it can be seen that the final SO_4^{2-} content in the acid stack is just around 10% lower when using nanocomposite membranes and there is not a statistical significant difference among the nanocomposite membranes with different loadings of functionalized iron oxide nanoparticles. To further explain this drop in the SO_4^2 concentration, Table 2 includes the SO_4^2 flux in the acid stack for nanocomposite and commercial membranes, where it can be observed that the use of nanocomposite membranes can diminish the SO_4^{2-} flux from 9% to 15% in the acid stack when compared to commercial membranes. However, the improvement in acid quality is lesser than expected regarding the permselectivity of the nanocomposite AEM. A potential damage of the modification layer and the consequent deterioration in the performance of the nanocomposite membranes is readily discarded as FTIR spectra before and after 93 h of operation in EDBM is the same. Additionally, permselectivity tests were performed after 31 h, 62 h and 93 h of operation in EDBM for the membrane AM-0.4NP (reference membrane) and the monovalent selectivity of the membrane was confirmed as very stable (see Section 3.3 Stability of nanocomposite membranes). Thus, the improvement of just around 10% observed in the quality of the acid stack (instead of 34% expected from the permselectivity of the membranes) might be explained due to the low SO_4^{2-} concentration in the desalination brine in relation to Cl⁻ concentration. When monovalent selectivity between Cl^{-} and SO_{4}^{2-} ions is evaluated, the feed solution usually have the same molar concentration of both ions [27,28]. Thus, a solution composed of NaCl 0.05 mol·L⁻¹ and Na₂SO₄ 0.05 mol·L⁻¹ (ratio 1:1) was used for permselectivity experiments in this work. However, the concentration of Cl^- and SO_4^{2-} in the brine used in this study is $Cl^ 0.9 \text{ mol} \cdot L^{-1}$ to $SO_4^2 - 0.055 \text{ mol} \cdot L^{-1}$ (ratio 16.4:1). This difference between Cl^{-} and SO_4^{2-} concentrations might have an important impact on the performance of the nanocomposite membranes, as its monovalent selectivity is based on the electrostatic interaction between the negatively charged surface of the membrane and the species in the solution [24,28,29] instead of the increase on the hydrophobicity of the membrane [27,30,31].

From Fig. 4 it can be confirmed that the addition of the negative layer over the surface of the AEM does not decrease the Cl⁻ concentration. Final concentrations of Na⁺ concentration in the acid stack showed half of the values for the modified membranes (around $4 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ to $6 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) than for the non-modified commercial membrane (9.5 $\cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$). This confirms that the interaction between the negatively charged membrane and the positively charged cations in the solution is not augmented and thus, Cl⁻/Na⁺ permselectivity is not modified.

3.1.1. Influence of current density over acid production, main impurities and current efficiency using nanocomposite membranes

In order to evaluate the influence of J over the acid production and the content of impurities in the acid stack, experiments were performed at current densities from $80 \text{ A} \cdot \text{m}^{-2}$ to $750 \text{ A} \cdot \text{m}^{-2}$. The SO_4^{2-} and Cl^- concentration increased linearly versus time for the different studied

current densities. As the evolution is linear, the SO₄²⁻ and Cl⁻ fluxes from the brine stack to the acid stack can be straightforwardly fitted from the slope. This calculation allows the comparison of the performance of the different membranes and in this case, the different nanocomposite membranes AM-0.2NP, AM-0.4NP and AM-0.6NP. A complete summary of SO₄²⁻ and Cl⁻ fluxes for the different current densities using different nanocomposite membranes is included in Tables 3 and 4 respectively. The linear behavior of SO₄²⁻ and Cl⁻ concentration versus time is supported by the goodness of the fitting presented in Tables 3 and 4 (R² around 0.99). The performance of the nanocomposite membranes in terms of SO₄²⁻ and Cl⁻ fluxes is very similar in the present experimental conditions as displayed in Tables 3 and 4. Thus the



Fig. 5. Evolution of the concentration of a) Cl^- b) H^+ and c) SO_4^{2-} in the acid stack at different current densities using the membrane AM-0.4NP.



Fig. 6. Evolution of concentration of Cl⁻ in the brine stack at different current densities using nanocomposite membranes AM-0.4NP.

membrane with more promising characteristics, AM-0.4NP, will be chosen for stability tests as reference membrane. The evolution of the concentration of H^+ , SO_4^{2-} and CI^- at different current densities when using the membrane AM-0.4NP is presented in Fig. 5.

From Fig. 5a) and b), it can be concluded that the production of HCl is highly dependent on the J showing that the higher the applied J, the better the production rate. Similar trends has been reported previously in acid and base generation from desalination brines [16,18,19]. The rise in acid concentration at the different current densities matches well with the drop in the Cl⁻ concentration in the brine stack (as shown in Fig. 6).

To further analyze the influence of J in acid generation, Cl^{-} and SO_{4}^{2-} fluxes of the AM-0.4NP membrane were plotted against J in Fig. 7. Once again, the evolution of the fluxes with I can be properly fitted to a linear relationship (R² over 0.99). This is due to the high concentration of Cl⁻ and SO_4^{2-} in the brine, which avoid mass transport limitations between the dilute compartment and the acid stack. The ionic flux that occurs in EDBM is a combination of migration due to the electric field and diffusion due to the difference of concentrations between stacks. A previous study [13] reported that the contribution of the diffusion to the total ion flux depends on the difference of concentration between the concentrated stack and the dilute stack (brine stack and acid stack in the present study). It was reported that it can account up to a 25% of the ionic flux when working at relatively high current densities (250 A \cdot m⁻²– 1000 $A \cdot m^{-2}$) being the difference of concentration between stacks around 2 mol \cdot L⁻¹. The contribution of ionic flux due to diffusion to the total ionic flux increase as the current density decrease thus becomes the ionic flux contribution at no current density, thus the fitness



Fig. 8. Evolution of η for Cl⁻ with a) time and b) J in the acid stack using the membrane AM-0.4NP.

has no zero intercept. In the case of Cl⁻, the mathematical linear relationship is simply given by $F_{Cl^-} = a_{Cl^-}J + b_{Cl^-}$ being F_{Cl^-} the Cl⁻ flux and the fitting parameters for Cl⁻ $a_{Cl^-} = 0.02 \text{ mol} \cdot h^{-1} \cdot A^{-1}$ and $b_{Cl^-} = 0.83 \text{ mol} \cdot h^{-1} \cdot m^{-2}$. This means that the increase of Cl⁻ flux is favored by incrementing the J value. Necessarily, a decrease in η is noticed when enlarging J. The difference between the raising of the J value and the increase of Cl⁻ flux is more significant at low J values than at high J values, as the parameter that is not influenced by J related to diffusion phenomena, b_{Cl^-} , lose importance in the total Cl⁻ flux at high fluxes. This explains the decrease in η when increasing J as observed in Fig. 8a), which is more pronounced at low J and very small as J goes up.



Fig. 7. Evolution of the flux of a) Cl^- and b) SO_4^{2-} versus J in the acid stack using the nanocomposite AM-0.4NP.

Table 5 Fraction of the η for the transport of different ions at different J values in the acid stack using the nanocomposite AM-0.4NP. Results expressed as percentage by means of Eq. (3).

η				
J	Cl ⁻	SO_4^{2-}	Na ⁺	Total
$(A \cdot m^{-2})$	(%)	(%)	(%)	(%)
80	85.18	5.50	1.75	92.43
120	71.55	6.16	0.47	78.18
250	61.53	8.31	1.50	71.34
500	63.82	9.00	0.22	73.05
750	56.20	9.02	0.19	65.40

The H⁺ leakage has been reported to have a pronounced influence in EDBM process [15]. This leakage can explain the decrease of η versus time observed in Fig. 8b). A decrease of η with conversion of NaCl into HCl has also been reported recently [19]. For further discussion and understanding of the reasons behind how the applied current is used in the EDBM at the different I values, Table 5 includes the relative contribution of current used in the transport of the most important ions in the acid stack (Na⁺, Cl⁻ and SO_4^{2-}) as a percentage (other ions add up to 100%). Thanks to Table 5 it can be observed that the utilization of current for SO_4^{2-} transport increase when J does. In the case of SO_4^{2-} , the mathematical relationship is also linear: $F_{SO_4^2} = a_{SO_4^2} J + b_{SO_4^2}$ being $F_{SO_4^2}$ the SO₄² flux and the fitting parameters $a_{SO_4^2} = 8.45 \cdot 10^{-4} \text{ mol} \cdot \text{h}^{-1} \cdot \text{A}^{-1}$ and $b_{SO_4^2} = -2.84 \cdot 10^{-2} \text{ mol} \cdot \text{h}^{-1} \cdot \text{m}^{-2}$. 2. Similarly to the case of Cl⁻, this difference becomes less important with increasing J. Thus, low current densities will allow lower SO₄²⁻ content in the product. Final concentrations of Na⁺ in the acid stack at the different current densities varied from $2.1 \cdot 10^{-3} \text{ mol} \cdot L^{-1}$ to $12.6 \cdot 10^{-3} \text{ mol} \cdot L^{-1}$. Taking into account that Table 5 includes the η value of the main ions of the acid stack, and the presence of CO_3^{2-} and HCO_3^{-} is very low in the brine $(120 \text{ mg} \cdot \text{L}^{-1} \text{ and } 170 \text{ mg} \cdot \text{L}^{-1} \text{respectively})$, the H⁺ leakage can be estimated from 8% at 80 A \cdot m² to 35% at 750 A \cdot m². A larger H⁺ leakage due to J has already been reported in the literature [32]. The results of η reported in this work for acid production (Fig. 8a) and Table 5) are very similar to the previously reported in the literature for valorization of desalination brines, namely 70%–77% for 15 V–25 V [15], 70%–45% for 200 A \cdot m⁻²–1000 A \cdot m⁻² [18], and 51%–55% for 340 $A \cdot m^{-2}$ –570 $A \cdot m^{-2}$ [19].

3.2. Base generation using commercial membranes. Influence of current density over base production, main impurities and current efficiency

The evolution of the Na⁺, OH⁻ and K⁺ concentration in the base stack for different *J* values using commercial membranes is

presented in Fig. S1 of the supplementary data. Similarly to acid production, the evolution of the ions is linear versus time and the production rate is also faster when increasing the J values. This allows the calculation Na^+ and K^+ fluxes at different J values. As expected, the increase of Na^+ concentration in the base stack (supplementary data, Fig. S1) matches with the decrease of Na^+ concentration in the brine compartment (supplementary data, Fig. S2).

After plotting the Na⁺ and K⁺ fluxes versus J, once again a linear relationship is obtained (Fig. 9). In this case, the same trend is observed for both ions thus $a_{Na^+} = 0.041 \text{ mol} \cdot h^{-1} \cdot A^{-1}$; $b_{Na^+} = 2.973 \text{ mol} \cdot h^{-1} \cdot m^{-2}$; $a_{K^+} = 1.07 \cdot 10^{-3} \text{ mol} \cdot h^{-1} \cdot A^{-1}$; and $b_{K^+} = 7.63 \cdot 10^{-2} \text{ mol} \cdot h^{-1} \cdot m^{-2}$. Similarly to Cl⁻ evolution in the acid stack, the increase of the flux of cations is proportional to the applied J values, giving to a lower η as J goes up (see Fig. 10 and Table 6). This difference tends to disappear when increasing J and thus the decrease of η is slower at higher J values. Final concentrations of Cl⁻ in the base stack at the different current densities varied from $3.9 \cdot 10^{-3} \text{ mol} \cdot L^{-1}$ to $9.7 \cdot 10^{-3} \text{ mol} \cdot L^{-1}$. Fig. 10 shows the results of η for the base stack at different J values, which is between 66% and 90%. This η is more stable versus time (Fig. 10b) than in case of the acid stack (Fig. 8b)). The η values reported in this work in the base stack are very similar to the ones reported in the literature (38–88% for 150–900 A · m⁻² [16], 70–77% for 15–25 V [15], 55–80% for 200–1000 A · m⁻² [18]).

If the performance of EDBM for base and acid production is compared in terms of η , it can be stated that it is slightly higher for the base than for the acid (66%-90% for the base and 56%-85% for the acid). This is due to a higher Na⁺ flux in the base stack (2.7 mol·h⁻¹·m⁻², 3.7 mol·h⁻¹·m⁻², 7.6 mol·h⁻¹·m⁻², 13.4 mol·h⁻¹·m⁻² and 18.5 mol·h⁻¹·m⁻² at 80 A·m⁻², $\begin{array}{l} 120 \text{ A} \cdot \text{m}^{-2}, 250 \text{ A} \cdot \text{m}^{-2}, 500 \text{ A} \cdot \text{m}^{-2} \text{ and } 750 \text{ A} \cdot \text{m}^{-2} \text{ respectively} \\ \text{than } \text{ Cl}^{-} \text{ flux in the acid stack } (2.5 \text{ mol} \cdot \text{h}^{-1} \cdot \text{m}^{-2}, \\ 3.1 \text{ mol} \cdot \text{h}^{-1} \cdot \text{m}^{-2}, 5.7 \text{ mol} \cdot \text{h}^{-1} \cdot \text{m}^{-2}, \\ 15.7 \text{ mol} \cdot \text{h}^{-1} \cdot \text{m}^{-2} \text{ for } 80 \text{ A} \cdot \text{m}^{-2}, 120 \text{ A} \cdot \text{m}^{-2}, 250 \text{ A} \cdot \text{m}^{-2}, \end{array}$ 500 $A \cdot m^{-2}$ and 750 $A \cdot m^{-2}$ respectively) and thus, a better performance of CEM. This could be due to a higher ion exchange capacity of the CEM [18] and the facilitated transport of co-ions observed in this work in the case of AEM (see Tables 5 and 6). Although the η values are slightly higher for the base, the total drop of η when increasing the I is very similar (24% for the base versus 29% for the acid). Consequently the η values are influenced by the leakages of OH⁻ in the base stack and H⁺ in the acid stack (4%-30% for the base (estimated from Table 6) and 8%-35% for the acid).



Fig. 9. Evolution of flux of a) Na⁺ and b) K⁺ in the base stack versus the J values using commercial membranes.



Fig. 10. Evolution of η for Na⁺ with a) time b) J in the base stack using the membrane AM-0.4NP.

3.3. Stability of nanocomposite membranes

The stability of the nanocomposite membranes has been evaluated in two ways. First, the existence of the negatively charged layer after 3 cycles of operation in EDBM (93 h of operation in total) was confirmed using FTIR. Then, their functionality was checked by doing permselectivity experiments after finishing each of the 3 cycles of 31 h of operation. The nanocomposite membrane AM-0.4NP, the one with more promising properties according to Table 1 (best monovalent selectivity, lower water contact angle and tied for lowest electrical resistance), was chosen as a reference for the evaluation of the stability of the nanocomposite membranes used in this work.

Fig. 11 includes the FTIR spectrum of commercial AEM AM-PP (Fig. 11a)), nanocomposite membrane AM-0.4NP before operation in EDBM (Fig. 11b)) and nanocomposite membrane AM-0.4NP after 93 h of operation in EDBM (Fig. 11c)). In this Fig. 11 it can be seen that the spectrum of the commercial AEM and the nanocomposite membrane is totally different. In the case of the commercial AEM, two characteristic peaks of C—H stretch in $-CH_2$ - and CH_3 - substitutes can be seen at

Table 6 Fraction of the η for the different ions after applying different J values in the base stack. Results expressed as percentage by means of Eq. (3).

η				
J	Na ⁺	K ⁺	Cl ⁻	Total
$(A \cdot m^{-2})$	(%)	(%)	(%)	(%)
80	89.62	5.03	0.89	95.54
120	81.99	4.92	1.34	88.24
250	78.88	3.64	0.93	83.45
500	71.91	3.42	0.61	75.94
750	66.15	3.08	0.47	69.70



Fig. 11. FTIR spectra of anion exchange membranes a) RALEX AM-PP, b) AM-0.4NP t_{operation EDBM} = 0 h, c) AM-0.4NP t_{operation EDBM} = 93 h.

2917 cm⁻¹ and 2849 cm⁻¹ respectively [33]. These peaks correspond to the two main components of the AM-PP membranes, polyethylene and polypropylene. However, in the case of the membranes AM-0.4NP (Fig. 11b) and c)) the transmittance bands observed at 1173 cm⁻¹, 1061 cm⁻¹ and 1394 cm⁻¹ correspond to the C—O—C stretch of the sPPO, $-SO_3H$ substitute in the aromatic ring of PPO and S=O stretch of the SO_4^2 - attached to iron oxide nanoparticles respectively [22,33]. This confirms the existence of the layer of sPPO and Fe₂O₃-SO₄² - nanoparticles in the membrane AM-0.4NP before and after 93 h of operation in EDBM.

Regarding the functionality of the nanocomposite membranes, Fig. 12 includes the evolution of the monovalent selectivity of the membrane AM-0.4NP with operation time in EDBM. The monovalent selectivity remained unmodified, even after 93 h of operation in EDBM. Thus, from the results presented in Fig. 11 and Fig. 12 it can be concluded that the negative layer on the surface of the nanocomposite AEM is very stable and the functionality of the membranes AM-0.4NP has not been deteriorated by the operation in EDBM.

Other studies have recently reported good stability of a negatively charged layer on the surface of commercial AEM [34]. However, in this previous work the stability of the membrane was evaluated by measuring its antifouling performance after the storage of the membranes in deionized water for some time. In the case of this work, we evaluate the stability of the coating in a very much demanding environment. Additionally, regarding the conventional storage of the membranes, due to the number of tests that have been performed, first characterization and then operation in an EDBM stack, the nanocomposite membranes have been storage in NaCl 0.5 mol \cdot L⁻¹ solution for almost a year. No significant change in performance in terms of monovalent selectivity has been observed since its synthesis, even after starting to operate in acid and base generation by EDBM. Thus, these nanocomposite membranes are very stable and suitable for operation in EDBM. These results also suggest a very promising stability and long lifetime when working in regular ED operation for desalination of water. Additionally, the good stability working with hydrochloric acid showed in this study can be of interest as a good resistance regarding the chemical cleaning that is usually performed in desalination processes [21].

4. Conclusions

EDBM has not developed its full potential for the valorization of desalination brines yet. This work addresses one of the most important remaining challenges, which is the increase of the quality of the obtained acids and bases. A reduction of 10% in the SO_4^2 – concentration in the acid stack was achieved using nanocomposite AEM under the experimental conditions of this work. These membranes were synthesized by direct coating of a commercial polyethylene AEM with a negatively charged layer made of sPPO and different loads of functionalized iron oxide nanoparticles. An in-depth analysis of the evolution of the main



Fig. 12. Evolution of monovalent selectivity of the membrane AM-0.4NP versus operation time in EDBM.

components and impurities in the acid and the base stack was performed. The evolution of Cl^- , SO_4^{2-} and H^+ in the acid stack was found to be linear versus time. The Cl⁻ and SO₄²⁻ fluxes increased linearly when the current density did. In the case of Cl⁻, the effect of current density in the flux showed a linear relationship with non-zero intercept. Similar trends for Na⁺, K⁺ and OH⁻ were observed in the base stack. The current efficiency was found to be slightly higher for the base stack (66%–90%) than for the acid stack (56%–85%). A similar decrease on current efficiency was observed in both stacks due to proton and hydroxyl ion leakages, being the current utilization associated to these leakages 8%–35% for H^+ in the acid stack and 4%–30% for OH^- the base stack. The nanocomposite membranes showed a good stability when working with acid and bases as their monovalent selectivity remained unchanged after 31 h, 62 h and 93 h of operation in EDBM. The stability of the nanocomposite membrane AM-0.4NP was also confirmed by the FTIR spectrum. Thus these membranes, which allow a better quality in the produced acid, are suitable for operation in EDBM and valorization of brines into acids and bases. The stability of the nanocomposite membranes at longer operation times and a techno-economic analysis regarding the sustainability of their use in EDBM should be performed.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.desal.2016.07.033.

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Supplementary information of the article "Valorization of desalination brines by electrodialysis with bipolar membranes using nanocomposite anion exchange membranes"



Figure S1. Evolution of the concentration of a) Na^+b OH⁻ and c) K⁺ in the base stack at J values using commercial membranes.



Figure S2. Evolution of the concentration of Na⁺ in the brine at different J values using commercial membranes.



"Son los problemas sin resolver, no los resueltos, los que mantienen activa la mente"

"They are the unresolved problems, not the solved ones, those that keep the mind active"



Erwin Guido Kolbenheyer (1878-1962)

Escritor/Writer

CAPÍTULO 3: RESUMEN DE RESULTADOS Y CONCLUSIONES

3.1. Resumen de los principales resultados

En esta tesis doctoral se han desarrollado un conjunto de estrategias de carácter innovador para la mejora de la sostenibilidad ambiental de la desalación mediante electrodiálisis (ED). Para ello se ha incidido sobre dos elementos de la ED responsables de los principales impactos ambientales directos e indirectos de esta tecnología sobre el medio ambiente: su alto consumo energético por unidad de producto y el vertido de cantidades significativas de concentrados de desalación como subproducto.

En cuanto al consumo energético y sus emisiones de gases de efecto invernadero asociadas, se han abordado dos tipos de acciones estratégicas. Por un lado, se ha estudiado la sostenibilidad de la integración de la ED con energías provenientes de fuentes renovables y por otro lado se han desarrollado membranas de intercambio aniónico *nanocomposite* para mejorar la eficiencia del proceso de desalación mediante ED.

En relación al estudio de la sostenibilidad de la ED con energías provenientes de fuentes renovables, y de forma específica con la energía solar fotovoltaica (PV), la integración ED-PV supone una mejora de los aspectos ambientales al producirse una reducción de un orden de magnitud de las emisiones de CO₂ equivalente. En cuanto a los elementos económicos se refiere, la previsión a medio-largo plazo se basa en dos hipótesis: una bajada en los costes de inversión de las membranas y los módulos solares fotovoltaicos y en un aumento en el precio de la electricidad. Dicha previsión ha mostrado la posible rentabilidad de la integración ED-PV en un contexto similar al que puede encontrarse en las Islas Canarias antes del 2020 en el escenario más favorable y antes del 2050 en el escenario más desfavorable, estimando el precio del agua producida mediante ED-PV entre 0,15 €·m⁻³ y 0,40 €·m⁻³ justo después del punto de rentabilidad. En cuanto a los aspectos sociales, la desalación utilizando energías renovables genera más puestos de trabajo directos e indirectos gracias precisamente a la integración de la PV. Se puede asumir un amplio rango de generación de empleo entre 1,03·10⁻ ⁴ puestos permanentes por m³·día⁻¹ y 4·10⁻³ puestos permanentes por m³·día⁻¹ durante la operación de la planta. Como principales barreras que evitan una mayor penetración de la integración de la ED con energías provenientes de fuentes renovables destacan el ajuste del suministro de energía intermitente de las energías renovables con la demanda de agua, la eficiencia de los módulos solares y el alto coste de producción del agua dulce en comparación con su bajo coste en el mercado como commodity.

En relación al desarrollo de membranas de intercambio aniónico, en esta tesis doctoral se propone el tratamiento de membranas comerciales de polietileno con una película cargada negativamente. Esta película *nanocomposite* está formada por polióxido de sPPO y un nanomaterial: nanopartículas de óxido de hierro sulfonadas Fe₂O₃-SO₄²⁻ (NPs) o nanotubos de

carbono multipared oxidados CNTs-COO⁻ (CNTs), cada uno con una geometría completamente distinta. La introducción de la película *nanocomposite* en la membrana de polietileno causó un cambio significativo en las características físico-químicas de la superficie de la membrana como su composición, hidrofilicidad, rugosidad y carga dando como resultado una mejora de su resistencia frente al *fouling* y su selectividad hacia iones monovalentes. Todas las membranas *nanocomposite* mostraron una superficie más hidrofílica que las membranas sin modificar, con descensos del ángulo de contacto del agua de entre 36° y 42°. La superficie de las membranas *nanocomposite* fue más homogénea y menos rugosa. Se consiguió un cambio de carga superficial de positiva a negativa (de 10 mV a -10 mV). Estos cambios superficiales se traducen en mejoras en la resistencia frente al *fouling* de las membranas *nanocomposite* de entre 25% y un 53% en función de la carga y el tipo de nanomaterial utilizado. Esta mejora se mantuvo estable durante 12 horas de operación en contacto con el *foulant* modelo traduciéndose en una bajada del consumo energético de entre un 49% y un 60% en el sistema experimental utilizado.

Así mismo se incrementó la selectividad Cl⁻/SO₄²⁻ entre un 21% y un 34%, con un aumento simultáneo del flujo de Cl⁻ de hasta un 17,4%. Todos estas mejoras se consiguieron sin producir un aumento en la resistencia eléctrica de las membranas de intercambio aniónico. La carga óptima de nanomateriales que presentó una mejor resistencia frente al fouling fue la misma con la que se obtuvo una mayor selectividad Cl^{-}/SO_{4}^{2-} para los dos nanomateriales, 0,4% $g \cdot g^{-1}$ en peso de NPs y 0,6% $g \cdot g^{-1}$ en peso de CNTs. Las membranas AM-0.4NP y AM-0.6CNT se seleccionaron como las mejores disponibles y se estudió su comportamiento eléctrico mediante Espectroscopía de Impedancia Eléctrica (EIS) en comparación con las membranas sin modificar. Las membranas nanocomposite mostraron un carácter capacitivo que no se observó en el caso de las membranas de intercambio aniónico sin modificar. Este carácter capacitivo es debido a la coexistencia en la membrana de una región cargada positivamente (membrana de intercambio aniónico) y una región cargada negativamente (película nanocomposite) que provoca la generación de una capa de agotamiento en la unión de las dos regiones. Los datos experimentales de impedancia se ajustaron satisfactoriamente a un modelo matemático tipo Maxwell-Wagner con el que se propuso un circuito eléctrico equivalente para cada membrana en el rango de frecuencias estudiado. Las membranas comerciales heterogéneas aniónicas y catiónicas se describieron a través de un circuito equivalente formado por una única conductancia correspondiente a una única capa equivalente. Por su parte, las membranas nanocomposite AM-0.4NP y AM-0.6CNT se describieron mediante un circuito eléctrico equivalente formado por tres elementos en serie: una conductancia correspondiente a la membrana *nanocomposite*, una conductancia en paralelo con una capacitancia asociada a la capa de agotamiento formada en la interfase del área positiva, y una conductancia en paralelo con una capacitancia asociada a la capa de agotamiento formada en la interfase del área negativa. La obtención de dos capas de comportamiento eléctrico distinto, identificadas con la capa de agotamiento, se debe principalmente a la gran diferencia en el valor de la constante dieléctrica entre la capa *nanocomposite* y la membrana de intercambio aniónico provocada por la existencia de nanomateriales. El estudio de la concentración de iones en disolución sobre los resultados de impedancia mostró que tanto la conductancia como la capacitancia de las membranas aumentaron con el incremento de la concentración de la disolución de una forma lineal.

En cuanto a la generación de grandes cantidades de concentrados de desalación, se ha propuesto la electrodiálisis con membranas bipolares (EDBM) como una alternativa prometedora que permite el tratamiento y valorización de estos concentrados en forma de HCI y NaOH. Se han identificado las principales barreras de esta tecnología para esta aplicación, entre las que destacan la baja pureza de los productos obtenidos, su alto consumo energético y el coste de inversión derivado de las membranas bipolares. Esta baja pureza provoca que los productos generados no lleguen a los reguerimientos del mercado teniendo que ser destinados a autoconsumo en plantas de desalación. Las estimaciones realizadas en esta tesis indican que el tratamiento de un 1% de los concentrados de desalación generados sería potencialmente suficiente para el autoabastecimiento del HCI necesario. Por ello se focalizaron los esfuerzos en la mejora de la pureza de dichos productos para facilitar su salida en el mercado utilizando las membranas nanocomposite con nanopartículas de óxido de hierro desarrolladas en la presente tesis y estudiando la evolución con el tiempo y la densidad de corriente de las principales impurezas. Utilizando membranas nanocomposite se consiguió una reducción del 10% en la concentración del SO₄²⁻, principal impureza del HCl producido. La evolución de Cl⁻, SO₄²⁻ y H⁺ en el compartimento del ácido fue lineal con tiempo. Los flujos de Cl⁻ y SO₄²⁻ aumentaron de forma lineal con la densidad de corriente. En el compartimento de la base se observaron tendencias similares para Na⁺, K⁺ y OH⁻. El compartimento de la base presentó una eficiencia de corriente ligeramente superior a la del ácido, con un rango de valores entre el 66% y el 90% y del 56% al 85% respectivamente. Los dos compartimentos presentaron un descenso en la eficiencia de corriente similar debido a fugas de H⁺ y OH⁻ estimadas entre un 8% y un 35% en el ácido y entre un 4% y un 30% en la base. Las membranas nanocomposite mostraron una buena estabilidad trabajando con ácidos y bases, presentando una selectividad monovalente estable después 93 horas de operación en EDBM.

3.2. Conclusiones

Las conclusiones obtenidas a lo largo de la presente tesis doctoral han sido difundidas a través de 10 comunicaciones presentadas en congresos internacionales (4 de las mismas recogidas en libros o *proceedings* con ISBN) y 5 artículos en revistas científicas incluidas en el InCites[™] *Journal of Citation Reports-Science Edition* (JCR) de Thomson-Reuters[™], 4 de ellos publicados y 1 en proceso de revisión en la fecha de elaboración del presente documento. El listado completo de comunicaciones en congresos se detalla en el anexo. Las 5 publicaciones en revistas científicas se listan a continuación, indicando lista de autores por orden de firma, título del artículo, título de la revista, número de la revista, año de publicación, números de la primera y última página, último índice de impacto disponible correspondiente a 2015 (IF), denominación del área temática de la revista, cuartil en el área temática y posición relativa en el área temática:

- <u>C. Fernandez-Gonzalez</u>, A. Dominguez-Ramos, R. Ibañez, A. Irabien. Sustainability assessment of electrodialysis powered by photovoltaic solar energy for freshwater production. Renewable and Sustainable Energy Reviews, 47 (2015) 604-615. IF: 6.789. Energía y combustibles, Q1, 6/88.
- <u>C. Fernandez-Gonzalez</u>, A. Dominguez-Ramos, R. Ibañez, A. Irabien. Electrodialysis with bipolar membranes for valorization of brines. Separation and Purification Reviews, 45 (2016) 275-287. IF: 5.824. Ingeniería Química, Q1, 5/135.
- <u>C. Fernandez-Gonzalez</u>, A. Dominguez-Ramos, R. Ibañez, Y. Chen, and A. Irabien. Valorization of desalination brines by electrodialysis with bipolar membranes using nanocomposite anion exchange membranes. Desalination, 406 (2017) 16-24. IF: 4.412. Ingeniería Química, Q1, 12/135.
- <u>C. Fernandez-Gonzalez</u>, B. Zhang, A. Dominguez-Ramos, R. Ibañez, A. Irabien, Y. Chen. Enhancing fouling resistance of polyethylene anion exchange membranes using carbon nanotubes and iron oxide nanoparticles. Desalination, 411 (2017) 19-27. IF: 4.412. Ingeniería Química, Q1, 12/135.
- <u>C. Fernandez-Gonzalez</u>, J. Kavanagh, A. Dominguez-Ramos, R. Ibañez, A. Irabien, Y. Chen, H. Coster. Electrochemical impedance spectroscopy of enhanced layered nanocomposite anion exchange membranes containing iron oxide nanoparticles and carbon nanotubes. Journal of Membrane Science, (en revisión). IF: 5.557. Ingeniería Química, Q1, 7/135.

Es destacable el hecho de que no sólo el conjunto de los artículos pertenece al primer cuartil del área temática seleccionada sino que, como puede observarse, el conjunto de las 5 publicaciones pertenece al primer decil de dicha área temática, lo cual puede usarse como evidencia de calidad de los trabajados aceptados.

Las principales conclusiones recogidas en los citados artículos relacionadas con el desarrollo e implementación de estrategias para mejorar la desalación de agua mediante ED son:

i. <u>Respecto a la sostenibilidad de la integración de la ED con energías</u> renovables:

- El alto consumo energético del proceso de desalación de agua (de 0,4 kWh·m⁻³ a 27 kWh·m⁻³ en función del tipo de agua tratada y tecnología utilizada) provoca que para conseguir una desalación sostenible, el desarrollo de las tecnologías de desalación debe producirse en paralelo a un aumento en el uso e integración de energías provenientes de fuentes renovables.
- La probada sostenibilidad de las energías renovables, y en particular la PV, junto con una disminución esperada en sus costes de inversión, pone de manifiesto que la integración de tecnologías de desalación con energías renovables será muy común en un futuro cercano en diferentes escenarios.
- El menor consumo energético de la ED con respecto a la RO para el tratamiento de aguas con bajo contenido en sólidos en suspensión, provocará un aumento en el uso de ED a corto-medio plazo.
- La integración ED-PV se espera que juegue un papel relevante como una alternativa sostenible para la desalación de agua salobre.
- El uso extendido de ED-PV tendrá lugar entre el 2020 y el 2050, una vez que la desalación renovable sea más económica que la desalación convencional, estimando el precio del agua producida mediante ED-PV entre 0,15 €·m⁻³ y 0,40 €·m⁻³.

ii. <u>En relación a la mejora de membranas de intercambio aniónico utilizando</u> <u>nanomateriales:</u>

- La introducción de la película *nanocomposite*, que contiene nanopartículas de óxido de hierro sulfonadas o nanotubos de carbono multipared oxidados, en membranas de intercambio aniónico comerciales causó un cambio significativo en la composición, hidrofilicidad, rugosidad y carga superficial de las membranas dando como resultado una mejora de su resistencia frente al *fouling* (del 25% al 53%) y su selectividad hacia iones monovalentes (del 21% al 34%).
- Los dos nanomateriales utilizados en la película *nanocomposite* presentaron un comportamiento muy similar durante el proceso de caracterización de las membranas (hidrofilicidad, rugosidad y carga superficial) y durante la evaluación de la mejora de propiedades de las membranas *nanocomposite* tanto en resistencia contra en *fouling* como en transporte de iones.
- Las mejoras en la resistencia frente al *fouling* se tradujeron en disminuciones significativas de hasta un 60% del consumo energético de la ED en las condiciones experimentales utilizadas en esta tesis.
- La introducción de la película *nanocomposite* en la superficie de la membrana provocó un cambio significativo en su comportamiento eléctrico en presencia de corrientes alternas, mostrando las membranas *nanocomposite* cierto carácter capacitivo no observado en membranas comerciales de polietileno.
- Los valores de impedancia se modelaron satisfactoriamente mediante el modelo Maxwell-Wagner. Se propuso un circuito eléctrico equivalente para membranas comerciales y otro para membranas *nanocomposite*. Se observaron evidencias de la formación de una capa de agotamiento en el interior de las membranas *nanocomposite* como resultado de la coexistencia de cargas positivas y negativas. Esta capa de agotamiento tiene diferente comportamiento eléctrico en la parte positiva y negativa de la membrana, lo cual se entiende posible debido a diferentes valores en la constante dieléctrica de las dos regiones, motivado por el uso de nanomateriales.
- Se ha demostrado la importancia, desde el punto de vista eléctrico, de la interfase generada entre una membrana con cargas positivas y la capa *nanocomposite* de cargas negativas.

iii. En cuanto al tratamiento de salmueras mediante EDBM:

- La EDBM es una tecnología viable para la generación de HCl y NaOH a partir de salmueras de distintas aplicaciones a escala de laboratorio, la cual, con la I+D que ayude a superar las barreras técnicas identificadas en esta tesis, estará lista para su escalado desde laboratorio a planta piloto y posterior implantación industrial.
- La calidad de los productos obtenidos y su concentración dependen fuertemente del origen de las salmueras, siendo los productos aceptables para autoabastecimiento. La pureza y concentración requeridas para alcanzar el grado comercial es aún un reto.
- Un aumento significativo de la selectividad de las membranas de intercambio iónico, junto con una limitación de los fenómenos de electroósmosis, llevarían a una mayor pureza de los productos obtenidos mejorando la eficiencia del proceso.

iv. <u>Respecto a la valorización de concentrados de desalación en HCI y NaOH</u> mediante EDBM utilizando membranas *nanocomposite:*

- El uso de membranas *nanocomposite* mejoró la pureza del HCl obtenido, disminuyendo en un 10% la concentración de SO₄²⁻ como principal impureza.
- La evolución de Cl⁻, SO₄²⁻ y H⁺ en el compartimento del ácido durante el tiempo del experimento presentó un comportamiento de tipo lineal. Los flujos de Cl⁻ y SO₄²⁻ aumentaron también de forma lineal con la densidad de corriente. En el compartimento de la base se observaron tendencias similares para Na⁺, K⁺ y OH⁻.
- El compartimento de la base presentó una eficiencia de corriente ligeramente superior al del ácido (del 66% al 90% para la base y del 56% al 85% para el ácido). Los dos compartimentos presentaron un descenso similar en la eficiencia de corriente debido a fugas de H⁺ y OH⁻.
- Las membranas *nanocomposite* mostraron una adecuada estabilidad trabajando con ácidos y bases, y por tanto, son adecuadas para trabajar en la tecnología EDBM.

3.3. Trabajo futuro

En relación a los resultados de esta tesis doctoral, se consideran relevantes las siguientes líneas para el progreso científico-técnico futuro:

- 1. Profundizar en el estudio de la estabilidad de las membranas nanocomposite a tiempos largos. Es necesario ampliar los estudios de estabilidad realizados en esta tesis doctoral con experimentos con mayores tiempos de operación para estimar la vida útil de las membranas nanocomposite tanto trabajando con ácidos y bases en EDBM como en desalación de agua mediante ED. Para este estudio, a la vista de los resultados de la presente tesis doctoral en lo referente a la identificación de cambios estructurales en las membranas nanocomposite a partir de cambios en su comportamiento eléctrico, se propone la utilización de la Espectroscopia de Impedancia Electroquímica como nueva herramienta para la investigación y caracterización de membranas avanzadas multicapa.
- II. Avanzar en el estudio de los mecanismos de influencia de los nanomateriales sobre las propiedades de las membranas. Es necesario profundizar en la comprensión de los mecanismos que hacen que la introducción de nanomateriales en membranas suponga mejoras significativas en sus propiedades para diferentes aplicaciones, ya que estos mecanismos aún no están claros. En esta tesis se propone seguir estudiando la influencia de la geometría de los nanomateriales y su funcionalización sobre las propiedades de las membranas. De esta forma sería posible, en su caso, confirmar que la mejora en las membranas de intercambio aniónico es independiente de la geometría y la funcionalización de los nanomateriales utilizados.
- III. Evaluación del comportamiento de las membranas nanocomposite con aguas y concentrados reales. Se propone la evaluación del comportamiento a medio y largo plazo en escenarios reales de las membranas nanocomposite para determinar con mayor exactitud su comportamiento frente a fenómenos indeseables como el fouling y la mejora de su rendimiento al trajabar en ED y EDBM.
- IV. Integración de la EDBM con energía solar fotovoltaica. Una vez evaluada la sostenibilidad de la integración ED-PV para la desalación de agua, se propone la integración de EDBM-PV para el tratamiento y valorización de concentrados de desalación. Para que esta integración sea posible, es necesario realizar experimentos en continuo a escala de laboratorio así como un modelado matemático del comportamiento eléctrico de la celda de EDBM que permita un acoplamiento óptimo de la producción de ácidos y bases con la energía solar variable recibida.

V. Análisis económico para la valorización de concentrados de desalación. Por último, como paso previo a una etapa de escalado, sería necesario llevar a cabo un análisis económico que optimice: las etapas adicionales de tratamiento y purificación para aumentar la pureza y concentración de los productos obtenidos, el encarecimiento de los productos al aumentar las etapas de tratamiento y el tipo de aplicaciones para las que se pueden utilizar estos ácidos y bases en función de su pureza.

3.2. Conclusions

The conclusions obtained in this doctoral thesis have been divulged in 10 communications in international conferences (4 of which are published in books or proceedings with ISBN), and 5 papers in scientific journals indexed according to InCitesTM Journal Citation Reports-Science Edition (JCR) from Thomson ReutersTM, being 4 of them published, and 1 under review in the date of elaboration of this document. The full list of communications in conferences is included in *ANEXO I*. The list of scientific articles is included next, indicating the authors, article title, journal title, volume, year of publication, number of first and last page, impact factor available corresponding to 2015 (IF), area of knowledge of the journal, quartile in the area of knowledge and relative ranking in the area of knowledge:

- <u>C. Fernandez-Gonzalez</u>, A. Dominguez-Ramos, R. Ibañez, A. Irabien. Sustainability assessment of electrodialysis powered by photovoltaic solar energy for freshwater production. Renewable and Sustainable Energy Reviews, 47 (2015) 604-615. IF: 6.789. Energy and fuels, Q1, 6/88.
- <u>C. Fernandez-Gonzalez</u>, A. Dominguez-Ramos, R. Ibañez, A. Irabien. Electrodialysis with bipolar membranes for valorization of brines. Separation and Purification Reviews, 45 (2016) 275-287. IF: 5.824. Chemical Engineering, Q1, 5/135.
- <u>C. Fernandez-Gonzalez</u>, A. Dominguez-Ramos, R. Ibañez, Y. Chen, and A. Irabien. Valorization of desalination brines by electrodialysis with bipolar membranes using nanocomposite anion exchange membranes. Desalination, 406 (2017) 16-24. IF: 4.412. Chemical Engineering, Q1, 12/135.
- <u>C. Fernandez-Gonzalez</u>, B. Zhang, A. Dominguez-Ramos, R. Ibañez, A. Irabien, Y. Chen. Enhancing fouling resistance of polyethylene anion exchange membranes using carbon nanotubes and iron oxide nanoparticles. Desalination, 411 (2017) 19-27. IF: 4.412. Chemical Engineering, Q1, 12/135.

 <u>C. Fernandez-Gonzalez</u>, J. Kavanagh, A. Dominguez-Ramos, R. Ibañez, A. Irabien, Y. Chen, H. Coster. Electrochemical impedance spectroscopy of enhanced layered nanocomposite anion exchange membranes containing iron oxide nanoparticles and carbon nanotubes. Journal of Membrane Science, (under review). IF: 5.557. Chemical Engineering, Q1, 7/135.

It is worth mentioning that not only the set of articles belongs to the first quartile of the selected area of knowledge, but also are included in the first decile, which can be used as an evidence of the quality of the accepted manuscripts.

The main conclusions included in the cited articles related to the development and implementation of strategies to improve the desalination by ED are:

i. <u>Regarding the sustainability of the integration of ED with renewable</u> <u>energies:</u>

- The high energy consumption of desalination technologies (from 0.4 kWh·m⁻³ to 27 kWh·m⁻³ as a function of the feedwater and used technology) cause that in order to achieve a sustainable desalination, the development of desalination technologies should be done in parallel to an increase in the use of energies from renewable sources.
- The proven sustainability of renewable energies, and particularly PV, together with the expected decrease in their investment cost, makes clear that the integration of renewable energies with desalination technologies will be usual in the future in different scenarios.
- The lower specific energy consumption of ED in relation to RO for the treatment of water with low suspended solids will promote an increase in the use of ED in the short-medium term.
- The combination ED-PV is expected to play a relevant role as a sustainable alternative for the desalination of brackish water.
- The widespread use of ED-PV will take place between 2020 and 2050, once renewable desalination is cheaper than conventional desalination. The price of the water produced by ED-PV is estimated within a range from 0.15 €·m⁻³ to 0.40 €·m⁻³.

ii. <u>In relation to the improvement in anion exchange membranes using</u> <u>nanomaterials:</u>

- o The introduction of the nanocomposite film, containing sulfonated iron oxide nanoparticles or oxidized multiwall carbon nanotubes, in commercial anion exchange membranes caused a significant change in their composition, hydrophilicity, roughness and surface charge, causing a significant improvement in their resistance against fouling (from 25% to 53%) and selectivity towards monovalent anions (from 21% to 34%).
- The two nanomaterials used in the nanocomposite film showed a very similar performance during the characterization process of the membranes (hydrophilicity, roughness and surface charge) and during the evaluation of the enhanced properties of the nanocomposite membranes for both fouling resistance and ion transport.
- The improvements in the fouling resistance were translated into significant reductions up to 60% in the energy consumption of ED under the experimental conditions used in this thesis.
- The introduction of the nanocomposite film in the membrane surface caused a significant change in their electrical performance in the presence of alternating current. The nanocomposite membranes showed certain capacitative character not observed in commercial polyethylene membranes.
- A Maxwell-Wagner model satisfactorily modeled the impedance data. Two different equivalent electric circuits were proposed for commercial and nanocomposite anion exchange membranes. Evidences of the formation of a depletion layer in the nanocomposite membrane were observed due to the coexistence of positive and negative charges. This depletion layer has a different electrical performance in the positive and the negative region of the membrane caused by different dielectric constants in these two regions due to the use of nanomaterials.
- The importance, under an electrical point of view, of the interface generated between the positively charged anion exchange and the negatively charged nanocomposite film has been proved.

iii. Regarding the treatment of desalination brines by EDBM:

- The EDBM is a viable technology for the generation of HCI and NaOH from brines of different applications in laboratory scale. Additional R&D will be ready for the scale-up from laboratory scale to pilot plant and industrial implementation to overcome the technical barriers identified in this thesis.
- The quality and concentration of the obtained products strongly depend on the origin of the brine, being the products acceptable for self-supply. The purity and concentration of industrial grades is still a challenge.
- A significant upgrade of the selectivity of ion exchange membranes, in combination with a limitation of the electro-osmotic processes, would lead to a higher purity of the obtained products improving the efficiency of the process.

iv. <u>In relation to the valorization of desalination concentrates by means of</u> <u>EDBM using nanocomposite membranes</u>

- The use of nanocomposite membranes enhanced the purity of the obtained HCI, diminishing in 10% the concentration of $SO_4^{2^-}$.
- The evolution of Cl⁻, SO₄²⁻ and H⁺ in the acid compartment during the operation time showed a linear trend. The fluxes of Cl⁻ and SO₄²⁻ also increased linearly versus current density. Similar trends were observed in the base compartment for Na⁺, K⁺ and OH⁻.
- The base compartment presented a slightly higher current efficiency than the acid compartment (from 66% to 90% for the base and from 56% to 85% for the acid). Both compartments presented similar decreases in current efficiency due to H⁺ and OH⁻ leakages.
- The nanocomposite membranes showed a suitable stability in acids and bases so they are appropriate for operation in EDBM.

3.3. Future work

Based on the results reported in this PhD thesis, the following relevant lines are proposed for future scientific-technical progress:

- I. Going in depth in the study of the stability of nanocomposite membranes. The preliminary stability studies performed in this thesis must be completed with experiments featuring longer operation times in order to estimate the lifetime of the nanocomposite membranes both working with acids and bases in EDBM and in desalination of water by ED. For this study, in view of the results of this thesis in relation to the identification of structural changes in nanocomposite membranes from changes in their electrical performance, the use Electrochemical Impedance Spectroscopy is proposed, as a new tool for the research and characterization of advanced multilayered membranes.
- II. Advancing in the study of the mechanism of influence of nanomaterials over membrane properties. It is necessary to go deeper in the understanding of the mechanism causing improvements in membrane properties, in different applications, when introducing nanomaterials in their structure, as these mechanisms are still uncertain. We propose carry on studying the influence of the nanomaterial geometry and functionalization over the membrane properties in order to confirm, if the case, the observation of this doctoral thesis: the improvement in anion exchange membrane properties were independent of geometry and functionalization of the used nanomaterials.
- III. Evaluation of the performance of nanocomposite membranes with real waters and brines. The evaluation of the performance of the nanocomposite membranes in the medium and long term in real scenarios is proposed in order to determine more accurately their performance facing undesired phenomena such as fouling and the improvement of their performance working in ED and EDBM.
- IV. Integration of EDBM with photovoltaic solar energy. After the assessment of the sustainability of the integration of ED-PV for water desalination, the integration EDBM-PV is proposed for the valorization of desalination brines. For this integration to be possible, experiments of operation in continuous mode should be performed at laboratory scale. Additionally, a modeling of the electrical performance of EDBM is necessary for the proper coupling of the production of acids and bases with the intermittent received solar energy.

V. Economic analysis of the valorization of desalination brines. Finally, as a previous step for the scale-up of the process, an economic evaluation should be done optimizing: additional treatment and purification stages to increase the purity of the obtained products, the increase in the price of products when increasing the number of treatment stages and the type of applications where these products can be used when rising their purity.

Difusión de resultados

"La mayoría de las ideas fundamentales de la ciencia son esencialmente sencillas y, por regla general, pueden ser expresadas en un lenguaje comprensible para todos"

"Most of the fundamental ideas of science are essentially simple, and may, as a rule, be



expressed in a language comprehensible to everyone"

Albert Einstein (1879-1955)

Físico, Premio Nobel de Física (1921)/ Physicist, Nobel Prize in Physics (1921)

ANEXO I: DIFUSIÓN DE RESULTADOS

AI.1 Contribuciones a congresos relativos a la tesis doctoral

A continuación se listan las contribuciones a congresos internacionales del ámbito de la Ingeniería Química a través de los cuales se ha realizado la difusión de los resultados de la presente Tesis, indicando lista de autores por orden de firma, título de la contribución, congreso, fecha de celebración, lugar de celebración, ISBN (en su caso) y tipo de comunicación:

- C. Fernandez-Gonzalez, J. Kanavagh, H. Coster, A. Dominguez-Ramos, R. Ibañez, Y. Chen, A. Irabien. *Enhancing the performance of polyethylene based anion exchange membranes using nanomaterials for desalination of water by electrodialysis.* 3rd *International Conference on Desalination using Membrane Technology.* 2-5 abril 2017, Gran Canaria (España). Comunicación oral.
- C. Fernandez-Gonzalez, J. Kanavagh, H. Coster, A. Dominguez-Ramos, R. Ibañez, Y. Chen, A. Irabien. *Enhancing the performance of polyethylene based anion exchange membranes using functionalized iron oxide nanoparticles and oxidized multiwalled carbon nanotubes: mechanism and comparison between nanomaterials.* 5th *International Conference on Multifunctional, Hybrid and Nanomaterials.* 6-10 marzo 2017, Lisboa (Portugal). Comunicación póster.
- <u>C. Fernandez-Gonzalez</u>, B. Zhang, A. Dominguez-Ramos, R. Ibañez, A. Irabien, Y. Chen. *Improving the Performance of Commercial Polyethylene Based Anion Exchange Membranes in an Electrodialysis Process Using Functionalized Iron Oxide Nanoparticles*. Reunión anual del AICHE 2016. 13-18 noviembre 2016, San Francisco (EE.UU.). ISBN: 978-0-8169-1097-7. Comunicación póster.
- M. Herrero, B. Muñiz-Rodríguez, <u>C. Fernández-González</u>, A. Domínguez-Ramos, R. Ibáñez, A. Irabien. *Evaluation of performance of tailored nanocomposite anion exchange membranes in the valorization of desalination brines by means of bipolar membranes electrodialysis. 6th European Chemistry Congress.* 11-15 septiembre 2016, Sevilla (España). Comunicación oral.









- <u>C. Fernandez-Gonzalez</u>, A. Mazón, A. Dominguez-Ramos, R. Ibañez, A. Irabien, Y. Chen. Valorization of desalination brines by means of electrodialysis with bipolar membranes using nanocomposite anion exchange membranes. 2nd International Conference on Desalination and Environment. 23-26 enero 2016, Doha (Qatar). Presentación Oral.
- <u>C. Fernandez-Gonzalez</u>, A. Mazón, A. Dominguez-Ramos, R. Ibañez, A. Irabien. Integration of electrodialysis with bipolar membranes with photovoltaic solar energy for the autonomous and continuous production of acid and bases from desalination brines. 2nd International Conference on Desalination and Environment. 23-26 enero 2016, Doha (Qatar). Presentación Oral.
- <u>C. Fernandez-Gonzalez</u>, A. Mazón, A. Dominguez-Ramos, R. Ibañez, A. Irabien. Electrodialysis with bipolar membranes powered by photovoltaic solar energy for the continuous production of acid and bases from desalination brines. 10th European Congress of Chemical Engineering (ECCE10). 27 septiembre 1 octubre 2015, Niza (Francia) <u>ISBN</u>: 978-2-910239-82-4. Comunicación oral.
- <u>C. Fernandez-Gonzalez</u>, A. Dominguez-Ramos, R. Ibañez y A. Irabien. The state-of-the-art of the electrodialysis for the treatment and valorization of desalination brines. 7th European meeting on Chemical Industry and the Environment (EMCHIE). 10-12 julio 2015, Tarragona (España) <u>ISBN</u>: 978-84-8424-3670. Comunicación póster.
- <u>C. Fernandez-Gonzalez</u>, A. Dominguez-Ramos, R. Ibañez, A. Irabien. Electrodialysis powered by photovoltaic solar energy: a sustainability assessment. 13th Mediterranean Congress of Chemical Engineering. 30 septiembre 3 octubre 2014, Barcelona (España). Comunicación póster.











<u>C. Fernandez-Gonzalez</u>, A. Dominguez-Ramos, R. Ibañez, A. Irabien. About the sustainability of the electrodialysis powered by photovoltaic solar energy. IX Ibero-american congress on membrane science and technology. 25-28 mayo 2014, Santander (España). <u>ISBN</u>: 978-84-697-0397-7. Comunicación poster y presentación flash.

AI.2 Producción científica anterior al doctorado

Artículo científico

A. Urtiaga, <u>C. Fernández-González</u>, S. Gómez-Lavín, I. Ortiz. Kinetics of the electrochemical mineralization of perfluorooctanoic acid on ultrananocrystalline boron doped conductive diamond electrodes. Chemosphere, 129 (2015) 20-26.

Comunicaciones a congresos

- <u>C. Fernandez</u>, S. Gómez-Lavín, I. Ortiz y A. Urtiaga. Electrochemical Degradation of Perfluorooctanoic Acid in Water by BDD Anodes. 5th International Workshop on Per-and Polyfluorinated Alkyl Substances- PFAS. 27-29 octubre 2013, Helsingør (Dinamarca). Comunicación póster.
- <u>C. Fernandez</u>, I. Ortiz, A. Urtiaga. Electrooxidación de ácido perfluorooctanoico (PFOA) mediante electrodos UNCD (borondoped ultrananocrystalline diamond). : XXXIV Reunión de la Real Sociedad Española de Química. 15-18 septiembre 2013, Santander (España). Presentación flash.





AI.3 Difusión divulgativa y premios

Como complemento a la difusión científica, en esta tesis doctoral también se ha realizado la siguiente difusión divulgativa de los resultados de la tesis:

- <u>C. Fernández González</u>, A. Domínguez Ramos, R. Ibáñez, A. Irabien. Tratamiento y valorización de concentrados de desalación: Hacia una desalación más sostenible.
 II Jornada de Jóvenes Investigadores de Cantabria. 5-6 de noviembre del 2015, Santander (España). Comunicación Póster.
 - Premio al mejor póster por el jurado.
 - i. Presentación oral como póster ganador a los asistentes a las jornadas.
 - ii. Entrevista en la radio Onda Cero (difusión regional).
- <u>C. Fernández González</u>, H. Coster, Y. Chen, A. Domínguez Ramos, R. Ibáñez y A. Irabien. Tratamiento y valorización de concentrados de desalación: Hacia una desalación más sostenible. V Jornadas Doctorales del grupo G9 de Universidades. 8-10 de febrero del 2017, Palma de Mallorca (España). Comunicación Póster.
 - Póster seleccionado por la Universidad de Cantabria para asistir a las V Jornadas Doctorales del grupo G9 de Universidades y representar a la Universidad de Cantabria como estudiante de doctorado en el área de Ingeniería.
- Difusión de resultados y actividad investigadora mediante diversas jornadas de puertas abiertas de los laboratorios organizadas por el Departamento de Ingenierías Química y Biomolecular de la Unviersidad de Cantabria.
