Universidad de Alcalá
COMISIÓN DE ESTUDIOS OFICIALES
DE POSGRADO Y DOCTORADO

UNIVERSIDAD DE ALCALÁ, PATRIMONIO DE LA HUMANIDAD

ACTA DE EVALUACIÓN DE LA TESIS DOCTORAL

(FOR EVALUATION OF THE ACT DOCTORAL THESIS)

Año académico (*academic year*): 2016/17

DOCTORANDO (*candidate PHD*): **GARCÍA PACHECO, RAQUEL**
D.N.I./PASAPORTE (*Id.Passport*): ******0178Q**
PROGRAMA DE DOCTORADO (*Academic Committee of the Programme*): **D336 DOCTORADO EN HIDROLOGÍA Y GESTIÓN DE LOS RECURSOS HÍDRICOS**
DEPARTAMENTO DE (*Department*): **QUÍMICA ANALÍTICA, QUÍMICA FÍSICA E INGENIERÍA QUÍMICA**
TITULACIÓN DE DOCTOR EN (*Phd title*): **DOCTOR/A POR LA UNIVERSIDAD DE ALCALÁ**

En el día de hoy 11/05/17, reunido el tribunal de evaluación, constituido por los miembros que suscriben el presente Acta, el aspirante defendió su Tesis Doctoral **con Mención Internacional** (*In today assessment met the court, consisting of the members who signed this Act, the candidate defended his doctoral thesis with mention as International Doctorate*), elaborada bajo la dirección de (*prepared under the direction of*) ELOY GARCÍA CALVO // JUNKAL LANDABURU AGUIRRE.

Sobre el siguiente tema (*Title of the doctoral thesis*): *NANOFILTRATION AND ULTRAFILTRATION MEMBRANES FROM END-OF-LIFE REVERSE OSMOSIS MEMBRANES A STUDY OF RECYCLING*

Finalizada la defensa y discusión de la tesis, el tribunal acordó otorgar la CALIFICACIÓN GLOBAL[1] de (**no apto, aprobado, notable** y **sobresaliente**) (*After the defense and defense of the thesis, the court agreed to grant the GLOBAL RATING (fail, pass, good and excellent)*): Sobresaliente

Alcalá de Henares, a 11 de mayo de 2017

Fdo. (*Signed*): Susana Luque Rodríguez

Fdo. (*Signed*): João Crespo

Fdo. (*Signed*): Arcadio Sotto

FIRMA DEL ALUMNO (candidate's signature),

Fdo. (*Signed*): Raquel García Pacheco

Con fecha 31 de mayo de 2017 la Comisión Delegada de la Comisión de Estudios Oficiales de Posgrado, a la vista de los votos emitidos de manera anónima por el tribunal que ha juzgado la tesis, resuelve:

☒ Conceder la Mención de "Cum Laude"
☐ No conceder la Mención de "Cum Laude"

La Secretaria de la Comisión Delegada

---

[1] La calificación podrá ser "**no apto**" "**aprobado**" "**notable**" y "**sobresaliente**". El tribunal podrá otorgar la mención de "cum laude" si la calificación global es de sobresaliente y se emite en tal sentido el voto secreto positivo por unanimidad. (*The grade may be "**fail**" "**pass**" "**good**" or "**excellent**". The panel may confer the distinction of "cum laude" if the overall grade is "Excellent" and has been awarded unanimously as such after secret voting.*).

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En aplicación del art. 14.7 del RD. 99/2011 y el art. 14 del Reglamento de Elaboración, Autorización y Defensa de la Tesis Doctoral, la Comisión Delegada de la Comisión de Estudios Oficiales de Posgrado y Doctorado, en sesión pública de fecha 31 de mayo, procedió al escrutinio de los votos emitidos por los miembros del tribunal de la tesis defendida por *GARCÍA PACHECO, RAQUEL*, el día 11 de mayo de 2017, titulada *NANOFILTRATION AND ULTRAFILTRATION MEMBRANES FROM END-OF-LIFE REVERSE OSMOSIS MEMBRANES A STUDY OF RECYCLING*, para determinar, si a la misma, se le concede la mención "cum laude", arrojando como resultado el voto favorable de todos los miembros del tribunal.

Por lo tanto, la Comisión de Estudios Oficiales de Posgrado **resuelve otorgar** a dicha tesis la

MENCIÓN "CUM LAUDE"

Alcalá de Henares, 5 de junio de 2017
EL PRESIDENTE DE LA COMISIÓN DE ESTUDIOS
OFICIALES DE POSGRADO Y DOCTORADO

Juan Ramón Velasco Pérez

Copia por e-mail a:
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DILIGENCIA DE DEPÓSITO DE TESIS.

Comprobado que el expediente académico de D./Dª RAQUEL GARCÍA PACHECO reúne los requisitos exigidos para la presentación de la Tesis, de acuerdo a la normativa vigente, y habiendo presentado la misma en formato: ☐ soporte electrónico ☒ impreso en papel, para el depósito de la misma, en el Servicio de Estudios Oficiales de Posgrado, con el nº de páginas: 295 se procede, con fecha de hoy a registrar el depósito de la tesis.

Alcalá de Henares a 28 de MARZO de 2017

Fdo. El Funcionario

RESTAURAR IMPRIMIR

Universidad de Alcalá

Escuela de Postgrado de la Universidad de Alcalá
Programa de Doctorado en Hidrología y Gestión de los Recursos Hídricos

Nanofiltration and ultrafiltration membranes from end-of-life reverse osmosis membranes

A study of recycling

Tesis Doctoral presentada por:

Raquel García Pacheco

Dirigida por:

Dr. Eloy García Calvo

Dra. Junkal Landaburu Aguirre

Departamento de Química Analítica, Química Física e Ingeniería Química
Universidad de Alcalá

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CERTIFICAN:

Que el trabajo descrito en la presente memoria, titulado “Nanofiltration and ultrafiltration membranes from end-of-life reverse osmosis membranes. A study of recycling”, ha sido realizado por **Dª Raquel García Pacheco** bajo su dirección. Asimismo, autorizan su presentación para que sea defendido como Tesis Doctoral.

Y para que conste y surta los efectos oportunos, firman el presente en Alcalá de Henares a ……. de Marzo de 2017.

Eloy García Calvo

Junkal Landaburu Aguirre

Universidad de Alcalá

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Alberto Escarpa Miguel, Profesor Titular de Universidad de Química Analítica y Director del Departamento de Química Analítica, Química Física e Ingeniería Química de la Universidad de Alcalá,

CERTIFICA:

Que el trabajo descrito en la presente memoria, titulado "Nanofiltration and ultrafiltration membranes from end-of-life reverse osmosis membranes. A study of recycling" ha sido realizado por **Dª. Raquel García Pacheco** bajo la dirección del **Dr. Eloy García Calvo** del Área de Ingeniería Química, con la codirección de la **Dra. Junkal Landaburu Aguirre** del grupo de Tecnología de Membranas del Instituto Madrileño de Estudios Avanzados del Agua (IMDEA Agua), y autoriza su presentación para que sea defendido como Tesis Doctoral.

Y para que conste y surta los efectos oportunos, firma el presente en Alcalá de Henares a ……….. de Marzo de 2017.

Alberto Escarpa Miguel

A mis abuelos.
A Casimira Pescador.

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I would like to note the tight collaboration between Valoriza Co. and Sadyt Co. staff developed during these years. It is being a pleasure working with Domingo Zarzo Elena Campos, Patricia Terrero, Paco Molina, Diego Martinez, José Manuel Caparrós and Jesús Durán within the Life-Transfomem project framework.

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I would like to thank to everyone at IMDEA Agua Institute. In particular thanks to Virtu María, M.A, Julito, Rubén, Alberto Blanco and Alberto de Tomás, because we have grown together. You have been always animating me, supporting me psychologically and we have spent such a wonderful time out of work. Thank you to Raffaella and Angelito for all the aforementioned and indeed, for the linguistic corrections and advises during the Thesis.

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Finally I would also like to thank to all my family, from the youngest to the oldest, for all the time spend together that was an incredible help to disconnect. Above all, the warmest thanks go to my parents Carol and Vicente because I owe them everything. They have supported all my decisions and have taught me how to live and how to face difficult times positively. Thank you very much to my sister Laura for her unconditional love and energy that always recharges me. I would also like to give a big thank you to Ioni for his patient, for understanding me always and being so generous sharing his time with me. Special thanks to my closest friends Carlotta and JuanP, because I learn everyday from you and I love discovering the World with you. Big thanks to my friends Ali, Bea, Carol, Don Jose Manuel, Laura, Sarita and Tania for the good time spent together (I love our “photo album covers”). Thank you also to Urs family for being there and sustain us with amazing food. Thanks to Pedro, Yolanda and Steve for the amazing time skying and thank you also to Angelo, my Italian “father”. Definitively, thank you to all the people that has shared time with me during these 7 years, specially to Rafael Luque, Erasmus friends and ERU Watsan Unit members from Spanish Red Cross, because each one of them has help me to grow in different ways.

Abstract

Reverse osmosis (RO) is the most employed technology for water desalination. However, membrane fouling is inevitable and one of the main reasons for a regular membrane replacement. Due to the continuous growth of this technology, end-of-life RO membrane management has created an economic and environmental concern. Therefore, alternative management routes need to be faced by the industry and academia. The overall aim of this study is to investigate the direct recycling process as a feasible alternative to produce nanofiltration (NF) and ultrafiltration (UF) recycled membranes.

In this study membrane fouling was characterized through thermo-gravimetric, spectrometric and microbiological techniques. Brackish and seawater RO membranes were subjected to the chemical attack of free chlorine. The main objective was altering their selective active layer of polyamide (PA). Recycling process was carried out by membrane passive immersion in sodium hypochlorite solutions, at room temperature with no pressure and no agitation. The TM720-400 BW membrane was selected as the case study at laboratory scale. It was investigated the effect of exposure time, pH solution and membrane storage (dry and wet) on the recycling process. It was observed that recycled membrane permeability values and rejection coefficients were affected by the storage condition. Indeed, 124 ppm free chlorine at basic pH solution during 50 h (equivalent to 6,200 ppm·h) were the initial selected conditions to transform RO membrane performance into NF membrane. In addition, longer exposure time (242 h) was chosen for obtaining UF membrane performance. Afterwards, the recycling method was optimized aiming at decreasing the aforementioned exposure time required. Therefore, the exposure dose concept (ppm·h) was evaluated, i.e. diverse solution concentrations and exposure times were combined to achieve fixed exposure doses (6,200; 30,000 y 300,000 ppm·h). The impact created on the membranes was evaluated in terms of permeability and rejection coefficients, during brackish water treatment. Some experiments were repeated using other end-of-life RO models to evaluate the reproducibility of the selected conditions. Moreover, results were compared with several pristine commercial membranes (RO, NF and UF). In fact, recycled membrane performance values were within the range values observed using NF90-

400 and NF270-400 nanofiltration membrane models. Moreover, membranes exposed to high exposure level were also compared to a commercial UF membrane (10 KDa). Recycled membranes showed rejection coefficients similar or higher than the commercial one, when treating urban wastewater. The recycling process at pilot scale required analogous exposure doses (ppm·h) to those used at laboratory scale.

At both scales, membrane scaling affected significantly the recycling process. Membranes that were fouled by inorganic clay, organic and microbiological matter did not show difficulties in the recycling process. Surface characterization was conducted to confirm the degradation of the PA layer by the attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and scanning electron microscopy (SEM). From 50,000 ppm·h exposure doses, ATR-FTIR spectra of recycled membranes were different than RO pristine membrane. SEM micrographs showed pores on the recycled membranes surfaces, with a Feret Diameter ranges from 8 to 14 nm (calculated by *ImageJ* software). Beside, the molecular weight cut off determined at laboratory scale ranges from 10,000 to 38,000 g/mol. Finally, a business model of end-of-life RO membranes of a hypothetical recycling membrane plant was developed identifying potential user, investors, technical drawback, market competition and social barriers.

This study demonstrates that direct passive recycling could be a feasible alternative that can further boost the RO membrane technology towards circular economy approach.

Resumen

La tecnología más empleada para la desalación de agua es la ósmosis inversa (OI). Sin embargo, el ensuciamiento de las membranas de OI es un hecho inevitable que provoca su periódica sustitución. El continuo crecimiento de esta tecnología ha generado una preocupación ambiental y económica entorno a la gestión de las membranas desechadas. Por ello, el estudio de alternativas de gestión que afronten este reto es necesario tanto a nivel académico como industrial. El objetivo de esta Tesis es investigar el proceso de reciclaje directo para la producción de membranas recicladas con propiedades de nanofiltración (NF) y ultrafiltración (UF).

En este estudio se caracterizó el ensuciamiento depositado sobre las distintas membranas a través de técnicas termogravimétricas, espectrométricas y microbiológicas. Las membranas de OI, que en su vida útil trataron agua de mar y agua salobre, se expusieron al ataque químico del cloro libre. El objetivo principal fue alterar las propiedades de su capa selectiva de poliamida (PA). El proceso de reciclaje se llevó a cabo mediante la inmersión pasiva de las membranas en soluciones de hipoclorito de sodio a temperatura ambiente, a presión atmosférica y sin agitación. Se seleccionó el modelo de membrana de agua salobre TM720-400 como caso de estudio a escala laboratorio, para investigar el efecto del tiempo de exposición, las condiciones de pH y la conservación previa de las membranas (secas o húmedas) en el proceso de reciclaje. Se observó que el método de conservación afecta a los valores de permeabilidad y los coeficientes de rechazo de las membranas recicladas. Así, se seleccionó la solución básica de 124 ppm de cloro libre y el tiempo de exposición de 50 h (equivalente a 6,200 ppm·h) para transformar las propiedades de las membranas de OI en propiedades de NF. Se requirió un tiempo de exposición mayor (242 h) para obtener propiedades filtrantes de UF. Posteriormente, el proceso de reciclaje se optimizó con el propósito de reducir dichos tiempos de exposición empleando el concepto de dosis de exposición (ppm·h). Se combinaron diferentes concentraciones de cloro libre y tiempos de contacto de las membranas para alcanzar una dosis de exposición fija (6,200; 30,000 y 300,000 ppm·h). El impacto generado sobre las membranas se evaluó en términos de permeabilidad y coeficientes de rechazo al tratar agua salobre. Se replicaron ensayos con distintas membranas deterioradas con el fin de evaluar la

reproducibilidad de las condiciones de reciclaje elegidas. Además, los resultados se compararon con datos adquiridos en la caracterización de membranas nuevas comerciales (OI, NF y UF). Se obtuvieron membranas recicladas con propiedades filtrantes intermedias a dos de los modelos comerciales estudiados (NF90-400 y NF270-400). Por otro lado, las membranas expuestas a altas dosis de exposición obtuvieron coeficientes de rechazo similares o mayores a los de una membrana de UF comercial (10 KDa) cuando trataron agua residual urbana. El proceso de reciclaje a escala piloto requirió dosis de exposición de cloro libre análogas a las observadas a escala laboratorio.

En ambas escalas, se determinó que el ensuciamiento por precipitación de sales es el que más interfiere en el proceso de reciclaje. Sin embargo, las membranas con ensuciamiento por depósito de matrices arcillosas, materia orgánica o microbiológica, permitieron la transformación de sus propiedades filtrantes sin dificultades. La degradación de la PA de la superficie de las membranas fue además confirmada mediante espectroscopía de infrarrojo lejano por transformada de Fourier (ATR-FTIR) y microscopía electrónica de barrido (SEM). A partir de 50,000 ppm·h de exposición los espectros de ATR-FTIR obtenidos de las membranas recicladas fueron diferentes a los de las membranas de OI nuevas. En las imágenes de SEM se detectaron poros sobre las superficies de las membranas recicladas. El diámetro Feret de los poros calculado mediante el software *image J*, alcanzó valores entre 8 y 14 nm. Además a escala laboratorio el peso molecular de corte de las membranas recicladas osciló entre valores de 10,000 y 38,000 g/mol. Por último, se discute sobre el modelo de negocio de una hipotética planta de reciclaje de membranas, identificando usuarios, inversores, inconvenientes, competencia de mercado y barreras sociales.

Este estudio demuestra que el reciclaje directo a través de la metodología de inmersión pasiva puede ser una alternativa viable de gestión que impulse la tecnología de membranas de OI a una tecnología basada en el concepto de economía circular.

List of original publications

The Thesis is based on the publications cited below, where it is explained author contribution. Among the manuscript, each publication is referenced as “Paper”,

PAPER I) Scientific paper.

Landaburu-Aguirre, J., **García-Pacheco, R**., Molina, S., Rodríguez-Sáez, L., Rabadán, J., García-Calvo, E. (2016). Fouling prevention, preparing for re-use and membrane recycling. Towards circular economy in RO desalination, Desalination 393 16–30.

García-Pacheco contributed writing Table 2 of the Section 3.2.2 entitled *“Chemical cleaning”*, Section 4 entitled “*Membrane re-use and recycling”* and Section 5 entitled *“Disposal: Spain as a case study”.*

PAPER II) Book Chapter.

García-Pacheco, R., Lawler, W., Landaburu-Aguirre, J., García-Calvo, E., and Le-Clech, P. End-of-Life Membranes: Challenges and Opportunities, In Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, Elsevier, 2017.

García-Pacheco designed the structure and wrote the manuscript excepting the following parts: Energy Recovery in Main Alternatives for end-of-life Membranes Section and the Road Map for Better Management Section.

PAPER III) Scientific paper.

García-Pacheco, R., Landaburu-Aguirre, J., Molina, S., Rodríguez-Sáez, L., Teli, S. B., & García-Calvo, E. (2015). Transformation of end-of-life RO membranes into NF and UF membranes: Evaluation of membrane performance, Journal of Membrane Science 495 305–315.

García-Pacheco is the corresponding author. She designed all the experiments, conducted the assays, evaluated the results and wrote the manuscript.

PAPER IV) International Congress proceeding.

Molina, S., **García-Pacheco, R.**, Rodríguez-Sáez, L., García-Calvo, E., Campos, E., Zarzo, D., et al. Transformation of end-of-life RO membranes into recycled NF and UF membranes: surface characterization (15WC-51551). Previously published as part of The International Desalination Association (IDA) World Congress Proceedings, San Diego, California, USA 2015.

García-Pacheco designed all the experiments and carried out the membrane autopsies. In addition, she contributed writing the part of the results and discussion, mainly regarding to Fujiwara analysis, bacteria detection and enumeration and inductively coupled plasma mass spectrometry (ICP-MS). Finally, García-Pacheco was the speaker of the oral presentation at the international IDAWC'15 Congress.

PAPER V) Scientific paper.

García-Pacheco, R., Landaburu-Aguirre, J., Rodríguez-Sáez, L., Molina, S., García-Calvo, E. Effect of ppm·h sodium hypochlorite exposure dose in the transformation of end-of-life RO membranes into NF and UF membranes. Manuscript is ready to be submitted.

García-Pacheco designed the experiment managed the results and wrote the manuscript. She will be the corresponding author.

PAPER VI) International Congress proceeding.

García-Pacheco, R., Rabadán, F. J., Terrero, P., Molina, S., Martínez, D., Campos, E., et al.. Life+13 Transfomem: a recycling example within the desalination world. In Proceeding XI AEDYR International Congress (pp. VAL–112–16), Valencia, 19-21 October 2016.

García-Pacheco contribution was the experimental design, the evaluation of the results and writing the abstract. In addition she was the speaker of the oral presentation.

PAPER VII) Patent.

Proceso de transformación de membranas de poliamida con enrollamiento en espiral que han agotado su vida útil en membranas de utilidad industrial. In English: Transformation of spiral wound polyamide membranes after its industrial lifespan. Spanish Patent P201630931, 08 July 2016.

García-Pacheco is one of the patent inventors. Her contribution was the experimental design of end-of-life membrane recycling at pilot scale, monitoring and evaluating results and she was the main responsible author writing the document.

All publications have been developed within the framework of the European Project Life+13 Transfomem (June 2014-June 2018), in which the author actively participated in the design and writing process of the project proposal. Furthermore, she is the technical responsible of the project, which is focused on recycling end-of-life RO membranes at pilot scale by using passive immersion methodology (similar to investigated at laboratory scale) and active methodology. Active methodology investigated in the Life+13 Transfomem project is out of the scope of this Thesis.

Contents

List of Figures

List of Tables

Symbols

C_p: solute concentration value in the permeate stream (ppm)

C_f: solute concentration value in the feed stream (ppm)

L: membrane permeability ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)

Log_{10}: decimal logarithm

N: number of experimental replicates

Q: permeate flow ($L \cdot h^{-1}$)

R: rejection coefficient (%)

S: membrane active area (m^2)

t: time needed for collecting the permeate (h)

T: temperature in Celsius grades (ºC)

W: weight of permeate sample (g)

ρ: solution density (g/L)

Abbreviations

ABS: acrylonitrile butadiene styrene

ATR-FTIR: attenuated total reflection-Fourier transform infrared spectroscopy

BSA: bovine serum albumin

BW: brackish water

BWRO: brackish water reverse osmosis

CA: cellulose acetate

CFU: colony formed unit

E. coli: Escherichia coli

EC: electrical conductivity

ED: electrodialysis

IC: Ion chromatography

ICP-MS: inductively coupled plasma mass spectrometry

LCA: life cycle assessment

LRV: log removal value

ND: not detected

NF: nanofiltration

NMP: n-methyl-2-pyrrolidone

N/A: not available

MED: multi-effect distillation

MF: microfiltration

MPD: m-phenylenediamine

MSF: multi-stage flash evaporation

MWCO: molecular weight cut off

PA: polyamide

PBS: phosphate buffered saline solution

PEO: poly(ethylene oxide)

PES: polyethersulfone

PET: polyester

PP: polypropylene

PSF: polysulfone

RO: reverse osmosis

SEC: size exclusion chromatography

SEM: scanning electron microscopy

SUWW: synthetic urban wastewater

SW: seawater

SWRO: seawater reverse osmosis

TC: total carbon

TFC: thin film composite

TGA: thermo gravimetric analysis

TMC: trimesoyl chloride

TMP: transmembrane pressure

TOC: total organic carbon

UF: ultrafiltration

WW: wastewater

Chapter 1: Introduction

1. Justification

This Chapter is based on Paper I and Paper II. It is introduced the motivation of the present investigation. The research framework was based on an environmental concern relaying with searching alternative to end-of-life reverse (RO) membrane landfill disposal. In addition, in this Section it is detailed the main objectives of this research and it is described the scientific activities that have been contributed to this Thesis as a compendium of publications.

1.1. End-of-life RO membranes: a waste management challenge

Access to clean water resource continues to be one of the most urgent and pressing global issue [1]. All economic sectors need water for their activities. In fact, 69% of the world's freshwater withdrawals are committed to agriculture. The industrial sector accounts for 19% while only 12% of water withdrawals are destined for households and municipal use [2]. Therefore by coupling water demand and water scarcity it is estimated that 50% of the world's population will be living in water-stressed regions by 2025 [3]. In this context, diverse type of fresh water sources such as local and imported surface water, groundwater, desalinated brackish water (BW), desalinated seawater (SW) and recycled water will be most necessary [4].

There are a number of different technologies available for desalination including: Multi-stage Flash evaporation (MSF), multi-effect distillation (MED), vapour compression distillation, RO, nanofiltration (NF), and electrodialysis (ED) [5]. Among these technologies, pressure-driven membranes (RO and NF) are playing an important role to manage water in integral cycles, mainly due to their modularity and the high quality of the treated water [1]. At international level, the installed desalination capacity in 2015 was 86.5 Hm^3/day. About the 65% of this total capacity corresponded to RO membrane processes [5].

Desalination of SW and BW by RO is largely applied and established in the industry for freshwater generation. Aromatic polyamide-based (PA) composite membranes currently account for over 95% of existing RO desalination plants [6]. During XX century, large desalination plants were typically designed to supply between 5% and 10% of the drinking water for coastal cities. More recently, regional or national SW desalination projects in countries such as Spain, Australia, Israel, Algeria and Singapore have been designed to increase these coefficients till 20 to 50% [7]. Indeed, by 2019 the market for RO system components is projected to reach \$8.8 billion, with a compound annual growth rate of 10.5% [8].

The major cost in desalination is related to energy, which can represent between 30% and 50% of the operating cost [9]. Therefore, large amount of investigation have been focused on this topic. As a result, the amount of power needed to drive desalination in SWRO plants has declined dramatically in the past decades, approaching the theoretical minimum energy (1.06 kWh/m^3 [10]). However, the overall energy consumption is still three to four times higher than the theoretical value [10]. The RO process itself, consumes between 2.2 and 2.8 kWh/m^3, depending on the type of energy recovery device used [9]. This decrease in energy consumption is attributed to a continuous technological improvement such us the use of higher-permeability membranes, installation of energy recovery devices, the use of more efficient pumps, pretreatment and post-treatment improvements and operation during off-peak periods [11,12].

Additionally, the rapid expansion of desalination capacity has required further attention on its environmental impacts. Research on specific effects of desalination plants include the impact and interference of organisms (due to the intake of large quantities of SW) and the emission of air pollutants (due to a considerable energy demand of the processes) [13]. The potential consequences of brine effluents discharge, which contains generally high salinity, high temperature, and dissolved chemicals is also under study [14,15].

Moreover, another important research line, which is in continuous study is the membrane fouling. Even though membrane physical damage and compression have a big impact on the membrane, fouling is one of the main reasons for the reduction of the membrane lifespan, causing membranes to become waste. The major types of fouling in RO membranes are: i) scaling (inorganic salt precipitates on the membrane surface [16,17] ii) organic fouling (deposition organic compounds such as proteins and humic substances) [18,19] iii) colloidal fouling (deposition of colloids such as clay, silt, particulate humic substances) [20–22] and iv) biofouling (adhesion and accumulation of microorganisms and biofilm formation) [23].

Considering the adverse impacts of membrane fouling, approaches for its mitigation have promoted great research efforts [1]. In fact, numerous academic and industrial works have focused on extending the usable time of RO membranes by developing improved manufacturing materials [24] and operating/cleaning practices [25]. Cleaning cycles are conducted when transmembrane pressure (TMP), permeate flow and/or permeate quality vary between 10% and 15% with respect to the initial values [26]. However despite many prevention strategies applied, fouling remains inevitable [27].

Membranes are generally replaced once their performance (permeability and rejection coefficients) declines significantly and beyond recovery. However in other cases, membranes are simply replaced because they reach the useful lifespan advised by the manufacturers or because the financing for membrane replacement is approved. Therefore with an expected life time of 5 to 8 years, the RO membranes used in desalination have to be considered as a frequently consumable, and as a consequence, a quite unique solid waste stream [9]. Annual replacement, together with the continuous growth of RO technology, is creating a non-stop accumulation of end-of-life modules. In desalination, the annual membrane replacement coefficient is around 5%–20% of the installed membranes [28,29]. However these coefficients vary depending on the nature of the feed water (e.g. SW, BW or wastewater (WW)) [29]. Table 1 shows the rarely reported costs related to membrane replacements.

Table 1. Membrane replacement costs for SW and BW desalination plants (Paper II © Elsevier).

Water source	**Total cost produced water**	**Membrane replacement cost**	**Replacement cost (%)**	**Reference**
SW	0.525 ($\$/m^3$)	0.028 ($\$/m^3$)	5.3	[30]
BW	0.248 (€/m^3)	0.020 (€/m^3)	8.1	[31]
BW	-	0.008-0.050 ($\$/m^3$)	-	[28] and references in.

Usually, it is considered that an average of 100 RO modules (8" diameter) are needed to produce 1,000 m^3/d of product water [32]. By fixing the annual replacement coefficient and supposing that end-of-life RO membranes average weight is 17 kg (from Paper I), it is possible to estimate the number of discharged RO modules and tons of waste. As an example, Table 2 shows the capacity of membranes installed in Spain and the estimation of end-of-life membranes discharged annually (>81,000 membranes, equivalent to >1,000 tonnes). Considering the installed capacity at worldwide scale and 15% replacement coefficient rate, >840,000 end-of-life membranes (equivalent to >14,000 tonnes) are potentially discarded every year.

Table 2. Spanish desalination capacity (according to AEDYR database) and estimated number of end-of-life RO membranes (Adapted from Paper I © Elsevier)).

Spanish desalination plants: water type, facility numbers		**Installed capacity (m^3/d)**	**Replacement rate (%)** [28,29]	**End-of-life membrane modules per year**	
SW	289	3,826,549	15	57,398	>81,000 total modules or >1,000 tonnes of plastic material
BW	349	1,064,485	10	10,645	
WW	26	208,670	33	6,886	
Other fluids	23	197,457	25	4,936	
Unknown	24	103,953	15	1,559	

Industrial processes relying on membrane technology follow the current linear economy. Generally, end-of-life membranes are handled according to the laws of each country and old membranes usually end up in landfills [32]. Landfill disposing can be viewed as wasteful, environmentally damaging and a costly waste management option. Furthermore, this practice goes against the EU goals to move towards a circular economy system and to achieve a cross continental recycling society. To accomplish an alternative management, changes in domestic practices are needed along with sustained industrial efforts, and legislation and social awareness to accept recycling products. Nowadays, water treatment plant managers are the responsible people deciding the fate of their end-of-life membranes. The lack of alternatives and the still convenient price of membrane disposal drive this common practice. Table 3 shows disposing cost depending on the membrane waste classification (dangerous or not dangerous) and transportation cost. Even though disposing cost does not seem to be expensive, both economic and environmental impacts should also be taken into account by conducting a sustainability assessment.

Table 3. Membrane waste classification according to the European List of Waste [33] and estimated cost of membrane disposal and transport (Paper II © Elsevier).

	Membrane type	**Codes of European list of waste**	**Cost**
Disposal	Non-dangerous material	150203 Filters with non-dangerous materials	45€/tonnes
	Dangerous materials	150203* Filter other than those mentioned in 15 02 02 190808* Membranes containing heavy metals	425€/tonnes
Transport	30 m^3 container costs about 100-150€ within the provinces areas*. Volume of a membrane module (0.314 m^3)		1-1.6 €/module

* Case of Spain with 50 provinces, with an average extension around 10,200 km^2 per area [34].

Membrane market tendency, particularly of RO membranes, together with the improvable management of the end-of-life modules have raised the interest towards more environmental friendly alternative management routs. Among several alternatives, which are summarized in Section 2.2.3, direct recycling process of end-of-life RO membranes into NF and ultrafiltration (UF) recycled membranes is raising interest within the research and development community. In this sense, this Thesis has investigated how to create NF and UF membranes from end-of-life RO modules, aiming to reach adequate performance for further reuse. Thus, the recycled membrane could be introduced again in industrial processes such us i) the pretreatment of RO membranes within desalination processes, ii) BW treatment and iii) Urban and industrial WW treatment. This would be not only attractive for saving industrial cost but also for boosting pressure-driven membrane technology towards a circular economy approach.

1.2. Objectives

The general aim of this Thesis is to investigate the direct recycling process as an alternative to the current waste management (landfill disposal) and to provide an overview of the current membrane waste challenge in desalination.

The specific objectives can be summarized as follows,

i) To examine the feasibility of recycling end-of-life RO membranes into NF and UF membranes by a controlled exposure to free chlorine.

ii) To determine the recycling conditions defining the borderline between RO, NF and UF recycled membrane performance.

iii) To investigate the effect of the combination of diverse free chlorine solution concentrations and exposure times used to achieve NF and UF recycled membrane performance.

iv) To scale up the recycling process.

v) To compare the recycled membrane performance to commercial membrane performance.

vi) To determine which type of fouling is critical for the recycling process.

1.3. Chapters description and scope

This Thesis is structured in 6 Chapters and one Appendix:

Chapter 1. Justification serves a general introduction and presents the objectives and scope of the Thesis.

Chapter 2. Literature Review introduces challenges and opportunities of end-of-life membrane management and gives an approach of RO membrane technology towards circular economy.

Chapter 3. **Material and Methods** shows the methodology employed during this investigation for: fouling detection, identification of membrane performance changes and membrane surface characterization.

Chapter 4. Results summarizes the main results obtained.

Chapter 5. Conclusions, Future Work and Research Directions shows the main outcomes and proposes activities within the recycling research line.

Chapter 6. References cites all the literature employed during the manuscript.

Appendix provides supplementary SEM micrographs and quantitative results relaying on the Chapter 4 and includes all publications that support this Thesis.

The Thesis consists of 2 peer-reviewed journal articles, one manuscript to be submitted to a scientific journal, 2 International Congress Proceedings, 1 patent and 1 book chapter (see list of original publications at page 15). Their scope and contribution to the Thesis are summarized in Fig. 1.

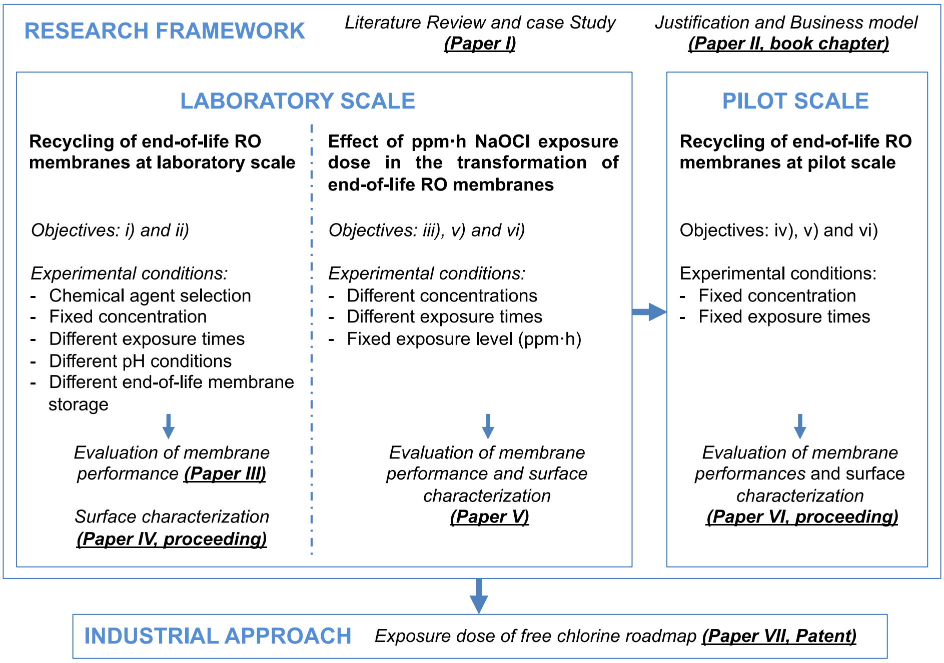


Fig. 1. Interconnection between the scientific contributions published relying on the present Thesis.

Paper I (review) and the Paper II (book chapter) describe the general framework of the Thesis. In one hand, Paper I is focused on the circular economy approach to be followed in the RO desalination process, covering the whole life cycle of RO membranes. Therefore, it summarizes the new development of antifouling membranes, the optimized membrane use and some of the membrane waste management routes such as membrane reuse and recycling. On other hand, the book chapter (Paper II) deals with challenges and opportunities of end-of-life membranes. It analyzes more deeply than Paper I the waste management alternatives, summarizing the most representative management routes of discarded end-of-life-membranes investigated to the date: landfill disposal, re-use, direct recycling, indirect recycling and energy recovery. A decision-making tool and a business model of a hypothetical recycling membrane plan are also provided in Paper II.

The experimental work and results have been reported from Paper III to VII. Laboratory scale results correspond to Papers III, IV and V. Paper III deals with the selection of an appropriate chemical agent to achieve the optimal changes in end-of-life RO membrane performance. NaClO was selected as the most effective oxidizing agent and its concentration was fixed. Two variables of the transformation condition were studied: solution pH, and exposure time. The main aim was to find out the exposure dose (ppm·h) required to convert end-of-life RO membranes into NF and UF membranes. The evaluation of the membrane process performance was conducted by using synthetic BW.

In a parallel investigation, which results are reported in Paper IV, it was identified membrane fouling and it was characterized the surface properties of the recycled membranes in terms of i) PA degradation and ii) molecular weight cut off (MWCO).

In Paper V, more realistic exposure times were further investigated. The scope was to research the effect of the combination of diverse free chlorine solution concentrations and exposure times at fixed exposure doses (ppm·h). In addition, synthetic urban wastewater (SUWW) solution was used for evaluating the recycled membrane performance. Commercial pristine RO, NF and UF membranes process performance was also evaluated and compared with recycled membrane performance.

Paper VI and VII deal with recycling end-of-life RO membranes at pilot scale, maintaining their original spiral-wound structure. The main objective of these investigations was to scale up the methodology developed at laboratory scale and to systematize the protocols of actions. Membrane fouling identification is shown in Paper VI. Finally, compilation of all results obtained at both scales made possible to patent a decision-making roadmap (Paper VII). It summarizes the requirement of free chlorine exposure dose depending on i) the initial end-of-life RO membrane performance, which is related to membrane fouling and ii) the type of membrane (SW vs BW membrane designed). A detailed description of the recycling pilot plant is also shown at Paper VII.

Chapter 2: Literature Review

2. Literature Review

The literature review shows basic concept of pressure driven membranes and the most relevant advances to prolong the membrane or membrane components lifespan. This Section provides information related to development of antifouling membranes, membrane use optimization and alternative actions to end-of-life membrane disposal in landfill. This Chapter is based on Paper I and Paper II.

2.1. Pressure driven membranes

Membrane filtration requires a semi-permeable membrane to separate compounds according to their physical and chemical properties. The membrane performance is determined by two parameters: i) its selectivity, which is often calculated by the rejection coefficients and ii) the permeation rate, defined as the volume flowing through the membrane per unit area and time. [35]. In pressure driven membrane processes, a differential pressure is required in order to obtain the desired separation. Moreover, the type of process is usually classified according to the membrane pore size, filtration mechanism, and size of particles removed. According to these parameters membranes can be classified as microfiltration (MF), UF, NF and RO (Table 4).

Table 4. Pressure driven membrane classification (Adapted from [35,36]).

Membrane	**RO**	**NF**	**UF**	**MF**
Pore size (μm)	<0.001	0.001-0.01	0.01-0.1	0.1-10
Permeability ratio ($l/h \cdot m^{2} \cdot bar$)*	0.05 – 1.4	1.4 -12	10 - 50	> 50
Pressure range (bar)	10-100	5-20	1-5	<2
Rejection (%)	Low molecular compounds (amino acid) and monovalent ions	150-2000 Da (MWCO) for neutral compounds Divalent ions	0.3-500 KDa organic compounds, colloidal and viruses	Bacteria and Suspended particles

*Depending on experimental conditions and scale of the characterization test.

Commercially available modules include spiral wound, hollow fibre, tubular and plate-and-frame modules. Industrially, amongst these configurations, spiral wound modules is often favored because they offer a good balance between fouling control, permeation rate, packing density and its ease operation [37]. Spiral-wound modules consist in two membrane sheets with the active layer facing out and containing the permeate spacer in the back layer. Between the membrane sheets feed channel spacers are placed. They provide turbulence and create space between the membrane sheets for the feed water to flow [37]. Moreover, the sheets are roll around a central tube (permeate tube). The feed water is forced to the feed spacer channel and the permeate (high quality water) flows in a spiral direction being collected in the central permeate tube [35]. Fig. 2 shows one example of an RO spiral wound.

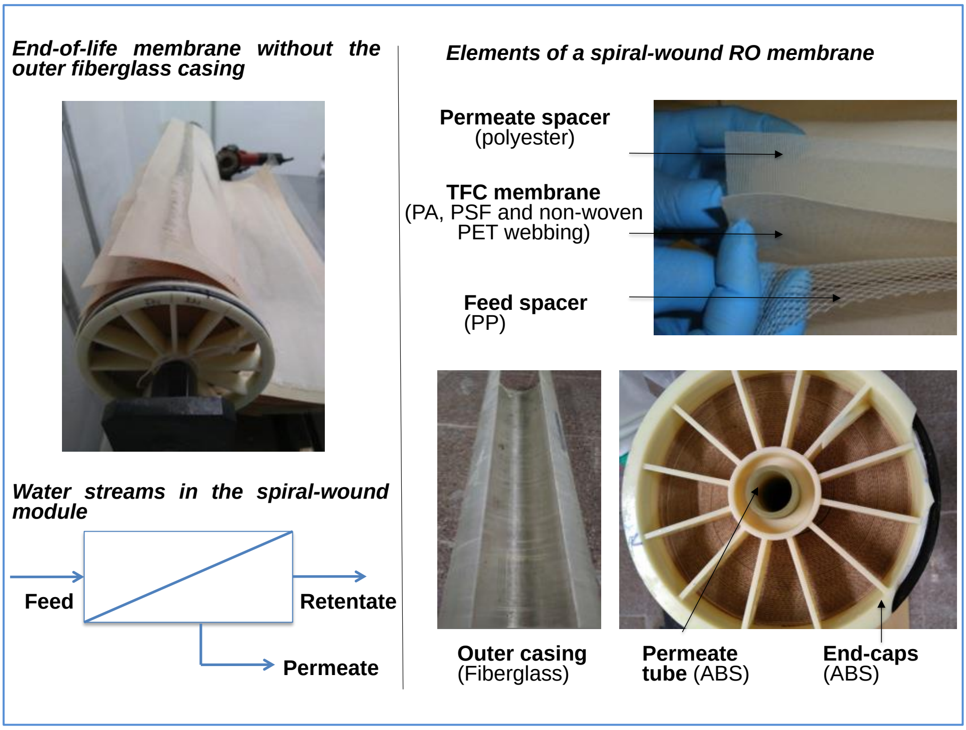


Fig. 2. Elements of a spiral-wound RO membrane module.

Membrane performance is mainly affected by i) concentration polarization, which is caused by the increased concentration of some compounds at the membrane surface due to the selective transfer and ii) membrane fouling, which is strongly related to factors such as quality of the water, level of pretreatment, membrane properties (roughness, hydrophilic character, surface charge) and operating conditions [35,38].

2.1.1. Reverse osmosis membranes

In RO separation process water and salt transport mechanism across the membranes is governed by a solution-diffusion mechanism, where species first partition into the PA layer and then diffuse down by a concentration gradient [39]. An applied pressure greater than the osmotic pressure of the feed solution is required to drive the process and water starts flowing from concentrated salt solution to dilute solution through the membrane [40]. The performance of RO desalination membranes is highly dependent on the composition of the membrane, which determines the main properties such as salt rejection, fouling propensity and water permeability [1]. The first commercially viable RO membrane was an asymmetric cellulose acetate (CA) membrane developed in the early 1960 [41]. However, the development of Thin Film Composite (TFC) membranes revolutionized the RO membrane market due to the higher water permeability achieved whilst maintaining the selectivity of RO membranes [10].

TFC membranes (Fig. 3) generally consists of a cross linked fully aromatic dense PA active layer (0.2 µm), a microporous polysulfone (PSF) supporting layer (40 µm), and a considerably thicker (120-150 µm) non-woven polyester (PET) base [42]. Moreover, the PA TFC membranes are generally manufactured by interfacial polymerisation. In interfacial polymerization two monomers react in a two-phase system, where polymerization takes place in the interface between the aqueous and organic phases. The most commonly used polymer for the water phase is m-phenylenediamine (MPD), whilst trimesoyl chloride (TMC) dissolved in hexane is commonly used as the organic phase [43].

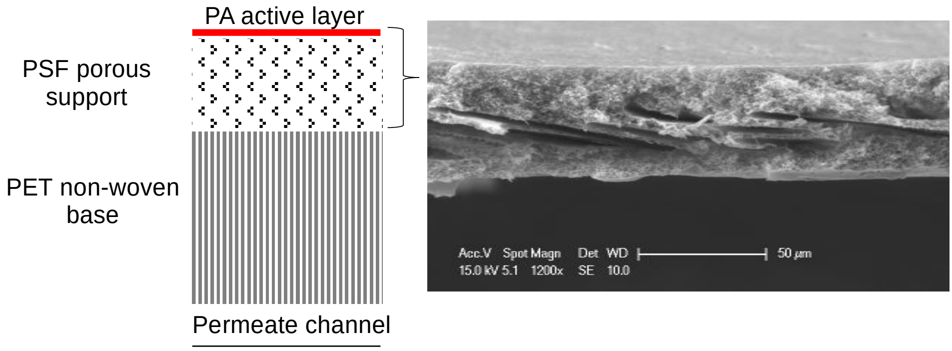


Fig. 3. Schematic drawing of a TFC membranes and micrograph cross section of the TFC of an end-of-life BWRO membrane (TM720-400) (Adapted from [35]).

The current RO membranes can achieve an average of 99.6% NaCl rejection coefficient (data estimated from 89 RO membranes datasheets of Toray, Hydranautics, Dow Filmtec and Koch). Therefore, they are widely implemented by the desalination industry. However, the hydrophobic aromatic groups and the still limited water flux due to the PA high cross-linking degree exhibits weakness that could be further solved in the near future by using new emerging materials (see Section 2.2.1.).

2.1.2. Nanofiltration membranes

NF membranes were recognized in the late 80's as “a process intermediate between RO and UF that rejects molecules which have a size in the order of one nanometer” [44]. However, they are also catalogued as typical non-porous membranes (as RO membranes) [45]. NF membranes show low rejection coefficients of monovalent ions, high rejection coefficients of divalent ions and higher permeate flux than RO membranes [35]. Mohammad et al. [46] summarized the characteristic of commercial NF membranes showing the manufactures specifications. Contrary to RO membranes, NF membranes show a wide spectrum of rejection coefficients ([10-95]% NaCl and [50-99]% $MgSO_4$, [100-800] Da of neutral organic compounds). Generally at industrial level, it is widely used NF membranes with TFC PA membranes in spiral-wound configuration such as NF90 and NF270 (Dow Filmtec) and ESNA membrane series (Hydranautics) [47].

There is a great market size of application for NF membranes. Some examples summarized by Van der Bruggen et al. [48] include drinking water production (softening), partial desalination, WW treatment and water reuse, arsenic removal, removal of endocrine disruptors and other chemicals (processing industry and pharmaceutical) and food industry.

2.1.3. Ultrafiltration and microfiltration membranes

UF membranes were originally developed in the late 1960s [49]. Since then, this technology has been continuously developed being applied in different fields such as chemical compounds recovery, water treatment, WW reclamation, juice concentration, dairy industry or medical usage [47]. In UF membrane processes, the separation occurs by size exclusion, retaining compounds that are bigger than the membrane pore size [50]. UF membranes can typically reject organic compounds with molecular weight ranged between 0.3 and 500 KDa [51] and are also effective rejecting bacteria, viruses and colloidal particles [52]. Even though they were developed at the time of RO membranes, UF membranes market is much more heterogeneous than RO membranes market. In this sense, diverse type of UF membranes can be found in the market based on different materials (ceramic, polymeric, metallic, etc.) and configurations (hollow fibre, flat-sheet, tubular, spiral-wound, etc.).

MF membranes are also low pressure filtration membrane used to remove suspended particles, bacteria and some viruses. The membrane geometry most commonly used is hollow fine polymeric fibre [53].

2.2. Towards membrane circular economy

The current economy is based on a linear model, which assumes that resources are abundant and with the pattern of “take-make-consume and dispose”. Industrial processes that use membrane technology are not an exception of the current economy model and membranes tend to be discarded when the flow rate and or water quality is unrecoverable.

In desalination, the continuous growth of the installed capacity per year, the membrane replacement rate and the current management have created a challenging scenario where thousands of tonnes of membranes are discarded into landfills. However end-of-life RO membranes have further potential uses that could drive the desalination industry towards a more circular economy approach. The main objective of the circular economy is to keep the value of the materials and energy used in products for as long as possible, minimizing waste and the use of resources [54]. For this purpose, actions must be taken at all stages of the life cycle of the product, from the extraction of the raw materials, through material and product design until the waste management.

In membrane processes, developments are continuously being achieved to keep the membranes as long as possible within the value chain of their processes. Some example of these actions are i) manufacturing novel membrane materials that show enhanced process performance ii) applying more efficient integrated pretreatment and cleaning processes and iii) developing innovative membrane recycling. All these actions make the membrane industry to move towards a more circular economy (Fig.4).

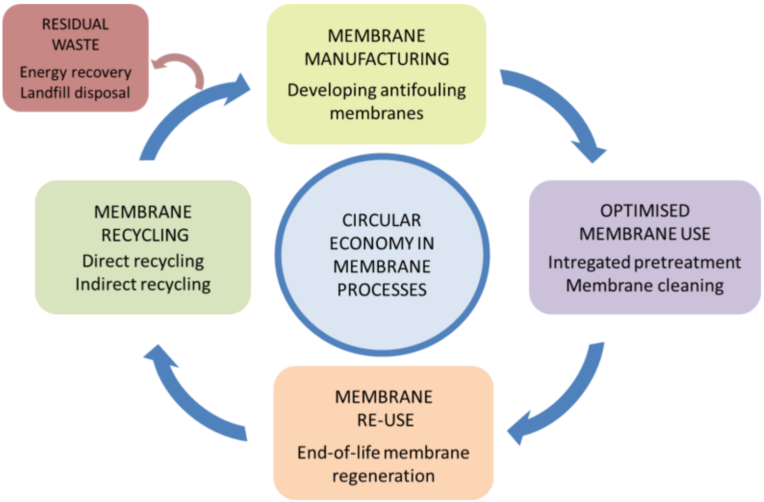


Fig. 4. Towards a circular economy in membranes used in desalination (Paper I © Elsevier).

2.2.1. Membrane manufacturing: developing antifouling membranes

The principal aim of the antifouling membranes is to enhance surface hydrophilicity as well as to reduce surface roughness, in order to lower the energy usage, enhance process reliability and minimize the environmental impact of membrane technology [55]. There are two routes that have gained interest for preparing antifouling membranes: i) preparation of tailor made new generation antifouling membranes and ii) surface modification of membranes.

In the first case, interfacial polymerization is still the dominant method to prepare the ultrathin barrier of the TFC membranes [56]. Some research are based on adding polyfunctional amine monomers [57] and new monomers that contain more functional polar groups [58,59]. Interfacial polymerization let also the incorporation of nanoscale inorganic particles as additive in the membrane polymer matrix [60,61] such as TiO_2, Zeolite, SiO_2 and silver. In addition, it has been also included carbon nanotubes (CNTs) grapheme-based nanomaterial [62–64] and aquaporin-based protein vesicles [65]. In fact membrane manufacturer NanoH_2O has launched to the market QuantumFlux thin-film nano-composite (TFN) membranes with 50–100% increase in permeability compared with traditional thin-film RO membranes [66].

In the second case, surface modification can be conducted by chemical (covalent attachment of polymer brushes by surface graft polymerization) and physical process. The latter is the most used and can be categorized by i) physical adsorption of compounds (such as surfactants [67] and charged polyelectrolytes [68], which enhances the electrostatic repulsion of cationic foulants) and ii) surface coating, using hydrophilic polymers that contain hydroxyl groups [69] and ethylene groups [70]. These polymers acts as a protective layer to reduce or eliminate the adsorption and deposition of foulants onto membrane surface [71].

2.2.2. Optimized membrane use

The optimization of membrane processes is an indispensable step to keep the membrane performance. In fact, water quality conditions, the type of pretreatment and the membrane cleaning protocols will determine the overall membrane process performance.

- ***Pretreatment***

Pretreatment is an indispensable and critical part of the desalination process and its design determines the costs of maintenance and operation of the plants. Pretreatment can be divided into two groups: i) conventional pretreatment or physicochemical and ii) unconventional pretreatment.

Some of the most used conventional pretreatment are: pre-chlorination [72], ozonation [73], dissolve air flotation [74], coagulation-flocculation, addition of antiscalants and sand filtration [31]. Generally, they require high space and elevated chemical additive doses such as chlorine and sodium bisulfite (pre-chlorination), aluminum or ferric salts (coagulation-flocculation process) or polyacrylates, organophosphonates or sodium hexametaphosphate (antiscalants). It is important to note that some of the aforementioned pretreatment are currently in the spotlight due to the negative effects that can provoke. For example, pre-chlorination can promote the formation of trialomethanes [75], the promotion of colloidal fouling [76] and the PA aging. Moreover it is not well demonstrated its efficiency against biofouling [77]. Consequently, the use of non-conventional pretreatment processes has gained interest in the past years.

Alternative techniques such as MF, UF and NF have emerged as RO pretreatment technologies. In addition, membrane pretreatments have significant benefits versus conventional pretreatments such us significant higher RO flux, lower space and decrease the RO elements replacement [78–81]. This technology is included in some large desalination plants installed in the last decades. The Umm-Lujj SWRO plant uses NF membranes prior to the RO process [82]. Indeed, different membrane models in the same pressure vessel begin to be used to improve operation and maintenance cost [83]. In addition, there are already desalination plants using UF membranes as pretreatment prior to the RO process. Some examples are the Mantoverde plant in Chile with a water production capacity of 12,000 m^3/day, Perth II plant in Australia with a capacity of 306,000 m^3/day and Ashdod plant in Israel producing 384,000 m^3/day of fresh water. This last example is the biggest plant in the world having UF membranes as pretreatment method.

- ***<u>Membrane cleaning</u>***

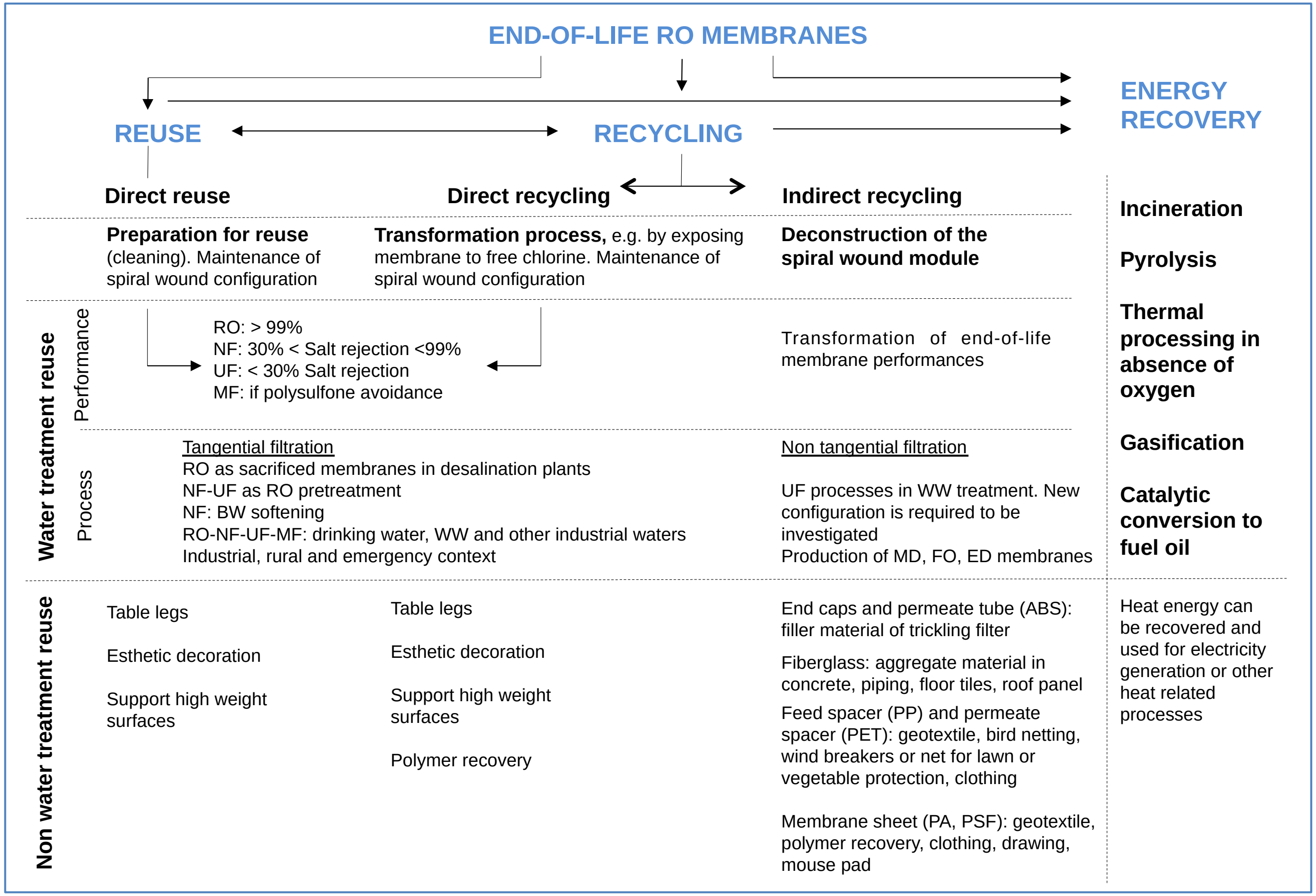
Despite the research and industrial efforts to develop new antifouling membranes and to optimize the pretreatment processes, membrane fouling is a phenomenon that will always occur at some extend. Therefore, membrane cleaning becomes a crucial step within the membrane processes. Cleaning cycles are recommended to be conducted when TMP pressure, permeate flow and/or permeate quality vary between 10-15 % respect to the initial values [26]. Membrane cleaning process can be i) physical, ii) chemical or iii) a combination of both (physio-chemical).

Physical cleaning depends upon mechanical forces to displace and remove foulants from the membrane surface [84]. Conventional physical cleaning methods used for RO membranes are i) forward flushing (permeate water is pumped through the feed side), ii) reverse flushing (permeate water is pumped from the retentate to the feed side) and iii) backwashing (permeate is flushed from the permeate side to the feed side) [25]. In RO membranes backwashing is conducted by direct osmosis, however it has not commonly been used because it would require a high back-hydraulic pressure that might damage the membrane [25].

Nevertheless in RO desalination, chemical cleaning is the most applied method [25]. Chemical cleaning methods depend on the chemical reactions that weaken the cohesion forces between the foulants and the adhesion forces between the foulants and the membrane surface [84]. The cleaning agents used must be able to dissolve the majority of the fouling materials and remove them from the membrane layer without causing surface damage [85]. In addition, the cleaning agents should be low-cost, safe and show chemical stability and the ability to be removed with water. Generally there are six common categories of chemical cleaning agents: alkalis, acids, metal chelating agents, surfactants, oxidizing agents and enzymes. Table 2 of Paper I (see Appendix) summarizes the main chemical agents (basic compounds and commercial products) that are used depending on the type of fouling observed in RO membranes in desalination. Besides choosing the correct chemical agent it is also important to apply a correct cleaning procedure such as temperature, chemical concentration, pH and time [84,86]. Indeed, in the cleaning method the cross flow velocity should be higher than the one used in the normal operation [25]. Moreover, zero TMP is recommended to achieve maximum foulant removal [87].

2.2.3. End-of-life RO membrane management

Membrane lifespan can be prolonged in industry by capital investment on fouling prevention processes. However, fouling is inevitable and once the membranes do not fulfill the objectives set at the industrial process they are considered as a waste, ending up mostly in landfills. According to the main pyramidal waste management principles of the European Directive 2008/98/EC on waste, preferred options are: material prevention, re-use, recycling, recovery and disposal [88]. The constant disposal of end-of-life membranes in landfills and the consequent environmental impact has raised interest on looking for other alternative management routes. Fig. 5 shows a roadmap of the various options currently considered. Although direct re-use of old membranes without any additional treatment is obviously preferred, appropriate assessment of their current performance, further validation and potential chemical cleaning protocols will be crucial in order to identify the optimal alternative routes [32].



END-OF-LIFE RO MEMBRANES

REUSE ⟷ RECYCLING

		Direct reuse	Direct recycling	Indirect recycling	ENERGY RECOVERY
		Preparation for reuse (cleaning). Maintenance of spiral wound configuration	**Transformation process,** e.g. by exposing membrane to free chlorine. Maintenance of spiral wound configuration	**Deconstruction of the spiral wound module**	**Incineration** **Pyrolysis** **Thermal processing in absence of oxygen** **Gasification** **Catalytic conversion to fuel oil**
Water treatment reuse	Performance	RO: > 99% NF: 30% < Salt rejection <99% UF: < 30% Salt rejection MF: if polysulfone avoidance		Transformation of end-of-life membrane performances	
	Process	Tangential filtration RO as sacrificed membranes in desalination plants NF-UF as RO pretreatment NF: BW softening RO-NF-UF-MF: drinking water, WW and other industrial waters Industrial, rural and emergency context		Non tangential filtration UF processes in WW treatment. New configuration is required to be investigated Production of MD, FO, ED membranes	
Non water treatment reuse		Table legs Esthetic decoration Support high weight surfaces	Table legs Esthetic decoration Support high weight surfaces Polymer recovery	End caps and permeate tube (ABS): filler material of trickling filter Fiberglass: aggregate material in concrete, piping, floor tiles, roof panel Feed spacer (PP) and permeate spacer (PET): geotextile, bird netting, wind breakers or net for lawn or vegetable protection, clothing Membrane sheet (PA, PSF): geotextile, polymer recovery, clothing, drawing, mouse pad	Heat energy can be recovered and used for electricity generation or other heat related processes

Fig. 5. Scheme of some alternative options for end-of-life membranes (Adapted from Paper II © Elsevier).

One of the primary considerations when selecting an end-of-life option for exhausted membrane modules is its relative environmental impact. Life cycle assessment (LCA) can be used to quantity the impact of different manufacturing processes, and disposal options. LCA is a systematic tool that considers a wide range of inputs including, the burden of raw material extraction and processing, energy consumption and transportation. Recently Lawler et al. [89] conducted a LCA of several end-of-life membrane disposal options (landfill, incineration, gasification, energy recovery, direct reuse and recycling) to quantify and compare their environmental impact. The results of this study showed that direct reuse is the most environmentally favorable option, whilst the current landfill disposal is the least favorable one. To bring this information together and to help selecting the optimum end-of-life options, a decision making tool has been created by the same team of researchers at UNSW Australia (the University of New South Wales) in collaboration with the National Centre of Excellence in Desalination Australia (NCEDA) [90]. This membrane end-of life (MemEOL) tool, which can be found online [91], aims promoting better practices in the desalination industry by helping users identify and select the optimum end-of-life option for their used RO membranes. This dynamic and interactive educational tool is based on a discrete multi-criteria decision analysis system, which is a powerful method for modeling and solving problems with multiple inputs [92]. It uses inputs on membrane condition and the relative importance of a number of key criteria to provide recommendation and further information about available end-of-life options.

- ***Reuse***

In waste hierarchy, ‘re-use’ includes “checking, cleaning or repairing recovery operations, by which products or components of products that have become waste are prepared so that they can be re-used without any other pre-processing” [88]. According to some studies, end-of-life RO membranes present similar performance to NF membranes [93]. Based on desalination plant experiences (Sadyt and Valoriza Agua Cos.), aged membranes are often re-used internally as “sacrificed” elements (placing them to the first or last position), in order to support the major fouling effect. Recently, Aqualia Co. has leaded the investigation in mechanical and chemical treatments to clean end-of-life RO membranes, at pilot scale during the Life-Remembrane project [29]. The main objective of the project was to recover RO membrane performance for further re-use by employing cleaning procedures without damaging the PA layer. In this way, membranes were studied to be re-used in the same desalination process where they came from or in other applications that need lower water quality such as urban tertiary WW treatment. In both cases, the industrial facilities were managed by Aqualia Co, demonstrating an example of centralize management of end-of-life membranes. Following this trend, the European project Life-Releach was initiated in 2014, aiming to re-use regenerated RO membrane in the treatment of landfill leachates.

Moreover to date WaterSurplus, a US-based company, appears to be the only commercial supplier of second-hand RO, NF and UF membrane elements. Watersurplus purchases, cleans and tests, repackages and repurposes these elements at significant cost savings to the user. The unit cost ranges from USD 150 to 400, with batches of up to 400 elements available to be purchased (WaterSurplus in [32]). By 2016, the company had acquired and re-used over 25,000 surplus RO membrane elements that can be used in diverse applications such mining, agriculture, industrial water re-use and chemical manufacturing [94].

Besides all of these examples and the growing interest for end-of-life RO membrane re-use, this option is not always possible due to the high membrane fouling or physical damage caused by abrasion of suspended particles. In these cases, membrane recycling becomes another potential strategy.

- ***Recycling***

According to the European Union Waste Framework Directive (2008), ‘recycling’ relates to “any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It includes the reprocessing of organic material, but does not include energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations” [88]. Under the framework of membrane technology, this category can be divided into two recycling types: direct recycling and indirect recycling, depending if recycled membranes conserve its original module structure or not.

Direct recycling

In the present context, direct recycling refers to “the conversion of the end-of-life RO membranes through partial or complete degradation of the dense PA layer”. The relative vulnerability of the PA layer towards conventional oxidative agents have been widely studied in the context of ageing/chemical degradation [95–97]. In case of direct recycling, PA oxidation is usually used as the recycling mechanism that changes the membrane morphology and performance. In fact, membrane direct recycling by chemical modification is gaining interest at academic and industrial level. Most of the direct recycling studies conducted in the last 15 years are summarized in Table 5 (published also in Paper I).

In 2002 Rodríguez et al. [98,99] introduced the concept of transforming end-of-life membranes into UF membranes and their further use in WW treatment processes. In this early work, sodium hypochlorite (NaClO) and other strongly oxidative chemicals, such as hydrogen peroxide (H_2O_2) and potassium permanganate (K_7MnO_4) were used to degrade the active layer from the membrane. This study was conducted under different operating conditions: active recirculation versus passive immersion by soaking membranes. Among the chemical agents used, they identified K_7MnO_4 as the most successful one with an optimal dose of approximately 1,000 mg/L for 1 to 2 hr. The recycled membranes were then tested as a pretreatment prior to RO process removing up to 96% of the suspended solids. Although a high level of fouling was recorded during the filtration, a nearly complete recovery of the permeability was possible [99]. Following this recommendation, more recently Ambrosi and Tessaro used K_7MnO_4 to modify the end-of-life PA layer with a more controlled degradation [100].

Following the above studies, higher permeability values of recycled membranes have been found by Lawler et al. [101] using higher exposure dose (ppm·h) of free chlorine at basic pH condition as PA degradant. Raval et al. [102] used free chlorine solution at pH 12 to degrade tailor-made membranes at laboratory scale. Free chlorine concentration was ranged between 1,000 to 3,000 ppm employing exposure times up to 48 h. Both NF and UF performance were obtained achieving high rejection coefficients of *Escherichia coli (E. coli)* bacteria (> 99.99% or > 4 Log removal). In addition it was presented one single case of end-of-life RO (SWC4) membrane conversion at pilot scale by recirculating a solution containing 2000 ppm free chlorine during 1 to 4.5 h. In this case, after 9,000 ppm·h of exposure dose membrane still showed 63.72% of NaCl rejection.

Afterwards, Lawler et al. [103] demonstrated the transformation of end-of-life RO membranes into UF membranes using 6 different types of membranes stored in wet, moist and dry conditions. This works highlights the importance of proper storage conditions of RO membranes intended for direct reusing or/and recycling. This study showed for the first time a potential reuse of the recycled membranes for gravity driven force UF processes. However, this study presents very little membrane surface characterization analysis to complement the permeability and rejection results.

Table 5. Research studies focused on end-of-life membranes recycling (Adapted from Paper I © Elsevier).

Main reuse propose	Process condition	Validation test
Recycled RO membrane for RO processes [104]. Pristine membranes: ACM1-TSA (Trisep), BW30-2514 (Dow FilmTec). End-of-life membrane: ACM1-TSA (Trisep).	Chemical agent: tannic acid. Concentration solution range: 80, 160, 240 y 400 ppm. Exposure time: 1 h. Tested different pH solution: 2.1, 2.4, 3.0, 4.0, and 5.0. Transformation: active process recycling solution.	Lab scale. Crossflow system, flat sheet membrane. Active surface: 56 cm^2. Pilot scale. Spiral wound element. Membrane active surface 0.7 m^2. Solution for both filtering test: 2,000 ppm NaCl. Operating pressure 11.77 bar, 22ºC.
Recycled UF membrane for waste water tertiary treatment [98,99]. End-of-life membranes.	Chemical agents: NaClO, K_7MnO_4, NaOH, H_2O_2. Concentration solution range: 180-8,208 ppm. Exposure time: 1-2 h. Transformation: - By Active process: recycling oxidizing solution under pressure. - By passive process: soaking the membrane in a bath without recirculation and no pressure.	Pilot scale. Spiral wound elements of 20.32 cm diameter. Membrane active surface 37 m^2. Solution for filtering test: waste water with secondary effluent quality: 5-10 NTU, 10-30 ppm SS, 1,500-2,500 µS/cm conductivity. Operating pressure 4-5.6 bar.
Recycled UF membrane for their reuse in water treatment [101]. Pristine membrane: BW30FR (Dow FilmTec). End-of-life membranes: TM700 (Toray).	Chemical agent: NaOH, K_7MnO_4, NaClO. Concentration solution range: 6,250 and 62,500 ppm (only for NaClO). Exposure dose: 28,000 to 500,000 ppm. Exposure time: was varied to achieve the exposure dose. Transformation: passive process at atmospheric pressure.	Lab scale. Dead end filtration system stirred cell. Solution for filtering test: 2,000 ppm NaCl. Pressure of 10 bar. (Characterization of active layer degradation). Solution for filtering test: solution of 10 ppm bovine serum albumin (BSA). Operating pressure of 2.5 bar, 2h. (Reused membrane fouling assessment).

Table 5 (continuation). Research studies focused on end-of-life membranes recycling (Adapted from Paper I © Elsevier).

Main reuse propose	Process condition	Validation test
Recycled RO and UF membranes for new applications like BW and bacteria elimination [102]. Taylor made membranes (Pilot plant at CSIR-Central Salt Marine Chemicals Research Institute) and SWC+4 end-of-life membrane.	Chemical agent: NaClO 4% (free chlorine). Concentration solution range: 1,000-3,286 ppm free chlorine. Exposure time: 0.5-144 h. pH: 12 (kept constant). Transformation: - By Active process: solution passed through membrane module. - By passive process: dipping in free chlorine solution.	Lab scale. Dead end filtration system stirred cell. Membrane active surface 18.9 cm^2. Solution for filtering test: 1,500 ppm NaCl. Pressure of 13.8 bar and 3.5 bar (UF test), 25 ºC. Solution for filtering test transformed UF case: aqueous polymer solution (15,000-100,000 Da) for molecular weight cut off (MWCO) determination.
Recycled RO for their reuse in other application different to RO processes [100]. End-of-life membrane: LFC3-LD-Hydranautics.	Chemical agent: K_7MnO_4. Concentration solution range: 2,000 ppm. Exposure time: 2 h. Transformation: active process recycling solution at 4 bar pressure.	Lab scale. Crossflow test unit. Membrane active surface 60 cm^2. Solution for filtering test: NaCl. Operating pressure 4, 6 and 8 bar, 25ºC.
Recycled UF membrane for their reuse in water treatment [103]. Pristine membrane: BW30FR (Dow FilmTec). End-of-life membranes: 8822HR (Koch), RE8040-FE (CSM), CPA5-LD (Hydranautics), TML820 (Toray), TFC-SW (Koch)	Chemical agent: NaClO 12.5% (free chlorine). Exposure dose: 300,000 ppm free chlorine, pH 12. Exposure time: 2.4 h.	Dead end filtration system stirred cell (HP4750 Sterlitech). Solution for filtering test: 2,000 ppm NaCl. Pressure of 1 bar. Advanced rejection characterization: solution of 10 ppm·humic acid and 10 ppm BSA.

Polyamide oxidation pathway by free chlorine

NaClO is a strongly oxidative chemical used for PA modification due to the reactivity of the free chlorine species towards functional groups of the PA layer [105,106]. This is why most PA RO membrane manufacturers recommend a exposure dose less than 1,000 ppm·h or, during their use, a feed water solution with a free chlorine concentration lower than 0.1 ppm [107,108]. The chemistry of aqueous NaClO solutions is largely dependent on pH. In water, NaClO is totally dissociated, forming sodium hydroxide (NaOH) and hypochlorous acid (HOCl), which is in equilibrium with two other species, hypochlorite (OCl^-) and chlorine gas (Cl_2 (g)) [109]. There is abundant literature about PA degradation by NaClO. Generally, it is accepted that it is a complex process closely related to the major chlorination species within the free chlorine solution (which depends on pH) and their concentration [95,110,111].

The chemical structure of PA has numerous amide linkages, which are random copolymers consisting of repeating units of the amide (-O=C-N-H-) group. N-H group of amide linkage are sensitive to the attack of chlorine radicals because of their high electron density [112]. In fact, the pathway for the oxidative membrane degradation has been reported in the literature (Fig. 6). Firstly, the reversible chlorination of amide occur and N–H groups are substituted by chlorine atoms to form amide N–Cl groups (N-halogenation). In addition, overcome a certain exposure dose, irreversible chlorine substitutions in aromatic rings are formed through the Orton rearrangement of the amide N–Cl groups, forming various aromatics subproducts [112,113]. This causes the failure of the PA RO membranes. Overall, it has been widely observed that at basic pH (ClO^- is the dominant specie) this PA degradation provoke the reduction of salt rejection capability and the increase of water permeability [97,103,114,115].

Between pH conditions, at acid pH (HClO is the dominant specie), the N-Cl formation is more effective [97,113]. Do et al., [116] also found that using hypochlorite solution ranged between 10 to 24,000 ppm·h the amount of chlorine attached onto the PA surfaces is dependent on its nature. In fact they observed that the chlorine amount attached was higher in fully aromatic PA (BW30 and NF90 models) than PIP based semi aromatic NF membrane (NF270). The inclusion of chlorine onto the PA could decrease the hydrophilicity of the surface [113] and could tight and compact the surface [117]. Usually, the consequence of all of those effects is the loss of membrane permeability and salt rejection [95,96,118].

On the other hand, at basic pH, at low exposure dose of free chlorine, only the highly reactive end amine groups are chlorinated and the carboxylic group (R-COOH) turn to (R-COO-) groups in the linear part of crosslinked aromatic PA [113,117]. This pH condition let increase the hidrophility of the surfaces and in consequence, exist less resistance to water passage through the membrane [117].

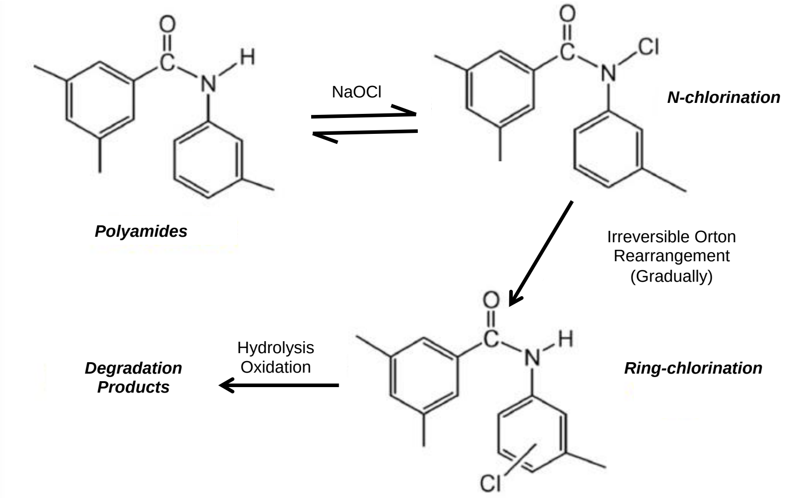


Fig. 6. PA degradation mechanism by free chlorine (From [95]).

Indirect recycling

Indirect recycling relate to module deconstruction to reprocess the whole membrane or some sections into industrial products. Therefore, it would be an alternative for end-of-life membranes that cannot be directly recycled and for spent recycled membranes.

Membranes are generally made of a number of polymeric materials. For example, RO membranes are thin film composites including aromatic PA dense layer supported by microporous PSF inner layer and non-woven PET webbing. In addition, feed spacers and permeate spacers are made by polypropylene (PP) and PET respectively. Acrylonitrile butadiene styrene (ABS) is used for the permeate tubes and end-caps. Fiberglass is used for the outer casing, along with glued parts containing proprietary epoxy-like components [119]. As a result, each of those materials could be extracted and recycled (mechanically and/or chemically).

Some of the indirect recycling activities cover options, from exotic fabric, decoration for clothing [120] or jewelry accessories, to more realistic use as aggregate material in composite concrete and wood fillers. PET permeate spacer and ABS permeate tube remain the most likely candidates to be recycled as these materials are only exposed to clean water during their lifespan. PET is widely and routinely recycled. Therefore, this material could be separated and sent to a PET recycling plant. In case of PP feed spacer, the main challenge remains in the high level of foulants on the membrane and that extensive cleaning would be required. Direct re-use of some of the membrane elements have also been reported. For example, sheets and spacers have been recycled as geotextiles in home gardens under a layer of gravel in order to maintain the position of decorative rocks and eliminate weed growth [93]. Additionally, potential agricultural applications for the spacers, including bird netting, wind breakers or nets for lawn protection have also been proposed [119]. The use of feed spacers and ABS caps could be particularly interesting in WW treatment as filler material of conventional trickling filter to promote microbiological growth. Although no report on the recycling of the module fiberglass could be found, there are studies focus on recycling fiber reinforced plastic composites [121,122]. Fiberglass could be recycled using physic-mechanical recycling method, converting it into a thermo-set material [123]. Another potential possibility would be to use the inert granular material for the partial substitution of aggregates in cementous mixtures [121].

So far, as reported in Paper II, only one business (MemRe GmbH Co., Germany) offers indirect recycling of end-of-life RO membranes (Fig. 7). The company manages the transportation and labeling of end-of-life membranes, from the pick-up on site until the recycling plant. Indeed, the company provides the certificate of disposal to its customers, confirming conclusively the process and completes the documentation requirements of customers, e.g. regulators, official or governmental authorities or the board of control.

Fig. 7. Industrial recycling process developed by MemRe GmbH (Adapted from [124]).

Energy recovery

According to the European Union Waste Framework Directive (2008), ‘recovery’ relates to “any operation the principal result of which is waste serving a useful purpose by replacing other materials which would otherwise have been used to fulfill a particular function, or waste being prepared to fulfill that function, in the plant or in the wider economy” [88].

The energy recovery option mainly concerns combustion of the polymer components of the membranes by oxidation of the organic material to produce energy. Earlier consideration of using old membranes in thermal processes has been initiated with the study of the thermal decomposition of RO membranes [119]. Thermo gravimetric analyses of the membrane components performed under nitrogen atmosphere showed that all material (excepting the fiberglass outer casing) had a coefficient carbon content ranged between 60% and 90% [119]. Therefore waste incinerators would be capable of removing all combustible material, excepting the residual inorganic filler contained in the fiberglass casing [32]. If it is considered also the volume of waste reduction and the potential energy recovery [89], incineration could be an alternative to the landfill disposal of the membranes that can not be reused or recycled. It could be also an option for the recycled and again spent membranes.

Chapter 3: Materials and Methods

3. Material and Methods

Chapter III describes the methodology employed during the investigation, detailing how to do a membrane autopsy, the techniques used for membrane surface fouling identification, the equipment employed for evaluating the membrane process performance and the recycling systems utilized in both laboratory and pilot scales.

3.1. Membranes and chemical reagents

All transformation assays were performed on several end-of-life PA RO membranes. All membrane models used in both laboratory and pilot scale and their original manufacture specifications are summarized in Table 6. At laboratory scale, coupons of 216 cm^2 were taken from 8" diameter spiral wound modules. In the pilot scale, the transformation was conducted in the entire 8" diameter spiral wound modules. During their life span, the membranes were used for treating BW or SW. End-of-life RO modules were conserved in sodium bisulphite (500-1,000 ppm). At laboratory scale, once the membranes coupons were extracted from the modules, they were conserved in Milli-Q water prior to be characterized and evaluated.

One potential challenge of the end-of-life RO membranes recycling process is the method of storage and transportation [103]. In order to evaluate the effect of dry end-of-life membrane conservation, the BW-10 (TM720-400) membrane was stored at dry conditions during two months. The performance of dry and wet membranes was compared at laboratory scale.

All chemicals used in this study are listed in Table 7, indicating the study purpose, the implemented scale and the paper where the data was published.

Table 6. Manufacture information of spiral wound membranes used to conduct the experiment in both laboratory and pilot scale.

Code	Commercial membrane brand	Membrane Model	Water Source	Nominal area (m^2)	Permeate flow rate (m^3/d)	Salt rejection coefficients (%)	Maximum chlorine tolerance(d)	Type of experiment where membrane was used
SW-0	Hydranautics	RO / HSWC3 (a)	SW	34	22.3	99.70	<0.01 ppm	Laboratory / Pilot
SW-1								
BW-2	Toray	RO / SU820-FA (a)	BW	32	19.0	99.75	0.00	Pilot
BW-3	Toray	RO / TM 720-400 (b)	BW	37	38.6	99.70	ND	Laboratory / Pilot
BW-6								
BW-9								
BW-10(e)								
BW-4	Dow Filmtec	RO / BW30-XFR-400 (b)	BW	37	43.0	99.65	<0.10 ppm	Laboratory / Pilot
BW-11(e)	Dow Filmtec	RO / BW30-400 (b)	BW	37	40.0	99.50	<0.10 ppm	Laboratory
BW-14								Pilot
BW-5	Toray	RO / SU-720F (b)	BW	35	32.0	99.40	N/A	Pilot
BW-7								
BW-8	Toray	RO / SU-720L (b)	BW	28	22.0	99.00	N/A	Pilot
SW-12(e)	Dow Filmtec	RO / SW30HRLE-440i(a)	SW	41	31.0	99.80	<0.10 ppm	Laboratory
SW-13(e)	Toray	RO / TM820C-400 (a)	SW	37	24.6	99.75	ND	Laboratory
SW-15 (f)	Dow Filmtec	RO / SW30XHR-440i (a)	SW	41	25.0	99.82	<0.10	Laboratory
NF-16 (f)	Dow Filmetc	NF / NF90-400 (c)	BW	37	38.0	>97.00	<0.10 ppm	Laboratory / Pilot
NF-17(f)	Dow Filmtec	NF / NF270-400/34i (c)	BW	37	47.0	>97.00	<0.10	Laboratory / Pilot
UF-18(f)	Koch	UF / 10KDa	N/A	N/A	N/A	N/A	N/A	Laboratory

(a) Values are normalized to the following conditions: 32,000 ppm NaCl, 55 bar applied pressure and 25ºC operating temperature; (b) Values are normalized to the following conditions: 1,500-2,000 ppm NaCl, 15.5 bar applied pressure and 25ºC operating temperature; (c) Values are normalized to the following conditions: 2,000 ppm MgSO$_4$, 4.8 bar applied pressure and 25ºC operating temperature; (d) Manufacture recommendation. The presence of free chlorine and other oxidizing agents will cause premature membrane failure; N/A means not available, ND means not detected. (e) These membranes were kindly donated by Genesys International Co. The rest of end-of-life membranes were kindly donated by SADYT Co. and Valoriza Agua Co, (f) Pristine membranes

Table 7. Chemical reagents employed during the Thesis.

Study purpose		Reagent	Purity (%)	Commercial brand	Paper
Membrane storage	Laboratory scale	$NaHSO_3$	40	Scharlab	Lab. Scale
	Pilot scale	$NaHSO_3$	<40	T.Q Aosta	Pilot scale
Bacteria to be analysed in: - Membrane autopsies - SUWW treatment	*E. coli* and total coliforms	Chromogenic coliform agar and CV Selective Supplement (CV-06-140-LYO)	N/A	Scharlab	Paper IV Paper V
	Aerobic	R2-A agar	N/A	Scharlab	Paper IV
	Pseudomonas	CromoMagar Pseudomonas	N/A	Scharlab	Paper IV
	Reducing iron sulphite bacteria	Iron sulphite modified agar	N/A	Scharlab	Paper IV
	Molds and yeast	Malt extract agar No.1	N/A	Scharlab	Paper IV
	PBS buffer solution	NaCl, KCl, Na_2HPO_4 (anhydrous) and KH_2PO_4 (anhydrous)	≥98, ≥99,≥98,≥98	Scharlab	Paper IV
Recycling process at laboratory scale	Transformation solutions	N-methyl-2- pyrrolidone (NMP)	≥99	Sigma Aldrich	Paper III Paper IV Paper V
		Acetone (C_3H_6O)	≥99	Scharlab	
		Sodium hypochlorite (NaClO)	10	Scharlab	
	pH adjustment	HCl	35-39	Scharlab	
Recycling process at pilot scale	Transformation solutions	NaClO	14	Lejías Navarro	Paper VI Paper VII
	Inhibition solutions	$NaHSO_3$	<40	T.Q Aosta	
Membrane performance evaluation at laboratory scale	Synthetic BW	NaCl	≥98	Scharlab	Paper III Paper V
		$MgSO_4$ (anhydrous)	≥98	Scharlab	
		Dextrose	Extra pure	Scharlab	
Validation of recycled membranes at laboratory scale	Synthetic urban wastewater (SUWW)	NaCl	≥98	Scharlab	Paper V
		$MgSO_4$ (anhydrous)	≥98	Scharlab	
		$NaHCO_3$	≥99	Scharlab	
		KNO_3	≥98	Scharlab	
		$NaNO_2$	≥99	Scharlab	
		NH_4Cl	≥99	Scharlab	
		$CaCl_2$ (anhydrous)	≥95	Scharlab	
		K_2HPO_4 (anhydrous)	≥98	Scharlab	
		Peptone & Meat extract	-	Scharlab	
		BSA	≥98	Sigma Aldrich	

3.2. Membrane autopsy and fouling identification

End-of-life RO membrane elements were placed vertically to drain the water excess during 1 h. Then, membranes were weighed. One membrane from each desalination plant was selected, packed in plastic bags, and shipped to the laboratory for membrane autopsy. Membrane autopsies consist in internal/external visual inspection and fouling and membrane surface analysis. Consequently, an entire destruction of the module was required. This practice is usually carried out to identify the main causes of membrane exhaustion.

Membranes donated by Genesys International Co. were already provided in sheet coupons. Membranes donated by Sadyt and Valoriza Companies were unrolled at the laboratories of IMDEA Agua. In this case, the extraction of fouled membrane sheets were carried out in five-step process: i) membranes model were open with a power saw, ii) the epoxy-fiberglass casing cover and ends caps were extracted, iii) membranes sheets were unrolled, iv) fouled membrane coupons were cut out for further analyses and v) the remaining module was conserved in sodium bisulphite (Fig. 8 or online video [125]).

Fig. 8. End-of-life RO membrane autopsy: a) dissection of membrane module; b) extraction of membranes coupons.

After the autopsy, fouling material was scraped off from the membrane surface and was dried at 110º C overnight. Dried fouling was then analyzed by thermo gravimetric analysis (TGA) and inductively coupled plasma mass spectrometry (ICP-MS). For microbiological analysis the collected fouling was not dried.

3.2.1. Thermo gravimetric analysis

TGA was used to assess the thermal decomposition of the fouling to identify its organic or inorganic nature. TGA was completed using TGA Q500 analyzer under an oxidative (air) atmosphere. The furnace was bought from 45 to 800ºC at a heating rate of 5ºC/min. The weight of each fouling sample was approximately 5 mg.

3.2.2. Inductively coupled plasma mass spectrometry

ICP-MS technique was utilized for estimating inorganic element concentration of fouling by using a quadrupole ICP-MS spectrometer device 7700x series from Agilent Technologies (Santa Clara, United States). The mass calibration of the ICP-MS instrument was tuned daily with a solution containing 1µg L^{-1} of Ce, Co, Li, Mg, Tl and Y in 1% (v/v) HNO_3. Accurately weighed samples (50 mg) were digested with 4:1 ratio of HNO_3:H_2O_2 and then diluted in 100 ml of Milli-Q water. Solutions obtained after digestion and dilution were analyzed by ICP-MS. A wide spectrum method of inorganic element detection was employed. Therefore, semi-quantitative results were given in relative coefficient, which was calculated by dividing the inorganic element detected mass by the total sample mass analyzed.

3.2.3. Microbiological identification

For bacterial identification, fouling material samples of 36 cm^2 were aseptically scraped off and transferred to a sterile Pyrex flask with 100 mL of phosphate buffered saline solution (PBS buffer). Samples were mixed in a vortex mixer during 4 min. *E. coli*, total coliform, *pseudomonas* and *clostridium* were detected following membrane filtration technique (Standard Methods: 9215 D) [126]. Each microorganism was grown in a specific medium: chromogenic coliform agar for *E. coli* and total coliform, CHROMagar for *pseudomonas* and iron sulfite modified agar for Clostridium. Aerobic mesophilic bacteria, molds and yeasts were detected and enumerated following pour plate count technique (Standard Methods: 9215 B) [127]. R2-A agar and malt extract agar No.1 were employed, respectively. When necessary, serial 10-fold dilutions were carried out. Incubation time and temperature were specifically adjusted according to agar medium. The detected colony forming units (CFU) bacteria were enumerated and divided by the surface area employed.

3.3. Recycling protocol

The conceptual scheme employed to conduct the recycling process is shown in Fig.9. A chemical agent, mainly NaClO, was used to carry out controlled degradation of the selective PA layer of the end-of-life membranes. In this way, end-of-life RO membranes were converted into NF or UF membranes, depending on the degree of exposure of the membrane to free chlorine. Passive immersion methodology was conducted in both laboratory and pilot scale experiments and their details are described in the following subsections.

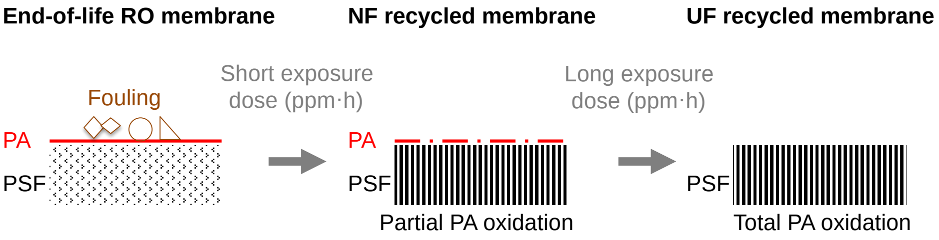


Fig. 9. Conceptual scheme of the controlled degradation of the PA RO active layer.

3.3.1. Laboratory scale

Membrane coupons of 216 cm^2 (dry and wet stored) were hydrated in fresh Milli-Q water for 24 h. Then, membranes were immersed in the transformation solution in sealed, opaque PP plastic containers at room temperature (≈21°C) with no agitation. Exposure time varied depending on the objective of the experiment. Then, the coupons were taken out of the containers and thoroughly rinsed with Milli-Q water until reaching Milli-Q pH. Membranes were conserved wet until membrane performance was evaluated. Table 8 summarizes the experimental conditions of the recycling process studied at laboratory scale. Results were compared with blank experiments, which involved the same protocol but exposing the membranes only to Milli-Q water. As Table 8 shows, the following issues were evaluated:

i) Type of Chemical agent

ii) The effect of NaClO exposure time and pH on dry stored BW-10 (TM720-400) membrane performance.

iii) The reproducibility of recycling process in diverse end-of-life membrane models (wet stored).

iv) The effect of the end-of-life RO storage conditions on the final recycled membrane performance.

v) Study of the exposure dose (ppm·h) concept. Three fixed exposure doses of free chlorine were set: 6,200; 30,000 and 300,000 ppm·h. Concentration and time were varied to achieve the exposure doses set.

In the cases where the NaClO was used, the free chlorine concentration was analyzed prior and after membrane exposure, using a Pharo 100 Spectroquant spectrophotometer (Merck).

Table 8. Experimental conditions used at laboratory scale to carry out the recycling study of end-of-life RO membranes.

Main objective	End-of-life membranes	Chemical agent	Concentration (ppm)	pH	Exposure time (h)	Exposure dose (ppm·h)
Preliminary study of chemical agent selection (Paper III)	BW-10 (TM720-400) (dry storage)	Acetone NMP	10,000	N/A	0.083	830
					20	200,000
					92	920,000
		Free chlorine (NaClO)	124	10.5	0.083	10,290
					20	2,480
					92	11,400
Selection of pH condition (Paper III)	BW-10 (TM720-400) (dry storage)	Free chlorine (NaClO)	124	3*-7*-10.5	1	120
					20	2,500
					36	4,500
					50	6,200
					122	15,000
Reproducibility study (Paper III)	BW-10 (TM720-400) BW-11 (BW30-400) SW-12 (SW30-HRLE) SW-13 (TM820-400) SW-0 (HSWC3) (wet storage)	Free chlorine (NaClO)	124	10.5	1	124
					20	2,500
					36	4,500
					50	6,200
					122	15,000
					242	30,000
					410	51,000
Study of ppm·h concept and recycled membrane validation (Paper V).	BW-10 (TM720-400) BW-11 (BW30-400) SW-12 (SW30-HRLE) SW-13 (TM820-400) SW-0 (HSWC3) (wet storage)	Free chlorine (NaClO)	1240	12	5	6,200
			6,200		1	
			12,400		0.5	
			124	12	24.2	30,000
			6,200		4.84	
			12,400		2.42	
			6,200	12	48.4	300,000

*pH was adjusted using 0.1 M HCl.

3.3.2. *Pilot scale*

The pilot recycling system (Fig. 10) consists of the following parts: i) passive recycling reactor, which at the same time has a structure that can contain vertically 6 spiral wound membranes. The structure is hold by a cylindrical PP container that is filled with the solutions; ii) low pressure pumps, iii) valve circuits, iv) 1 m^3 containers that storage the NaClO and $NaHSO_3$ solutions and v) 10 m^3 container used to carry out the neutralization of free chlorine with sodium bisulphite.

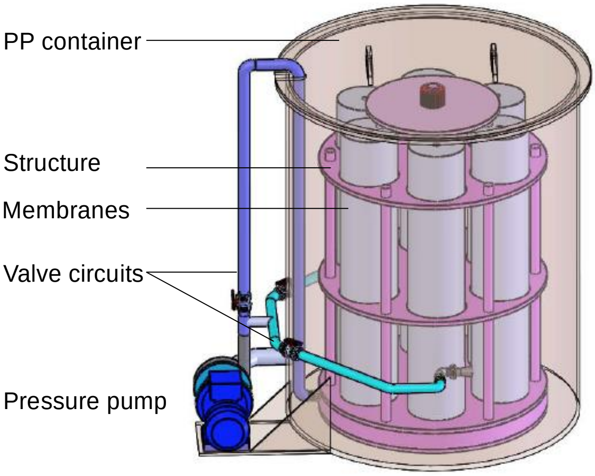


Fig. 10. Pilot scale recycling reactor containing 6 spiral wound membranes in the structure. Virtual design kindly facilitated by Valoriza Agua Company.

The direct protocol used is outline below:

NaClO was prepared by diluting the commercial product in water (permeate of Cuevas del Almanzora Desalination Plant) until achieving the free chlorine concentration set for the experiments (ranged between 6,000 and 16,000 ppm). This solution was reused for all the transformation experiments and its free chlorine concentration was regulated according to the in situ determination of pH, conductivity and redox. Therefore, commercial NaClO was added when necessary in order to guarantee a constant concentration in each assay. Moreover, sodium bisulphite ($NaHSO_3$) solution was prepared by diluting the commercial reagent (around 3 mg of $NaHSO_3$ per 1 mg free chlorine) with water and it was stored in other chemical storage container.

Six end-of-life membranes were placed in the structure (using a hoist when necessary). Then, NaClO solution was transferred to the membrane container. When the reactor was fulfilled ¾ parts of its volume, transversal circulation was applied in order to homogenize the solution. When the membranes were completely submerged, the solution was circulated during 10 min across the membrane to expel the air contained within the membrane sheets. No agitation was applied during the rest of the experiment providing static conditions. Temperature and pH were not adjusted.

Exposure time varied depending on the objective of the experiment. In one hand, selected exposure levels used at laboratory scale were also tested in this Section in order to validate them at pilot scale. On the other hand, it was evaluated if the PSF layer of the UF recycled membranes was damaged with longer exposure doses. Therefore, additional experiments were conducted in 6 membrane elements exposing them up to 1.700.000 ppm·h. All experimental conditions are summarized in Table 9.

Once the recycling protocol was finalized, the transformation solution was transferred again into the chemical container storage. Afterwards, the recycling reactor was filled with the $NaHSO_3$ solution to reduce completely the residual free chlorine remaining on the membranes. Finally, recycled membranes were taken out from the recycling reactor to be stored in $NaHSO_3$ solution until their process performance was evaluated.

Table 9. Free chlorine exposure doses used in the recycling process at pilot scale.

Main objective of research	**Free chlorine Concentration (ppm)**	**Estimated Exposure dose (ppm·h)**
Validation of the exposure dose set at laboratory scale	7,446 ± 1292	6,200, 12,500 33,500, 42,000, 46,000
	12,385 ± 3,040	350,000
Effect of long exposure dose on the recycled UF membrane performance and surface	12,385 ± 3,040	600,000, 800,000 1,000,000, 1,700,000

3.4. Evaluation of membrane performance

After the exposure to the chemical agent, membrane performance was evaluated in both laboratory (Paper III and V) and pilot scale (Paper VI and VII). Three individual steps were carried out as following: The step-1 consisted in evaluating the end-of-life RO membrane performance in terms of permeability and rejection coefficients. The step-2 was focused on membrane recycling following the protocols described in Section 3.3. Finally, the step-3 consisted in the characterization of the recycled membranes using the same procedure as in the step-1. Step-2 and step-3 were repeated several times for the same membrane (either coupon or spiral wound module) until the exposure time series was completed. Both permeability and rejection coefficients were calculated after the relative error of the measurements (standard deviation divided by the average) was less than 5%.

The permeability (L_p, $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$), was calculated following the Equation (1), where Q ($L\cdot h^{-1}$) is the permeate water flow, S (m^2) is the active membrane surface and the TMP (bar) is the transmembrane pressure. At laboratory scale, permeate water flow was calculated by measuring permeate weight (W, g) with time (t, h) and considering 1,000 g/L solution density (ρ) (Equation (2)).

$$L_p = \frac{Q}{S \cdot TMP} \quad (1)$$

$$Q = \frac{W}{\rho \cdot t} \quad (2)$$

Salt rejection coefficients (%R) were calculated using Equation (3), where C_f and C_p are the salt concentration found in the feed and permeate, respectively. The salt concentrations were calculated by measuring the conductivity using a conductivity meter CM 35 (Crison Instrument, Barcelona). At least six measurements of permeability and rejection coefficients were averaged for each representative data point.

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \cdot 100 \quad (3)$$

Individual ion rejection coefficients were determined by measuring the corresponding concentrations. For this purpose, ion chromatography (IC) was employed using an 861 advanced compact Metrohm ionic chromatograph with an autosampler 838 Advanced Sample Processor. Organic compounds rejection coefficients were determined by measuring the total organic carbon (TOC) concentration using a TOC-V CSH Shimadzu device. The results were introduced into Equation 3, where C_p and C_f now represent the concentrations of the corresponding analytes.

3.4.1. Laboratory scale cross flow filtration equipment

A laboratory-scale cross-flow system (Fig. 11), with a high-pressure pump, a 25 L feed reservoir and a tubular heat exchanger with a temperature controller was used in total recycle mode. The desired pressure and flow rate were achieved by adjusting the valve located after the membrane cell and the frequency pump regulator, respectively. The effective membrane filtration area was 84 cm^2. The membrane coupons were placed into a flat-sheet stainless steel RO test cell, containing permeate and feed spacers from each original RO modules.

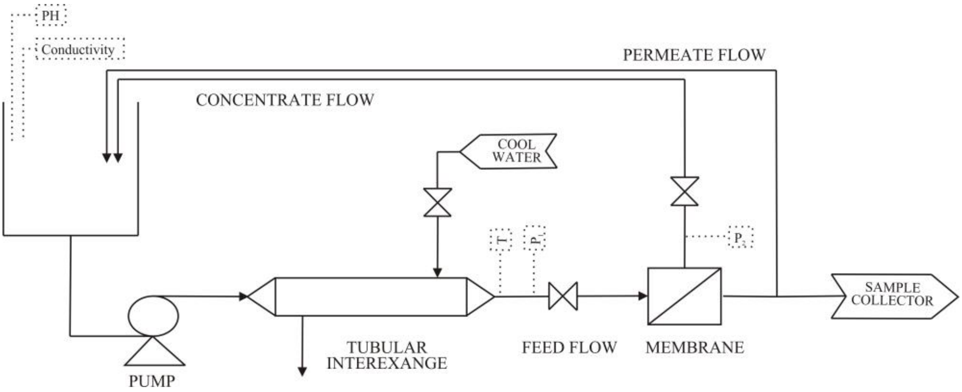


Fig. 11. Schematic diagram of the filtration setup (Paper III © Elsevier).

- ***Recycled membrane performance***

Milli-Q water (5 L) and synthetic BW solution (5 L) containing NaCl (2,000 ppm), $MgSO_4$ (2,000 ppm) and dextrose (250 ppm) were employed to test membrane performance. NaCl and $MgSO_4$ were chosen since they are the standard inorganic salts used by membrane manufactures for performance tests. Dextrose was chosen as an organic solute. It is an uncharged, hydrophilic, low molecular weight compound (180.16 $g\cdot mol^{-1}$) that is retained at 90-100% by dense PA membranes and it is not absorbed on the membrane [128]. All coupons were first compacted at 15 bar TMP. Table 10 shows the mean values and standard deviation of the filtering operation conditions and the physical and chemical parameters of the synthetic BW solution.

Table 10. Operation conditions and water quality parameters of the synthetic BW used to characterize the recycled membrane performance. Average and standard deviation values are shown.

Operation condition for membrane performance characterization					
Filtration in cross flow filtering system			Feed flow ($L\cdot h^{-1}$)	TMP (bar)	T° (C)
			240	5	30 ± 1
Water quality parameters					
EC µm/cm	6,350 ± 155	Cl^-	1,192 ± 131	Na^+(ppm)	785 ± 67
pH	6.2 ± 0,4	SO_4^{2-}	1,604 ± 115	Mg^{2+}(ppm)	395 ± 60
TOC (ppm)	104 ± 6				

• *Validation of recycled membrane for urban wastewater treatment*

The validation of recycled membranes (Paper V) was conducted by reusing the recycled membranes to treat a secondary synthetic urban wastewater (SUWW) solution (Table 11). The SUWW was prepared by using NaCl, $MgSO_4$, $NaHCO_3$, KNO_3, $NaNO_2$, NH_4Cl, $CaCl_2$, K_2HPO_4, NaClO, peptone and meat extract, bovine serum albumin (BSA) protein and natural *E. coli*. Chromogenic coliform agar with the Coliform CV Selective Supplement was employed for detection and enumeration of bacteria.

This study was only carried out using the TM720-400 commercial model from El Campillo desalination Plant (BW-10 membrane). TM720-400 was selected because it was the most representative model of the membrane stock (Table 6). Filtration conditions using SUWW (temperature, pressure and feed flow) were set equal than in synthetic BW assays (see Table 10). Two different cases were evaluated: a) NF recycled membrane and b) UF recycled membrane.

Table 11. Water quality of the SUWW solution used to validate a) recycled NF and b) UF recycled membranes. Average and standard deviation values are shown.

Analytical parameter	**SUWW (a)**	**SUWW (b)**
pH	7.9 ± 0.2	7.8 ± 0.3
EC (µS/cm)	1212 ± 38	1135 ± 101
Cl^- (ppm)	96 ± 48	156 ± 12
NO_2^- (ppm)	5 ± 1	7 ± 5
NO_3^- (ppm)	44 ± 1	34 ± 10
PO_4^{3-} (ppm)	32 ± 0	10 ± 2
SO_4^{2-} (ppm)	118 ± 6	101 ± 11
HCO_3^- (ppm)	259 ± 18	181 ± 37
Na^+ (ppm)	141 ± 3	108 ± 10
NH_4^+ (ppm)	9 ± 3	7 ± 3
K^+ (ppm)	58 ± 2	35 ± 3
Mg^{+2} (ppm)	33 ± 2	32 ± 10
Ca^{+2} (ppm)	11 ± 5	36 ±13
Organic matter (ppm)	26 ± 17 (meat extract and peptone, TOC value)	1051 ± 171 (BSA)
E. coli (FCU/100mL)	[10^5-10^7]	[10^5-10^7]

In case of using NF recycled membranes, five different end-of-life RO membranes coupons were used: three coupons were used for control assays (end-of-life membranes without chemical exposure to free chlorine) and two coupons after membrane recycling. End-of-life membranes were recycled using 4,500 ppm·h free chlorine (124 ppm solution). Then, membranes were reused filtering SUWW solution during 24 h (8 hours per day) without applying any cleaning procedures.

In case of using UF recycled membranes, end-of-life RO membranes were exposed at 30,000 and 300,000 ppm·h free chlorine exposure dose combining diverse concentration and exposure times (see Section 3.3.1, Table 8). Five end-of-life membrane coupons were employed. A commercial membrane (Koch, 10 KDa) was also tested in order to compare permeability results with recycled membranes. The experiments were conducted with the following filtering steps: i) Milli-Q water (1h), ii) SUWW solution (4h), iii) Milli-Q water (1h) and iv) cleaning procedures. Different cleaning procedures at room temperature were explored. First day of the experiment, membranes were cleaned by flushing 20 ppm free chlorine solution during 5 min (the washing flow was pumped in the same direction as that of the feed stream during filtration). In the second day, membranes were taken out from the filtration system and were cleaned in a PP plastic container by stirring 200 ppm free chlorine solution. This was conducted in order to preserve the stainless steel filtration system to free chlorine attack. In the third day, membranes were cleaned by reverse flushing using 20 ppm free chlorine solution during 5 min (the flushing flow was pumped in the reverse direction to the feed stream direction used during filtration).

To quantify the rejection coefficients, several samples of permeate and feed were collected periodically and individual ion concentration were analyzed by IC and TOC analysis. Moreover, total Alkalinity was analyzed by Titrator Titrando, Metrohm 809. The concentration of BSA was measured by using UV-vis spectrophotometer (Hitachi UV-2800) at 280 nm. In each single case, rejection coefficients were calculated by using Equation 3.

Wild strains of *E. coli* were previously isolated from a natural WW sample using the methodology reported in Vivar et al. [129]. All influent samples were diluted to obtain between 20 and 200 colonies formed unit (CFU) per filter, with dilution factors up to 10^3 using sterilized Milli-Q water. Quantitative results referred to CFU/100 mL were converted into $\log_{10}$ counting forming unit per 100 mL of filtered solution. *E. coli* removal efficiency was calculated as log removal value (LRV) by Equation 4. Equivalent rejection coefficients were calculated by Equation 3.

$$LRV = -Log_{10}\left[\frac{CFU_{fi}}{CFU_{pi}}\right] \qquad (4)$$

3.4.2. Pilot scale filtration equipment

A pilot-scale cross-flow test system (Fig. 12) was used to characterize the membranes prior and after free chlorine exposure. The pilot system consisted in a 1,000 L feed tank with thermal control, a low pressure pump, high pressure pump, a pressure vessel to contain one spiral wound 8” membrane and an electrical control panel. The desired pressure and the permeate flow rate were achieved by adjusting the valve located in the retentate and permeate streams, respectively. The effective membrane area was varied in each case according to the membrane brand (from 32 to 37 m^2). The system was used in total recycled mode. Natural BW, taken from Cuevas del Almanzora Desalination Plant, was previously pre-filtered (sand filter) and used to evaluate the membrane process performance. Table 12 shows operation conditions and the water quality used.

Fig. 12. Pilot membrane performance characterization system.

Table 12. Operation conditions and water quality parameters of the natural BW used to characterize the recycled membrane performance. Average and standard deviation values are shown.

Operation for membrane performance characterization			
Membranes	Feed flow (L·h^{-1})	TMP (bar)	Tº (C)
RO & NF	8,400 ± 1,164	14 ± 2	24.0 ± 3.0
UF	10,559 ± 1,300	2 ± 1	20.5 ± 1.3

Water quality parameters					
EC µm/cm	10,280 ± 1,226	Cl^- (ppm)	2,074 ± 404	Na^+ (ppm)	1,434 ± 43
pH	7,0 ± 0,2	NO_3^- (ppm)	147 ± 22	K^+ (ppm)	43 ± 8
TC (ppm)	55 ± 10	SO_4^{2-}(ppm)	2,345 ± 381	Ca^{2+}(ppm)	434 ± 75
IC (ppm)	53 ± 9			Mg^{2+}(ppm)	364 ± 62

3.5. Membrane surface characterization

The surface morphology of recycled membranes was characterized in order to further evaluate the level of membrane transformation. In all cases, recycled membranes were compared with end-of-life membranes results.

3.5.1 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy

Membrane surface was characterized by ATR-FTIR spectroscopy using a Perkin-Elmer RX1 spectrometer equipped with an internal reflection element of diamond at an incident angle of 45°. Prior to the ATR-FTIR analysis the membrane samples were dried at 110ºC to remove moisture for two days. Then an adequate pressure was applied on the membrane placed on the crystal surface. The spectra were recorded at a resolution of 2.0 cm^{-1} in the frequency region of 4000–650 cm^{-1} with an average of 4 scans per sample.

3.5.2. Scanning electron microscopy

Membrane samples were dried overnight at 110ºC and were imaged using two devices: XL30 ESEM Model (Phillips) and S-8000 Model (Hitachi). The first one was used to observe the cross section of the membranes. For this, the membranes were broken properly after being frozen into liquid nitrogen. The samples were dried and later were gold sputtered with a Sputter Coater Polaron SC7640 model to achieve 13–15 nm thickness prior to the scanning electron microscopy (SEM) analysis. The second device (S-8000 Model (Hitachi)) was employed to examine the membranes surface.

Afterwards, Digital Image Analysis (DIA) was used to determine the average pore Feret diameter of UF recycled membranes by Image J software (Java-based image processing program). Feret pore diameter is defined as the diameter that a pore should have if it had a circular section in the surface [130]. The analyses were conducted over SEM micrographs at 500 nm scale. The threshold used ranged between 80 and 83% and the FFT bandpass filter was adjusted as following: filter large structures down to 20 pixels, filter small structures up to 3 pixels and tolerance direction 5%.

3.5.3. Molecular Weight Cut Off

The MWCO is defined as the molecular weight corresponding to a retention coefficient of 90%. In this study a laboratory-scale cross-flow system described previously [131] was used. TMP was fixed at 3 bar and the effective membrane area was 5 cm^2. Filtering assays were conducted during 2h using poly(ethylene oxide) (PEO) feed solution (10 L, 1,000 ppm). The feed solution contained PEOs of different molecular weights (1,000; 2,000; 3,000; 4,000; 6,000; 8,000; 10,000; 20,000; 35,000 and 100,000 g/mol). Permeate samples obtained during the filtration experiments were collected and analyzed using a Size Exclusion Chromatography (SEC), which allows the estimation of the retention coefficient for each membrane [132–134]. A PerkinElmer Series200 SEC device with a column from Polymer Labs (PL MIXED aquagel-OH) of nominal pore size 8 µm was used. Milli-Q water was used as the eluent with a flow rate of 1 mL/min. The calibration was carried out with narrow standards of PEO with molecular weights between 194 and 490,000 g/mol.

Chapter 4: Results and Discussion

4. Results and discussion

This Section summarizes all experimental results obtained in this Thesis (Papers III, IV, V, VI and VII). Some of the membranes used are common for both laboratory and pilot scale. Therefore, in Section 4.1. fouling identification results at both scales are summarized. Sections 4.2. and Section 4.3. are focused on the recycling process at laboratory scale, whilst Section 4.4. deals with the recycling process results obtained at pilot scale. Section 4.5. is focused on fouling interaction in the recycling process and Section 4.6. discusses about a hypothetical business plant of a recycling RO membrane plant (Paper II).

4.1. Fouling identification

Fouling identification experiments were performed on membrane coupons that were obtained from 8” diameter spiral wound end-of-life RO membranes. The end-of-life membranes had originally been used for water desalination (Section 3.1. Table 6). This subsection is based on Paper IV and Paper VI.

4.1.1. Membrane weight and visual inspection

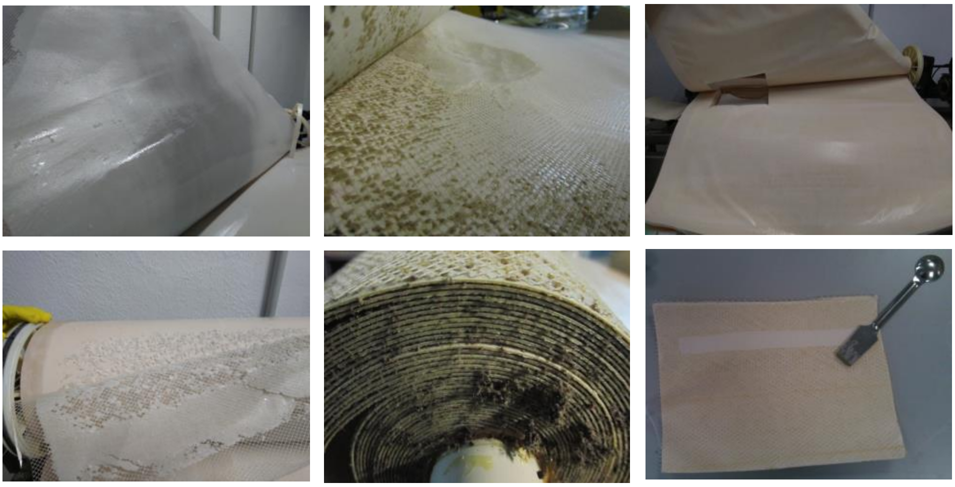
Membrane weight is rarely reported in the membrane manufacture data sheet. However normally, dry weight of pristine spiral wound membranes is between 11 kg and 16 kg. Membrane weight differences depend mainly on the number of membrane sheets and the type of outer casing fiberglass.

During their lifespan, membrane weight tends to increase due to the fouling. Therefore, end-of-life membrane weight can be used for a preliminary identification of fouling level type. As shown in Table 13, more than 3-fold weight increment from the original weight is usually found due to a thick layer of salt deposition (high level of scaling). Nevertheless, when the old module weight does not exceed 1.5 times the original weight value, the fouling might be organic or/and inorganic and other characterization techniques such as TGA, microbiological, ICP-MS or ATR, should be applied to identify membrane foulants.

Table 13. End-of-life membrane weight average, standard deviation and quantity of modules tested (Adapted from Paper VI).

Code	Membrane model	Desalination plant origin	End-of-life Membrane weight (Kg)	Nº modules	Weight increment x-fold	Odor	Color	Fouling Texture		Appearance Fouling nature
SW-0	HSWC3	IDAM Carboneras	16.8 ± 0.2	4	1.1	No	Orange	Slime		Organic & Biofouling
SW-1	HSWC3	Sta Cruz de Tenerife	17.0 ± 0.4	6	1.1	No	No	ND		No fouling
BW-2	SU-820FA	Cuevas del Almanzora	38.0 ± 2.8	6	3.5	Yes	White	Scab		Scaling
BW-3	TM 720-400	El Atabal	19.2 ± 2.8	6	1.7	No	White & Brown	Scab & Colloidal		Scaling & organic
BW-4	BW30-400	El Atabal	18.8 ± 0.4	3	1.7	No	White & Brown	Scab & Lump		Organic & Scaling
BW-5	SU-720F	Classified	15.2 ± 0.2	2	1.4	-	-	-		-
BW-6[a]	TM720-400	Codeur	40.3 ± 0.9	6	3.7	Yes	White	Scab		Scaling
BW-6[b]	TM720-400	Codeur	16.6 ± 1.1	24	1.5	N/A	N/A	N/A	N/A	N/A
BW-7	SU-720F	El Cocón	14.6 ± 0.4	4	1.3	N/A	N/A	N/A	N/A	N/A
BW-8	SU-720L	El Cocón	16.0 ± 0.0	1	1.5	N/A	N/A	N/A	N/A	N/A
BW-9	TM720-400	Classified	16.2 ± 1.6	17	1.5	No	Dull brown	Colloidal		Clay matrix
BW-10	TM720-400	Classified	N/A	1	N/A	No	Dull Brown	Colloidal		Clay matrix
BW-11	BW30-400	Classified	N/A	1	N/A	No	Light Brown	Colloidal		Clay matrix
SW-12	SW30-HRLE	Pristine	16.7	1	1.5	No	Brown	Colloidal & slime		Organic-biofouling
SW-13	TM820-400	Classified	16.9	1	N/A	No	Dark purple-black	Colloidal		Inorganic
BW-14	BW30-400	Pristine	11.2 ± 0.0	3	1.0	-	-	-		-

Visual inspection provides also information that allows distinguishing between the diverse types of fouling such us scaling, clay matrix, organic colloidal fouling or biofouling. Table 13 also shows parameters collected during the membrane visual inspection such as fouling color, texture, appearance and odor. In addition, Fig. 13 shows typical pictures taken during the membrane autopsies representing inorganic fouling and organic fouling of three membranes from distinct BWRO plants. Biofouling texture can be identified due to the slimy texture of the fouling. In addition, clay matrix and organic matter has a colloidal texture whilst salt precipitates tend to be stuck on the membrane and/or the feed spacer surfaces.



Inorganic fouling (scaling).
Over the feed spacer and membrane sheets.
Membrane: BW- 2 (SU-820FA).

Organic fouling and inorganic fouling. Over the feed spacers and membrane sheets.
Membrane: BW-3 (TM720-400).

Inorganic fouling (clay-colloidal matrix). Over the membrane sheets.

Membrane: BW-9 (TM720-400).

Fig. 13. Inorganic scaling (left), organic fouling (middle) and inorganic clay fouling (right) from different membranes installed in Spanish BWRO desalination plants (Paper II © Elsevier).

4.1.2. *Thermo gravimetric analysis*

TGA of the fouling samples were carried out under an oxidative atmosphere to obtain the coefficient composition of organic and inorganic fouling. Decomposition process occurred in several steps. Fig. 14 shows the thermograms of the membrane fouling extracted from BW and SW membranes and their derivatives. Diverse derivative temperature curves of material degradation can be distinguished according to their nature.

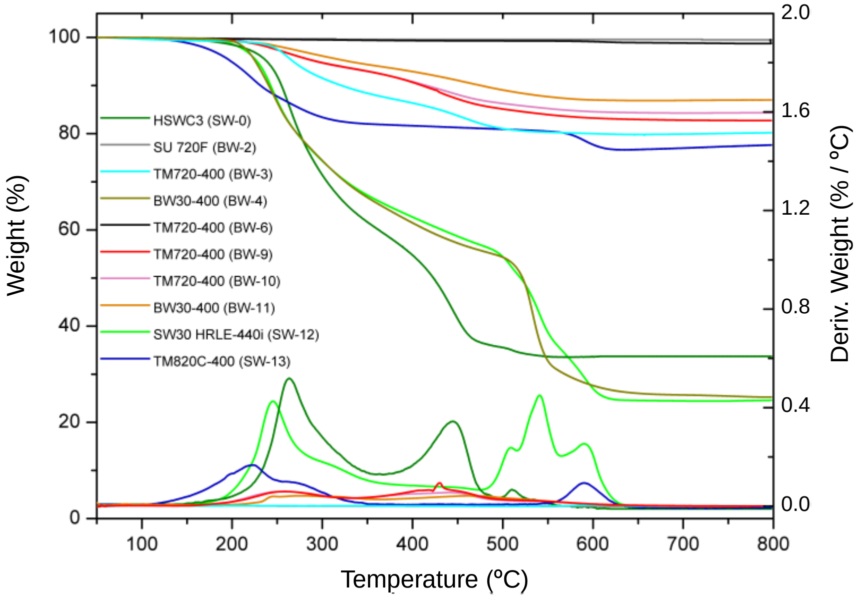


Fig. 14. TGA curves of fouling materials (Heating rate 5 ºC/min from 45 to 800 ºC) (Adapted from Paper IV and Paper VI).

Table 14 shows the temperature of initial decomposition, which was detected between 175 and 235 °C, and the percentage of the fouling nature for each membrane tested. As Table 14 shows, the majority of the fouling found on the BW membrane surfaces was inorganic. In fact, 3 end-of-life membranes had a white scab over the feed spacer. This usually occurs because BW membranes have higher flux than SW membranes, exacerbating the fouling by scaling when salts reach their saturation limit [10]. Fouling of SW-0, BW-4 and SW-12 membranes was ranged between 66% and 76% organic matter, which is the most common category of fouling of RO membranes according to the review published by Genesys International [135].

Table 14. Initial decomposition temperature and coefficient (%) of organic and inorganic fouling obtained by TGA analysis (Adapted from Paper IV and Paper VI).

Code	**Membrane Model**	**T_d (ºC)[a]**	**% Inorganic fouling[b]**	**% Organic fouling[c]**
SW-0	HSWC3	240	33.70	66.30
BW-2	SU-820FA	ND	99.49	0.51
BW-3	TM 720-400	235	80.10	19.90
BW-4	BW30-400	215	25.20	74.80
BW-6[a]	TM720-400	ND	98.73	1.27
BW-9	TM720-400	235	82.72	17.28
BW-10	TM720-400	210	84.30	15.70
BW-11	BW30-400	235	82.00	18.00
SW-12	SW30-HRLE	220	24.40	75.60
SW-13	TM820-400	175	77.00	23.00

[a] Onset temperature of initial weight loss (T_d). [b] Char residue at 800 ºC ($R_{800ºC}$ (%).
[c] 100% - $R_{800ºC}$ (%).

4.1.3. Inductively coupled plasma mass spectrometry

In order to get a better understanding of the inorganic fouling, ICP-MS analyses were also performed. As Table 15 shows, aluminium (Al), iron (Fe), potassium (K), phosphorus (P), silicon (Si) and magnesium (Mg) were elements commonly detected. Some of the end-of-life BW membranes that had a visual appearance of colloidal fouling (BW-9, BW-10, BW-11 membranes) showed higher relative coefficient of Al, K and Fe than the rest of the membranes. Al and Fe are elements naturally present in groundwater, however they also could have been introduced in the filtration process by the use of flocculants like aluminum sulphate, ferrous sulphate or ferric chloride. In case of the BW membranes fouled by precipitation of inorganic salts (visual white scab), the major inorganic elements presents were calcium and sulphate. In fact, BW-3 membrane showed the most representative example of scaling based on calcium sulphate (39.4% Ca and 56.55% S of the inorganic fouling).

In case of SW membranes diverse metals were found. The SW-13 membrane showed a specific fouling problem, probably related to the quality of the feed water to be treated. Manganese has been the main inorganic foulant found in this membrane (30%). Manganese salts are less frequently found than iron [136], however, some illustrative cases have been reported in literature. Fernandez-Alvarez et al., [137] reported about the autopsy of RO membranes after 8 years of operation treating SW from Ceuta, Spain. ICP-MS analysis revealed a great variety of metals like Ba, Cr, Sr, V, Zn, Ni, including Mn. According to TGA results obtained, overall membranes tested SW-12 membrane has the lowest inorganic coefficient. The most representative metallic elements were P, Iodine (I) and sodium (Na), which are elements naturally present in SW. Finally, the inorganic fouling of HSWC3 membrane is mainly due to Si, P, Fe and Al.

Results are consistent with other literature works [135,137,138]. In fact, after considering 150 elements autopsies, Darton et al. [135] revealed that around 50% of membrane fouling was organic. The rest of inorganic foulants were distributed in 10.2% Fe_2O_3 and $CaSO_4$, 13.5% SiO_2, 3.8 Al_2O_3, 2.7% $CaPO_4$, 2.4% $CaCO_3$. Remaining inorganic elements (15%) were considered as other category.

4.1.4. Bacteria detection and enumeration

Fouling matter was extracted from the end-of-life membranes in order to detect and enumerate bacteria, yeasts and molds, usually categorized as biofouling. Table 16 shows the estimated colony-forming unit detected by cm^2 of end-of-life membrane tested. All membranes showed a biofilm on their surfaces since none of them operated with sterile water. The most frequently microorganism found in all membranes were *pseudomonas bacteria,* yeast, aerobic bacteria and molds. Mold population was the highest ($[10^4$-$10^5]$ CFU/cm^2) in all the membranes studied. *E. coli* and *clostridium* bacteria were detected only in BW membranes. Very low concentrations of other coliforms bacteria were detected in the case of BW-3, BW-4, BW-10, BW-11 and SW-13 membranes. All values can be considered as normal values according with other works [135], which reported that problematic biofouling occurs when bacterial amounts is higher than 10^5 CFU/cm^2.

Table 15. Inorganic elements percentages (%) contained in the membrane fouling (Adapted from Paper IV and Paper VI).

Inorganic Elements	**SW-0** **HSWC3**	**BW-2** **SU820FA**	**BW-3** **TM720-400**	**BW-4** **BW30-400**	**BW-6** **TM720-400**	**BW-9** **TM720-400**	**BW-10** **TM720-400**	**BW-11** **BW30-400**	**SW-12** **HRLE440-i**	**SW-13** **TM820C-400**
Mn	0.01	< 0.01	< 0.01	0.01	< 0.01	0.01	0.01	0.06	0.17	***30.58***
Mg	0.55	< 0.01	**0.33**	**1.33**	< 0.01	**0.18**	**0.32**	**3.68**	**0.68**	***1.83***
Ca	ND	**11.4**	**39.4**	**4.11**	**11.40**	**0.18**	0.08	1.95	0.53	***0.93***
K	0.29	< 0.01	0.05	0.46	< 0.01	**0.84**	***2.06***	***7.47***	0.27	0.19
P	***2.69***	0.01	**0.84**	**6.26**	< 0.01	0.23	0.66	**1.02**	***1.44***	0.32
Fe	***1.86***	< 0.01	**0.05**	**1.67**	< 0.01	**2.6**	***2.22***	***13.80***	**0.36**	**0.19**
Si	***6.17***	< 0.01	**0.57**	**2.13**	< 0.01	**0.09**	**0.66**	**3.87**	**0.40**	**0.13**
I	0.02	< 0.01	0.06	1.01	< 0.01	< 0.01	ND	0.01	***1.55***	0.13
Al	***1.59***	< 0.01	**0.18**	**1.04**	< 0.01	**3.36**	***10.53***	***32.20***	0.35	0.04
S	ND	**12.3**	**56.55**	**3.41**	**10.20**	ND	ND	0.31	***1.93***	0.04
Na	ND	< 0.01	0.08	0.64	0.01	0.03	0.10	1.29	***2.46***	0.03
Cu	0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	ND	0.03	0.15	0.02
Ti	0.02	< 0.01	< 0.01	0.01	ND	0.04	0.11	0.47	0.03	ND
B	0.08	< 0.01	< 0.01	0.02	ND	< 0.01	0.01	0.02	0.01	ND
As	ND	ND	< 0.01	< 0.01	ND	< 0.01	ND	ND	ND	ND
Ba	0.00	< 0.01	< 0.01	0.01	< 0.01	0.04	ND	0.06	ND	ND

Table 16. Estimated colony-forming unit (CFU) bacteria in 1 cm^2 of end-of-life RO membranes tested (Adapted from Paper IV and Paper VI).

Microorganism	**SW-0** **HSWC3**	**BW-2** **SU820FA**	**BW-3** **TM720-400**	**BW-4** **BW30-400**	**BW-6** **TM720-400**	**BW-9** **TM720-400**	**BW-10** **TM720-400**	**BW-11** **BW30-400**	**SW-12** **HRLE440-i**	**SW-13** **TM820C-400**
E. coli	ND	ND	[0-10]	[0-1]	ND	ND	ND	[0-1]	ND	ND
Other coliforms	ND	ND	[10-10^2]	[10-10^2]	ND	ND	[0-1]	[10-10^2]	ND	[1-10]
Clostridium	ND	ND	[10^3-10^4]	[10-10^2]	[10-10^2]	[0-1]	ND	[10^3-10^4]	ND	ND
Pseudomonas	[10^2-10^3]	ND	ND	ND	[10^2-10^3]	[0-1]	[10^2-10^3]	[10^2-10^3]	[10^2-10^3]	[10-10^2]
Aerobic bacteria	[10^3-10^4]	ND	[10^4-10^5]	[10^3-10^4]	[10^3-10^4]	[10^2-10^3]	[10^4-10^5]	[10^3-10^4]	[10^3-10^4]	[10^3-10^4]
Molds	[10^4-10^5]	ND	[10^3-10^4]	[10^3-10^4]	[10^3-10^4]	[10^4-10^5]	[10^4-10^5]	[10^3-10^4]	[10^4-10^5]	[10^4-10^5]
Yeast	[10-10^2]	[10-10^2]	[10-10^2]	[10-10^2]	[10-10^2]	[10-10^2]	[10-10^2]	[10-10^2]	[10-10^2]	[10-10^2]

4.2. Transformation of end-of-life RO membranes into NF and UF recycled membranes using low free chlorine concentration solutions

First aim of this Section was to select the chemical agent to be further used during the work presented in this Thesis. BW-10 (TM720-400) membrane was used to conduct great amount of experiments creating a baseline of results. Moreover, the study was extended to other membrane models (BW and SW) in order to evaluate the reproducibility of the recycling process. This Section is based on Paper III.

4.2.1. Chemical ageing agent selection

Preliminary tests were conducted with chemicals that could degrade the PA layer of the end-of-life RO membranes. The chemical reagents selected were NaClO, which oxidizes the PA; NMP, which dissolves PA and acetone, which strips PA from membrane support layers. Fig. 15 shows the Milli-Q water permeability values achieved after the dry stored BW-10 (TM720-400) membrane coupons were exposed to these solutions. The longer the membranes were left immersed in the transformation agent, the better the permeability obtained. However, it has to be mentioned that a 27% increased in permeability was achieved in one of the blank samples (coupons immerse only in Milli-Q water) after 92 h exposure. Hence, a minimum of 30% increment was considered as a significant effect. The increment observed in the control samples might be due to several factors such us pore swelling and experimental error. Furthermore, acetone and NMP did not provoke substantial changes in Milli-Q membrane permeability. Moreover, it was observed that only the NaClO treatment led to increase noticeable the Milli-Q water permeability: around 4.8-fold at 20 h (from 2.90 to 14.08 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$), and 9.3-fold at 92 h (from 2.90 to 26.90 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$). Then NaClO was selected for further studies.

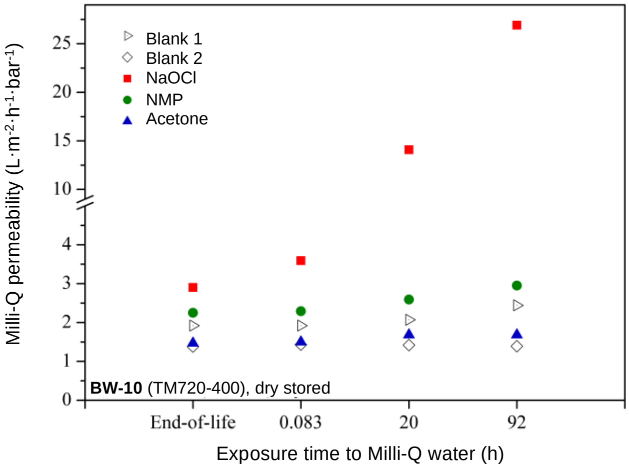


Fig. 15. Milli-Q permeability changes vs. exposure time of different chemical reagents (acetone, NMP, NaClO). Membranes exposed to Milli-Q water are considered blanks (Paper III © Elsevier).

4.2.2. Effect of NaClO exposure time and pH on dry stored TM720-400 membrane performance

As it was explained at Section 2.2.3 (Polyamide oxidation pathway by free chlorine), the chemistry of aqueous NaClO solutions is largely dependent on pH. The present Section relies on membrane exposure to free chlorine at pH-3, pH-7 and pH-10.5. Filtering assays were conducted using synthetic BW in order to evaluate recycled membrane performance. Five coupons (dry stored) were extracted from BW-10 (TM720-400) membranes and transformed at pH-3 (one coupon), at pH-7 (one coupon) and at pH-10.5 (three coupons, replicates). In these experiments the free chlorine concentration was fixed at 124 ppm and a serial time was employed to achieve from 124 ppm·h to 15,000 ppm·h exposure dose. All data were reported at Table A1 Paper III (see Appendix).

- ***Permeability and salt rejection coefficients of recycled membranes***

Fig. 16 (a) and 16 (b) show the permeability and salt rejection coefficients. Prior to the recycling process, the performance of all end-of-life membranes was similar. Further, at pH-3 no significant change was found in permeability (less than 30% of increment). Since the main objective was to achieve higher permeability values, the experiments were stopped at 36 h exposure time. Similar results of this study have also been found [97,116]. However it has been widely reported in literature that at acid pH conditions the membrane permeability declines severely [117,118]. Controversial results can be explained due to the differences in the membrane material studied such as the origin of the PA membrane layer (commercial or tailor made). PA can be full aromatic, partial aromatic and functional modified PA layer. These all aforesaid conditions could produce different interactions with hypochlorite acid solution [113].

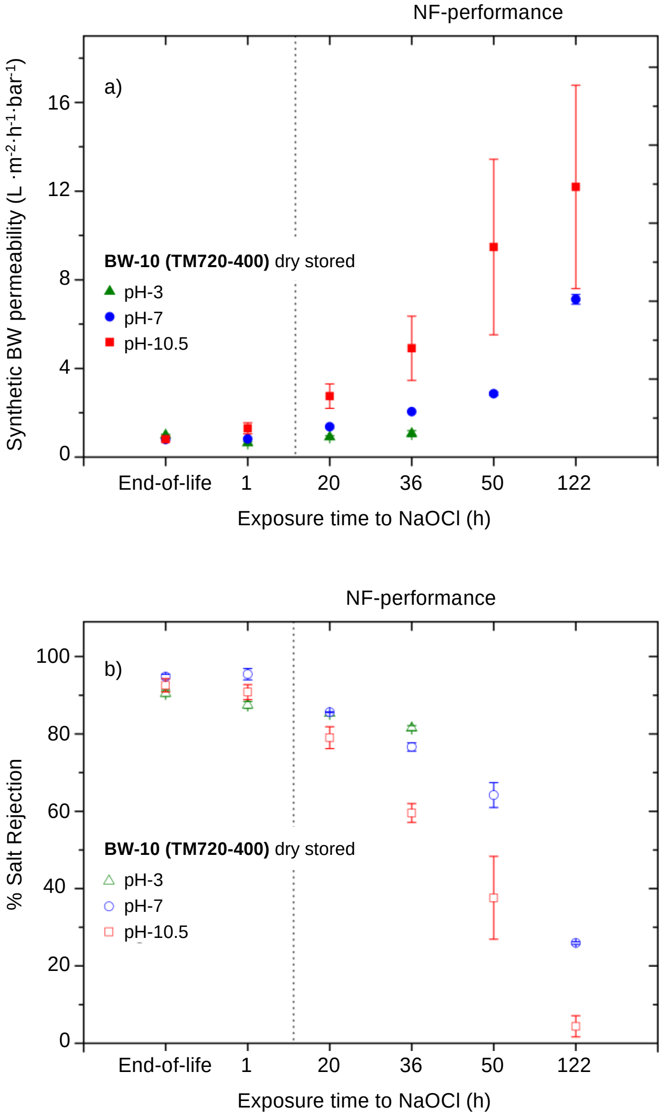


Fig. 16. Effect of pH recycling condition and exposure time to NaClO; Permeability values (a) and salt rejection coefficients (b). In case of pH-10.5 result are shown as average values obtained by repeating the experiments 3 times with 3 different membrane coupons (Paper III © Elsevier).

On the contrary to pH-3, pH tested at neutral (pH-7) and basic condition (pH-10.5) showed significant performance changes on the recycled membranes. After low exposure time (1 h, equivalent to 124 ppm·h exposure dose) at neutral and alkaline conditions, the membrane permeability values increased slightly >1-fold (from 0.79 to 0.82 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) and 1.6-fold (from 0.81 to 1.30 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$), respectively. Salt rejection coefficient was kept almost constant at neutral pH (rise 3.8%, from 94.82% to 95.45 %) and slightly decreased at basic pH (drop 2%, from 92.57% to 90.75%). This can be due to the fact that at low exposure level of ClO^- at pH-10.5, only the highly reactive end amine groups are chlorinated and the carboxylic group (R-COOH) turn to ($R\text{-}COO^-$) groups in the linear part of crosslinked aromatic PA [113,117]. This pH condition let increase the hydrophilic character of the membrane surfaces and in consequence, exists less resistance to water passage through the membrane [117]. The same behavior has also been observed in other experiment assays using NaClO, where low chlorine exposure concentration (100-6,000 ppm·h) was applied [97,112,139]. Results of these studies address that the NaClO is not only a good organic fouled membrane cleaner but also increases membrane permeability values without compromising dramatically their rejection coefficients.

Moreover, in both neutral and basic pH recycling conditions, after 36 h of membrane exposure time (equivalent to 4,500 ppm·h exposure dose), the recycled membranes achieved the permeability rate of NF membranes. In this case the transformation mechanism could be based on the irreversible chlorine substitutions in aromatic rings formed through the Orton rearrangement of the amide N–Cl groups [95]. Consequently, PA layer degradation occurred and the permeability of the exposed membranes increased, whilst the rejection coefficients decreased.

It is interesting to note that the effect of the exposure time was dependent on the pH (Fig. 16). As an example, after 50 h of contact with chlorine solution (equivalent to 6,200 ppm·h exposure dose) at pH-7 the membrane showed a permeability of synthetic BW 3.6 times higher than the initial end-of-life values (from 0.79 to 2.86 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$). At basic pH the membrane permeability was 11.7 times higher (from 0.81 to 9.48 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$). This can be explained by the chemistry of aqueous NaClO solutions. At basic pH the ClO^- is the main specie present in the solution (around 100 % at pH>10) and at neutral pH the ClO^- is around 22% [140]. Therefore, the effect of ClO^- on the PA is more significant at basic pH. These results are in concordance with other works found in the literature, which reported PA membranes degradation by hypochlorite ion exposure [101,103,115].

At 122 h exposure to NaClO at basic pH (equivalent to 15,000 ppm·h exposure dose), the salt rejection capability decreased 95% (from 92.57 to 4.4%) showing UF properties. However, the initial permeability increased up to 12.19 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, which is in the NF permeability range. This could be due to the fact that in the present experiments, end-of-life membranes were stored dry and the pore could be collapsed, achieving very low permeability values. However, SEM micrographs of the membrane surfaces confirmed there was still PA on the surface (see Appendix, Fig A.1).

- ***Rejection coefficients of mono/divalent ions and dextrose of recycled membranes***

Previous studies found in literature used only NaCl salt solution to evaluate the membrane performance changes after exposing the membrane to chlorine solutions [102–104]. In addition, the rejection coefficients were often calculated using only the electrical conductivity measurements at the feed and the permeate. In the present study, synthetic BW was used to obtain a more exhaustive membrane performance evaluation by calculating not only monovalent ion rejection coefficients but also divalent ion and organic compounds rejection coefficients. Consequently, it was possible to recognize the border line conditions between NF and UF conversion.

Figure 16-b shows that salt rejection coefficient at pH-7 and 50 h exposure time was 64.19%. Despite this relatively low rejection obtained by conductivity measurement, as Figure 17-b shows, SO_4^{-2} ion rejection was high (97.0%). The same behavior was observed when the membrane was transformed at pH-10.5, where the total salt rejection was 39.27% whilst the SO_4^{-2} rejection was 81.4%. The detection of successful divalent ions rejection coefficients indicates that the recycled membrane achieved NF performance. In fact, further characterization with dextrose (180 Da) showed that the transformed membrane had still capability to reject low molecular weight organic compounds. As an example, at 50 h exposure time at pH-7 and pH-

10.5 the rejection coefficients were 71.4% and 43.9%, respectively. Indeed, at 122 h exposure time and pH-10.5, almost no rejection of dextrose was observed (2.9%).

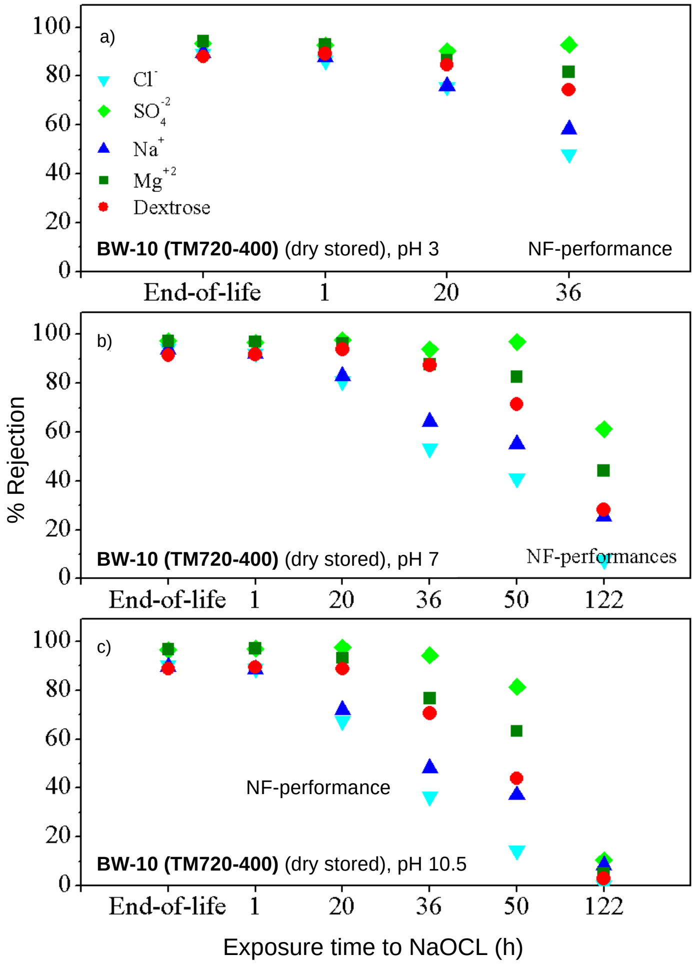


Fig. 17. Effect of pH transformation conditions and exposure time to NaClO on ions and dextrose rejection. In case of pH-10.5 result are shown as average values obtained by repeating the experiments 3 times with 3 different membrane coupons (Paper III © Elsevier).

As Fig. 17 denotes, divalent ions are rejected more efficiently than monovalent ions. This can be attributed to molecular size and charge of the membrane. It is well known that PA is an amphoteric and hydrophilic polymer which possess dissociable carboxylic groups [141]. As it has been reported in literature, chlorination process at the pH condition studied (pH-3, pH-7, and pH-10.5) should increase the negative charges on membrane surface [113,142,143]. Therefore it was assumed that recycled membranes had negative charged surface. The synthetic BW employed for membrane performance characterization contains symmetric salts (NaCl and $MgSO_4$). Cl^- and SO_4^{-2} have the same charge sign as the membrane therefore, they are the dominant ions (co-ions). Anions could be repelled by electrostatic repulsion mechanism due to the fixed negative charge density on the membrane surface [144]. This is attributed to the deprotonation of carboxylic acid group and chloride ion attached on the membrane after being exposed to free chlorine [113,145]. Between Cl^- and SO_4^{-2} exists a co-ions competition that would explain minor rejection of Cl^-, which has less charge and higher mobility than SO_4^{-2}. Furthermore, stronger electrostatic repulsion results in higher ions rejection [146], which explain the highest rejection coefficients obtained for SO_4^{-2} anion.

4.2.3. Reproducibility study of the transformation process (wet stored membranes)

According of the results obtained in the previous section, using NaClO basic pH solutions provoked the most significant changes on end-of-life membrane process performance. Therefore, NaClO solution at basic pH condition was selected for further recycling analysis. This Section is focused on the reproducibility of membrane recycling process by using 5 brands of end-of-life membranes, which were stored under wet conditions. Membrane performance in terms of permeability, salt, ion and dextrose rejection coefficients was evaluated filtering synthetic BW solution.

The recycling process was carried out following the same protocol as in Section 3.3.1. Membranes performance evaluation series (end-of-life, and after 36, 50, 122, 242 and 410 h exposure time) were repeated three times for BW-10 (TM720-400), SW-12 (SW30HRLE-440i) and SW-13 (TM820C-400) membranes, whilst only one series was done for SW-0 (HSWC3) and BW-11 (BW30) membranes. Fig. 18, shows the results of the permeability and the rejection coefficients obtained with the recycled membranes. All data are also summarized in Paper III (see Appendix).

Among all the membranes studied, recycling process applied for end-of-life BW membranes let achieve higher permeability values than in case of end-of-life SW membranes. This might be due to particular differences within membrane PA type and the process condition that the membranes suffered on its lifetime.

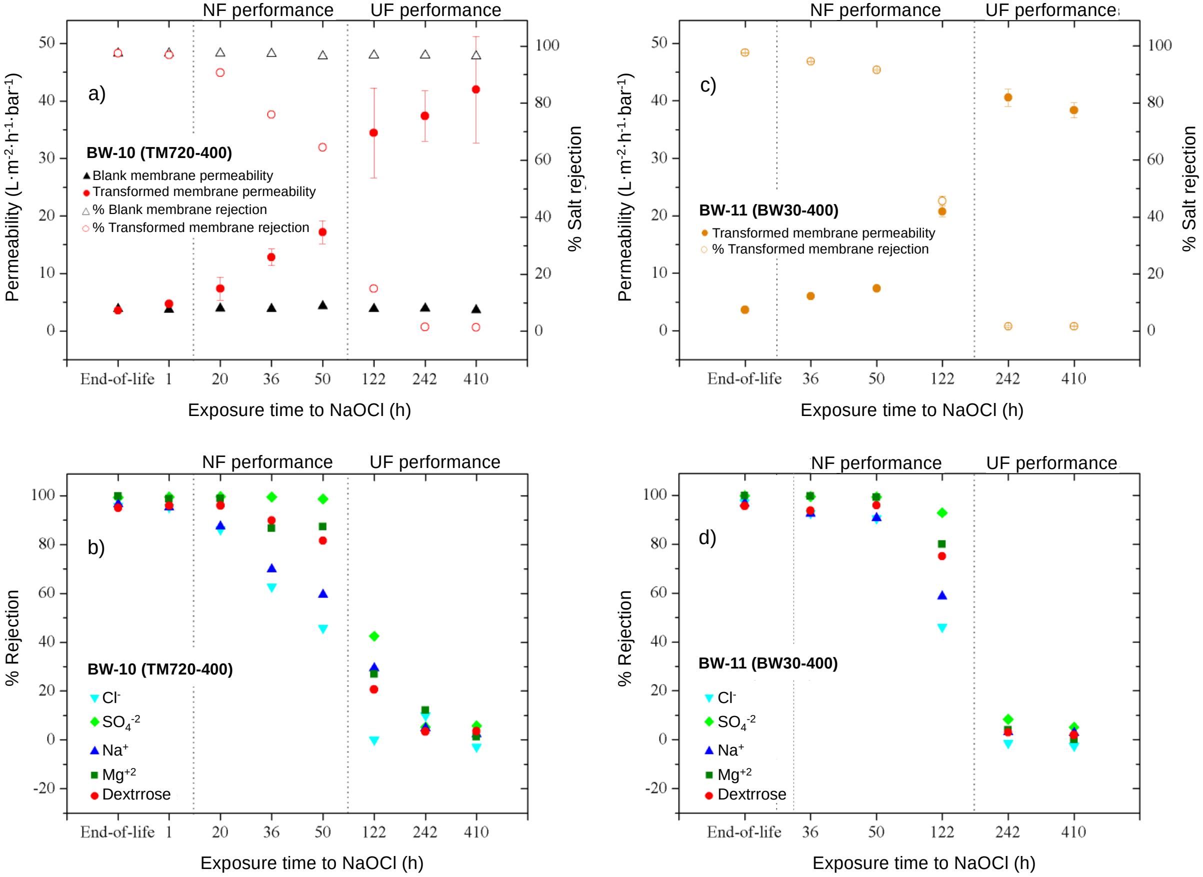


Fig. 18. End-of-life recycled membrane performance. Graphs at the top show permeability and salt rejection coefficients (measured by electrical conductivity). Graphs on the bottom show ion and dextrose rejection coefficients. In case of BW-10, SW-12 and SW-13 membranes, result are shown as average values obtained by repeating the experiments 3 times with 3 different membrane coupons (Paper III © Elsevier).

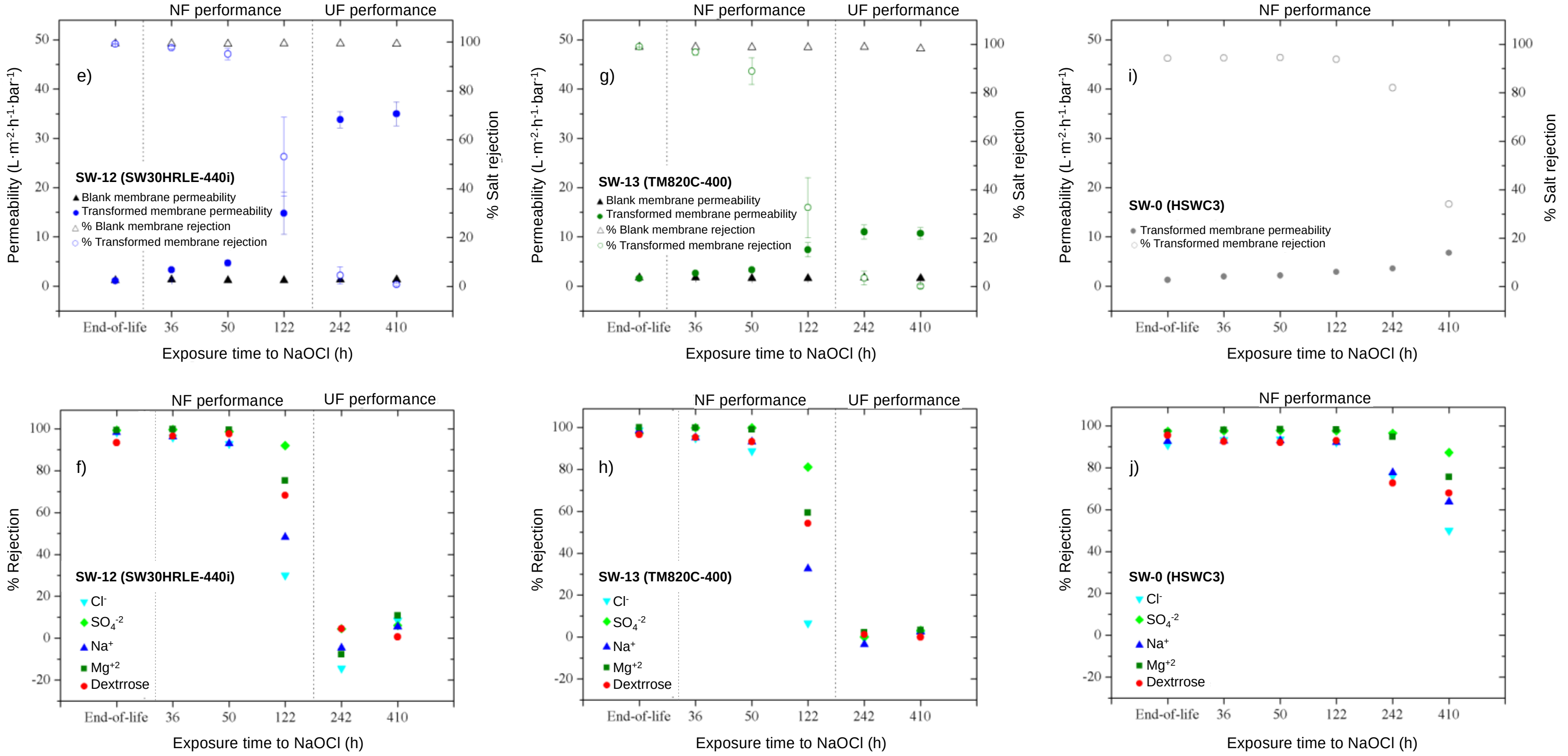


Fig. 18 (continuation). End-of-life recycled membrane performance. Graphs at the top show permeability and salt rejection coefficients (measured by electrical conductivity). Graphs on the bottom show ion and dextrose rejection coefficients. In case of BW-10, SW-12 and SW-13 membranes, result are shown as average values obtained by repeating the experiments 3 times with 3 different membrane coupons (Paper III © Elsevier).

At 50 h exposure time (equivalent to 6,200 ppm·h exposure dose), the permeability of the synthetic BW ranged between 3.32 and 17.17 L·h^{-1}·m^{-2}·bar^{-1}. Once the membranes were transformed, they showed similar performance in terms of rejection coefficients. The lowest rejection coefficients were obtained using the recycled BW10 (TM 720-400) membranes. However, even at this case, the average values were still successful (45.8 % Cl^{-}, 98.7% SO_4^{-2}, 59.4% Na^{+}, 87.3% Mg^{2+} whilst dextrose rejection was up to 81.6%). Hence, results showed that end-of-life RO membranes tested were transformed into NF membranes within the same recycling exposure time range.

Mostly, all the membranes showed an increment in permeability at 122 h exposure time (equivalent to 15,000 ppm·h exposure dose), achieving values up to 34.44 L·h^{-1}·m^{-2}·bar^{-1}. This value could be considered typical of UF membranes or a high permeable NF membrane. However, it is interesting to note that divalent ions were still well rejected. In most of the cases, SO_4^{-2} and Mg^{2+} rejection was higher than 80% and 59%, respectively. For these reasons, 122 h exposure time could be determined as the border line between the recycled NF and UF membranes for all the membranes tested, excepting for the SW-0 (HSWC3) module.

After applying 242 h exposure time (equivalent to 30,000 ppm·h exposure dose), 3 of the 5 commercial membrane brands tested were clearly transformed into UF membranes in terms of permeability. These were BW-10 (TM720-400), BW-11 (BW30) and SW-12 (SW30HRLE-440i). The permeability values achieved were ranged between 33.80 and 40.57 L·h^{-1}·m^{-2}·bar^{-1} (with a relative error less than 10%). The individual rejection coefficients were lower than 17%. In addition, at this transformation condition, SW-13 (TM820C-400) could be contemplated as a low permeable UF membrane.

After applying 410 h (equivalent to 50,000 ppm·h) permeability values were similar to results achieved 242 h for all the cases studied (excepting for HSWC3). SW-0 (HSWC3) membrane showed different behavior within the whole recycling process. After 242 h exposure time, the membrane performance was not equivalent to UF performance. Although membrane was exposed to the longest exposure time, the permeability was still within the NF range. The reasons could be attributed to several factors. In one hand, this membrane could present different PA composition (more resistant than the rest). On the other hand, certain type and degree of irreversible fouling could be present on the surface and it was not detected during the initial fouling characterization.

4.2.4. Comparison between dry and wet storage

Membrane conservation could be a challenge for recycling process. Dry storage simulates the condition in which end-of-life membranes are currently managed for being sent to the landfill (less membrane weight means transport cost saving). Wet storage simulates the ideal condition to preserve membranes after their industrial life has ended and prior to the recycling process.

At laboratory scale only one membrane model (BW-10 (TM720-400) membrane) was used for the comparison between both membrane storage types. Lawler et al. [103] showed the importance of proper membrane storage to maintain hydraulic performance, as the dry membranes results in lower average permeability than the membranes that were stored wet. However, the NaCl rejection coefficients were similar. In the present investigation, in general terms it was observed that wet stored membranes obtained higher permeability values and higher rejection coefficients than dry stored membranes. For these reasons, to guarantee membrane transformation it is essential to keep the end-of-life membranes under wet condition after the industrial process. In fact, for further analysis all membranes were stored in sodium bisulphite or in Milli-Q water.

4.2.5. Confirmation of membrane recycling by surface characterization

Membrane surface characterization was carried out to complement membrane performance results and for better understanding of the recycling process.

- ***Attenuated total reflectance-Fourier transform infrared spectroscopy***

The degradation of the PA layer was investigated by the ATR-FTIR spectroscopy. The most representative peaks of PA were compared with the spectra obtained from the membrane surfaces. Peaks at 1664 and 1542 cm^{-1}, corresponds to amide I and amide II bands respectively, and are mainly associated with C=O stretching and N–H plane bending. The peak at 1610 cm^{-1} is representative of the C=C stretching vibrations from the aromatic amide bonds [32,97,140]. Indeed, all the spectra were normalized to band at 1240 cm^{-1}, which corresponds to phenylene ether stretching vibration because it remains constant during the degradation of PA layer.

Fig. 19 shows a selected range of the spectra for BW-10 (TM720-400) and SW-0 (HSWC3) membranes. The spectra from the end-of-life membranes showed peaks at 1664 and 1542 cm^{-1}. In case of BW-10, the intensity of these peaks progressively were reduced and become nearly zero due to the elimination of PA layer when the exposure time to free chlorine increased from 36 h to 410 h (i.e., from 4,500 to 50,000 ppm·h). The lack of PA signal detection over recycled membranes was also observed in previous works such as Lawler et al. [103] where 300,000 ppm·h was used. In case of SW-0 (HSWC3) membrane a gradual peak reduction was observed, however it did not disappeared completely after membrane was exposed to hypochlorite solution. This fact explains the high ion rejection coefficients (>40%) obtained after 50.000 ppm·h exposure (see Fig. 18-j).

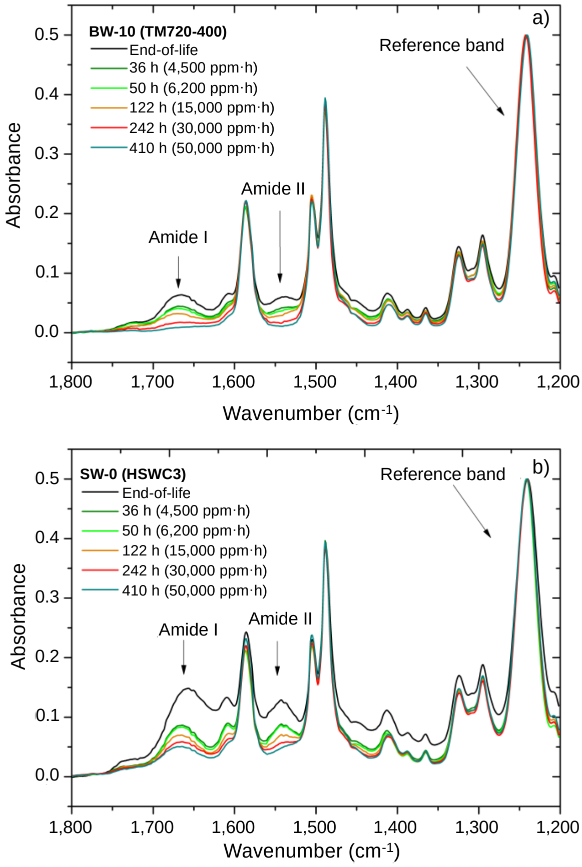


Fig. 19. ATR-FTIR spectra of a) BW-10 (TM720-400) membrane and b) SW-0 (HSWC3) membrane.

• *Scanning electron microscopy (SEM)*

SEM micrographs of the membrane surfaces were taken to verify the existence of pores after high exposure dose to free chlorine. Fig. 20 shows the SEM micrographs of pristine commercial RO (TM720-400 model) and UF PSF membranes. These micrographs had been used for recycled membrane surfaces comparison.

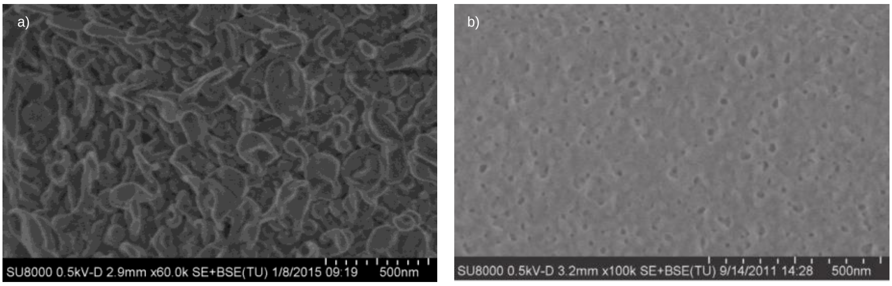


Fig. 20. SEM micrograph of pristine commercial RO (TM720-400 model) and UF membranes [131].

Fig. 21 shows micrographs of two membrane models, TM720-400 (BW-10) and TM820C-400 (SW-13) prior and after have been exposed to free chlorine.

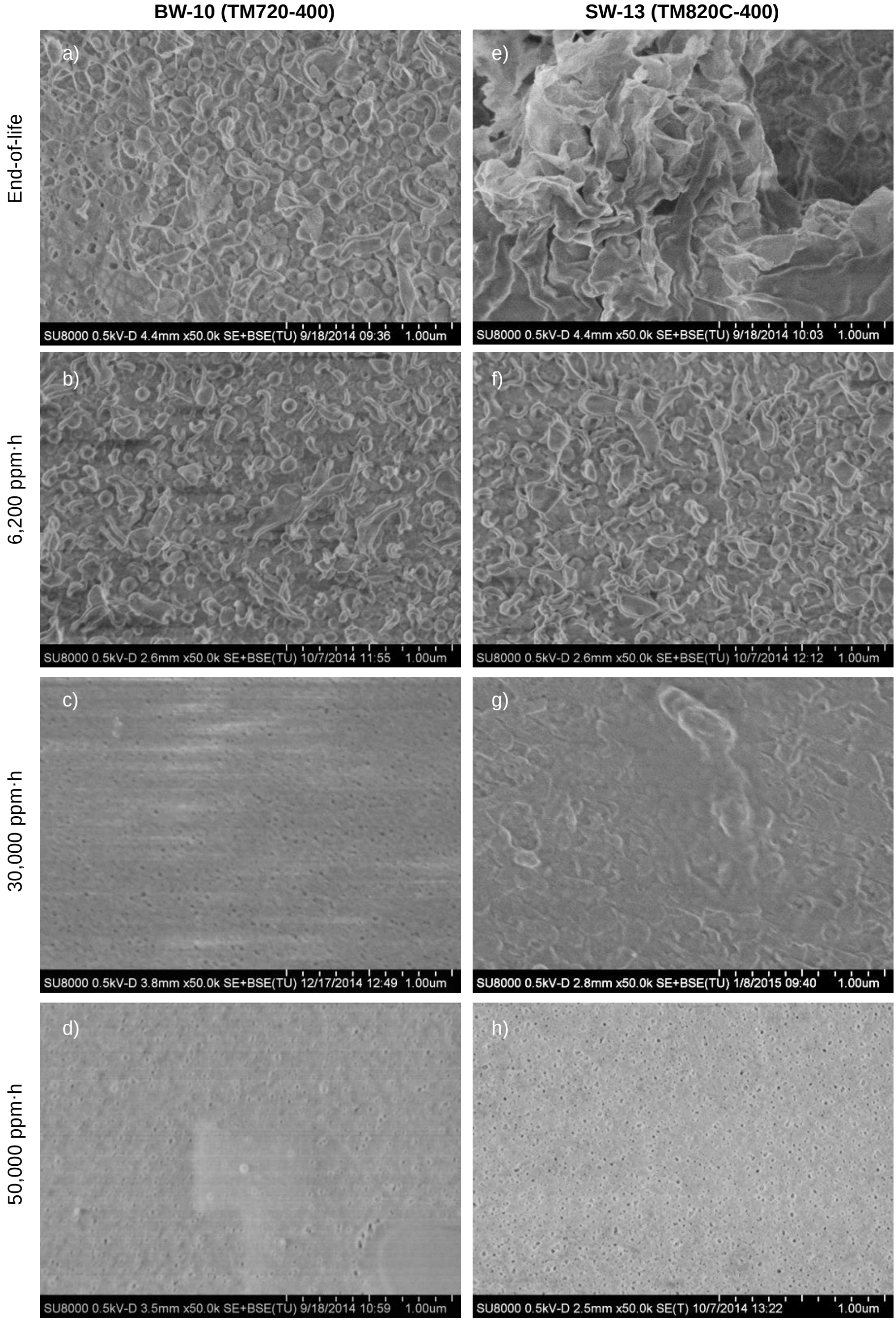


Fig. 21. SEM micrographs of BW-10 and SW-13 end-of-life membranes and recycled membranes exposed to 6,200, 30,000 and 50,000 ppm·h free chlorine (Adapted from Paper IV).

End-of-life membranes were partially (Fig. 21-a) or totally (Fig. 21-e) covered by a fouling layer. Exposing the membranes from 36 to 122 h (equivalent to 4,500 to 15,000 ppm·h) NF recycled membrane surfaces were similar to the TM720-400 pristine membrane surface (Fig. 21-b and Fig. 21-f). At 242 h (equivalent to 30,000 ppm·h) and 410 h (equivalent to 50,000 ppm·h) exposure dose, similar membrane performance and ATR-FTIR results were obtained. However as Fig. 21 shows there was a clear difference in terms of surface properties. At 30,000 ppm·h, SEM micrographs showed pores only in TM720-400 model, whilst at 50,000 ppm·h exposure dose pores were detected in both membrane models (Fig. 21 e and Fig. 21-h) having similar aspect to pristine UF membrane [131]. Same tendency as SW-13 membrane was observed for the rest of the membranes, excepting in case of SW-0 (HSWC3) membranes (see Appendix Fig A2-A4). This could be due to the fact that membrane suppliers do not provide spiral membrane module elements with the same TFC-PA formula.

In case of 50,000 ppm·h exposure dose, pores over the membranes were detected and quantified as Feret diameter (d_F) applying imageJ software to the SEM micrograph. Table 17 shows the average pore sizes obtained. Feret Diameter values are in concordance with Molina et al. [131], who characterized tailor-made UF membranes with high flux and antifouling properties from novel polymers. The analysis of the image surface of SW-0 (HSWC3) membrane could not be carried out because the pores were still not appreciated.

Table 17. Feret diameter values estimated for recycle membranes at 50,000 ppm·h exposure dose.

Membrane	**$d_{F,medio}$ (nm)**
BW-10 (TM720-400)	12.9 ± 6.1
BW-11 (BW30)	11.9 ± 5.8
SW-12 (TM820C-400)	12.8 ± 5.9
SW-13 (HRLE-440i)	14.2 ± 6.9

On the other hand, the cross-section micrographs allow observing the membrane porous structure, which contains some macrovoids. The most significant difference perceived between end-of-life RO membranes was the thickness (Fig. 22). In general, BW membranes have almost double thickness compared to SW membranes and this reality was also observed after chlorine exposure. Probably this difference in thickness may be due to the fact that BW water membranes have been subjected to less pressure than the SW membranes. Beside, this could be one of the reasons that explain the difference in terms of permeability for the both membranes types.

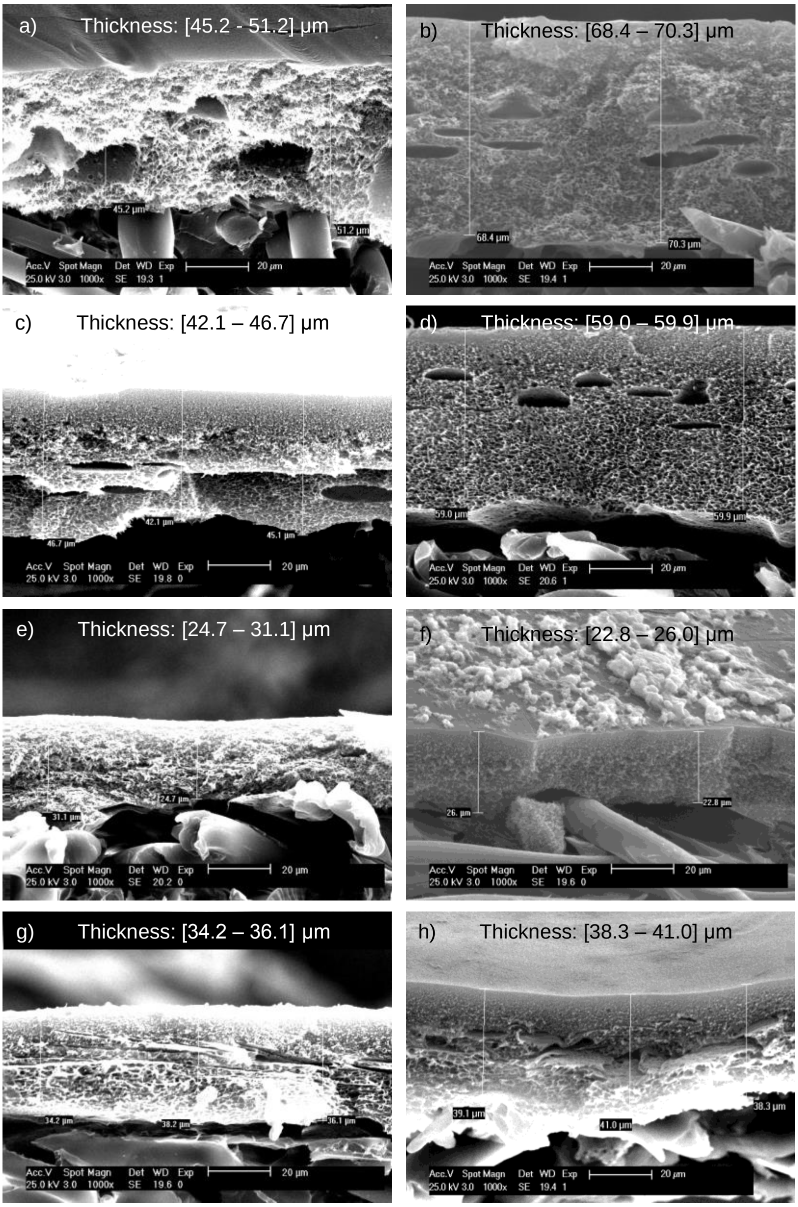


Fig. 22. Cross section of a) pristine RO membrane, b) pristine UF membranes and end-of-life membranes: c) BW-10 (TM720-400), d) BW-11 (BW30-400), e) SW-0 (HSWC3), f) SW-12 (TM820C-400) and g) SW-13 (SW30 HRLE-440i). Moreover, h) shows one example of recycled membrane (SW30 HRLE-440i exposed to 50,000 ppm·h) (Adapted from Paper IV)

- ***Molecular weight cut off***

The MWCO values (molecular weight of PEO 90% rejected) are listed in Table 18. It can be observed that the longer the membranes were exposed to NaClO the higher molecular weight cut-off was achieved. This can be attributed to the level of degradation of PA layer.

At 30,000 and 50,000 ppm·h the MWCO obtained were within the range of the commercial UF membranes. Some of them are listed by Antón et al [51]. Moreover, results are in concordance with other investigations on recycled UF membranes production. In one hand, Raval et al. [102] reported that the MWCO of membranes exposed to free chlorine were comparable to MF/UF membranes. On the other hand, Lawler et al. [90] compared UF recycled membrane performance with three commercial UF membranes (10, 30 and 100 KDa PAL Omega PES). Overall, the UF recycled membranes showed similar rejection coefficients than 10 and 30 KDa membranes.

Table 18. Molecular weight cut-off of different recycled membranes (From Paper IV).

MWCO (g/mol) after membrane was exposed at the following exposure dose:				
Code	**Membranes**	**15,000 ppm·h (122 h)**	**30,000 ppm·h (242 h)**	**50,000 ppm·h (410 h)**
BW-10	TM720-400	<1,000	8,900	22,400
BW-11	BW30-400	<1,000	1,900	10,100
SW-12	SW30HRLE440i	ND	19,000	37,800
SW-13	TM820C-400	<1,000	11,600	20,000
SW-0	HSWC3	ND	<1,000	16,000

4.3. Effect of ppm·h sodium hypochlorite exposure dose in the transformation of end-of-life RO membranes performance

This Section is based on Paper V. According to the results obtained in Paper III, low free chlorine concentration (124 ppm) and exposure time of 50 h (equivalent to 6,200 ppm·h exposure dose) was needed to obtain NF properties. Moreover, UF performance was clearly achieved in most of the cases at free chlorine concentration of 124 ppm and exposure time of 242 h (equivalent to 30,000 ppm·h exposure dose). Since these exposure times are long for being implemented at pilot scale, a further study was carried out fixing both exposure levels to 6,200 ppm·h and 30,000 ppm·h. Three diverse concentrations and exposure times were used (Table 8, Section 3.3.1). Moreover, additional experiment of 300,000 ppm·h exposure dose was tested in order to guarantee that UF performance is reached.

This Section is based on the exposure dose concept (ppm·h). The aim of this study was to determine if high concentration and short exposure times affect to membrane performance in an equivalent way than using low concentration and long exposure times, at the fixed exposure dose. Therefore, exposed membrane process performance was evaluated filtering synthetic BW and SUWW.

4.3.1. Recycled membrane performance at exposure dose of 6,200 ppm·h free chlorine

The ppm·h concept was consistent when a moderate exposure dose (6,200 ppm·h) was applied to produce NF recycled membranes. Considering each membrane brand separately, permeability (Fig. 23) and rejection coefficients achieved (Fig. 24) were similar for all the combinations of concentration solutions and exposure times. These results are comparable to previous works reported in literature, which evaluated the ppm·h concept by using NaClO at 1,000, 3,000 and 6,200 ppm·h [97]. Donose et al. [97] observed that at a fix dose of NaClO at pH 10, permeability was similar in most of the cases (maximum variation ±0,5 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$).

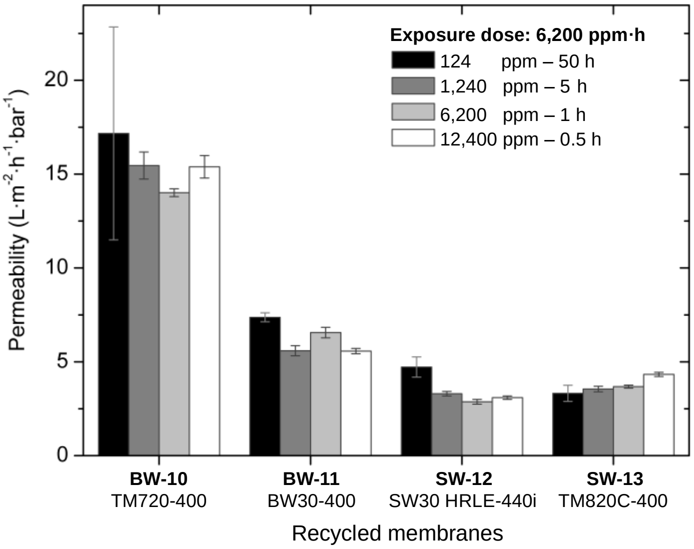


Fig. 23. Permeability of recycled membrane at 6,200 ppm·h exposure dose of free chlorine.

Similar performance was found between pristine commercial membranes (Table 19) and recycled membranes (Fig. 23 and Fig. 24). End-of-life RO membranes that were used to treat BW, achieved performance similar to pristine NF commercial membranes (NF270 and NF90 from Dow) after 6,200 ppm·h free chlorine exposure. Meanwhile, recycled SWRO membranes achieved similar performance to commercial BWRO (e.g., TM720-400 pristine).

Table 19. Pristine membrane performance after filtering a synthetic BW. Results show average value and standard deviation obtained in one experiment.

Pristine membranes	**Perm. ± sd ($L·h^{-1}·m^{-2}·bar^{-1}$)**		**Salt Rejection ± sd (%)**		**Cl^- ppm**	**SO_4^{-2} Ppm**	**Na^+ ppm**	**Mg^{+2} ppm**	**Dextrose. Ppm**
NF 90-400	7.92	± 0.22	90.91	± 0.23	87.5	99.8	87.1	99.7	98.8
NF 270-400/34i	13.34	± 0.57	53.53	± 0.65	42.8	99.6	54.8	86.2	92.4
RO TM720-400	3.85	± 0.21	94.78	± 0.15	93.9	97.8	97.7	99.3	N/A
SW30XH-R-400i	1.25	±0.07	98.45	± 0.35	97.4	99.6	98.3	91.7	97.5

The variability between diverse models was expected since as it was mentioned in Section 4.2., the PA of each membrane model seems to have diverse chlorine resistance. However, a wide range of rejection capability is also found in commercial NF membranes. According to manufacture specifications, rejection values for divalent salt rejection solution range between 50% and >99%, while monovalent rejection capacity is lower (range between 10% and 95%) [46].

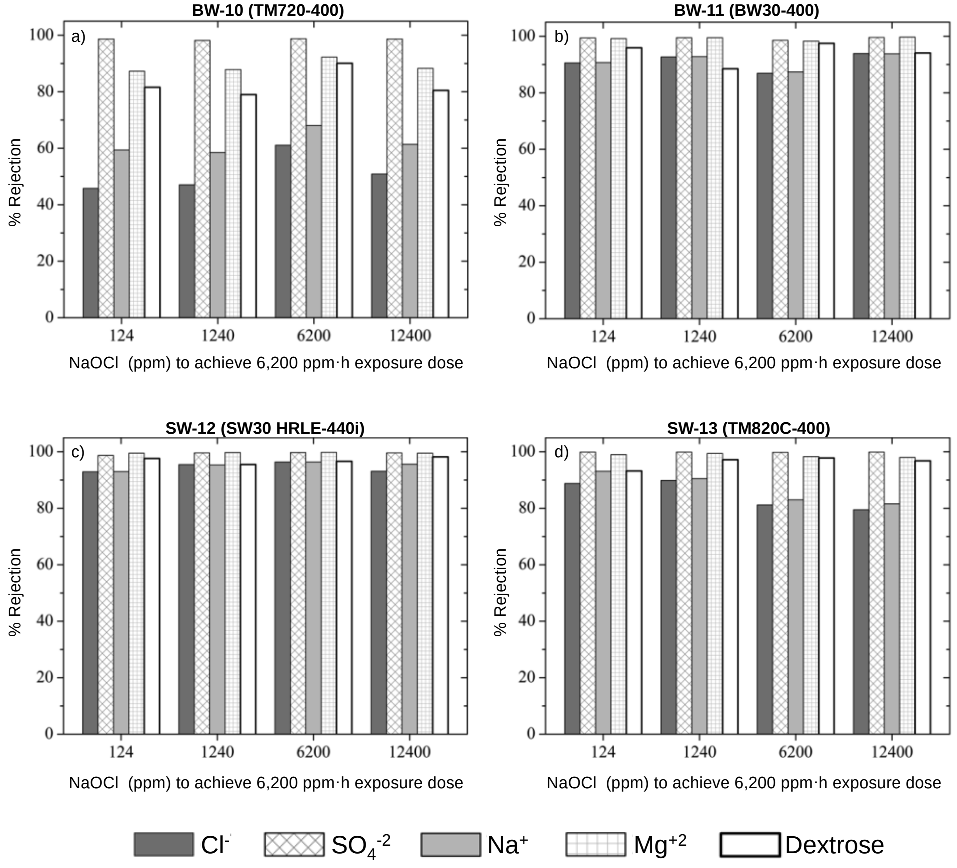


Fig. 24. Rejection coefficients of recycled membrane at 6,200 ppm·h exposure dose.

4.3.2. Recycled membrane performance at exposure dose of 30,000 ppm·h free chlorine

A remarkable variability of membrane performance was observed when fixing 30,000 ppm·h exposure dose. In this sense, ppm·h concept should be carefully used when UF performance is intended to be achieved. Fig 25 shows the permeability values and Fig 26 shows the rejection coefficients obtained. Considering each membrane brand separately, significant differences in membrane performance were observed.

Regarding rejection coefficients (Fig. 26), the lowest values (<5%) were achieved when applying the lowest free chlorine concentration (124 ppm) and the highest exposure time (242 h). Moreover, the permeability associated to < 5% rejection coefficients ranged between 11.03 and 44.55 L m^{-2} h^{-1} bar^{-1} (within the UF permeability range). However, when concentration and exposure time were moderate (1,240 ppm and 24.2 h), rejection coefficients were the highest in most of the membrane brands studied. In addition, when BW-10 (TM720-400), BW-11 (BW30) and SW-12 (SW30HRLE) membranes were exposed to 1,240; 6,200 and 12,400 ppm free chlorine (Fig. 26 a,b&c), the rejection coefficients achieved could still be compared with NF even though membrane permeability values were within the UF range.

As a results show, when ppm·h concept is used there is no a clear concentration and exposure time defining the borderline between NF and UF recycled membrane performance. Instead, it can be said that there is a transitional area between NF and UF, which is limited by the interaction between the exposure time and NaClO concentration.

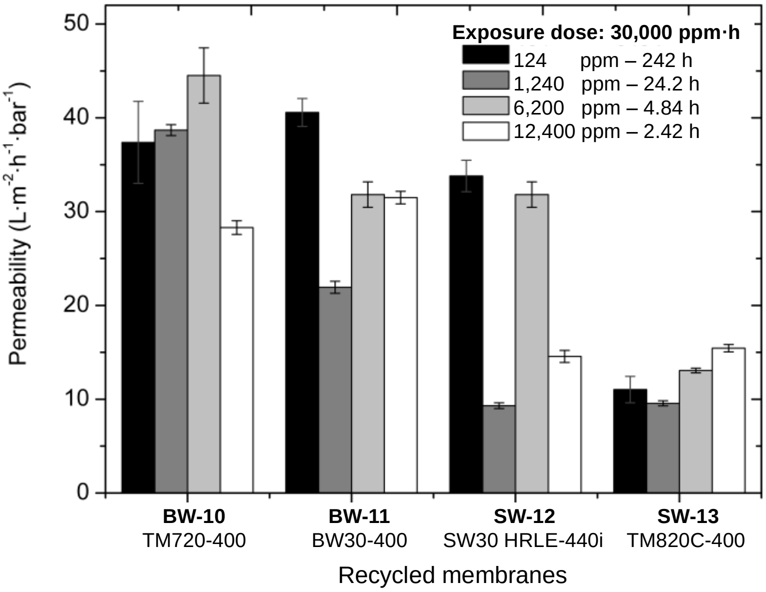


Fig. 25. Permeability of recycled membrane at 30,000 ppm·h exposure dose.

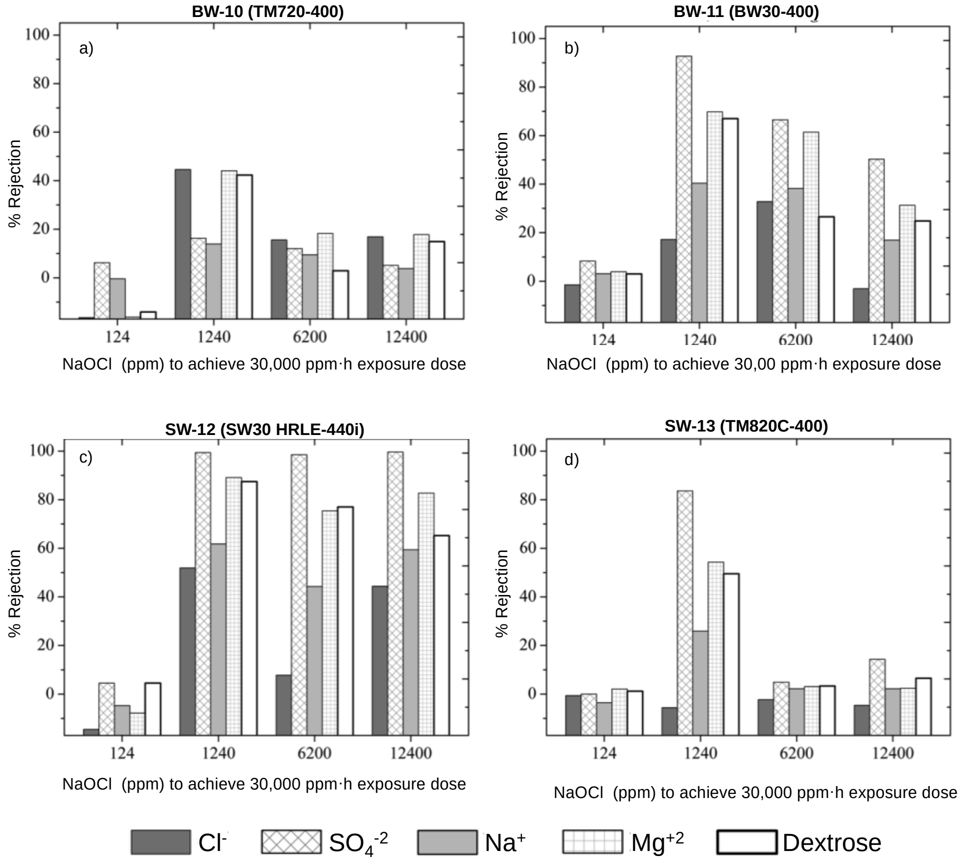


Fig. 26. Rejection coefficients of recycled membrane at 30,000 ppm·h exposure dose.

In order to complement the membrane performance results, further surface characterization was conducted for the BW-10 (TM720-400) membrane. Degradation of the PA layer was confirmed by the ATR–FTIR spectroscopy (Fig. 27). The spectra of the TM720-400 membrane surface showed that end-of-life and recycled membranes had peaks at 1,664 cm^{-1}, 1,542 cm^{-1} and 1,610 cm^{-1} corresponding to amide I and amide II bands and the C=C stretching vibrations from the aromatic amide bonds, respectively [140]). As Fig 27 shows, there are differences between the recycled membranes. It is observed the intensity of the peak signals varied. The lowest concentration and the highest exposure time degraded the most the PA layer. However, at the same exposure dose but using higher concentrations and lowers exposure times, the PA was not totally degraded. In fact for these cases, the peak obtained at 1664 cm^{-1} had similar intensity to the pristine RO membrane.

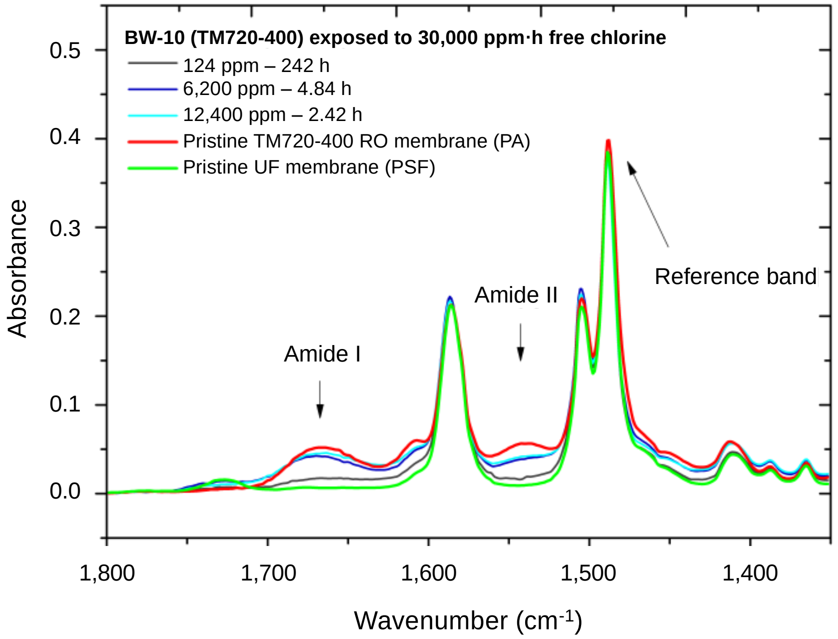


Fig. 27. ATR-FTIR spectra for TM720-400 membrane model (BW-10): pristine membrane, end-of-life membrane and the recycled membranes at 30,000 ppm·h.

Further SEM analysis (Fig. 28) was conducted in order to confirm ATR-FTIR results. As it was expected, micrographs of recycled membranes showed similar morphology to the pristine TM720-400 membrane surface due to the presence of PA. In fact, the lowest concentration (124 ppm free chlorine) and the longest exposure time (242 h) was the unique combination with which pores were detected on the membrane surface (Fig. 28-c).

According to Section 4.3.2, 124 ppm concentration solution could be proposed to be used for end-of-life RO membranes transformation into UF recycled membrane. However, the complete degradation of PA is not guaranteed in all end-of-life membrane models (see Fig. 21 and Appendix Fig A2-A4).

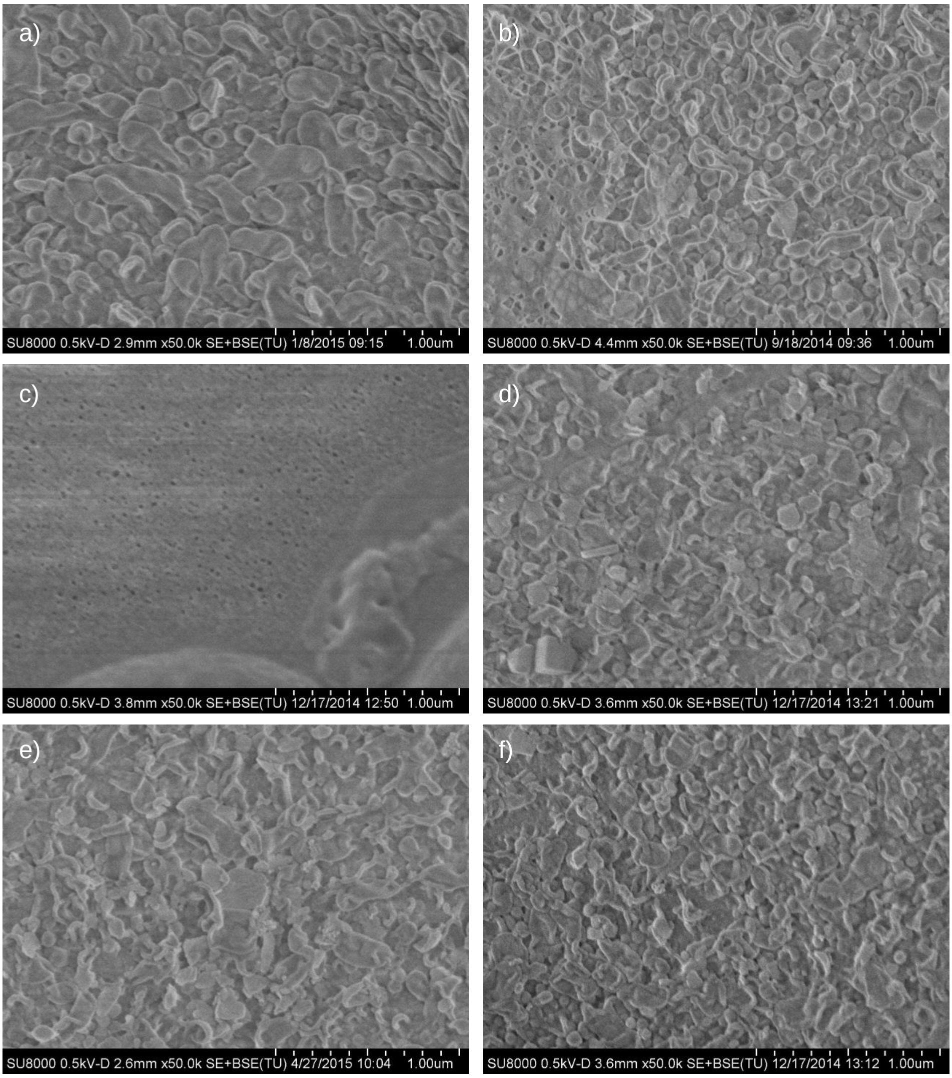


Fig. 28. SEM micrographs of (a) TM720-400 pristine membrane; (b) end-of-life BW-10 (TM720-400) membrane and BW-10 membrane exposed to 30,000 ppm·h free chlorine combining the following variables: c) 124 ppm and 242 h; (d) 1,240 ppm and 24.2 h; (e) 6,200 ppm and 4.84h and (f) 12,400 ppm and 2.42h.

4.3.3. Recycled membrane performance at exposure level of 300,000 ppm·h free chlorine.

Longer exposure dose to free chlorine was studied by using one concentration value (6,200 ppm) and one exposure time (4.84 h), resulting in the 300,000 ppm·h dose. Results show that permeability varied between 13.84 and 86.09 L m^{-2} h^{-1} bar^{-1} (Fig. 29). Moreover, end-of-life RO membranes used to treat BW achieved the highest permeability. Lawler et al. also showed a wide range in permeability values (between 10 and 110 L m^{-2} h^{-1} bar^{-1}) when comparing different recycling membranes [103]. Based on the low rejection coefficients obtained (<5%), a total degradation of PA layer was expected in all membranes.

The differences achieved in permeability values could be attributed to the diverse composition of the PSF support, diverse fouling type (within pores) and different operating pressure condition during the membrane lifespan.

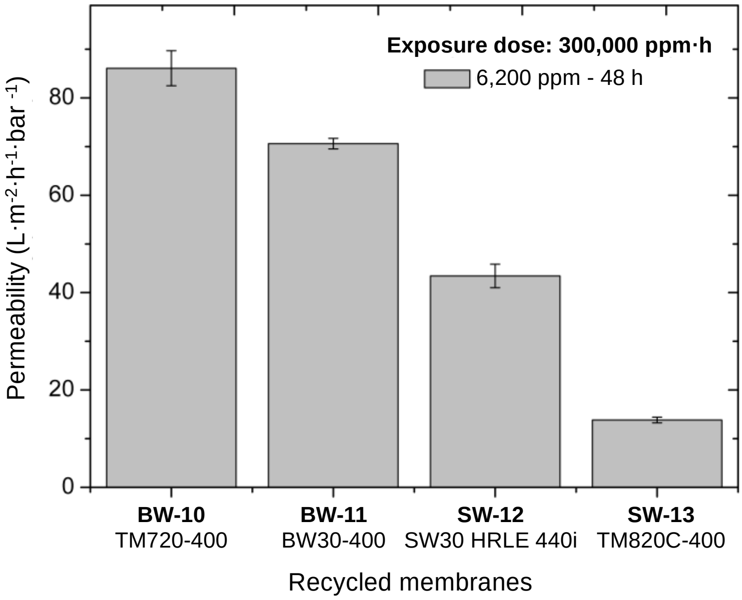


Fig. 29. Permeability values of recycled membrane at 300,000 ppm·h exposure dose.

4.3.4. Validation of recycled membrane process performance

An exhaustive monitoring of recycled NF and UF membrane performance was carried out by filtering SUWW (Section 3.4.1 (Table 11). For these validation assays, only BW-10 (TM 720-400 model) membrane was used since it was the most available model within the membrane stock.

- ***Recycled NF membrane for tertiary wastewater treatment***

End-of-life RO membranes were recycled by using 4,500 ppm·h exposure dose in order to transform them into NF membranes. Fig. 30 shows the permeability and salt rejection coefficient obtained during 24 h of filtration. Recycled membrane permeability was in the range of 3.5 and 6.5 $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$. In addition, permeability increased during the first 8 h of filtration and it remained constant during the following 16 h, even though no cleaning cycles were applied. Salt rejection coefficients oscillated between 88% and 95%. During the first 8 h of filtering time, the salt rejection capability decreased until reaching constant values. Ions rejection coefficients were also evaluated and are presented in Fig. 31. Recycled membrane presented monovalent ion rejection > 80% (Cl^-, Na^+, K^+), polyvalent ion rejection >94% (SO_4^{-2}, Mg^{+2}, PO_4^{-3}) and a total nitrogen rejection >75%. By comparing with the results obtained using end-of-life RO membrane (control membranes), only the divalent rejection coefficients did not vary substantially after the free chlorine attack.

The average rejection coefficients of COD and TOC during the first 3.5 h for the control membranes were 76% and 78%, respectively. In case of the recycled NF membranes, rejection coefficients were 64% and 56%, respectively. Other organic matter rejection values could not be calculated. Under the experimental studied conditions, the turbidity of the solution increased after 4-5 h of filtration probably due to meat extract and peptone denaturation. Consequently, samples had to be filtered through 0.45 µm compromising organic matter determination.

Similarities have been found with Antony et al. [147], who exposed fouled BW30 membrane to free chlorine by circulating 1,000 ppm free chlorine solution during 8 membrane cleaning cycles of 30 min each. Therefore, in this case, the total exposure dose was 4,500 ppm·h. Membrane permeability, measured at the beginning of the fouling cycle was 6 L·h^{-1}·m^{-2}·bar^{-1} and NaCl rejection coefficient was >90%.

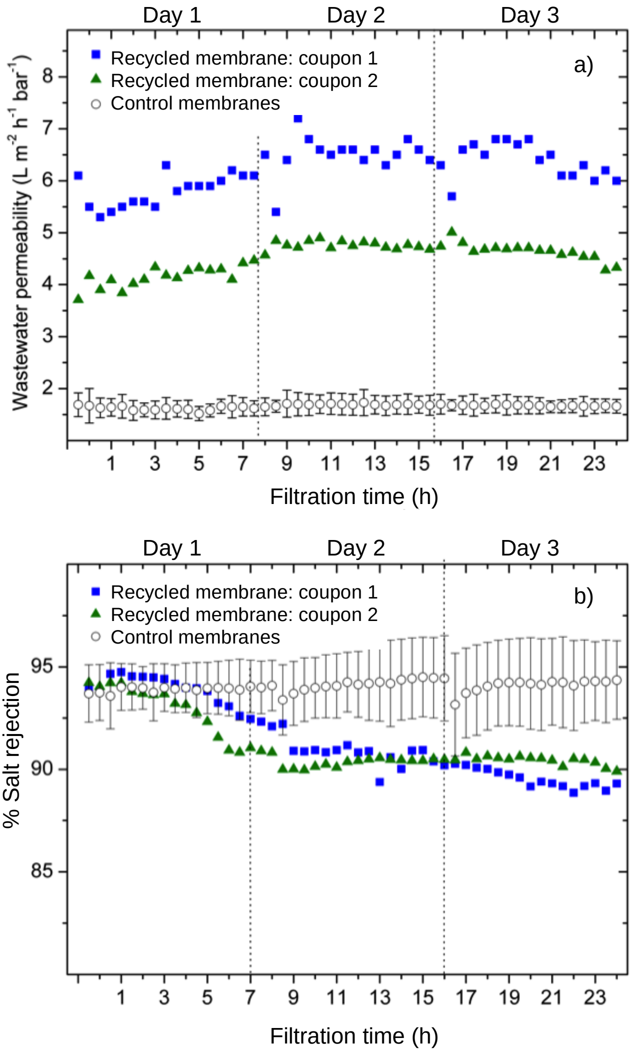


Fig. 30. Validation of end-of-life and NF recycled membranes performance during 24 h SUWW treatment a) Permeability values and b) Salt rejection coefficients.

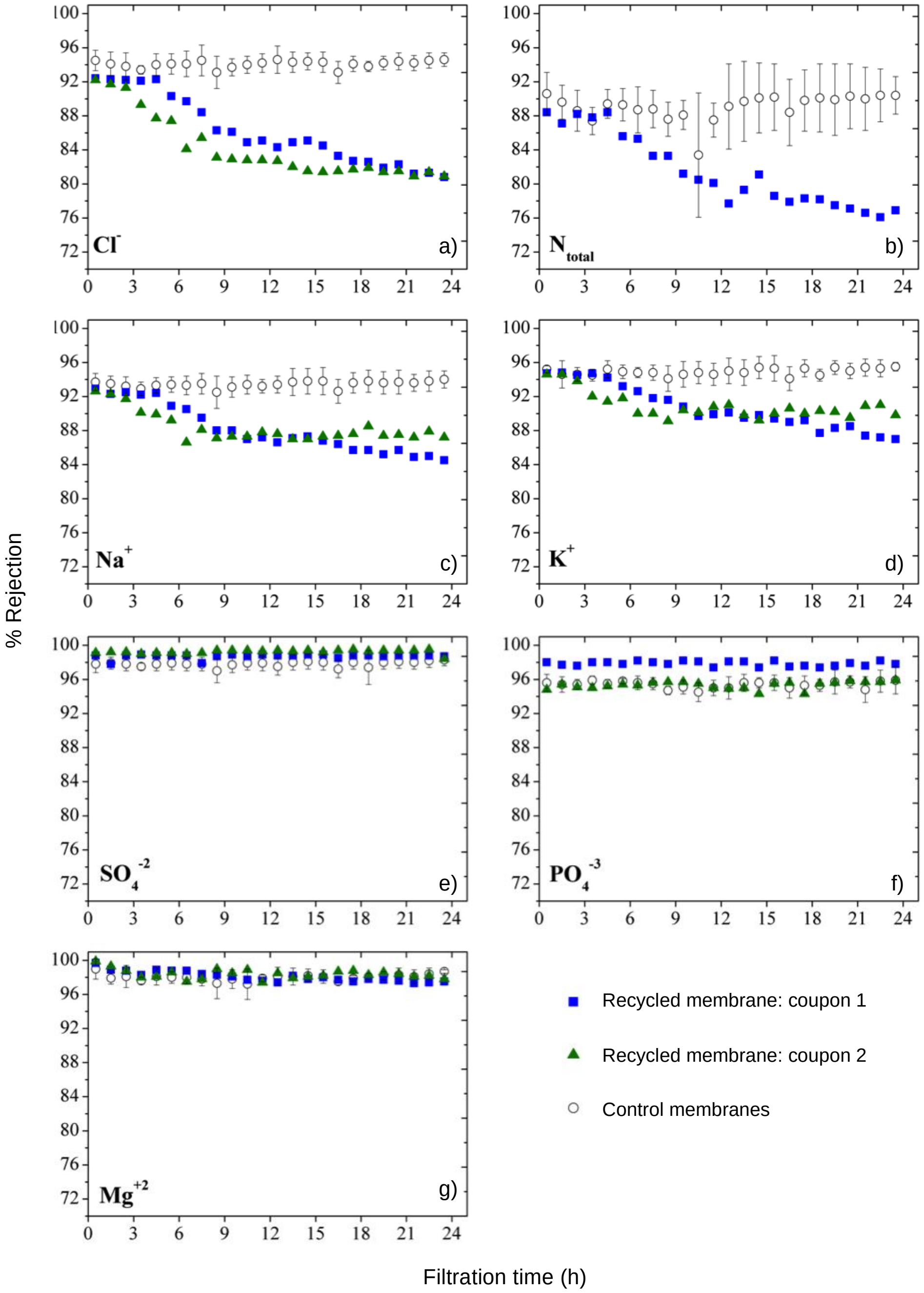


Fig. 31. Rejection coefficients of monovalent ions, divalent ions and total nitrogen for control membranes and recycled NF membranes.

E. coli removal efficacy was calculated as log removal value (LRV) and rejection coefficient (Table 20). Two control membranes and one recycle membrane coupon rejected *E. coli* bacteria totally. However in the rest of the cases, some bacteria were detected in the permeate stream. It is important to note that in all cases the concentration of *E. coli* in the permeate stream did not exceed 10^4 FCU/100 mL. Therefore, reclaimed water would accomplish the bacteria standard set on the European countries legislation (such as Spanish Royal Decree RD1620/2007 [148]) for some uses such us aquifer recharge, forest irrigation with no public access or silviculture.

Table 20. *E. coli* bacteria removal estimated by log removal value (LRV) and % rejection.

Membrane	Coupon	Filtering Time (h)	Log$_{10}$ feed FCU/100mL	Log$_{10}$ permeate FCU/100 mL	LRV	% R
End-of-life RO membrane (Control)	1	8	5.5	0.0	-5.5	100.0
		16	5.8	0.0	-5.8	100.0
		24	5.6	0.0	-5.6	100.0
	2	8	4.9	0.0	-4.9	100.0
		16	8.0	0.0	-8.0	100.0
		24	7.5	0.0	-7.5	100.0
	3	8	7.1	2.1	-5.0	70.8
		16	7.7	1.5	-6.1	80.0
		24	7.2	0.8	-6.4	89.0
Recycled NF membrane	1	8	4.6	0.0	-4.6	100.0
		16	5.4	0.0	-5.4	100.0
		24	4.7	0.0	-4.7	100.0
	2	8	6.2	0.0	-6.2	100.0
		16	6.5	1.8	-4.7	72.5
		24	6.9	2.8	-4.1	59.2

The worst rejection coefficient detected was 59.2% (equivalent to LRV of 4.1). The bacteria detection on the permeate stream could be due to several facts: i) unintentional post-filtration contamination or ii) batch operation condition (filtration plus stagnation) implying that bacteria and nutrients fixed onto the PA layer were stagnated during more than 16 h at room temperature. Bacteria growth may be enhanced and biofilm could be developed, provoking ineffective membrane bacteria rejection with the time. Antony et al. [147] after applying 4,500 ppm·h exposure dose to free chlorine observed LRV values between 4 and 5.5, using MS2 and *E.coli* microorganism. Moreover, bacteria in the permeate stream have been also found in other studies by using commercial NF membranes [149,150].

- ***Recycled UF membrane for tertiary wastewater treatment***

Attending the variable surface characterization results obtained for TM 720-400 membrane model (see Section 4.3.2., Fig. 28), the recycled membrane performance was further studied for its reuse in SUWW treatment. Fig. 32 shows permeability of a pristine UF membrane and one recycled membrane at 300,000. Fig. 33 shows the permeability of membranes recycled at 30,000 ppm·h free chlorine exposure dose. The concentration of free chlorine solutions and exposure times are shown in Section 3.3.1 (Table 8). The main aim of this study was to identify if residual PA layer on the surface of the UF recycled membranes has some positive impact in terms of membrane cleaning.

Recycled membrane permeability to both, Milli-Q and SUWW, decreased constantly over the time. None of the applied cleaning protocols recovered permeability performance to the initial values. However, the commercial UF membrane permeability regained better its initial performance after employing all the cleaning procedures. In addition, reverse flushing using 20 ppm free chlorine provided the worst results. However it should be considered that reverse flushing was applied after three cycles of filtering SUWW, when the membrane was at its dirtiest condition. Table 21 shows the flux recovery obtained for each membrane after applying the different cleaning protocols. More over, in case of using 300,000 ppm·h free chlorine exposure dose, the flux recovery was decreasing in each fouling and cleaning cycle. Therefore, the exposed PSF layer showed more sensibility to the fouling than the membranes with residual PA on their surface. Other authors have also reported fouling propensity of recycled membranes. In one hand, Veza et al. [99] reported that fouling was the most relevant drawback found when reusing recycled UF membrane (spiral wound) to treat wastewater. On the other hand, Lawler and co-workers [103] employed a filtering solution containing BSA, humic acid, alginic acid, colloidal silica and calcium carbonate (20 ppm TOC). It was observed on average that the cleaning process was 92% effective for the commercial UF membrane (10 KDa polyethersulfone (PES), but only 86% effective for the recycled membranes.

Table 21. Flux recovery values of recycled membranes and one pristine commercial UF membrane.

Cleaning type	Flux recovery values defined as the ratio of the pure water flux of the cleaned membranes to that of the initial recycled membrane exposed to:				
	124ppm 242h	1,240ppm 24.2h	6,200ppm 4.84h	6,200ppm 48h	UF 10 KDa,
5min 20 ppm (flushing)	0.50	0.65	0.53	0.60	0.77
1 h 200 ppm (out of filtering system)	0.71	0.65	0.58	0.26	0.91
5 min 20 ppm (Reverse flushing)	0.50	0.46	0.51	0.16	0.59

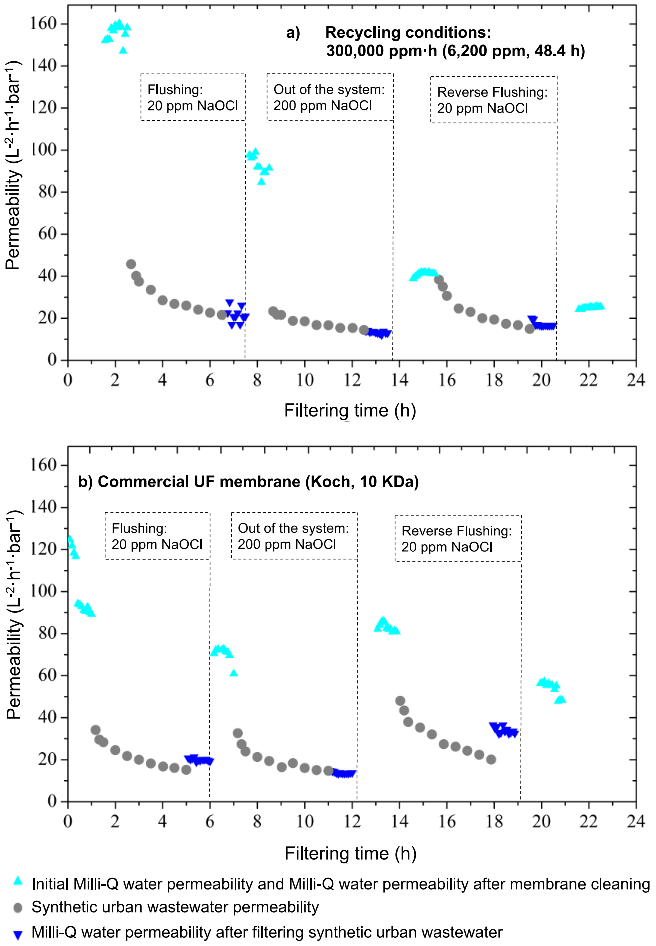


Fig. 32. Milli-Q water permeability of membranes before (light blue) and after (dark blue) treating SUWW (grey). Graphs show results of (a) recycled membrane exposed to free chlorine at 300,000 ppm·h and b) a pristine UF commercial membrane.

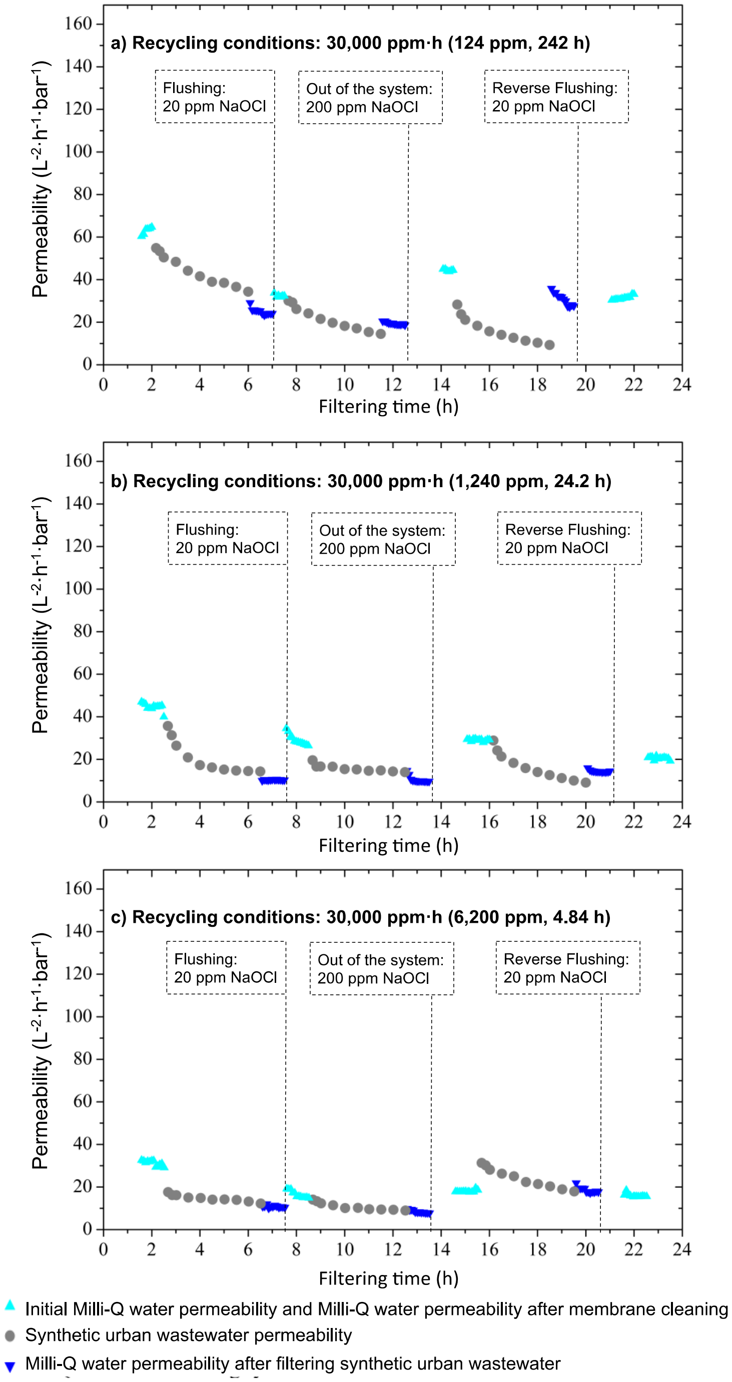


Fig. 33. Milli-Q water permeability of membranes before (light blue) and after (dark blue) treating SUWW (grey). Graphs show results of recycled membrane at 30,000 ppm·h exposure dose. a) 124 ppm free chlorine during 242 h; b) 1,240 ppm during 24.2 h and c) 6,200 ppm during 4.84 h.

As it was expected, residual PA contributes to achieve better ion rejection coefficients. Fig. 34 shows ion and protein (BSA) rejection coefficients of three over the five cases studied (Appendix, Table A1). The recycled membrane at 30,000 ppm·h got better capability of rejection than the commercial UF membranes, even in the case of BSA (> 98%). Meanwhile the recycled membrane at 300,000 ppm·h achieved rejection coefficients similar to the pristine UF membrane. Moreover, the best rejection coefficients were achieved when membrane was recycled using 1,240 ppm of free chlorine during 24.2 h and 6,200 ppm of free chlorine during 4.84 h. These membranes were still able to reject SO_4^{-2} (>85%), PO_4^{-3} (>65%), Ca^{+2} (>47%) and Mg^{+2}(>47%).

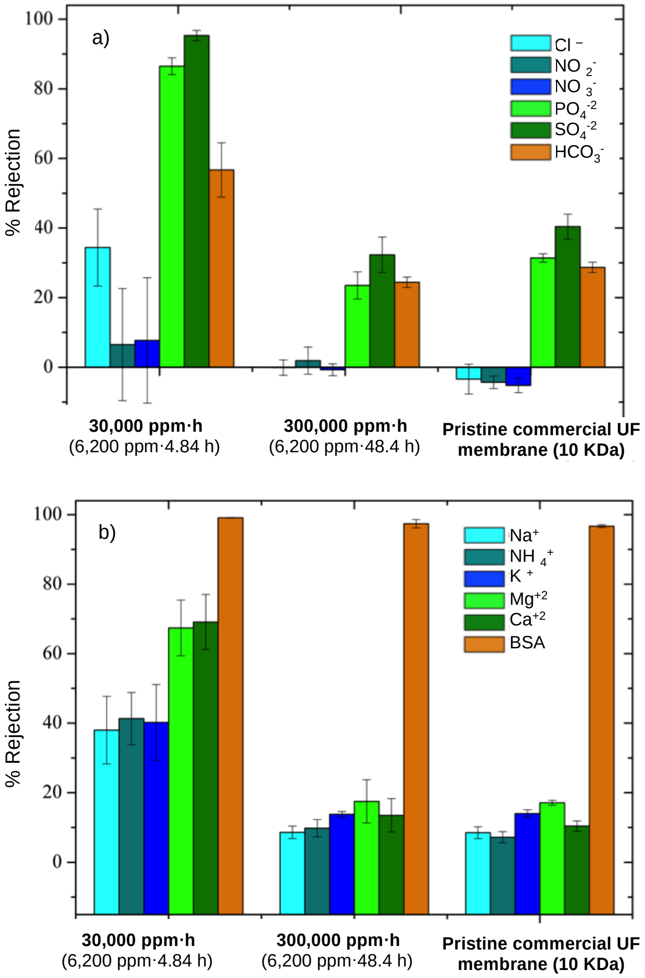


Fig. 34. Rejection coefficient of (a) anion and (b) cation and BSA protein obtained after filtering SUWW solution.

In most cases, no *E. coli* bacteria where detected in the permeate stream (rejection coefficient was 100%), which might indicate that the exposed PSF surfaces delays the biofilm growth over the membrane surface comparing to chlorinated PA (recycled NF membranes). There was only one case (300,000 ppm·h exposure dose of free chlorine) where it was counted 41 FCU per 100 mL in the composite sample of permeate, at the third filtering day (rejection coefficient was 76,6% equivalent to LRV of 5.6). However, when Milli-Q water was filtered prior to conduct SUWW assay, *E. coli* bacteria were also detected, indicating that probably the membrane cell was contaminated when the cleaned membrane was placed again in the filtration system. These results are in concordance with other microorganism removal studies by using recycled membranes. Raval et al. [102] also indicated that end-of-life RO membranes degraded by chlorine exhibit good bacterial separation performance (claiming 4 LRV or >99.99%) and their performance were comparable with pristine MF/UF membrane (Hydranautics HydraCap MF membrane and Zee Weed 1000 UF membrane). Lawler et al. [103] used silver nanoparticle as a model particle to simulate the virus removal of a recycled membrane. Membrane got a 99.62% (or 2.42 LRV), similar rejection than by using a 10 KDa UF pristine membrane (99.75%, or 2.57 LRV).

4.4. Recycling of end-of-life membranes at pilot scale

According to the results obtained at laboratory scale (Paper III, IV and V), it was demonstrated that the controlled exposure dose (ppm·h) of free chlorine let to transform end-of-life RO membranes into NF and UF recycled membranes. Therefore, similar procedure was applied using the pilot system in order to scale up the process to spiral-wound membranes. Thus, a concentration range from 6,000 to 16,000 ppm free chlorine solution was employed in order to use realistic exposure times. Exposure levels previously used at laboratory scale were tested.

4.4.1. Evaluation of recycled membrane performance

Recycled membrane performance was characterized in a cross flow pilot membrane system as it was explained in Section 3.4.2. (Fig. 12). Natural BW was used to determine salt, single ion and organic rejection coefficients (see Table 12, Section 3.4.2).

As well as it was observed at laboratory scale, the SW membrane model available (HWC3, SW-0 and SW-1 cases) offered resistance to the chemical attack by free chlorine. Fig. 35 shows permeability values and salt rejection coefficients obtained. Mean and standard deviation used were calculated by using from one membrane to 8 membranes depending on the stock availability. An exposure range of [33,000-46,000] ppm·h was required to observed NF performance and at around 350,000 ppm·h (same that laboratory scale) exposure dose was needed to reach UF-like rejection coefficients (Fig. 34). However, permeability of these membranes was also < 7 L $\cdot m^2 \cdot h^{-1} \cdot bar^{-1}$, which is lower than UF typical values.

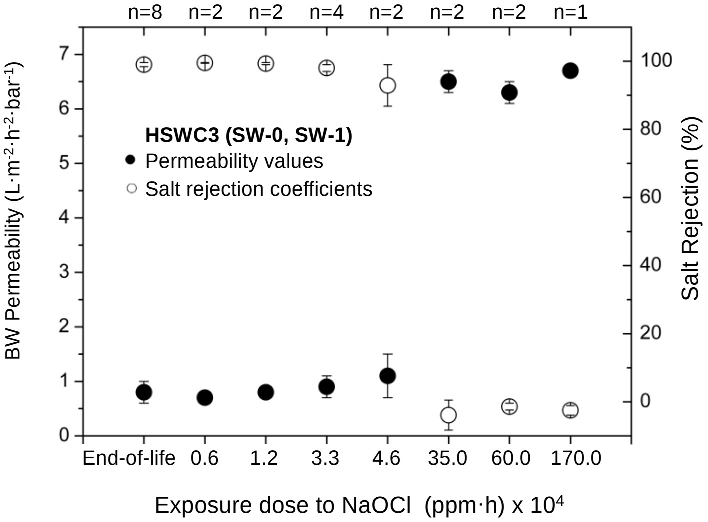


Fig. 35. Permeability and salt rejection coefficients SW-0, SW-1 (HSWC3).

Regarding BW end-of-life membranes, recycling process followed the same trend as laboratory scale. Table 22 shows permeability values, single ion and organic compound rejection coefficients for all the models tested. According to these results, by controlling the exposure dosage (6,200 and 12,500 ppm·h) two kinds of NF recycled membranes can be obtained. Recycled membrane performance was intermediate between the commercial NF90-400 and NF270-400 membranes. Generally, NF recycled membranes showed lower permeability values and higher rejection coefficients than the aforementioned commercial membranes. High selectivity of spiral wound RO membranes exposed to free chlorine up to 4,000 ppm·h (6.9 and 8.0 pH) was also observed by Ettori et al [108]. They reported a fully retention of divalent ions and rejection coefficients >95% in case of monovalent ions.

Table 22. Permeability and rejection coefficients of recycled membranes and pristine NF commercial membranes.

Code	**Model**	**Exposure dose (ppm·h)**	**Replicates (n)**	**Permeability ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)**	**Cl^- (%)**	**NO_3^- (%)**	**SO_4^{-2} (%)**	**Na^+ (%)**	**K^+ (%)**	**Ca^{+2} (%)**	**Mg^{+2} (%)**	**TC (%)**
NF90*	NF 90-400	0	1	4.5 ± 0.0	87.9	51.2	99.9	86.7	85.0	99.3	99.8	91.5
NF270*	NF 270-400	0	1	7.9 ± 0.2	23.0	1.9	99.6	28.7	30.9	73.6	88.8	57.5
BW-4	BW30-400	6,200	1	2.8 ± 0.1	76.8	71.4	87.9	75.4	76.1	89.3	88.5	77.4
BW-14*	BW30-400		1	1.8 ± 0.1	95.8	84.8	99.9	95.3	95.7	99.6	99.5	93.9
BW-7*	SU720-F		1	1.3 ± 0.1	96.1	83.4	99.9	95.4	95.8	99.4	99.8	91.7
BW-9	TM720-400		7	2.6 ± 0.6	86.9 ± 10.8	67.4 ± 17.1	98.8 ± 1.3	86.5 ± 10.2	88.4 ± 8.9	97.2 ± 3.3	97.1± 3,7	83.1 ± 11.0
BW-4	BW30-400	12,500	1	4.4 ± 0.1	44.9	39.1	62.8	44.4	46.1	59.7	58.7	47.9
BW-14*	BW30-400		1	3.8 ± 0.1	56.8	38.6	86.7	60.8	62.5	80.1	78.6	55.6
BW-7*	SU720-F		1	5.1 ± 0.2	71.3	34.8	99.6	70.7	73.5	95.3	95.1	71.3
BW-9	TM720-400		2	4.9 ± 0.3	44.7 ± 4.7	16.9 ± 2.7	95.2 ± 3.4	49.2 ± 3.2	53.9 ± 4.5	82.4 ± 3.8	80.2 ± 5.6	43.4 ± 5.0

* Pristine membranes. NF90 and NF270 were purchased for carrying out the assays, while BW-7 and BW-14 were membranes that have never been installed in the desalination facilities where they came from.

In case of UF transformation, UF performance was clearly achieved by exposing end-of-life BWRO spiral-wound membranes at around 42,000 ppm·h (intermediate to the 30,000 ppm·h and 50,000 ppm·h used at laboratory scale). That fact was observed using BW30-400 model (BW4, BW14), SU720F model (BW-7) and SU720L model (BW-8) (Table 23). Note that permeability values were similar to those observed at laboratory scale for UF recycled membranes.

Table 23. Permeability values of membranes: end-of-life and recycled membranes at 42,000 ppm·h exposure dose.

Code	**Membrane**	**Replicates (n)**	**Permeability $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$**	
			End-of-life	**UF-like recycled**
BW-4	BW30-400	1	2.1 ± 0.1	30.2 ± 0.3
BW-14*		1	1.6 ± 0.0	43.04 ± 0.5
BW-7*	SU 720F	1	1.4 ± 0.1	32.6 ± 0.1
BW-8	SU 720L	1	2.0 ± 0.4	42.3 ± 0.4

* Pristine membranes.

Moreover, permeability values obtained after membranes were overexposed to free chlorine did not show a clear tendency (Table 24). This fact might indicate that PSF layer (below the PA) is not completely affected by the free chlorine exposure. This reality would be favorable in case of scaling up the recycling process to the industrial level, since the production of UF recycled membranes could be conducted within a wide flexible range of exposure dose.

These results are in concordance with laboratory scale results of other authors. Lawler et al. [101] showed that UF membrane recycled at 300,000 ppm·h NaClO presented similar permeability than membranes exposed at higher ppm·h level. Permeability stability has also been reported by Rouaix et al. [109] using UF PSF membranes. However, they reported that long exposure to NaClO would produce chain breaking in the PSF polymer. Regula et al. [151] reported PSF chain breaking and permeability differences when exposing the hollow fibres PSF membranes to NaClO. In addition, Regula et al. [152] also reviewed different studies focused on the action of hypochlorite on the UF membranes. They showed cases where PSF UF membrane permeability increase after free chlorine exposure and emphasized the structural changes in the PSF molecules.

Table 24. Permeability of UF recycled membranes at pilot scale at the exposure doses of 350,000, [600,000-800,000] and 1,000,000 ppm·h. “n” represents the number of modules tested.

		Permeability L·m^{-2}·h^{-1}·bar^{-1}							
Code	**Membrane**	**(n)**	**End-of-life**	**(n)**	**350,000**	**(n)**	**[600,000[a] 800,000[b]]**	**(n)**	**1,000,000**
BW-3	TM720-400	4	2.7 ± 0.7	2	32.0 ± 1.8	2	38.5 ± 3.5[a]	1	43,7 ± 0.7
BW-6		6	2.1 ± 1.2	0	N/A	0	N/A	2	40,9 ± 1.7
BW-9		7	1.8 ± 0.4	0	N/A	3	48.8 ± 1.0[b]	1	44,7 ±1.6
BW-5	SU 720F	1	4.3 ± 0.1	1	28.5 ± 0.4	1	36.6 ± 0.1[a]	0	N/A
BW-7$_{\text{Pristine}}$		2	1.3 ± 0.1	1	31.6 ± 0.4	2	31.0 ± 2.5[a,b]	0	N/A

4.4.2. Confirmation of membrane recycling by surface characterization

In order to verify the complete elimination of the PA active layer SEM analysis (Fig. 36) were conducted for two selected membranes: SW-0 (HSWC3) and BW-9 (TM720-400). Recycling exposure level was >1,000,000 ppm·h. As Fig. 36 shows, pores were detected in both membranes surfaces even though residual fouling remained on the recycled surface. Feret diameters was 11.0 ± 5.3 nm for SW-0 (HSWC3) and 8.0 ± 3.8 nm for BW-9 (TM720-400). These results are in concordance to the laboratory results obtained after 50,000 ppm·h exposure dose (see Section 4.2.5.). Moreover, the spectra of both recycled membranes (Fig. 37) does not show peaks in the corresponding amide I and amide II wavenumber signal. Therefore it is confirmed that the porous PSF layer constitute the active layer or these recycled membranes.

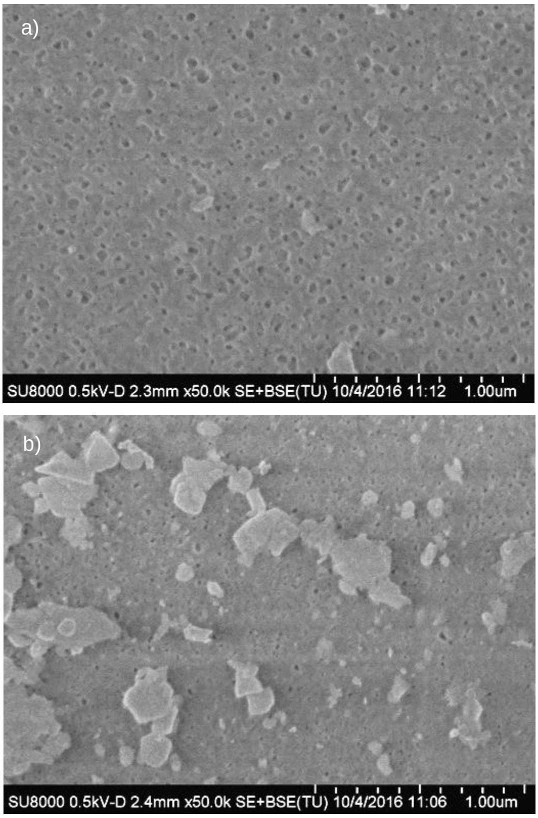


Fig. 36. SEM micrographs of a) SW-0 (HSWC3) recycled at 1,700,000 ppm·h exposure dose, b) BW-9 (TM720-400) membranes recycled at 1,000,000 ppm·h exposure dose.

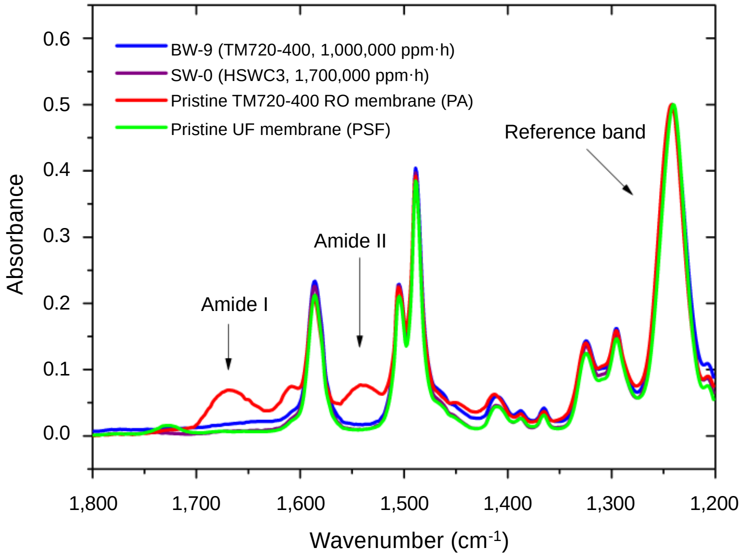


Fig. 37. ATR-FTIR spectra of pristine and recycled membranes at pilot scale.

4.5. Does fouling affect the membrane recycling process?

Performance of same membranes models that were installed in different desalination plants were also compared in order to evaluate how the fouling type can affect the recycling process. In this Section results obtained at laboratory scale (Paper V) and pilot scale (Paper VI) are discussed separately.

4.5.1. Laboratory scale assays

Table 25 shows permeability values obtained in case of three membrane models (TM7200, BW30-400 and HSWC3). Scaling reduces drastically the rejection coefficients as well as increases the permeability rates, which might be due to a mechanical and/or chemical degradation of the PA layer. This was observed in BW-3 (TM720-400 model), which had around 80% weight of inorganic fouling (salt deposition). In this case, the comparison of the membrane process performance with other models was only possible at 300,000 ppm·h exposure dose. The permeability of the UF-like recycled membrane was >2,4-fold higher when the fouling over the membrane was an inorganic clay matrix than scaling (Table 25 case A). Therefore, scaling fouling compromise the effectiveness of the recycling process showing the necessity of applying exhaustive cleaning protocols prior to the free chlorine exposure.

In case of BW30 model (Table 25 case B) two cases with diverse fouling were also studied: BW-11 had inorganic matrix of clay (>80% weight), while BW-4 had mostly organic fouling (>70% weight). Despite fouling nature, initial performance was similar. Besides, when both membranes were exposed to 6,200 ppm·h free chlorine, membrane recycling process worked in both cases and the achieved performance was similar to the pristine commercial NF-90 membrane. Thus, permeability increased around 1.7-fold and rejection capacity decreased less than 7% comparing with the end-of-life membranes values. However, in case of 300,000 ppm·h exposure dose, permeability of the UF recycled membrane that presented inorganic clay matrix was >1.18-fold than the membrane which had organic fouling. Even though permeability varied around 10 L m^{-2} h^{-1} bar^{-1}, the difference within both cases is less pronounced than in the last example (scaling). Therefore, both organic and clay matrix fouling seem not to hinder significantly the recycling process. Organic fouling is degraded by NaClO and therefore, there would not be any resistance for the free chlorine to attack the PA layer. In addition clay fouling is not linked to the PA and it could be removed due to the fact of i) decantation during the transformation process and/or ii) mechanical elimination through the continuous tangential flux during the filtering step.

Finally, end-of-life HSWC3 membrane models that treated SW from Mediterranean (SW-0 from Carboneras desalination plant) and Atlantic sea (SW-1 from Tenerife desalination plant) were also studied. SW-0 membrane had mostly organic fouling (66.3%), while SW-1 membrane did not present fouling over the surface. In these cases, fouling level was the lowest found between all the aforementioned examples and the end-of-life membranes performance could be still considered RO-like. Therefore, similar performance was achieved in most of the cases at the exposure dose tested. As Table 25 (case C) shows, after 6,200 ppm·h free chlorine exposure dose, membranes achieved permeability in the range between 1.72 and 2.93 L·m^{-2}·h^{-1} bar^{-1} and the salt rejection capability was higher than 94%. It is important to note that after 300,000 ppm·h exposure dose, permeability values achieved were around 17 L m^{-2} h^{-1} bar^{-1} in both cases. It might be that the operating conditions such as the TMP used during membrane lifetime compacted the membrane tremendously obtaining very low permeability values.

Table 25. Permeability values and standard deviation of membranes with diverse fouling type before and after being exposed to 6,200 ppm free chlorine.

Code	**Membrane model**	**Fouling type**	**Case study**	**Permeability (L m^{-2} h^{-1} bar^{-1})**		
				End-of-life	**6,200 (ppm·h)**	**300,000 (ppm·h**
BW-3	TM720-400	Scaling & organic	A	6.0 ± 0.2	N/A	35.5 ± 0.2
BW-10		Clay matrix		3.6 ± 0.1	14.0 ± 0.2	86.1 ± 3.6
BW-4	BW30-400	Organic & scaling	B	3.6 ± 0.1	5.8 ± 0.2	59.6 ± 1.5
BW-11		Clay matrix		3.6 ± 0.2	6.6 ± 0.3	70.6 ± 1.1
SW-0	HSWC3	Biofouling & organic	C	1.3 ± 0.1	N/A	17.2 ± 0.9
SW-1		N.D		1.5 ± 0.1	N/A	17.4 ± 0.5

4.5.2. Pilot scale recycling process

At pilot scale, initial characterization of permeability and salt rejection coefficients were conducted within the end-of-life membranes stock. The main objective was to create an end-of-life management route based on the type of fouling and initial membrane performance. In general terms, it was found that when the membrane weight increases, the water permeability increases and the salt rejection coefficient decreases. In this sense, a wide variety of membrane weight and initial rejection coefficients was observed, obtaining salt rejection coefficients from null to >99% and end-of-life membranes weight from 15 kg to 40 kg.

Fig. 38 shows permeability and rejection coefficients for several end-of-life membranes. In case of BW-2 (SU 820-FA, high level of scaling fouling), the membrane performance declined drastically obtaining low rejection coefficients and high permeability rates. In this case direct transformation to UF membrane could be the recycling route recommended. However, it should be considered the need of a previous intensive acid cleaning to reduce the membrane weight. Therefore, membranes that contain high amount of scaling (>30 kg of weight) might not be considered suitable to any direct recycling process. However, indirect recycling or valorization strategies are advised to be explored as disposal alternatives (see Section 2.2.3 “Indirect recycling”).

In case of BW-3 membrane (TM720-400, scaling and organic fouling), membranes showed salt rejection coefficient in the range of commercial NF membranes. In this case, these membranes could be cleaned and reused in NF processes or recycled, transforming them into UF membranes. Finally, in case of BW-4 membrane (organic fouling) and BW-9 membrane (TM720-400, inorganic clay fouling), end-of-life salt rejection coefficients were still acceptable, obtaining values >97%. In this case, the membranes could be reused as RO membranes in processes that require lower salt rejection coefficients than in SW desalination. Indeed, this type of fouling did not provoke difficulties during the recycling process.

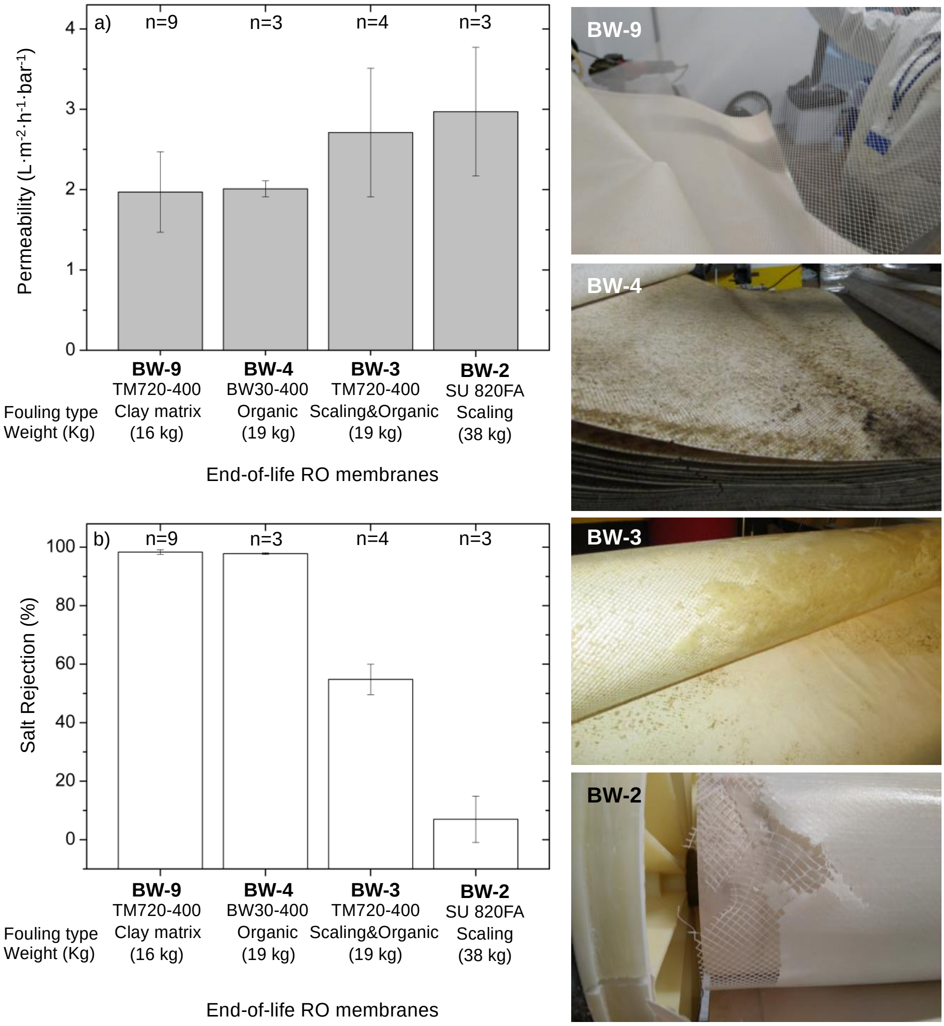


Fig. 38. Examples of membrane fouling and end-of-life membrane performance: (a) Permeability; (b) salt rejection coefficient and weight of four cases of end-of-life membranes (Adapted from Paper II © Elsevier).

4.6. Potential business model on membranes recycling

A potential business model of a recycling end-of-life RO plant was designed (Fig. 39) based on four main pillars: i) the recycling RO plant, ii) the potential clients that could be interested on purchasing the recycled membranes iii) investors and iv) stakeholders. This Section is based on Paper II (book chapter).

4.6.1. Recycling RO plant

Supposing that membrane direct recycling is feasible and expecting that the products obtained would be competitive with the commercial membranes existing on the market, the success of the direct recycling process would depend mainly on the supply and demand. In Fig. 39 a recycling membrane plant is considered. In the business plant developed, the recycling membrane plant is envisaged to be managed by a company from waste management, desalination or membrane manufacturing sectors. The recycling plant would be based on three main eco-innovative selling products: RO, NF and UF recycled membranes. These products could offer modularity, flexibility, smart monitoring, efficient treatment and market diversification with lower cost. Although some research has been developed during the last decade, the membrane recycling plant would improve laboratory and pilot operation conditions and would generate their own know-how for real scale implementation, including patents rights and intellectual property right ownership.

Different business model scenarios could be proposed. In one hand, a centralized business plan scenario may gain interest for membrane manufacture companies or waste management companies. They could collect membranes from desalination plants and generate a stock of recycled membranes with diverse performance. On the other hand, the big desalination companies (Veolia, GE, Doosan, IDE, SADYT, Acciona, etc.) that normally construct, manage and maintain also other industrial plants (such as BW and WW plants) could recycle their end-of-life RO membranes and further re-use them in their own industrial facilities (decentralized scenario).

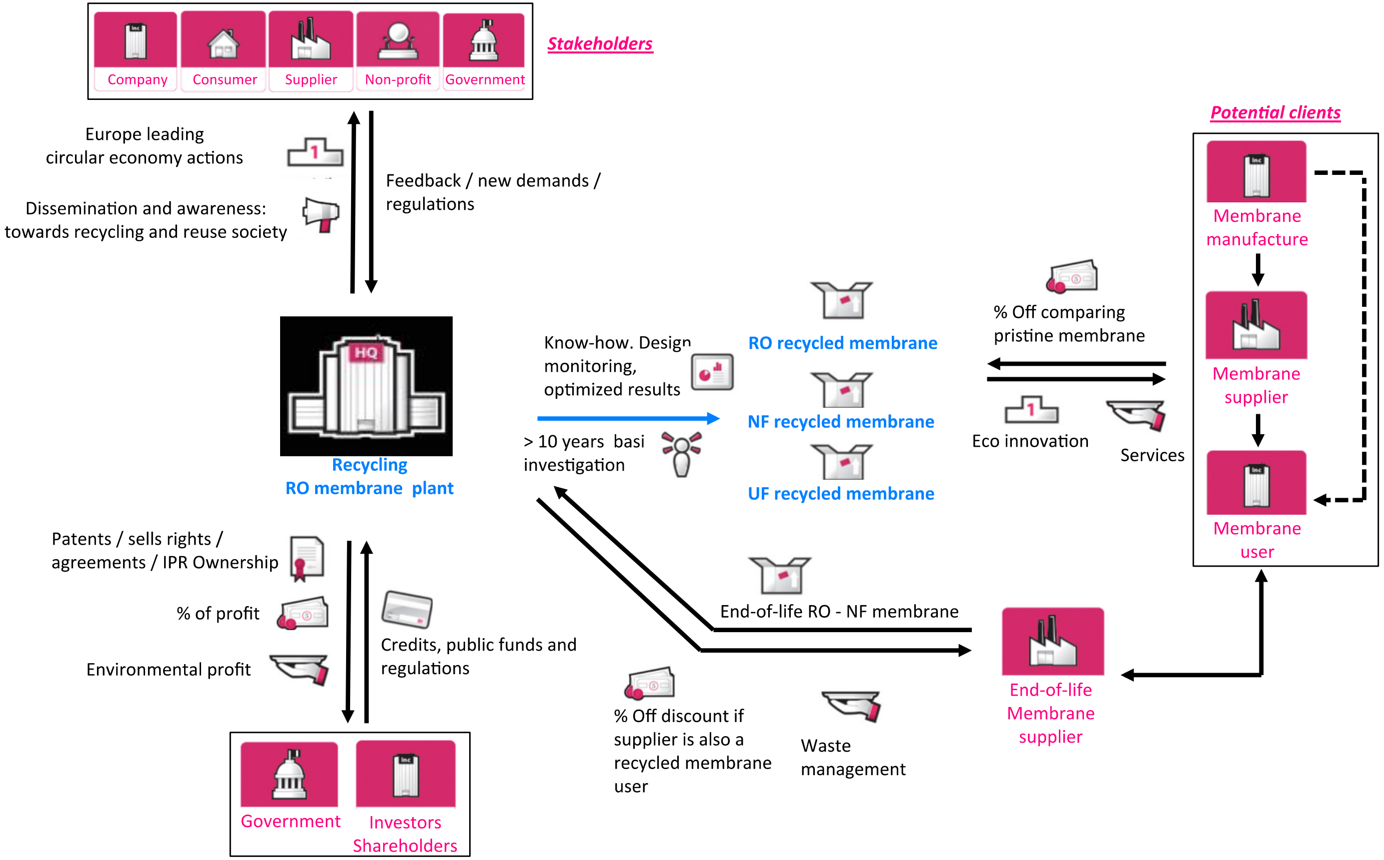


Fig. 39. Potential business model for a recycling RO membrane plant (Drawn using Board of Innovation Tool) (Paper II © Elsevier).

4.6.2. Potential clients

Potential customers have been identified as i) membrane manufacturers, ii) membrane suppliers and iii) membrane users. Membrane manufacturers produce their own membranes. However, including recycled membranes as an “second-hand brand” in their catalogue could increase their product diversification. Indeed, depending on the demand, membrane suppliers could acquire recycled modules for their stocks in order to distribute them to the membrane users. Both, manufacturers and suppliers could offer lower cost products compared to the conventional membranes due to the wide economic margin expected from the recycling process.

Membrane users can be grouped into two sectors: customers interested in long-term and short-term membranes. In the first case, old RO membranes (which still maintain RO performance) could be reused as sacrificed membranes in RO desalination plants placing them in the first or the last position, according to the main membrane fouling tendency. In this scenario, 16%–30% of the membranes used could be second-hand membranes, thereby reducing the replacement cost and reducing the raw material needed for manufacturing new pristine modules. Moreover for longer-term applications, substitution of NF commercial membranes could be considered by recycled NF membranes to treat BW or in other industrial proposes. Finally, recycled UF membranes could potentially be reused as RO pretreatment in desalination process.

In addition, recycled membranes could have a potential use in decentralized WW treatment facilities. As an example, in Spain, nearly 6,000 of over 8,000 existing municipalities are small communities (<2,000 equivalents inhabitants), which have normally WW treatment rates of less than 50% [153]. The implementation of advanced treatment facilities is often hindered due to economic reasons. Small communities do not benefit from the economy of scale effect and thus, implantation and exploitation cost per habitant is higher, being most of the time unaffordable. Under this context, there is a potential market for compact and low-cost WW treatment facilities, where recycled membranes could be used.

The second group of membrane users could be classified as those demanding punctual treatment cases where the low cost of membranes makes their use feasible. In addition recycled membranes could be applied in cases where the water quality with high organic matter content and/or high salinity provoke a rapid irreversible fouling, increasing the membrane replacement rate. Industrial WW from landfill leaches, animal husbandry, textile, pharmaceutical, or food industry are examples of problematic waters. Recycled membranes could assert for temporary treatment solution by using mobile plants or by renting temporary systems.

Other punctual users that could request low-cost membranes are the international cooperation agencies to work on assessing drinking water at both levels: household treatment and conventional drinking water production and distribution, especially in case of emergency response. Common systems deployed for water production and distribution are normally robust systems with easy replacement parts and simple operating technology. Mainly, they consist in batch coagulation and disinfection or sand-active carbon pressure filtration with disinfection. However, these kinds of systems show limitation on the treated water quality. As example, there is an enormous limitation to remove salts, which is a concern in typhoon or tsunami emergencies due to the salinization of water resources. In fact, there is a market behind the emergency response to treat BW and SW using membranes: 3E (SETA), Aquamove™ MORO (Veolia Water), Emergency Service-Mobile Water Services (GE POWER & WATER), Emergency SW 800 (Big Brand Water Filter). Moreover, military membrane purchases in mobile desalinations systems exceeded $15 million in 2004 [154].

It has already been recognized in literature that direct recycled end-of-life RO membranes have the potential to be used in low-cost humanitarian water treatment projects [32]. Moreover, preliminary studies conducted by Life-Transfomem consortium shows that one recycled UF spiral wound module would be appropriate for few families according to the international standard recommendation (15 L/person·day [155]). Indeed, recycled membranes could achieve the maximum microbiological reduction (> 4 Log_{10} reduction for bacteria and protozoa and >5 Log_{10} reduction for viruses) that WHO demands [156].

However, it has to be considered that “second-hand” recycled membranes might not be easily validated for high risk applications such potable water and water reuse in the pharmaceutical sector. Indeed, it is expected that high size desalination plants, which are the major membrane users, are not going to reuse the recycled membrane until guaranteeing zero risk for contamination.

4.6.3. Investors

In order to have a successful market penetration, further financial funds and regulation from governments should be investigated. This could place the products into the market and guaranty their sustainability thanks to the endorsement of the legislation. Some legal actions could promote the usage of recycled membranes such as promoting an environmental tax penalizing landfills option, the implementation of subsidies for recycled membrane users or credits with low interest for investments on recycling plants.

4.6.4. Stakeholders

Even though membrane recycling is demonstrated to be technically feasible, the wider application in industry and the market penetration is strongly dependent on overcoming further technical drawback, market competition and social barriers.

- ***Technical drawback***

The main drawback expected for recycled membrane technology would be similar to conventional membranes, such as the energy required for the filtration process [10], fouling [152], cleaning and concentrate stream management [13].

- ***Market competition***

RO technology dominates the desalination field and its market is well established. 65% over the total capacity correspond to RO membranes technology implementation [5]. The recycling membrane plant would receive end-of-life RO membranes after have being operating during 5 to 10 years in average. By this time, new enhanced membrane models could be implemented in the market. Therefore, recycled RO membranes would have to compete with the improved commercial membrane performance.

The successful implementation of NF mainly relies on its rejection capabilities, especially for divalent compounds. Even though NF process represent only the 2% of the installed desalination capacity at worldwide for BW treatment [5], it has numerous applications in other areas such as WW treatment, pharmaceutical and biotechnology, and food engineering [46]. Van der Bruggen et al. [48] described the need to improve NF membranes as the reduction of membrane fouling, increase in separation and rejection efficiency, membrane lifetime and chemical resistance. To achieve this improvements, diverse innovative methods in NF fabrication are being investigated [46]. However, thin film NF membranes obtained through interfacial polymerization method is expected to remain the benchmark in development of NF membranes in the upcoming years [46]. This is the same methodology used to create RO membranes. Therefore, end-of-life RO membrane that were recycled into NF membrane would find a relative market niche.

Nevertheless, the greatest implementation challenge is related to the UF membrane market. Spiral wound UF recycled membranes have to compete with hollow fiber, tubular and flat geometries. Between all, hollow fiber and spiral wound are still the most common used configurations for many industrial applications, such as milk and water filtration due to their low investment and energetic cost [152]. Improving antifouling properties of UF recycled membranes would give them a value chain and reinforce their position in the market.

Polymeric membranes account for 80%–90% of the global treatment capacity [152]. However, the demand of ceramic membranes is continuously showing an upward trend being expected an annual growth of 12% between 2015 and 2020 [157]. Therefore, they could also be big competitor for polymeric membranes such as the recycled UF membranes. In fact, companies such as Veolia (CeraMem®) and Nanostone (CM-151™) provide ceramic membranes.

• ***Social barriers***

Besides the technical and market barriers, social acceptance and regulatory support is crucial in order to have an attractive and successful second-hand product in the market. Recycled membranes have to demonstrate several key capabilities, such as safety (no traces of harmful compounds in the membrane), excellent removal, low prices, lower and/or similar energy consumption and similar lifetime as compared to the homologous RO, NF and UF commercial membranes. On the other hand, health risk assessment should also be conducted and strict validation methods should be applied in order to guaranty minimum risk of failure during the treatment process.

Chapter 5: Conclusions, Future Work and Research Directions

5. Conclusion, Future Work and Research Directions

In this Section it is summarized the conclusions of the Thesis study and it is proposed additional future work and research challenges to be faced.

5.1. Conclusions

The main aim of this study was to identify the conditions (agent, concentration, exposure time and pH) required to transform end-of-life RO membranes into recycled NF and UF membranes at laboratory scale and, to extent the process at pilot scale. Overall, this work shows that the recycling methodology employed (passive immersion) is a feasible alternative to end-of-life RO membranes landfill disposal.

The conclusions of the Thesis are described as following,

Does direct passive recycling methodology work using NaClO?

Results (Sections 4.2. - 4.4.) showed that NaClO was an effective reagent for membrane recycling, transforming successfully end-of-life RO membranes into NF and UF membranes. It was shown that free chlorine attacks the RO selective layer. Controlling the exposure dose allowed a partial or total degradation of the aromatic PA polymer. At a fixed free chlorine concentration, the longer the membranes were left immersed in the solution, the higher permeability values and lower rejection coefficients were obtained. However, it was observed that PA of SWRO membranes resist more the chlorine attack than BWRO membranes. Thus, permeability values achieved after the recycling process were usually higher in case of transforming BWRO membranes than in case of SWRO membranes.

Can the ppm·h concept be used freely in the recycling process?

At laboratory scale (Section 4.3.), it was observed that ppm·h concept was consistent for NF transformation conditions for each membrane model type. Therefore, at 6,200 ppm·h exposure dose set, similar performance was observed on membrane coupons regardless of the combination of exposure time and free chlorine concentration. However, results also showed that ppm·h concept should be carefully used for transforming RO performance into UF performance. This specially becomes critical when approaching the transition properties between UF and NF membranes. For example, fixing 30,000 ppm·h exposure dose, pores were observed when end-of-life BWRO (TM720-400 model) was exposed to 124 ppm free chlorine solution during 242 h. However when end-of-life RO membranes were exposed to higher concentration (1,240, 6,200 and 12,400 ppm free chlorine) and lower exposure time (24.2, 4.84 and 2.42 h), no clear UF properties were achieved, observing both NF and UF membrane performance. For this reason longer exposure dose (300,000 ppm·h) was chosen to guarantee UF conversion.

Can recycled membranes achieve similar process performance than commercial NF and UF membranes?

In Section 4.3., it was concluded that recycled membranes showed permeability values and rejection coefficients comparable to commercial membranes. End-of-life SWRO membranes achieved similar performance to pristine BWRO membranes. In addition, when end-of-life BWRO membranes were recycled into NF membranes at pilot scale (Section 4.5.), intermediate performance between NF90-400 and NF270-400 commercial membranes were found. At last, UF recycled membranes also showed similar behavior than a commercial 10 KDa UF membrane (Koch) when filtering SUWW.

Overall, the competitiveness of the recycled membranes in the market would be determined not only by the membrane process performance but also by other key factors such as the membrane lifespan, cleaning, cost and market-social acceptance.

Is the recycling process scalable?

At laboratory scale transformation assays were conducted in 216 cm^2 flat sheet coupons, whilst at pilot scale spiral-wound modules were used (37 m^2 in average of membrane surface). The results summarized in Section 4.4. have shown that the recycling process at pilot scale required exposure doses (ppm·h) similar to those used at laboratory scale. However, it was demonstrated that membrane recycling is not a standard process. Consequently, a roadmap (Fig. 40) has been created taking into account i) the RO membrane design (BW or SW); ii) the initial rejection coefficients of the end-of-life membranes and iii) the effect of the combination of free chlorine concentration and exposure time observed on membrane performance at laboratory scale. Therefore, Fig. 40 shows the exposure level dose proposed in order to cover a wide concentration range of 100 to 16,000 ppm free chlorine.

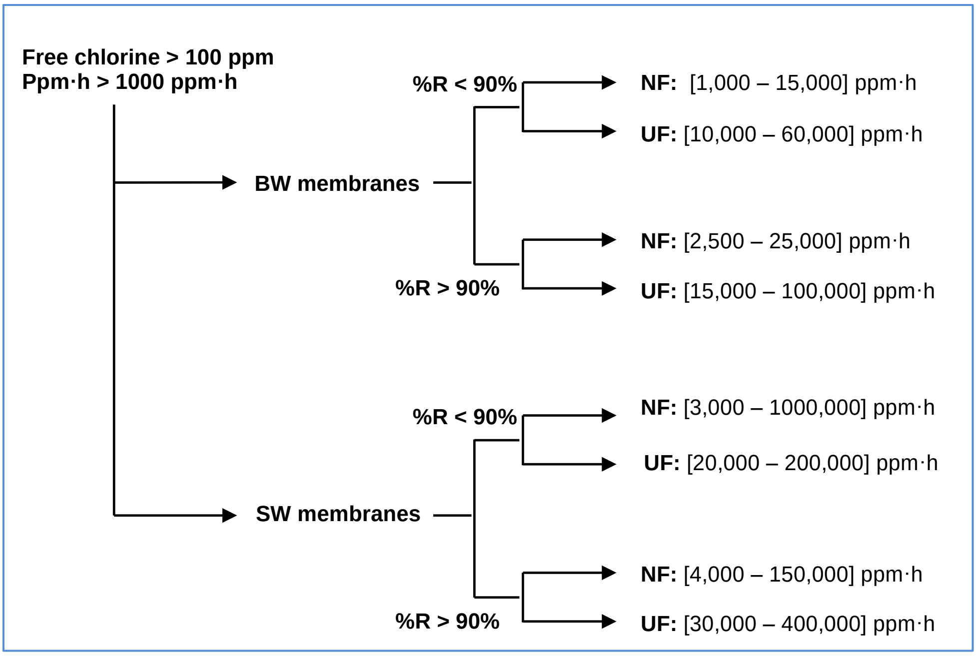


Fig. 40. Exposure dose of free chlorine roadmap to direct membrane recycling (from Paper VII, patent).

How does the fouling affect the recycling process?

At it was observed during the membrane autopsies and fouling analysis (Section 4.1.), fouling type affects the end-of-life membrane performance differently. Therefore, membrane weight and initial performance characterization (permeability and salt rejection coefficients) is useful to assess potential waste management options (i.e., cleaning, direct or indirect recycling, reuse, valorization or landfill disposal).

In addition from a comparative analysis conducted in Section 4.5., it was concluded that biofouling, organic fouling and clay matrix are the type of fouling that alter the less the recycling process. In fact, results showed that end-of-life membranes could be transformed with no previous cleaning step. Nevertheless in case of having fouling of clay matrix nature, fouling still remained on the membrane surface at pilot scale transformations after the free chlorine exposure.

Moreover, when the nature of fouling was scaling, recycled membrane performance varied more significantly obtaining, generally, lower permeability values. In addition, the exposure to NaClO did not remove the precipitated salts at all. Hence, scaling remained onto the membrane offering water resistance. To avoid this fact, an initial intensive chemical cleaning could be helpful, allowing a better interaction between the PA and the hypochlorite ion once the fouling is removed. Nevertheless, it should be considered that the addition of cleaning step would increase the total recycled membrane cost. In this way, membranes fouled by scaling that overcome 30 kg weight should not be considered to direct recycling.

5.2. Future Work and Research Directions

The initial membrane performance of end-of-life RO membranes varies significantly depending on their fouling degree or damage level. Therefore, more research on identifying alternative end-of-life membrane management routes is still necessary. The weight of end-of-life membrane can be used as a low-cost indicator of the fouling degree. However, it is not accurate enough and further characterization methods are usually needed. In-situ membrane rejection coefficient measurements during their operation in the desalination plant could provide reliable information for the decision making of end-of-life membrane management. In addition, identification tools such as online MemEol tool can help to promote better practices in the desalination industry by helping users to identify and select the optimum end-of-life options for their RO membranes. This tool could be updated by including valuable complementary information such as divalent and organic matter rejection coefficients and end-of-life membrane weight.

Membrane recycling process shows very promising results. However, the research regarding membrane recycling is relatively new and further studies are encouraged. In this Thesis, it has been confirmed the importance of proper storage of end-of-life membranes to maintain their properties. In addition, it has been demonstrated the feasibility of direct recycling membranes by using NaClO. However, the secondary effect of the organic matter reaction with free chlorine, the toxicology effect and how to treat this potential waste have not been studied yet. New chemicals can be investigated for membrane transformation and also for improving antifouling properties of recycled membranes. In addition, indirect recycling methodologies can be considered as the step to be followed after direct recycling. The deconstruction of the spiral wound modules could be also part of new research lines focused on re-using plastic parts or the development of new membrane configurations.

Moreover, Life Cycle Assessment (LCA) as well as the economic and financial studies of the recycling process should be further pursued.

Chapter 6: References

6. References

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Appendix

Fig A.1. shows surface characterization to complement the membrane performance results obtained in Section 4.2.2. (Effect of NaClO exposure time and pH on dry stored TM720-400 membrane performance). Non of the cases shows pores on the surface and indeed, the ATR-FTIR spectra confirm that there is still PA on the membrane.

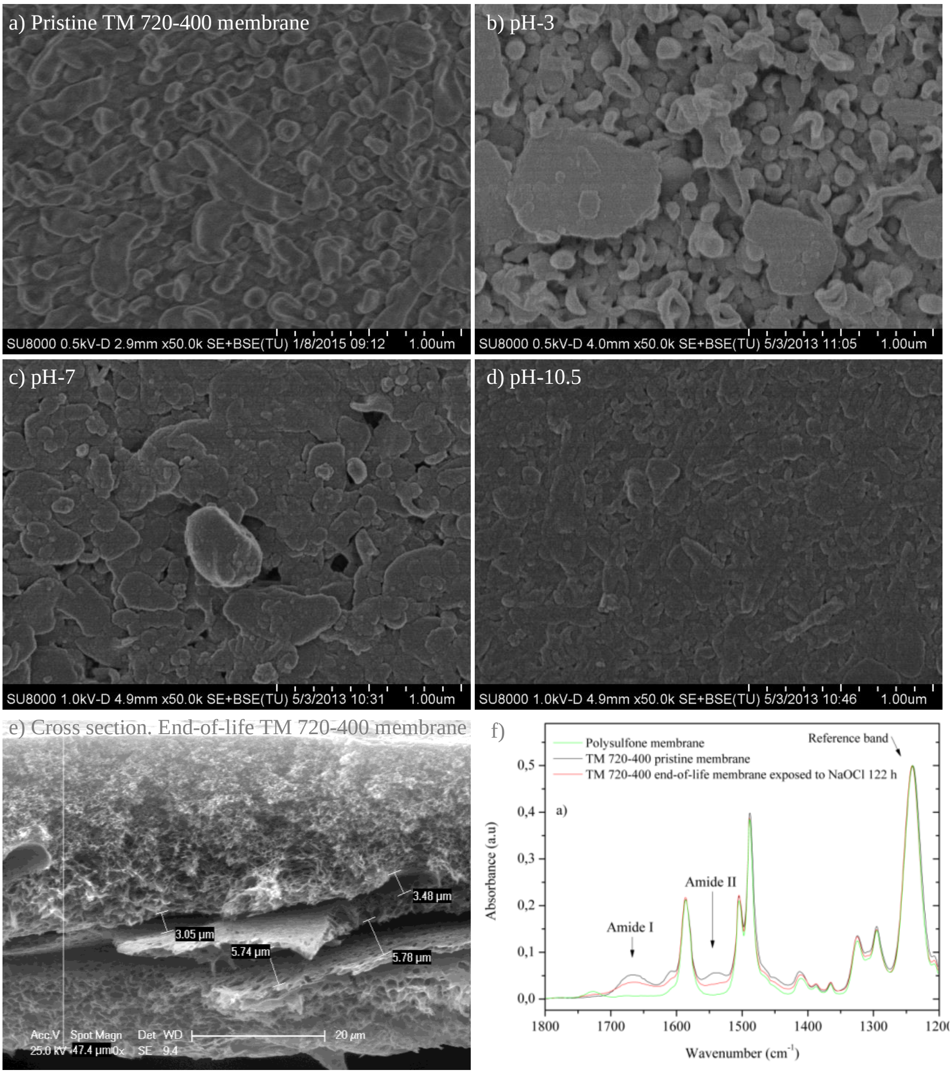

Fig. A.1. Surface characterization of TM720-400 membrane (dry stored). SEM images of a pristine membrane (a), exposed membranes to NaClO at 122 h at pH-3 (b), pH-7 (c) and pH-10.5 condition (d), cross section of end-of-life membrane (e) and ATR–FTIR spectra (f) for an end-of-life membrane, a transformed membrane and a pristine polysulfone membrane.

Fig A.2. shows SEM surface micrographs to complement the results discussed at Section 4.2.5. (Confirmation of membrane recycling by surface characterization).

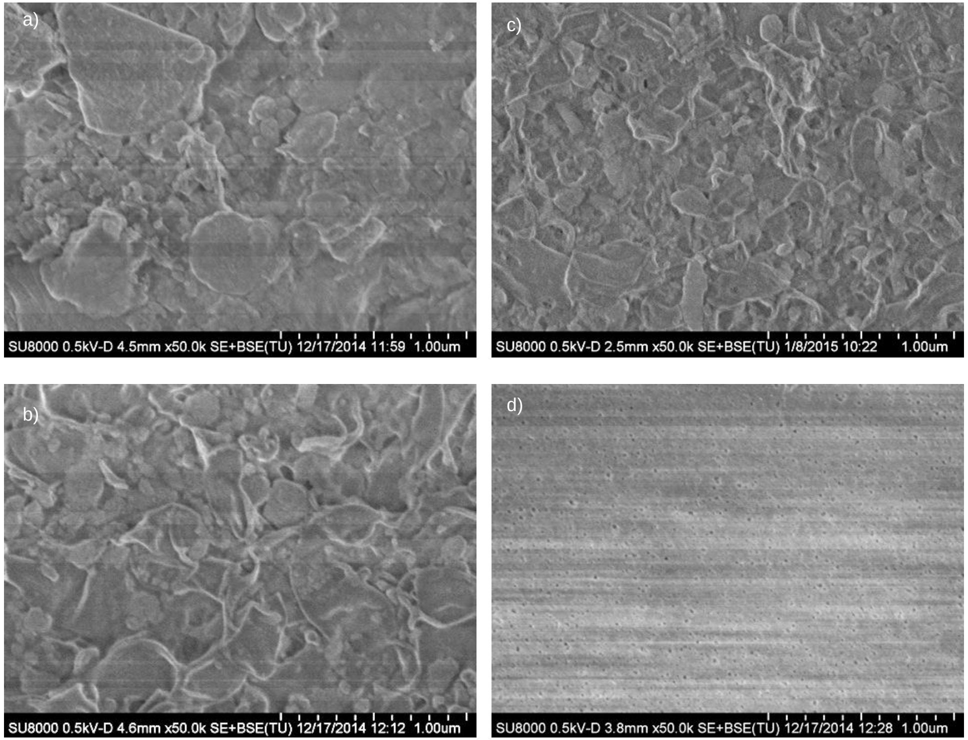

Fig. A2. SEM micrographs of BW-11 (BW30-400): a) end-of-life membranes and exposed membranes to b) 6.200, c) 30,000 and d) 50,000 ppm·h exposure dose.

Fig. A.3. shows SEM surface micrographs to complement the results discussed at Section 4.2.5. (Confirmation of membrane recycling by surface characterization).

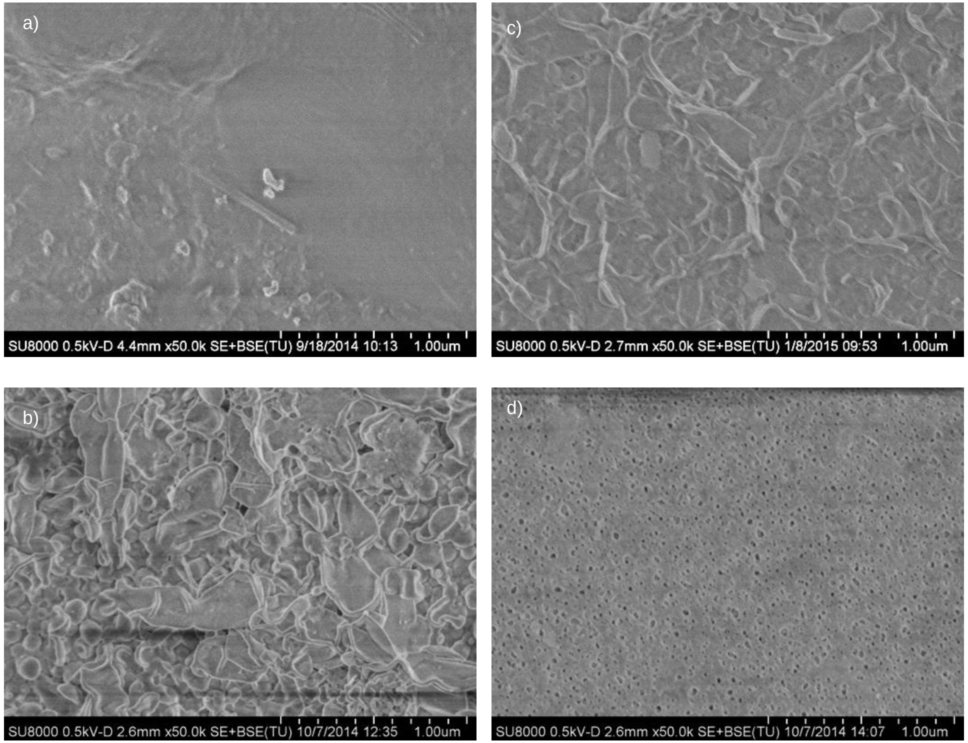

Fig A.3. SEM micrographs of SW-12 (SW30-HRLE440i): a) end-of-life membranes and exposed membranes to b) 6.200, c) 30,000 and d) 50,000 ppm·h exposure dose.

Fig A.4. shows SEM surface micrographs to complement the results discussed at Section 4.2.5. (Confirmation of membrane recycling by surface characterization)

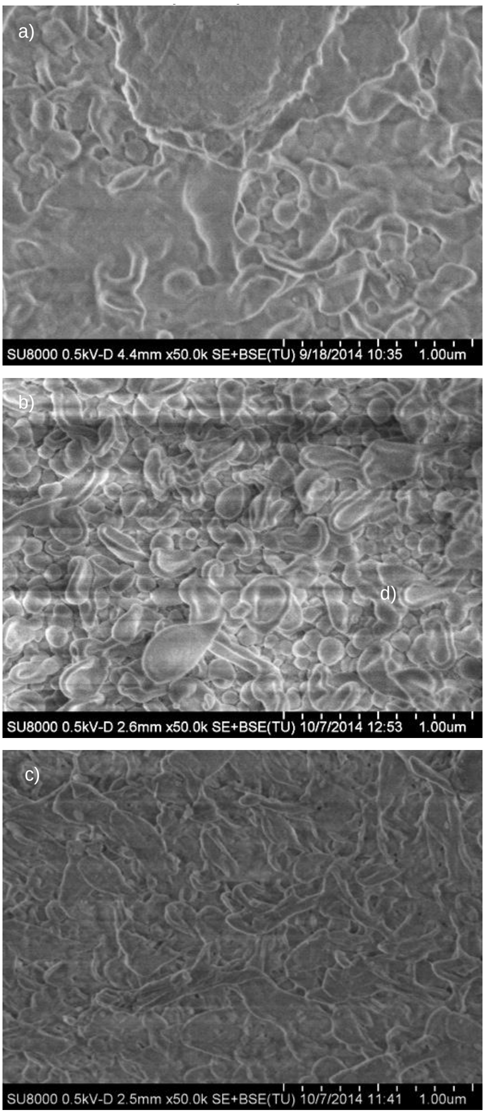

Fig.A.4. SEM micrographs of SW-0 (HSWC3): a) end-of-life membranes and exposed membranes to b) 6.200, c) 50,000 ppm·h exposure dose.

Table A.1. Rejection coefficients (%) obtained when treating SUWW solution with the BW-10 (TM720-400) membrane recycled at 30,000 and 300,000 ppm·h doses. Results achieved using a pristine UF commercial membrane are also shown. Values are measured from composite samples taken during all the experiment.

Table A.1. Rejection coefficients (%) obtained when treating SUWW solution with the recycled BW-10 (TM720-400) membranes and a pristine UF commercial membrane.

Cases		Anion rejection (%)					Cation rejection (%)					Rejection (%)
Ppm h	Free chlorine ppm	Cl- ± sd	NO^{-3} ± sd	PO_4^{-3} ± sd	SO_4^{-2} ± sd	HCO_3^- ± sd	Na^{+-} ± sd	NH_4^{+-} ± sd	K^+ ± sd	Mg^{+2} ± sd	Ca^{+2} ± sd	BSA ± sd
30,000	124 ppm 242 h	14.6 ± 24.5	16.4 ± 22.1	48.8 ± 8.8	64.8 ± 29.5	41.2 ± 14.0	27.4 ± 22.4	36.1 ± 25.9	31.3 ± 21.7	33.1 ± 21.4	38.3 ± 13.6	98.8 ± 0.5
	1240 ppm 24.2 h	20.3 ± 11.8	9.0 ± 16.2	65.0 ± 10.0	85.1 ± 5.0	45.7 ± 5.1	32.1 ± 10.5	41.3 ± 9.5	34.6 ± 11.3	47.0 ± 6.1	47.4 ± 5.0	98.7 ± 0.1
	6200 ppm 4.84 h	34.5 ± 11.1	7.7 ± 18.0	86.5 ± 2.4	95.3 ± 1.5	56.7 ± 7.8	38.0 ± 9.7	41.3 ± 7.5	40.2 ± 10.9	67.4 ± 8.0	69.1 ± 7.9	99.1 ± 0.1
300,000	6200 ppm 48 h	-0.1 ± 2.2	-0.7 ± 1.7	23.5 ± 3.9	32.3 ± 5.1	24.4 ± 1.5	8.6 ± 1.8	9.8 ± 2.5	13.8 ± 0.8	17.5 ± 6.2	13.5 ± 4.8	97.4 ± 1.2
UF Commercial*	0	-3.4 ± 1.7	-5.2 ± 2.1	31.4 ± 1.2	40.4 ± 3.6	28.7 ± 1.5	8.5 ± 1.7	7.2 ± 1.6	14.0 ± 1.1	17.1 ± 0.7	10.4 ± 1.5	96.7 ± 0.4

* No pressure compaction was applied; In the rest of cases, 15 bar of compaction was applied in order to operate at the same condition that the rest of the experiments conducted at laboratory scale (end-of-life RO and transformed NF membranes).

COMPENDIUM OF PUBLICATIONS

Paper I: Scientific paper

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Fouling prevention, preparing for re-use and membrane recycling. Towards circular economy in RO desalination

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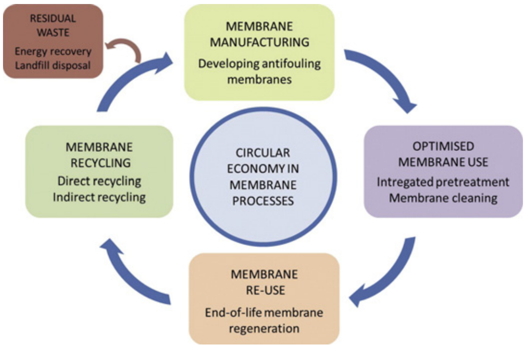
HIGHLIGHTS

- Circular economy can revolutionize membrane industry by designing recyclable modules.
- Antifouling membranes are based on higher hydrophilicity and less roughness.
- Pretreatment and cleaning are tailored processes in continuous research development.
- Near future discarded membrane management may include recycling and reuse.
- Sustainability assessment is necessary to decide other management alternatives.

GRAPHICAL ABSTRACT



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ABSTRACT

Reverse osmosis (RO) is the most employed technology for water desalination. Energy consumption and membrane fouling represent some of the major concerns in membrane technology because they increase the costs associated with treated water. Membrane lifespan is mainly correlated to the quality of the water and the operation condition and it is estimated that often membrane lifespan is 5 to 10 years. Remarkable advances have been made improving the reverse osmosis desalination by integrating pretreatment and cleaning processes. Attending to the membrane active layer, substantial research efforts have been conducted in preparing new antifouling RO membranes to i) enhance antifouling properties, ii) obtain high recovery flux and iii) have low energy requirements. However, scarce research has been detected in literature regarding end-of-life membrane management. This review summarizes the most representative research activities conducted to prevent membrane fouling. In addition, it highlights alternative routes to discarded end-of-life-membranes in order to prevent the uncontrolled disposal of fouled membranes in landfills. In this way, this review aims at summarizing research efforts found in literature in order to approach a more circular economy society, covering the whole life cycle of RO membranes: from the new development of antifouling membranes to the membrane waste management.

1. Introduction

Water is vital for human life, nature and economy. Around 97% of the total water mass on earth is salty water and 3% is fresh water. However, most of the fresh water on earth is captured as glaciers and ice caps.

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Therefore, readily available fresh water is a scarce and a valuable resource [1,2]. In addition, the increase in population, the water use in agriculture, industrial applications and water pollution has deteriorated the accessibility for safe and stable water supplies worldwide. Therefore, there is a need for alternative sources to obtain fresh water.

Desalination of sea and brackish water is broadly implemented in the industry to create fresh water. According to the International Desalination Association (IDA), in 2015, 18,426 desalination plants were installed in 150 countries with a global capacity of commissioned desalination plant of more than 86.8 million m^3 per day [3]. The seawater desalination capacity in Southern Europe represents around 10.6% of the global seawater desalination capacity [4]. Among the different technologies available, membrane technology such as reverse osmosis is very well established in the desalination industry and aromatic polyamide-based (PA) composite membranes currently are the most widely used membranes in RO desalination plants [5]. Energy consumption and membrane fouling represent some of the main concerns in membrane technology because they increase the associated financial cost for m^3 of treated water. Due to fouling, it is estimated that membrane lifespan is 5 to 10 years [6]. Hoek et al. [7] proposed a definition of RO membrane fouling comprising internal and external fouling. External fouling, also known as "surface fouling", is mainly affected by the quality of the water and the operation conditions. Some examples of process parameters to take into account are pH, temperature, chemical agents used as antiscalants or in cleaning steps, and either an effective pretreatment or not is used before the membrane system [8–10]. Internal fouling occurs due to a change in membrane structure due to physical compaction or chemical degradation, which alters solute and solvent transport through the membrane [7].

The current economy is based on a linear model, which assumes that resources are abundant and with the pattern of "take–make–consume and dispose". Industrial processes that use membrane technology are not an exception of the current economy model and membranes tend to be discarded when the flow rate/water quality is unrecoverable. In desalination, the annual membrane replacement percentage is around 10–20% [6,11]. This, together with the continuous growth of reverse osmosis technology, is creating a non-stop accumulation of end-of-life reverse osmosis membranes. Generally, end-of-life membranes are handled according to the laws of each country and unfortunately, membranes usually end up in landfills [12]. Landfill disposing is wasteful, environmentally damaging and costly. Furthermore, it is in direct conflict with EU goals to move towards a circular economy system and to achieve a cross continental recycling society. In this way, the main objective of the circular economy is to keep the value of the materials and energy used in products for as long as possible, minimizing waste and the use of resources. For this purpose, actions must be taken at all stages of the life cycle of the product, from the extraction of the raw materials, through material and product design until the waste management and recycling.

In membrane processes developments are continuously being achieved, both at industrial and scientific levels, to keep the membranes as long as possible within the value chain of their processes. Some examples of these actions are i) manufacturing novel membrane materials that show enhanced process performance, ii) applying more efficient integrated pretreatment and cleaning processes and iii) developing innovative membrane recycling. All these actions make the membrane industry to move towards a more circular economy. Under this framework, the objective of this review paper is to report a comprehensive overview of research efforts found in literature covering the whole life cycle of RO membranes: from the new development of antifouling membranes to the membrane waste management (Fig. 1).

2. Membrane design and manufacturing. Developments in antifouling membranes

Even though membrane physical damage and compression have a big impact on the membrane lifespan, fouling is one of the main reasons that reduce the lifespan of a membrane, causing membranes to become waste. In order to overcome the fouling drawback, in the last years, special research interest has grown in the scientific and industrial communities on the design and preparation of novel antifouling membranes [13].

In this review two main routes for preparing antifouling membranes are discussed: i) the preparation of tailor made new generation antifouling membranes and ii) surface modification of membranes (Fig. 2). Either one route or the other is chosen, the studies focused on the preparation of antifouling membranes generally aimed to enhance surface hydrophilicity as well as to reduce surface roughness (Table 1).

2.1. New generation antifouling membranes

Interfacial polymerization is still the dominant method to prepare the ultrathin barrier of the thin film composite membranes [14]. In

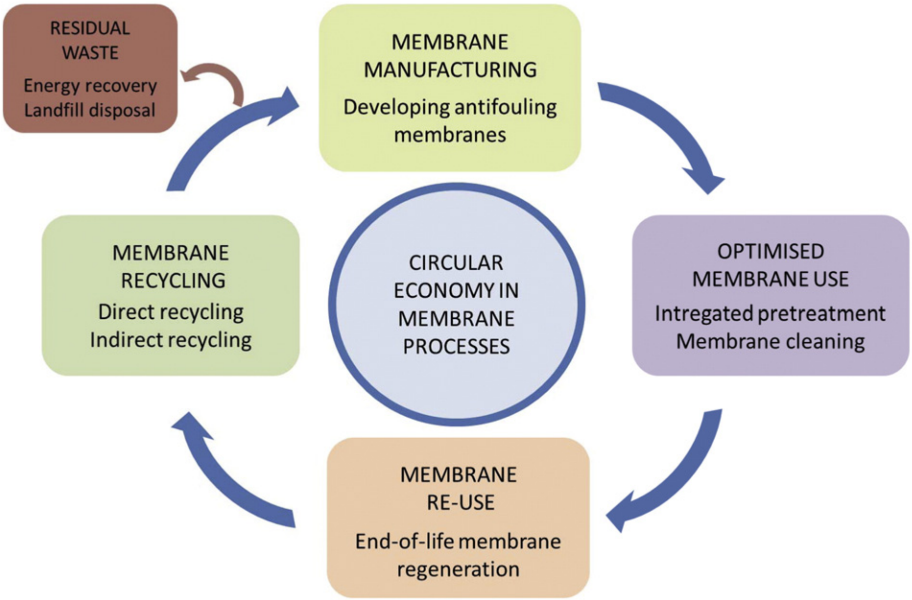

Fig. 1. Circular economy in desalination.

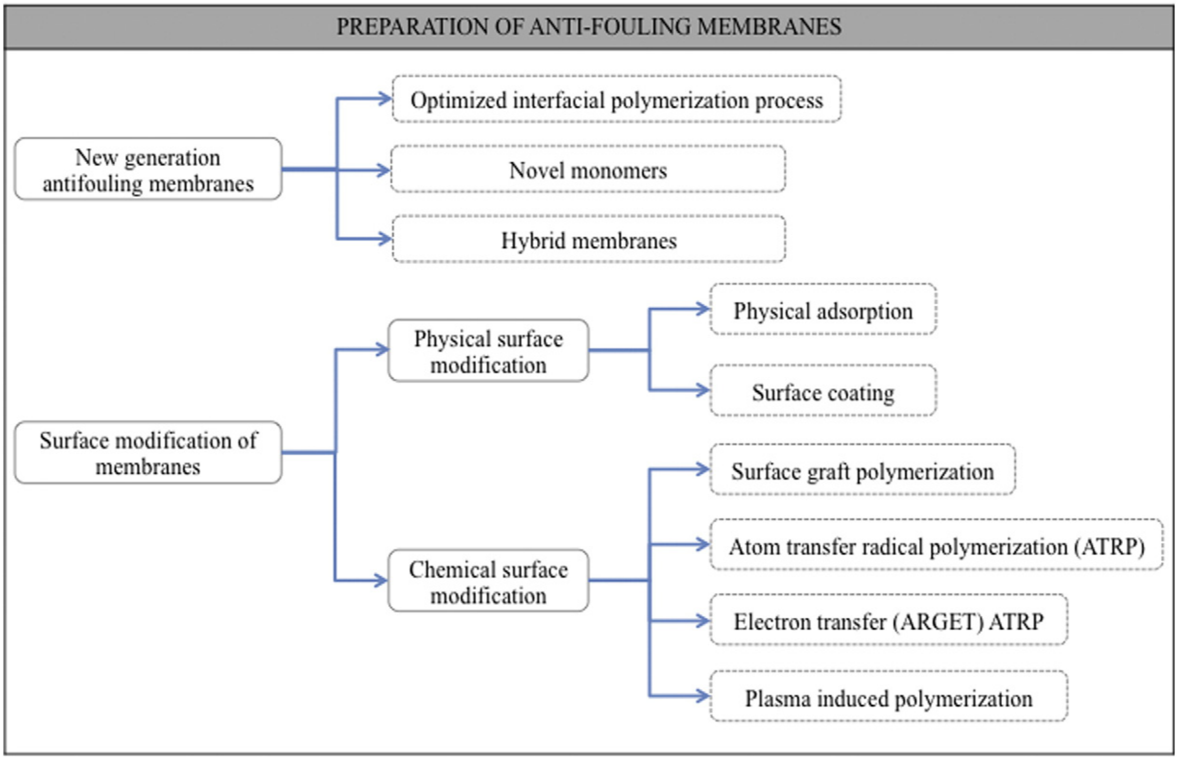

Fig. 2. Preparation of anti-fouling membranes.

interfacial polymerization two monomers react in a two-phase system, where polymerization takes place in the interface between the aqueous and organic phases. The most commonly used polymers for the water phase are m-phenylenediamine (MPD) and piperazine (PIP), whilst trimesoyl chloride (TMC) dissolved in hexane is commonly used as the organic phase [15].

Researchers have been able to achieve better antifouling membrane performance by improving the interfacial polymerization process. According to Zou et al. [16], during the interfacial polymerization, the polyamide thin film grows and behaves as an obstacle for the mass transfer of both monomers. This barrier would inhibit the complete reaction between both monomers, achieving an excess of unreacted polyfunctional acid chloride groups on the surface of the active skin layer. Consequently, there must be an excessive unreacted thin film layer formation. Following this research direction, they added polyfunctional amine monomers to the active skin layer to react with the unreacted acyl chloride groups existing on the surface. They reported to obtain RO membranes with smoother surface and relatively better antifouling behavior.

As Table 1 shows, the improvement of membrane surface properties has also been pursued by studying new monomers that contain more functional polar groups [17,18]. Further, active organic modifiers have been included into the commonly used TMC or MPD solution in order to introduce them to the functional barrier layer [19,20]. Kang et al. [13] presented an exhaustive table in their review summarizing novel monomers and modifiers studied until the date.

Another important development in antifouling RO membranes is the incorporation of nanoscale inorganic particles into the membrane. The use of nanoparticles in the synthesis of membranes can improve the membrane performance by decreasing the degree of membrane fouling [21,22]. In this way, in 2005 Hoek et al. [23] introduced for the first time and patented the preparation of thin film nanocomposite reverse osmosis membranes by interfacial polymerization. The patent describes the preparation of Zeolite A–polyamide nanocomposite membranes. For this purpose, Zeolite A (ZA) nanoparticles were added to the TMC–hexane solution, and the resultant suspension was ultrasonicated for 1 h in order to ensure good dispersion of the ZA nanoparticles. The polyamide layer was formed then by interfacial polymerization by pouring ZA–TMC–hexane solution on top of the MPD-water soaked UF support. After 1 min of reaction, the TMC solution was poured off, and the resulting membranes were then rinsed with de-ionized water. After Hoek's work, a wide range of studies has been performed regarding the preparation of thin film nanocomposite membrane with the objective of improving the overall membrane process performance. Commonly used nanoparticles are TiO_2 [24], Zeolite A [25], SiO_2 [26], and silver nanoparticles [27–29]. The preparation of thin film nanocomposite membranes can be separated in three main groups [30]: i) the nanoparticles are included in the thin film layer of the RO membrane via interfacial polymerization process [31,32], ii) the nanoparticles are included in the membrane polysulfone sublayer via immersion precipitation process [25,33] and iii) the nanoparticles are included both in the membrane sublayer and thin film layer [34]. It is interesting to note that nano enhanced membranes are also manufactured commercially. As an example, membrane manufacturer NanoH_2O has launched to the market QuantumFlux thin-film nano-composite (TFN) membranes, which incorporate benign nano-materials into its patented thin-film layer. The company reports to have obtained 50–100% increase in permeability compared with traditional thin-film RO membranes [35].

Following the same trend (to enhance surface hydrophilicity as well as to reduce surface roughness) many research studies have been focused on conducting membrane chemical or physical surface modification.

2.2. Surface modification of membranes

2.2.1. Physical surface modification

Physical modification is usually conducted by physical adsorption of compounds and surface coating. Physical adsorption is a simple tool for surface modification [13]. Researchers have carried out surface modification of reverse osmosis membranes by adsorption of compounds such as surfactants [36] and charged polyelectrolytes [37]. The reports show that the adsorption of surfactants on the membrane surface decreased the membrane surface roughness, improving the antifouling

Table 1
Research studies on the preparation of antifouling membranes.

Preparation route		Description	Reference
New generation antifouling membranes	Novel interfacial polymerization	Adding of polyfunctional amine monomer into the skin layer to react with the unreacted acyl chloride groups.	[16]
	Novel acid monomers:	3,4,5-Biphenyl triacyl chloride (BTRC) and 3,3,5,5-biphenyl tetraacyl chloride (BETEC). MPD was used as the amine monomer. BTEC–MPD membrane exhibited a smoother surface and similar hydrophilicity compared to TMC–MPD membrane.	[17]
		5-Isocyanato-isophthaloyl chloride (ICIC). Amine monomer used was MPD. ICIC–MPD membrane had favorable hydrophilicity and smoother surface, showing better fouling resistance.	[18]
	Organic modifiers	4,4′-Methylene bis(phenyl isocyanate) (MDI) and PEG into organic phase containing TMC.	[19]
		Polyvinyl alcohol (PVA) was incorporated into composite nanofiltration membranes in situ by adding different amounts of PVA into piperazine (PIP) during its interfacial polymerization with trimesoyl chloride (TMC).	[20]
	Hybrid nanocomposite membranes	Photocatalytic membrane. RO membranes were coated with TiO_2 by dipping method.	[24]
		Zeolite A–polyamide nanocomposite thin film RO membranes showed smoother, more hydrophilic surfaces, higher water permeability and salt rejection, and improved resistance to irreversible flux decline due to physical compaction.	[25]
		In situ formation of silver nanoparticles on top of the polyamide reverse osmosis membranes was proved to be a feasible and easy method to prepare nanocomposite membranes with a strong antibacterial activity. The incorporation of Bio-Ag0–6 nanoparticles into the PES membranes enhanced the membrane hydrophilicity, porosity, water uptake ratio and the smoothness were enhanced due to the introduction of Bio-Ag0–6 nanoparticles.	[26,27]
		The immobilization of silver on the silica improved silver distribution on the membrane surface and throughout the membranes. PES membrane showed higher hydrophilic character and improved biofouling performance.	[26]
Membrane surface modification	Physical surface modification	Adsorption of surfactants and polyelectrolytes such as polyethyleimine (PEI) enhanced the electrostatic repulsion of foulants, increasing membrane fouling resistance	[36,37]
		Surface coating using hydrophilic polymers such as PVA and PEG. All the coatings increased the hydrophilicity and decreased the surface roughness compared to uncoated membrane. In addition, all the coated membranes decreased the attachment of bacteria on the surface.	[39,40]
		Surface mineralization by depositing $BaSO_4$ on the surface of polyamide RO membrane. The coated membrane showed better antifouling performance when filtering BSA. The membrane was easily cleaned by a simple hydraulic washing.	[41]
		Surface coating using dopamine. Dopamine contains both amino and phenolic hydroxyl groups, which can be regarded as zwitterionic molecules for anti-fouling property. Due to the increase in hydrophilicity, the water permeability of the membranes increased, whilst the salt rejection was maintained.	[44]
	Chemical surface modification	Atom transfer radical polymerization (ATRP). Hydrophilic polymer brushes such as zwitterionic sulfobetaine methacrylate (SBMA) and poly(sulfobetaine methacrylate) [poly(SBMA) are added into the membrane surface to improve membrane antifouling performance.	[51]
		Electron transfer (ARGET)-ATRP. cellulose acetate (CA) reverse osmosis membranes were modified by reacting surface hydroxyl groups with an atom transfer radical polymerization (ATRP) initiator, 2-bromoisobutyryl bromide, followed by polymeric grafting of 2-hydroxyethyl methacrylate (pHEMA) using activators regenerated by electron transfer (ARGET) ATRP. Results showed a greater resistance to seawater microbial biofouling for pHEMA modified CA membranes with respect to pristine CA membranes.	[53]

property of the membranes. The adsorption of polyelectrolytes such as polyethyleneimine (PEI) enhances the electrostatic repulsion of cationic foulants, increasing the fouling resistance of the membranes.

In surface coating, the coating acts as a protective layer to reduce or eliminate the adsorption and deposition of foulants onto membrane surface [13]. In this way, the presence of the coating layer has shown to significantly enhance hydrophilicity and reduce surface charge and roughness of the membrane, achieving a better membrane fouling property [38]. Often, surface coating has been conducted using hydrophilic polymers that contain hydroxyl groups such as polyvinyl alcohol (PVA) [39] and ethylene groups such as polyethylene glycol [40]. Zhou et al. [41] conducted a novel coating approach called surface mineralization, where $BaSO_4$-based mineral coating was deposited on the surface of a polyamide reverse osmosis membrane. They performed an alternate soaking process using aqueous solutions containing barium chloride ($BaCl_2$) and sodium sulfate (Na_2SO_4), respectively. They reported that compared to the unmodified reverse osmosis membrane, the mineralized membrane showed improved antifouling property when filtering BSA aqueous solution. In addition, most of the adsorbed and deposited foulants could be easily removed from the mineralized membrane by a simple hydraulic washing.

Another cutting edge methodology on membrane coating is the deposition of polydopamine. It was in 2007 that Lee et al. reported for the first time the potential use of dopamine as a surface modifier [42]. Compared to other methods, the deposition of dopamine is simpler, controllable and the coating stays stable in a wide range of pH values. In addition, the coating process occurs in the solution without the need of an external stimulus such as light [43]. Furthermore, dopamine contains both amino and phenolic hydroxyl groups, which can be regarded as zwitterionic molecules for anti-fouling property [44]. Due to these advantages, dopamine has been used as a surface modifier of a wide range of materials such as carbon nanotubes [45,46], photocatalystis such as TiO_2 [47], and zirconia ceramics [48,49]. In membrane technology dopamine can be used as a surface modifier, intermediate layer, skin layer, filler and pre-modifier polymer [43].

2.2.2. Chemical surface modification

Covalent attachment of polymer brushes by surface graft polymerization is a promising method to modify the surface properties of a membrane [50]. In radical grafting, free radicals are produced from initiators and transferred to the living polymer chain to react with the incoming monomer, realizing the modification of the membrane surface. In general, the proposed grafting site on the polyamide surface is the hydrogen in amide bond [13].

Although conventional radical polymerization technique has been widely used in material synthesis, it is difficult to be controlled when synthesizing well-defined architecture polymers, compositions and functionalities. Overcoming these limitations, Atom Transfer Radical Polymerization (ATRP) has created research interest among the scientific community, using a catalyst [44,51]. In ATRP, the radicals are generated through the dormant species periodically reacting with transition metal complexes, which also work as catalysts. In membrane technology ATRP has been widely applied to modify membrane surfaces with antifouling properties by developing and using synthesized hydrophilic polymer brushes. In addition, the chain growth can be controlled allowing the preparation of less rough surfaces, enhancing the antifouling properties of the membranes [50]. Ran et al. summarized in their paper different monomers used in ATRP for the synthesis of antifouling surfaces [50].

However, the main drawback of using ATRP in a manufacturing process is that it requires inert conditions and a large amount of copper catalyst, which is difficult to remove from the final product [52]. Therefore, Matyjaszewski's group [52] developed the electron transfer (ARGET) ATRP polymerization technique. With ARGET ATRP only a very small amount of copper catalyst is required for the reaction and the experimental procedure is more simple because oxidatively stable Cu(II) can be used to regenerate Cu(I) (the activator) in situ [53].

Most of the research conducted using ATRP have been carried out to modify ultrafiltration and microfiltration membranes [50] and there is very scarce research regarding the surface modification of RO membranes using this technology. Worthley et al. used (ARGET) ATRP improved microbial biofouling resistance of commercially available cellulose acetate membranes by covalently grafting poly(2-hydroxyethyl methacrylate) (pHEMA) coating from the surface [53].

It is interesting to note that often surface grafting is performed after activating the surface to generate oxide or hydroxide groups by plasma treatment (plasma induced polymerization). Another possibility of plasma treatment is plasma polymerization, a one-step method where the plasma is used to deposit the polymer onto the membrane surface [13].

3. Optimized membrane use

As Fig. 1 shows, the optimization of membrane processes is an indispensable step to keep the membrane process performance. In desalination, the high quality of the feed water is crucial to assure the correct functioning of RO membranes. The purpose of pretreatments is to prepare brackish water and seawater to the requirements of desalination process by adapting the physicochemical and biological characteristics of collected water. The selection of a suitable treatment is essential and the quality of water and its characteristics must be taken into account. Therefore, pretreatment is an indispensable and critical part of the desalination process and its design determines the costs of maintenance and operation of the plants. Besides, an adequate design of pretreatment would avoid the corrosion, scaling and the premature damage of equipment and membrane fouling [10]. Another very critical step for the optimized membrane use is the conduction of membrane cleaning. Inappropriate cleaning protocols can cause corrosion in the system and membrane degradation [54,55].

3.1. Pretreatments

Pretreatments can be divided into two groups: i) conventional pretreatments or physicochemicals and ii) unconventional pretreatments (Fig. 3).

3.1.1. Conventional pretreatments or physicochemicals

Conventional pretreatments consist of a combination of chemical treatment with a media filtration to achieve a conditioned feed suitable as RO feed (Fig. 3). Generally, the water treatment plants use *chlorination* [56] before and after RO process (pre-chlorination and post-chlorination). Pre-chlorination improves the disinfection of polluted water because it helps to control the growth of algae on the walls of pipes and tanks inside the system [57]. However, pre-chlorination has become much less common in some countries such as United States, and it is only carried out in plants where there are no problems with the formation of trihalomethanes [58]. The formation of trihalomethanes occurs when chlorine reacts with the organic compounds in water during a longer contact time. Some authors believe that shock chlorination is better than continuous chlorination, which promotes destabilization and more coagulation of the natural colloidal polymers as well as irritates sea organisms in the intake system allowing their division to add foulants [59]. Nevertheless, others opine that with shock chlorination there is a greater risk of bacteria adhering to the surfaces of RO installations [60]. Therefore, considering that chlorine is not effective for deterring RO membrane biofouling and that it creates a high risk of generating toxic disinfectant by products, the use of chlorination in

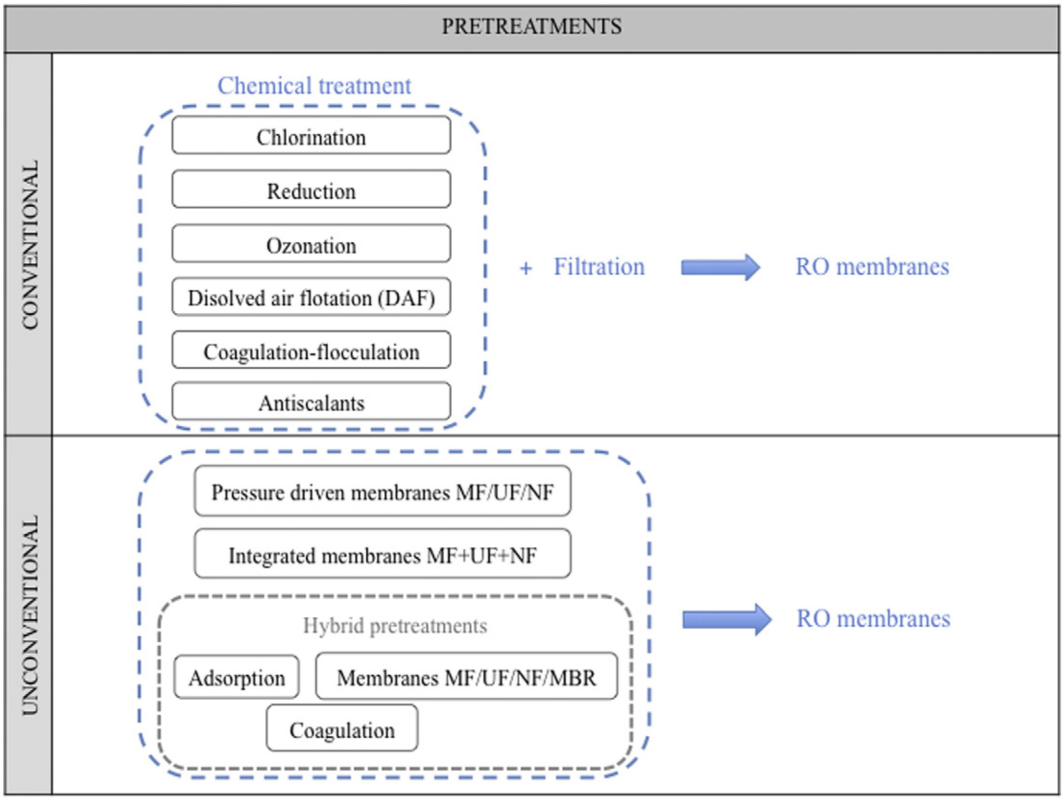

Fig. 3. Possible conventional and non-conventional pretreatments to avoid the membranes become waste.

the pretreatment stage of sea water reverse osmosis (SWRO) is not recommended. In addition, it is important to note that polyamide is not chemically resistant to chlorine. Consequently, sodium bisulfite or activated carbon is commonly used in order to remove free chlorine from water, preventing chlorine contact with membranes.

Ozonation may be a good alternative to chlorination, mainly in the pre-chlorination of plants with risk of formation of trihalomethanes, which can be destroyed by ozone. As disinfectant, ozone is more powerful and faster than chlorine and it can produce less flavor and smell of treated water [61]. However, the use of ozone in this field is not more widespread because of its higher cost compared to other commonly used disinfectants. In addition, when ozone is added to seawater hypobromous acid is formed which cause membrane damage [62,63].

Dissolved air flotation (*DAF*) involves dispersing air bubbles to increase the contact time of the particles suspended in the water with coagulants. As a consequence, the removal of algae and organic matter from water is higher. Some research studies suggest that the combination of this technique with coagulation is more economical for the water treatment [64]. In addition, other works explain the importance about the stratified flow and bubble size in DAF [65].

The *coagulation–flocculation* process is employed to remove both organic and inorganic colloidal substances from water. It is based on the neutralization of the charge associated with the colloidal particles by adding a coagulant (metal salts), generally aluminum or ferric salts. G. Di Bella et al. [66] explained the negative effects of the coagulant residuals that result from the pretreatment process on the performance of the RO membrane. As a consequence, they recommend the application of the coagulation process with a low coagulant dose (50–70 mg/L), particularly with aluminium sulfate because it is more versatile for the removal of the main water contaminants. On the other hand, other authors opine that the use of powdered activated carbon (PAC) is really efficient for humic acids removal [67].

Antiscalants are helpful conventional pretreatment used in reverse osmosis process to prevent membrane scaling. Several types of antiscalants can be employed in RO plants, such as polyacrylates, organophosphonates or sodium hexametaphosphate. However, it is acknowledged that the scale inhibitor is prone to contribute to the biofilm growth due to an alteration of membrane surface properties such as hydrophobicity and surface charge. Amer Sweity et al. [68] have studied how polyphosphonate-based antiscalants contribute to membrane biofouling because it is a phosphorous source of nutrients. As a consequence, these authors recommend strongly that antiscalants should be screened for their biofouling contribution prior to their application.

Generally, conventional pretreatments require high space and elevated chemical additive doses. In addition, the quality of the produced effluent is lower and requires larger manpower and higher chemical and operation costs than other non-conventional pretreatments with membranes [69,70]. Therefore, the use of non-conventional pretreatment processes has gained interest in the past years.

3.1.2. Unconventional pretreatments

Alternative techniques such as microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) have emerged as reverse osmosis pretreatment technologies. These technologies have been extensively used in water consumption for humans and in tertiary treatments of urban wastewater. However, the use of pressure driven membranes as a pretreatment process in desalination have been scarcer in the past and have gained a substantial interest in recent years. This is because membrane pretreatments are more effective than conventional ones obtaining a lower silt density index (SDI) to inhibit biofouling [29]. In addition, membrane pretreatments have significant benefits versus conventional pretreatments [71–74] because of the following:

- significantly higher RO flux,
- lower space,
- replacement of reverse osmosis membranes occurs rarely.
- it is possible to treat surface water with variable quality, and
- reduced requirement for RO disinfection and cleaning.

The Umm-Lujj SWRO plant uses nanofiltration membranes prior to the reverse osmosis process [75]. Indeed, different membrane models [76,77] or different element brands [78] in the same pressure vessel begin to be used to improve operation and maintenance cost. In addition, there are already desalination plants using UF membranes as pretreatment prior to the RO process. Some examples are the Mantoverde plant in Chile with a water production capacity of 12,000 m^3/day, Perth II plant in Australia with a capacity of 306,000 m^3/day and Ashdod plant in Israel producing 384,000 m^3/day of fresh water. This last example is the biggest plant in the world having UF membranes as pretreatment method.

Depending on the specific contaminants to be eliminated, it will be advisable to use a type of membrane or another. While MF membranes are appropriate for removal of larger particulate matter at higher permeate fluxes, NF membranes are used to remove dissolved contaminants, particulate and colloidal material. On the other hand, UF membranes offer better balance than MF and NF membranes, because they have greater fluxes than NF membranes and smaller pore sizes than MF membranes [11]. Recently, the European project Life + UFTEC has demonstrated the technical feasibility and the environmental and economic viability of direct UF membrane technologies as an alternative to conventional pretreatment schemes in Water Treatment Plants using RO membranes.

Several authors have suggested that the keystone of membrane pretreatment technology could be the combination of conventional and non-conventional pretreatments (hybrid technologies). In this way, it could be possible to unify the advantages from different types of pretreatments in order to produce better water quality and minimize the overall treatment cost. For instance, T. Chatkaew et al. proposed the application of the hybrid adsorption/UF process as a relevant pretreatment process before RO desalination [79]. This method may allow the organic matter removal of 75% and no flux decline for short-term experiments. Other research studies suggested the use of UF membranes in combination with coagulation because natural organic matter (NOM) can be effectively removed employing coagulation before UF membranes [80,81]. This could result in a mitigation of fouling in UF membranes and the fewer decline of ultrafiltration flux. Other advantages stated for this method are the low cost and the easy use of coagulation.

Although membrane bioreactor (MBR) has been widely used for the surface water and wastewater treatment, it is starting to be considered as seawater pretreatment [82]. As M. Lerner et al. reported, MBR allows the removal of chemical oxygen demand (COD) and biological oxygen demand (BOD), which could contribute to minimize the membrane biofouling in RO membranes [83].

3.2. Membrane cleaning

Despite the research and industrial efforts to develop new antifouling membranes and to optimize the pretreatment processes, membrane fouling is a phenomenon that will always occur at some extent. Therefore, membrane cleaning becomes a crucial step within the membrane processes. Cleaning cycles are recommended to be conducted when transmembrane pressure, permeate flow and/or permeate quality vary between 10 and 15% with respect to the initial values [84].

The type of membrane cleaning procedure will depend of the type of membrane fouling [85]. The major types of fouling in RO membranes are: i) inorganic/scaling (deposition inorganic salts precipitate on the membrane surface [86,87], ii) organic fouling (deposition organic compounds such as proteins and humic substances) [88,89], iii) colloidal fouling (deposition of colloids such as clay, silt, particulate humic substances) [90–92] and iv) biofouling (adhesion and accumulation of microorganisms and biofilm formation) [93]. Membrane cleaning process can be physical, chemical or a combination of both (physio-chemical). Physical cleaning methods prior to chemical cleaning methods are often used in membrane processes. However, in RO desalination, chemical cleaning is the most applied method [94].

3.2.1. Physical cleaning

Physical cleaning depends upon mechanical forces to displace and remove foulants from the membrane surface [95]. Conventional physical methods include sponge ball cleaning, forward and reverse flushing, backwashing, air sparging and CO_2 back permeation [96,97]. Conventional physical cleaning methods used for RO membranes are forward, reverse and backwashing [94]. As Fig. 4 shows, in forward flushing permeate water is pumped at high cross-flow velocity through the feed side (from feed to retentate) in order to remove foulants that are adsorbed on the membrane surface. In reverse flushing permeate is first flushed for a few seconds in the forward direction and afterwards, for few seconds in the reverse direction (from retentate to feed). In backwashing, permeate is flushed from the permeate side to the feed side (Fig. 4). In reverse osmosis membranes, backwashing is conducted by direct osmosis. This is achieved by i) reducing the operation pressure below the feed osmotic pressure or ii) by increasing the permeate pressure [98]. Backwashing has not commonly been used in RO desalination because it would require a high back-hydraulic pressure that might damage the membrane [94]. Following this idea, a non-conventional backwashing method called osmotic backwashed induced by hypersaline solution has been recently been developed for RO membranes. It is performed by introducing into the feed channel a highly concentrated solution (hypersaline solution, 5–10% NaCl solution) that can create an osmotic pressure more than 100 bar. The high osmotic pressure achieved will promote the direct osmosis and consequently the water would flow from the permeate side to the feed side [94]. Few research studies are available using other non-conventional physical cleaning methods for RO membranes. Some examples are the use of ultrasonic [99], electric [100] and magnetic fields [101].

3.2.2. Chemical cleaning

Chemical cleaning methods depend on the chemical reactions that weaken the cohesion forces between the foulants and the adhesion forces between the foulants and the membrane surface [95]. The cleaning agents used must be able to dissolve the majority of the fouling materials and to remove them from the membrane layer without causing surface damage [54]. In addition, the cleaning agent should be low-cost, safe and show chemical stability and the ability to be removed with water. Generally there are six common categories of chemical cleaning agents: alkalis, acids, metal chelating agents, surfactants, oxidizing agents and enzymes. Table 2 summarizes the main chemical agents (basic compounds and commercial products) that are used depending on the type of fouling observed in RO membranes in desalination. The choice of the cleaning type and products mainly depends on feed characteristics and autopsy information. For example, acid cleaning is suitable for the removal of precipitated salts, such as $CaCO_3$, $CaSO_4$ or aluminum hydroxides [102,103], while alkaline cleaning with or without surfactants and metal chelating are used to remove adsorbed organics [104–107].

Besides choosing the correct chemical agent it is also important to apply a correct cleaning procedure. In one hand, the cross flow velocity used in the cleaning method should be higher than the one used in the normal operation. On the other hand the pressure used should be lower than the pressure used in normal operations [94]. Moreover, zero trans-membrane pressure is recommended to achieve maximum foulant removal [108]. Other important parameters are the temperature, chemical concentration, pH and time [95,109]. As an example, Hydranautics recommends to use cleaning and flushing flow rate range of 91–151 dm^3/min for 8 in. RO elements. In addition, it is recommended not to exceed 4 bar. It is also very typical to recirculate cleaning chemicals through the membranes during 1 h if the temperature is less than 40 °C. When the temperatures used are more than 40 °C the exposure is limited to 30 min [110].

3.2.3. Physico-chemical cleaning

Physico-chemical cleaning methods consist on using physical cleaning methods with the addition of chemical agents. However, the simultaneous use of physical and chemical cleaning is not commonly used in RO industry. The most commonly combination method used is to conduct forward flushing between different chemical cleaning steps [94].

4. Membrane re-use and recycling

Membrane lifespan can be prolonged in industry by capital investment on fouling prevention processes. However, fouling is inevitable and once the membranes do not fulfill the objectives set at the industrial process they are considered as a waste, ending up mostly in landfills. The constant disposal of end-of-life membranes in landfills and the consequent environmental impact has raised interest on looking for other alternative management routes. Recently Lawler et al. [111] conducted a Life Cycle Assessment (LCA) of several end-of-life membrane disposal options (landfill, incineration, gasification, energy recovery, direct reuse and recycling) to quantify and compare their environmental impact. The results of this study showed that direct reuse is the most environmentally favorable option, whilst the current landfill disposal is the least favorable one. The same research team at UNSW Australia (the

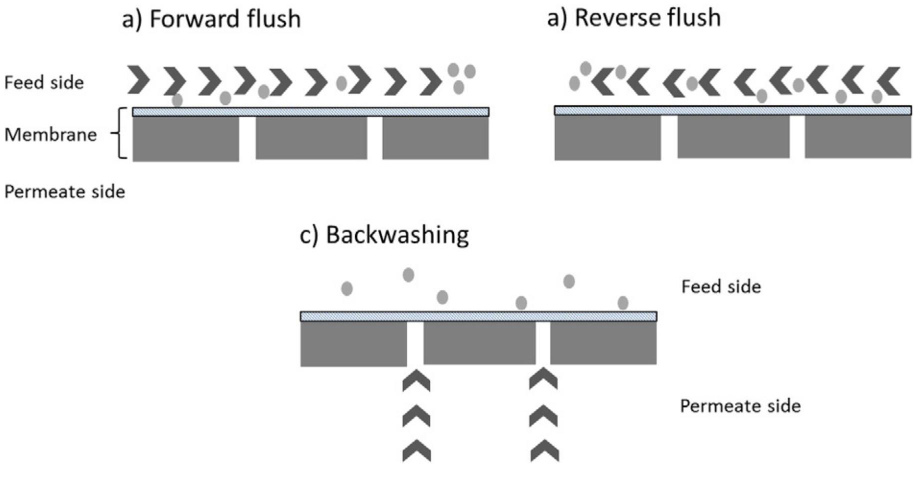

Fig. 4. Flow direction in forward flushing, reverse flushing and backwashing.

Table 2
Main chemical agents employed in chemical cleaning of membranes.

Type of fouling	Cleaning chemical agent	Commercial cleaning products for membrane application
$CaCO_3$ $MgCO_3$	- Cleaning of this type of scaling is relatively by the use of a hard acid. If the cleaning procedure is not conducted the membrane performance will decrease by achieving lower salt rejection coefficients. The appropriate hard acids to be used are: hydrochloric acid, citric acid, phosphoric acid, Ammonium hydroxide, EDTA [55,84,102].	Genesol 37, 701, 721 RoClean P303, L403, L404 AM-11 Decasol CA
$CaSO_4$ $BaSO_4$ CaF_2	- Scaling of sulfate compounds is much more challenging to clean because they are often not soluble in many cleaning products [110]. - The appropriate chemicals to be used in the cleaning processes are: hydrochloric acid, sodium hydroxide, sodium bisulfite, ammonium hydroxide, phosphoric acid sulfuric acid, sodium tripolyphosphate [102].	Genesol 50, 34,703 RoClean L811, L211 AM-11 Versene100 y 220 crystals Decasol SO
$CaPO_4$	- It is a common foulant in wastewaters. - The chemical agents to be used are surfactants and acidic solutions [110].	Genesol 37, 701–721 RoClean L403, P303, L404 Decasol DS
Iron, aluminum and magnesium hydroxide	- The cleaning pH conditions will depend on the type of hydroxide foulant [103]. - Chemical agents such as hydrochloric acid and sulfuric acid [102]. - Weak acids such as citric acid combined with a non ionic surfactant [105]. - Sodium bisulfite [110].	Genesol 34, 36, 37, 38 RoClean L404, L403, P303, P703 AM-11, AM-124 Decasol 940
Metal oxides	- Chelating agents such as EDTA [109]. - Sodium bisulfite, citric acid, EDTA, ammonium hydroxide [97].	Genesol 38, 701 RoClean L404, L403, P303, P703 Decasol CA
Silica scaling	- Chelating agents and alkaline compounds [84]. - Sodium hydroxide, citric acid, ammonium hydroxide [97].	Genesol 40 RoClean P112, L212 AM-99 Decasol SI
Colloidal foulants such as clay	- It is recommended to promote the chemical stability of the colloids present in the feed water. - The chemical agents to be used in case of colloidal fouling are: sodium hydroxide, anionic surfactant sodium dodecylsulphate (SDS), sodium bisulfite, EDTA, citric acid with phosphoric acid and hydrochloric acid [84].	Genesol 40, 703,704 RoClean P112, L212 AM-55 Decasol DS
Organic foulants such as humic acids	- Alkaline agents, surfactants and chelating agents [106]. - Sodium hydroxide, sodium tripolyphosphate, EDTA, sodium dodecylsulfate, sodium dodecylbenzenesulfonate [55,97,106,107]. - Hydrogen peroxide, sodium hypochlorite are used for cleaning the membranes that chemically are resistance to such compounds [105].	Gensol 34, 36, 40, 703, 704 RoClean L211 AM-22 Versene100 y 220 crystals Decasol DS
Biofouling	- Usually acidic and alkaline cleaning is used. EDTA inhibits the biofilm formation. EDTA also helps inhibits enzyme development [102]. - Biofouling could be reduced by using biocides agents, chelating agents, surfactants, citric acid and enzymes [109,105]. - Trisodium phosphate [84]. - Sodium hydroxide, anionic surfactant sodium dodecylsulphate (SDS), EDTA [84,106,107]. - Chlorine and formalin [97].	Genesol 40, 703, 704 RoClean P111 AM-22 *Productos enzimáticos* Memprotech-A100 Ultrasil 67 y 69 Decasol DS

Genesol products are form Genesys International Co.; AM products are from Applied Membrane Inc., Co.; Memprotech-A100 is from Wessex Chemical Factors Co.; Ultrasil products are from Ecolab Co.; Versene products are from Dow chemical Co.; Decasol products are from Aguasin Co.

University of New South Wales) has recently created the MemEOL tool, which aims to promote better practices in the desalination industry. It helps the users to identify and select the optimum end-of-life management option for their discarded reverse osmosis membranes [112].

Table 3 summarizes some alternatives routes to the end-of-life RO membranes disposal that had been studied in the last 15 years. These experiences will be further discussed in this section. More information of opportunities and strategies for end-of-life membranes has been published previously by Lawler et al. [113].

4.1. End-of-life membrane re-use

In waste hierarchy '*re-use*' *means checking, cleaning or repairing recovery operations, by which products or components of products that have become waste are prepared so that they can be re-used without any other pre-processing* [114]. Following this definition, there are some studies that employed end-of-life RO membranes as NF membranes without additional cleaning or treatment [115]. Indeed, based on desalination plant experiences (Sadyt and Valoriza Agua Cos.), membranes that are not completely blocked due to fouling are often reused internally as "sacrificed" membranes (placing them to the first position within the same pressure vessel membrane tubes). Membranes placed in the first position show more organic and metal oxide fouling and biofouling than the rest of membranes [84,97]. Aqualia Co., coordinator of the European project (Life-Remembrane), has recently leaded the investigation in mechanical and chemical treatments to clean end-of-life RO membranes, at pilot scale. The aim of the project was to attack the membrane fouling layer without damaging the polyamide layer. Membranes were recovered in order to be further reused in the same desalination process or in other applications that need a lower water quality. However, as stated above, the objective of this project was to re-use the end-of-life membranes in reverse osmosis processes [6]. In addition, another interesting case study of end-of life RO membranes reuse is at the Talavera de la Reina waste treatment plant (Spain). In this study, repaired end-of-life RO membranes are used as the tertiary treatment of wastewater for irrigation. Following this trend, in 2014 began the European project called Life-Releach, which aims to use repaired RO membrane in the treatment of landfill leachates. Besides the growing interest for end-of-life RO membrane reuse, it is not always possible due to the high membrane fouling or physical disruption caused by abrasion of solid particles. In these cases, membrane recycling becomes another potential route for the end-of-life membranes.

4.2. Recycling

According to the European Union Waste Framework Directive (2008) 'recycling' *means any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It includes the reprocessing of organic material but does not include energy recovery and the reprocessing into materials that*

Table 3
Alternatives routes to the end-of-life RO membranes disposal in the last 15 years.

Alternative to membrane landfill disposal	Main reuse propose	Process condition	Validation test	Reference
Preparation for reuse	*Recycled RO membrane for NF processes and other proposes* Pristine membrane: SW30HR-4040 (Dow Filmetc). End-of-life membranes: SW30HR-2540-A (Dow FilmTec).	No cleaning or recycling method were applied. End-of-life membranes were characterized with no previous treatment.	Lab scale: Tangential filtration method, cross flow test unit (Sepa II, GE Osmonics). Active surface: 138 cm^2. Solution for filtering test: NaCl. Total salinity 6 g/L. Operating pressure range of 0–30 bar, 22 °C.	[115]
	Recycled RO membrane for RO processes. End-of-life membranes (SW, BW) from Toray, Hydranautics, Dow FilmTec and Koch.	Chemical agent: acid cleaner (HCl, H_3PO_4), alkaline cleaner (NaOH, tensoactives and sequester) and oxidant (H_2O_2). pH solution: from 2 to 12. Regeneration: active process recycling solution.	Lab scale: Tangential filtration method, cross flow test unit (Sepa II, GE Osmonics). Solution for filtering test: 1500 ppm NaCl. Operating pressure 15 bar. Pilot scale: Membrane recovery plant for membrane testing and cleaning. Standard brackish water test before and after cleaning process.	[6]
Recycling for membrane filtration	*Recycled RO membrane for RO processes.* Pristine membranes: ACM1-TSA (Trisep), BW30-2514 (Dow FilmTec). End-of-life membrane: ACM1-TSA (Trisep).	Chemical agent: tannic acid. Concentration solution range: 80, 160, 240 y 400 ppm. Exposure time: 1 h. Tested different pH solution: 2.1, 2.4, 3.0, 4.0, and 5.0. Transformation: active process recycling solution.	Lab scale. Crossflow system, flat sheet membrane. Active surface: 56 cm^2. Pilot scale. Spiral wound element. Membrane active surface 0.7 m^2. Solution for both filtering test: 2000 ppm NaCl. Operating pressure 11.77 bar, 22 °C.	[140]
	Recycled UF membrane for waste water tertiary treatment. End-of-life membranes.	Chemical agents: NaOCL, K_7MnO_4, NaOH, H_2O_2. Concentration solution range: 180–8208 ppm. Exposure time: 1–2 h. Transformation: - by an active process: recycling oxidising solution under pressure. - by a passive process: soaking the membrane in a bath without recirculation and no pressure.	Pilot scale. Spiral wound elements of 20.32 cm diameter. Membrane active surface 37 m^2. Solution for filtering test: waste water with secondary effluent quality: 5–10 NTU, 10–30 mg/L SS, 1500–2500 μS/cm conductivity. Operating pressure 4–5.6 bar.	[123,124]
	Recycled UF membrane for their reuse in water treatment. Pristine membrane: BW30FR (Dow FilmTec). End-of-life membranes: TM700 (Toray).	Chemical agent: NaOH, K_7MnO_4, NaOCl. Concentration solution range: 6250 and 62,500 ppm (only for NaOCl). Exposure level: 28,000 to 500,000 ppm. Exposure time: was varied to achieve the exposure level. Transformation: passive process at atmospheric pressure.	Lab scale. Dead end filtration system stirred cell. Solution for filtering test: 2000 ppm NaCl. Pressure of 10 bar. (Characterization of active layer degradation). Solution for filtering test: solution of 10 mg/L bovine serum albumin (BSA). Operating pressure of 2.5 bar, 2 h. (Reused membrane fouling assessment).	[129]
	Recycled RO and UF membranes for new applications like brackish water and bacteria elimination. Taylor made membranes (Pilot plant at CSIR-Central Salt¬ Marine Chemicals Research Institute) and SWC + 4 end-of-life membrane.	Chemical agent: NaOCl 4% (free chlorine). Concentration solution range: 1000–3286 ppm free chlorine. Exposure time: 0.5–144 h. pH: 12 (kept constant). Transformation: - by an active process: solution passed through membrane module. - by a passive process: dipping in free chlorine solution.	Lab scale. Dead end filtration system stirred cell. Membrane active surface 18.9 cm^2. Solution for filtering test: 1500 ppm NaCl. Pressure of 13.8 bar and 3.5 bar (UF test), 25 °C. Solution for filtering test transformed UF case: aqueous polymer solution (15.000–100.000 Da) for molecular weight cut off determination.	[126]
	Recycled RO for their reuse in other application different to RO processes. End-of-life membrane: LFC3-LD-Hydranautics.	Chemical agent: K_7MnO_4. Concentration solution range: 2000 ppm. Exposure time: 2 h. Transformation: active process recycling solution at 4 bar pressure.	Lab scale. Crossflow test unit. Membrane active surface 60 cm^2. Solution for filtering test: NaCl. Operating pressure 4, 6 and 8 bar, 25 °C.	[125]
	Recycled UF membrane for their reuse in water treatment. Pristine membrane: BW30FR (Dow FilmTec). End-of-life membranes: 8822HR (Koch), RE8040-FE (CSM), CPA5-LD (Hydranautics), TML820 (Toray), TFC-SW (Koch)	Chemical agent: NaOCl 12.5% (free chlorine). Exposure level: 300,000 ppm free chlorine, pH 12. Exposure time: 2.4 h.	Dead end filtration system stirred cell (HP4750 Sterlitech). Solution for filtering test: 2000 ppm NaCl. Pressure of 1 bar. Advanced rejection characterization: solution of 10 mg/L humic acid (HA) and 10 mg/L bovine serum albumin (BSA).	[127]
	Recycled NF and UF membrane for their reuse in water treatment End-of-life membranes: TM720-400 (Toray), TM820C-400 (Toray), BW30 (Dow FilmTec), SW30HRLE-440i (Dow FilmTec), HSWC3 (Hydranautics).	Chemical agent: NaOCl 10%. Concentration solution range: 124 ppm. Exposure time range: 1–410 h. Transformation: passive immersion, room temperature, no agitation, no pressure.	Lab scale. Crossflow system, flat sheet membrane. Active surface: 84 cm^2. Solution for filtering test: 2000 ppm NaCl, 2000 ppm $MgSO_4$, 250 ppm dextrose. Pressure of 5 bar, 30 °C.	[12]
			Lab scale. Crossflow system, flat sheet membrane. Active surface: 5 cm^2. Solution for filtering test transformed UF case: aqueous polymer solution (1000–100.000 Da) for molecular weight cut off determination. Operating pressure 3 bar, 25 °C. Membrane surface characterization is also conducted.	[128]
Recycling	*Recycling RO material to be used as a*	Module deconstruction and flat sheet membranes	20 m^2 of end-of-life RO membrane and 20 m^2 of	[115]

Table 3 (*continued*)

Alternative to membrane landfill disposal	Main reuse propose	Process condition	Validation test	Reference
for other proposes	*geotextile.* End-of-life membranes: SWRO-30-4040 (Veolia).	and spacer extraction from spiral wound module.	permeate spacer were used in home garden before rock deposition to maintain rocks and totally eliminated grass growth.	
	Review of material recycling option and alternative to landfill disposal.	Module deconstruction and individual recycling consideration. Combustion and carbonization of the whole module and energy recovery.		[113]
	Assessment of end-of-life options for reverse osmosis membranes.	Simapro version 8 software to conduct a Life Cycle Assessment, (LCA) following the ISO 14040-44 guidelines. Databases used: Ecoinvent 3 and AusLCI.	Scenario models were developed for membrane manufacturing and end-of-life options (landfill, incineration, gasification, EAF, Recycling, Direct Reuse and Conversion to UF)	[111]

are to be used as fuels or for backfilling operations [114]. Under the framework of membrane technology authors considered to divide this category into two recycling types: direct recycling and indirect recycling.

4.2.1. Direct recycling

Direct recycling does not interfere in the module structure but acts over the active layer (polyamide) of the end-of-life RO membranes. The low polyamide tolerance for oxidants could be profited to change membrane morphology and performance. Therefore, membrane direct recycling by chemical modification is gaining interest at academic and industrial level.

Membrane with similar characteristics to pristine RO membranes can be obtained using low concentration and exposure time of oxidants [116,117]. Results showed a slight increment in membrane permeability with a slight decrement in the rejection of monovalent compounds. Those recycled membranes can be applied in RO processes, including desalination and wastewater treatment. However, the aim of these studies was to investigate the aging of the polyamide layer by sodium hypochlorite and membrane recycling was not the main target [118–122].

Rodríguez et al. introduced the concept of transforming end-of-life membranes into ultrafiltration membranes and their further use in wastewater treatment processes [123,124]. Among the chemical agent used, they identified K_7MnO_4 as the most successful one. Following this recommendation, more recently Ambrosi and Tessaro used K_7MnO_4 to modify the end-of-life polyamide layer with a controlled degradation [125]. Other researchers found that the best chemical agent was sodium hypochlorite at high exposure level (ppm·h) and basic pH [12, 126,127]. Lawler et al. demonstrated that the transformation of end-of-life RO membranes into UF membranes was possible due to the complete removal of the active PA layer. As an example, they reported an increase in permeability of 8.6-fold for the end-of-life membrane CSM RE8040-FE after exposing it to NaOCl at 300,000 ppm·h. The membrane salt rejection capability was null, achieving NaCl rejection coefficients less than 1% [127]. Molina et al. [128] have demonstrated that exposure level of 30,000 ppm·h removes completely the PA layer showing the polysulfone porosity. Four end-of-life RO commercial brands tested showed SEM micrographs with nanopores of Feret diameter around 13 nm.

Research efforts have been focused on the end-of-life membrane transformation into recycled ultrafiltration membranes. However, controlling the exposure time of the membrane to the chlorine agent could further lead the membrane transformation towards recycled nanofiltration membranes [129]. García-Pacheco et al. [12] used a mixed solution (synthetic brackish water) of monovalent, divalent and low molecular organic compounds that help to identify the borderline condition between reverse osmosis, nanofiltration and ultrafiltration properties. However, they also mentioned that there are challenges that will determine whether or not recycling is a successful alternative instead of landfill disposal. One challenge is to provide recycling solutions to end-of-life RO membranes despite their type of fouling and commercial brand. Another challenge is to achieve properties of recycled membranes that compete with commercial membranes in terms of cost, effectiveness, durability, energy requirements and maintenance. The same research group is leading a European Project (Life-Transfomem) that aims to demonstrate the viability of transforming end-of-life membranes into nanofiltration and ultrafiltration membranes, at pilot scale.

4.2.2. Indirect recycling

Commonly end-of-life RO membranes are thin film composites, which consist in an aromatic polyamide dense layer supported by a microporous polysulfone (PSf) inner layer and a non-woven polyester webbing. In addition, feed spacers and permeate spacers are made by polypropylene (PP) and polyester respectively. Acrylonitrile butadiene styrene (ABS) is used for the permeate tubes and end-caps, and fiberglass for the outer casing. Finally, there are also glued parts containing proprietary epoxy-like components [130]. According to this composite polymeric nature, each membrane material could be extracted and recycled in diverse recycling routes like mechanical recycling and chemical recycling.

Several strategies are being investigated for indirect recycling and all of them involve the deconstruction of the modules. Some examples for the potential indirect recycling of end-of-life RO membranes components are summarized by Lawler et al. [113]. Recently, National Centre of Excellence in Desalination from Australia (NCEDA) has also proposed to separate the membrane multiple layers and use them creatively as fabric and decoration for clothing [131]. However, according to the author's knowledge, there are no industrial applications yet. This lack of industrial studies could be because the interest for alternative management routes is rather new. Consequently, end-of-life membrane waste is poorly studied, and no demand and no market are associated yet.

There are scientific papers focused on fiber reinforced plastic composites recycling, including fiberglass. However, authors could not find any study that focuses on recycling of membrane module fiberglass. Even though landfill and incineration are the most commonly waste management route adopted for fiberglass [132], it could also be recycled using physic-mechanical recycling method, converting it into a thermoset material. This material could further be used as a filler in the manufacture of SMC (Sheet Moulding Compound), BMC (Bulk Moulding Compound), traditional pre-fabricated concrete and polymer concrete, acoustic and/or thermal panels, piping, kerbstones, floor tiles and similar products [133].

Another possibility is to use the inert granular material for the partial substitution of aggregates in cementous mixtures. Concrete reinforcement with commercial fiber is used in multiple applications such as the construction of tunnels, concrete, self-compacting concrete,

Table 4
Spanish desalination capacity and estimated number of discarded end-of-life membranes.

Spanish desalination plants	Total number	Installed capacity (m^3/day)	% Compared to the total installed capacity	Replacement rate [6]	Estimated end-of-life membrane modules per year
Sea water	289	3,826,549	71	15%	57,398
Brackish water	349	1,064,485	20	10%	10,645
Waste water	26	208,670	4	33%	6886
Other fluids	23	197,457	4	25%	4936
Unknown	24	103,953	2	15%	1559

lightweight concrete and roof panel [134]. Through chemical recycling (pyrolysis or metanoesis), resins can be transformed in new virgin resins [132] to be used in the manufacture of polymeric concretes (prefabricated, cladding, artificial stone, etc.), impermeable layers and even new glass fiber reinforced plastics components [134]. However, composite materials, as a special category of engineering materials have not yet been properly recycled, mainly due to their heterogeneous matrix and reinforcement. An overview of recycling technologies for different types of composites has been previous summarized by Yang et al. [135].

Thermogravimetric analyses of the membrane components performed under nitrogen atmosphere showed that all material (excepting fiberglass) had a percentage carbon content ranged between 60% and 80% [130]. Therefore, waste incinerators would be capable of removing all combustible material, excepting the residual inorganic filler in the fiberglass casing combustion [113]. If it is considered also the volume of waste reduction and the potential energy recovery [111], incineration could be an alternative to the disposal of the recycled and again spent membranes. However, it has to be mentioned that according to the waste hierarchy incineration cannot be considered recycling since it involves energy recovery.

5. Disposal: Spain as a case study

In Spain there are approximately 950 operating desalination plants, placing Spain in the fourth country worldwide in production capacity of desalinated water [136,137]. According to AEDYR database, in Spain, the total installed capacity is approximately 5.4 million m^3/day (3.8 million m^3/day in seawater desalination). Usually it is considered that an average of 100 of reverse osmosis (RO) modules (8 in. diameter) is needed to produce 1000 m^3/day of product water [113].

There are different reasons for membranes to be discarded. Peña-García et al. [138] published the results of 600 autopsies performed on reverse osmosis membranes and showed that the main cause of RO membrane failure is fouling followed by chemical damage (oxidation) and physical damage (abrasion). Even though there is no real data available regarding the main reasons for membrane replacement, in general terms, the most of the membranes are replaced once their performance declines (permeability and rejection coefficients). In some cases, membranes are spent due to functional treatment problems and often present high level of fouling. In other cases, membranes are simply replaced because they overcome the useful lifespan advised by the manufactures.

End-of-life membrane weight is one of the main parameters used to estimate how many tonnes of waste are produced. The weight of the end-of-life membranes depends on fouling. From the authors' experience, scaling can increase membrane weight 3–fold. In this way, after weighting 53 end-of-life RO membranes from 9 different Spanish desalination plants, the average weight obtained was 22 kg (the weight varied from 15 kg to 42 kg). Considering the median weight obtained (17 kg) and different membrane replacement rates [6], the authors have estimated the number of end-of-life membranes and tonnes of waste that are annually disposed at landfills in Spain (Table 4). As a result, it has been calculated that 81,425 end-of-life membranes are disposed annually in Spain (>1000 Tn). Considering that the 65% of the total worldwide desalination installed capacity (86.8 million m^3 per day) uses RO membrane technology [139] and a 15% membrane replacement rate, these results can be extrapolated at worldwide scale. Results show that >840,000 end-of-life membranes (>14,000 Tn/year) are discarded every year. These data are in concordance with previous estimations [113].

Initial end-of-life membrane characterization by means of salt rejection coefficients and recovery rates might be an excellent tool to assess alternative management routes of landfill disposal. Table 5 summarizes manufacture information about RO membranes from diverse Spanish desalination plants that are currently collaborating in the Life-Transfomem project. Prior to transformation, membrane performance is characterized in terms of recovery and rejection coefficient. For this purpose, natural brackish water (around 11 mS/cm) that was previously pre-filtered (sand filter and microfiltration) was used to conduct the filtering assays.

Recovery percentage (% Rec) was calculated from water flux from feed (F_f) and permeate (F_p) using Eq. (1). Salt rejection percentage (% R) was calculated by measuring the conductivity of the feed (C_f) and permeate (C_p) and using Eq. (2).

$$\%\text{Rec} = \frac{F_p}{F_f} \cdot 100 \tag{1}$$

Table 5
Manufacture information of the commercial RO membranes.

Manufacture information of the spiral wound membrane						
Commercial membrane brand	Membrane model	Water	Active area m^2	Permeate flow rate m^3/d	Salt rejection %	Maximum chlorine tolerance [d]
Hydranautics	HSWC3[a]	SW	34	22.3	99.7	<0.01 ppm
Toray	SU-820FA[a]	SW	32	19	99.75	0 ppm
	SU-720F[b]	BW	35	32	99.4	Not specified
	SU-720L[b]	BW	28	22	99.0	Not specified
	TM 720-400[a]	BW	37	38.6	99.7	Not detectable
Dow FilmTec™	BW30XFR-400/34i[c]	BW	37	40	99.5	<0.1 ppm

[a] Values are normalized to the following condition: 32,000 ppm NaCl, 55 bar applied pressure and 25 °C operating temperature.
[b] Values are normalized to the following condition: 1500 ppm NaCl, 10–15 bar applied pressure and 25 °C operating temperature.
[c] Values are normalized to the following condition: 2000 ppm NaCl, 15.5 bar applied pressure and 25 °C operating temperature.

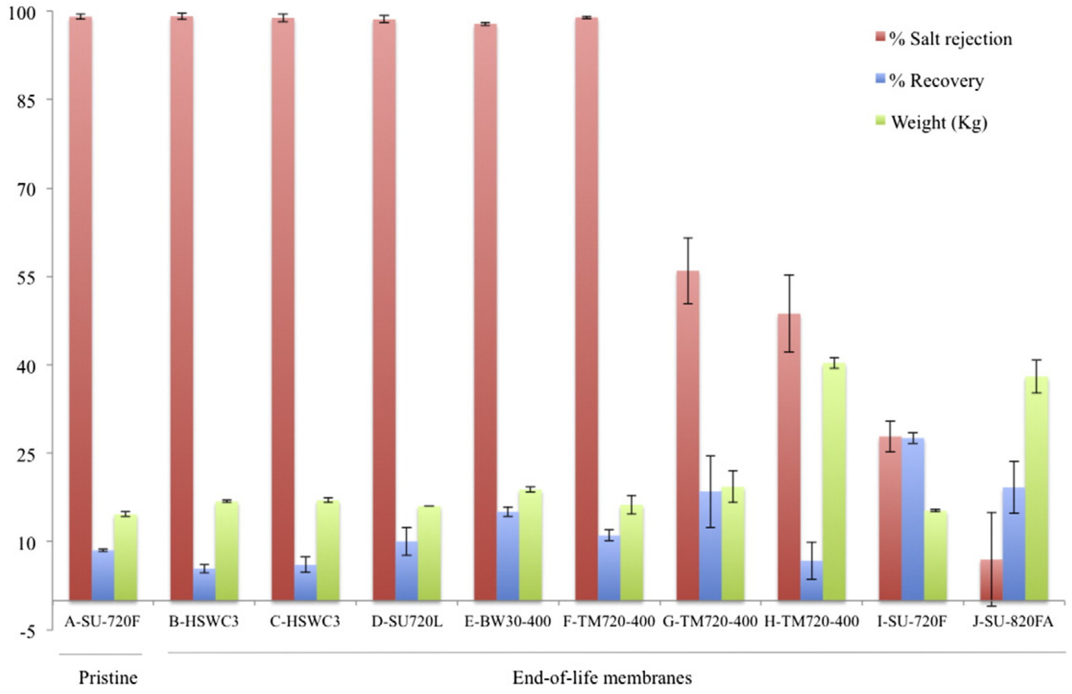

Fig. 5. Salt rejection and recovery average coefficients of end-of-life membranes associated to their weight.

$$\%\mathrm{R} = \left(1 - \frac{C_p}{C_f} \cdot 100\right) \quad (2)$$

Fig. 5 summarizes the salt rejection and recovery coefficients of the end-of-life membranes tested and associated to their weight. As Fig. 5 shows, there is a clear correlation between membrane weight and end-of-life membrane performance. When the membrane weigh increases, salt rejection coefficient decreases and the water recovery percentage increases. Results show that in some cases (from B to F) salt rejection coefficients are still acceptable, obtaining values >97%. Therefore, these end-of-life membranes could be appropriate to be re-used in RO processes once they are cleaned. Membranes from desalination plants G and H show rejection coefficients that are not acceptable for RO membranes. In these cases, they could be prepared for reuse in nanofiltration processes or could be transformed into ultrafiltration membranes. Finally, for the case I and J desalination plants, the membrane performance declined drastically obtaining low rejection coefficients as well as high recovery rates, which might be due to a mechanical and/or chemical degradation of the polyamide layer. In these cases the most appropriate alternative route would be the transformation of the end-of-life membranes into UF membranes.

Although there is a realistic potential for membrane recycling, the current price of membrane disposal is still convenient. Table 6 shows that disposing cost varies depending on the membrane waste classification (dangerous or not dangerous). In this way, membranes that are classified as dangerous waste would have a higher disposing cost because their management includes crushing and energetic valorization. It is important to note that in these cost estimations, transportation is not taken into account, which might be more expensive than the disposal cost itself. Even though disposing cost does not seem to be expensive, both economic and environmental impacts should be taken into account by conducting a sustainability assessment.

Table 6
Membrane waste classification according to the European List of Wastes [141] and estimated disposing cost.

Membrane foulant	Codes of European list of wastes	Estimated disposing cost
Non-dangerous	15 02 03 Filters with non-dangerous materials	45 €/Tn
Dangerous materials	15 02 03* Filters other than those mentioned in 15 02 02 19 08 08* Membranes containing heavy metals	425 €/Tn

6. Conclusions

Desalination of sea and brackish water by reverse osmosis is broadly implemented and established in the industry to create freshwater. In addition, the market of RO membranes is highly standardized and the membranes have well defined performance targets. Desalination membranes tend to be discarded when the flow rate/water quality is unrecoverable. The constant growth of the RO technology together with the significant annual membrane replacement percentage (around 15%) has created a non-stop accumulation of end-of-life reverse osmosis membranes. Generally, end-of-life membranes are handled according to the laws of each country and unfortunately, they usually end up in landfills.

The current economy is based on a linear model based on the assumption that resources are abundant. However, the society should move towards a more circular economy where a 'waste' can be turned into a resource. This review reports a comprehensive overview of research efforts found in literature covering the whole life cycle of RO membranes from the perspective of circular economy.

This paper shows that there is a big scientific interest to improve the membrane fouling phenomena and to avoid the early membrane aging. In this way, research efforts on improving the membrane process efficiency and avoiding membranes to become waste have been mainly focused on developing efficient pretreatment and cleaning processes as well as preparing novel antifouling membranes. In addition, it shows that hybrid systems are the cutting edge technologies applied for this purpose. However, as much as the fouling phenomenon is improved, membrane damaging and aging is a realistic fact that has to be considered by the scientific and industrial communities. Rather than membrane disposal, it was concluded that alternative membrane management routes are feasible. Scientific articles published on membrane recycling show very promising results. However, the research regarding membrane recycling is rather new (around ten years) and more efforts on this kind of studies should be further conducted and encouraged.

Furthermore, it is concluded that the feasibility of using recycled membranes could have a potential market at industrial level if the recycled membranes show to be competitive in terms of cost, effectiveness, durability, energy requirements and maintenance, showing once more the importance of this kind of research. New RO configurations may be designed from the beginning by the manufactures to be recyclable revolutionizing the RO desalination industry.

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Paper II: book chapter

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End-of-Life Membranes: Challenges and Opportunities

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Abbreviations

ABS	Acrylonitrile butadiene styrene
ATR-FTIR	Attenuated total reflection-Fourier transform infrared spectroscopy
BW	Brackish water
EAF	Electric arc furnace
LCA	Life cycle assessment
LCIA	Life cycle impact assessment
MCDA	Multi-criteria decision analysis
NF	Nanofiltration
PA	Polyamide
PET	Polyester
PP	Polypropylene
PSf	Polysulfone
RO	Reverse osmosis
SEM	Scanning electron microscopy
SW	Seawater
UF	Ultrafiltration

Introduction

Membrane technology can help to manage water in integral cycles, mainly due to their modularity and the high quality of the treated water. On the one hand, desalination of seawater (SW) and brackish water (BW) by reverse osmosis (RO) is largely applied and established in the industry for freshwater generation. RO is the most widely used desalination technology globally[1] and aromatic polyamide (PA)-based composite membranes currently account for over 95% of existing RO desalination plants.[2] Within the 2000s, large desalination plants were typically designed to supply between 5% and 10% of the drinking water of coastal cities.

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More recently, regional or national SW desalination projects in countries such as Spain, Australia, Israel, Algeria, and Singapore have been designed to satisfy 20% to 50% of long-term drinking water needs.[3] By 2019, the market for RO system components is projected to reach $8.8 billion, with a compound annual growth rate of 10.5%.[4]

The major cost in desalination is related to energy, which can represent between 30% and 50% of the operating cost,[5] and much investigations have been focused on this topic. As a result, the amount of power needed to drive desalination in SWRO plants has declined dramatically in the past decades, closing to the theoretical minimum energy (1.06 kWh m^{-3}). However, the overall energy consumption is still three to four times higher.[6] The RO process itself consumes between 2.2 and 2.8 kWh m^{-3}, depending on the type of concentrate energy recovery used.[5] This decrease in energy consumption is attributed to continual technological improvement, including higher permeability membranes, installation of energy recovery devices, use of more efficient pumps, pretreatment, posttreatment improvements, and operating during off-peak periods.[7,8]

Additionally, the rapid expansion of desalination capacity required further attention on its environmental impacts. Specific effects of desalination plants include the impact and interference of organisms due to the intake of large quantities of SW and the emission of air pollutants due to a considerable energy demand of the processes.[9] The potential consequences of brine effluent discharge and waste from chemicals used during pretreatment and membrane cleaning have to be also studied.

With an expected lifetime of 5–8 years, the RO membranes used in desalination have to be considered as a frequently replaceable consumable, and as a consequence a quite unique waste stream.[5] Much academic and industrial effort has focused on extending the usable time of RO membranes by developing improved materials and manufacturing and operating/cleaning practices. Ultimately, the management of the end-of-life membrane has shown to have growing interest among academia and industrial sector, with little information being published so far. A significant number of projects have recently been funded to address this gap. The aim of this article is therefore to provide an overview of the current membrane waste challenge in desalination and in other applications and to report on recent investigations, aiming at developing new opportunities for the fate of end-of-life membranes.

The Current Membrane Waste Challenge

Landfill Disposal

Despite many prevention strategies applied, fouling remains inevitable[10] and it is the main cause of the disposal of thousands of tons of RO membranes every year.[11] Cleaning cycles are conducted when transmembrane pressure, permeate flow, and/or permeate quality vary between 10% and 15% with respect to the initial values.[12] The current economy is based on a linear model, which assumes that resources are abundant and with the pattern of "take–make–consume and dispose." Industrial processes relying on membrane technology are no exception of the current economy model and membranes tend to be discarded when the flow rate/water quality is unrecoverable.[13] Annual replacement, together with the continuous growth of RO technology, is creating a nonstop accumulation of end-of-life modules. In desalination, the annual membrane replacement percentage is around 5%–20% of the installed membranes.[14,15] However this numbers vary depending on the nature of the feed water (e.g., SW, BW, or wastewater).[15] **Table 1** shows the rarely reported costs related to membrane replacements.

Generally, end-of-life membranes are handled according to the laws of each country and old membranes usually end up in landfills.[11] Landfill disposing can be viewed as wasteful, environmentally damaging, and a costly waste management option. Furthermore, this practice goes against the EU goals to move towards a circular economy system and to achieve a cross-continental recycling society.[13] To achieve this, changes in domestic practices are needed along with sustained industrial efforts, and legislation and social awareness to accept reuse recycling products. At present, managers from water treatment plants are responsible for the fate of their end-of-life membranes. The lack of alternatives and the still convenient price of membrane disposal drive this common practice. **Table 2** shows disposing cost depending on the membrane waste classification (dangerous or not dangerous) and transportation cost. Even though disposing cost does not seem to be expensive, both economic and environmental impacts should also be taken into account by conducting a sustainability assessment.[13]

On average, it is considered that around 100 RO modules (8″ spiral wound unit) are needed to produce 1000 $m^3 day^{-1}$ in case of medium to large SWRO plants.[11] Considering the median weight of 8″ membranes (17 kg) and different membrane replacement rates, Landaburu et al. estimated that in Spain (i.e., fourth country worldwide in production capacity of desalinated water) around 81,425 end-of-life membranes (equivalent to more than 1000 ton) are annually disposed in landfill.[13] These results can be extrapolated at worldwide scale, where the 65% of the total worldwide desalination installed capacity (86.8 million $m^3 day^{-1}$)

Table 1 Membrane replacement costs for SW and BW desalination plants

	Total cost to produce water	*Membrane replacement cost*	*Replacement cost (%)*	*Reference*
SW	0.525 ($\$ m^{-3}$)	0.028 ($\$ m^{-3}$)	5.3	[16]
BW	0.248 (€ m^{-3})	0.02 (€ m^{-3})	8.1	[17]
	—	0.0080.05 ($\$ m^{-3}$)	—	[14] and references there in

Table 2 Membrane waste classification according to the European List of Waste[18] and estimated cost of disposal and transport

Disposal	*Membrane type*	*Codes of European list of waste*	*Cost*
	Nondangerous	150203 Filters with nondangerous materials	45€ per ton
		150203[a] Filter other than those mentioned in 15 02 02	
	Dangerous materials	190808[a] Membranes containing heavy metals	425€ per ton
Transport	30 m^3 container costs around 100–150€ within the provinces areas[a]. Volume of a single-membrane module (0.314 m^3)		1–1.6€ per module

[a] Case of Spain with 50 provinces, with an average extension around 10,200 km^2 per area.[19]

Modified from Landaburu-Aguirre, J.; García-Pacheco, R.; Molina, S.; Rodríguez-Sáez, L.; Rabadán, J.; García-Calvo, E. Fouling prevention, preparing for re-use and membrane recycling. Towards circular economy in RO desalination. *Desalination* **2016**, *393*, 16–30.

uses RO membrane technology.[20] Considering a 15% membrane replacement rate, estimation shows that more than 840,000 end-of-life modules (or more than 14,000 ton) are discarded every year.[13]

Characteristics of End-of-Life Membranes

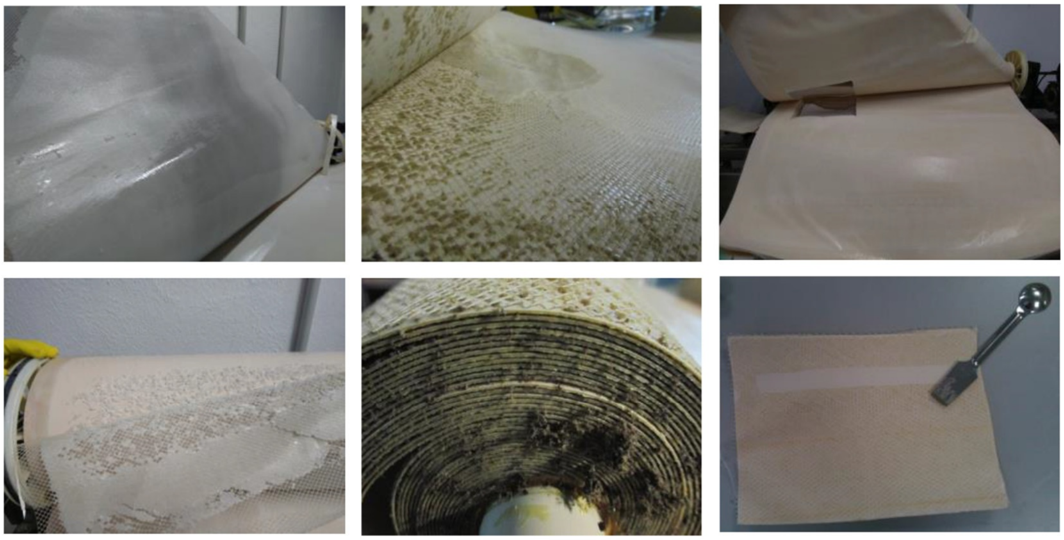
End-of-life membrane fouling and performance

Membranes are generally replaced once their performance (permeability and rejection coefficients) declines significantly and beyond recovery. However, in other cases, membranes are simply replaced because they reach the useful life span advised by the manufacturers or because financing for membrane replacement is approved.[13]

One method to identify the main causes of membrane exhaustion is through membrane autopsies. Membrane autopsies are a series of observations and scientific tests made on an end-of-life membrane element. Moreover, Peña-García et al.[21] published the results of 600 autopsies performed on RO membranes and showed that the main cause of failure is fouling, followed by chemical damage (oxidation) and physical damage (abrasion). Indeed, the majority of the end-of-life RO membranes of this study were treating BW. This can be due to the fact of BW membrane having higher fluxes than those of SW; therefore concentration polarization exacerbates fouling.[6] The major types of fouling in RO membranes are (i) inorganic/scaling (deposition inorganic salts precipitate on the membrane surface); (ii) organic fouling (deposition organic compounds such as proteins and humic substances); (iii) colloidal fouling (deposition of colloids such as clay, silt, particulate humic substances); and (iv) biofouling (adhesion and accumulation of microorganisms and biofilm formation). Fig. 1 shows typical pictures taken during end-of-life membrane autopsies representing inorganic fouling (clay-colloidal, scaling) and organic fouling of three membranes from BWRO plants.

Overall, membrane autopsy provides an exhaustive overview of one specific module representing a group of membranes. However, it is important to understand that membrane performance can vary significantly depending on their position within the treatment train due to the type and level of fouling. Fig. 2 shows diverse permeability and salt rejection coefficient for six membranes elements that were treating BW in the same pressure vessel. Position 1 is related on the inlet (first contact with the feed) and position 6 corresponds to the outlet (membrane is in contact with the more concentrated solution). For instance, membranes placed in the first position usually show more organic colloidal, metal oxide, fouling, and biofouling than the rest of membranes, while membranes placed into the last position can show more inorganic scaling fouling.[22] Therefore, membrane autopsies are generally conducted using the membranes placed in the first and last position. As a result, the information obtained after the membrane autopsy is usually used to design appropriate membrane cleaning procedures in order to reestablish membrane performance, prolonging their industrial operating life. However, autopsies require module deconstruction and a complete set of characterization, which can cost around \$4000–\$5000.

Nevertheless, there are some nondestructive techniques used that allow a preliminary identification of fouling level and type. One of the simplest is the membrane weight. In fact, based on the results obtained in the Life-Transfomem project, when the membrane weight increases around threefold the original weight is usually due to a thick layer of salt deposition (high level of scaling). However, when the old module weight does not exceed 1.5 times the original weight value, the fouling might be organic and/or inorganic and other characterization techniques such as membrane autopsies should be applied to identify membrane foulants. In addition, membrane performance characterization can also be useful. To assess potential waste management options (i.e., cleaning, recycling, reuse as described later in this article), Fig. 3 shows permeability and rejection coefficients (feed natural BW, 11 mS cm^{-1}) of the three end-of-life membranes showed in Fig. 1. When the membrane weight increases, salt rejection coefficient generally decreases and the water permeability increases. In case A (high level of scaling, 2.9-fold the original weight), the membrane performance declined drastically obtaining low rejection coefficients as well as higher permeability rates, which might be due to a mechanical and/or chemical degradation of the PA layer. In this case, indirect recycling strategies are advised to be explored as disposal alternatives (see section "Indirect recycling"). In case B (organic–inorganic fouling, 1.5-fold the original weight), membranes show rejection typical of some commercial nanofiltration (NF) membranes. In this case, these membranes could be cleaned and reused in NF processes or recycled converting them into ultrafiltration (UF) membranes (see section "Direct recycling"). Finally, in case



Inorganic fouling (scaling)
Over the feed spacer and membrane sheet
Case A: SU-820FA

Organic fouling and inorganic fouling
Over the feed spacer and membrane sheet
Case B: TM720-400

Inorganic fouling (clay-colloidal)
Over the membrane sheet
Case C: TM720-400

Fig. 1 Diverse fouling from different membranes installed in BWRO desalination plants collaborating in Life-Transfomem project.

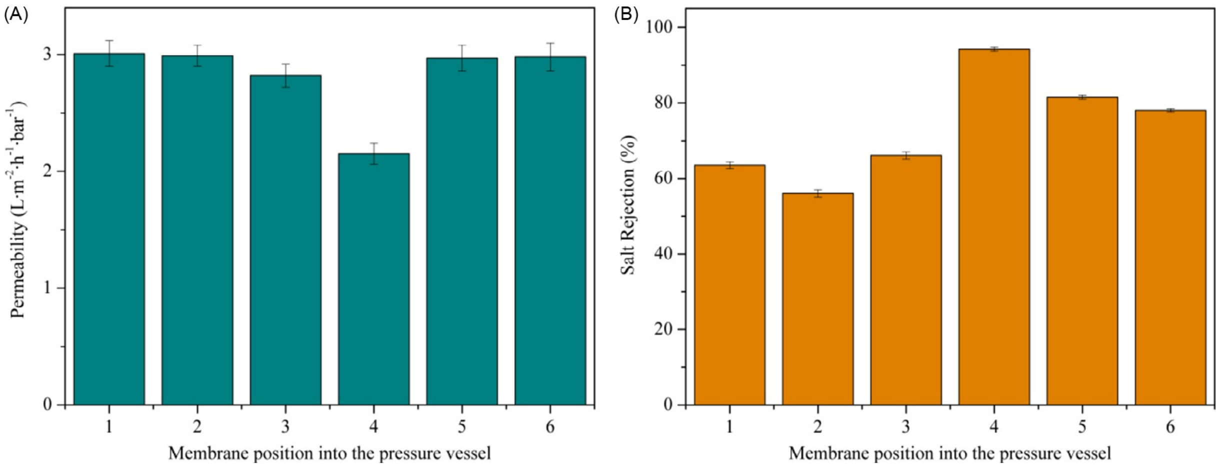


Fig. 2 Performance of membranes that were treating BW in the same pressure vessel at the indicated position, from a Spanish desalination plant.

C (inorganic-clay fouling, 1.3-fold the original weight), salt rejection coefficients are still acceptable, obtaining values >97%. In this case, the membranes could be reused as RO membranes, but in processes that require lower salt rejection coefficients than in SW desalination (see section "Reuse"). Defining the most appropriate alternative for end-of-life membranes remains the critical step in the process and will be further discussed later in this article.

Membrane storage and drying

One potential challenge with a number of the proposed end-of-life options for used RO membranes is the method of storage and transportation, and the resulting impact on future membrane performance.

The primary aim for developing and using appropriate storage protocols is to prevent biological growth, to which used membranes are extremely susceptible. The standard protocol for membrane storage relies on the use of a buffered 1 wt% solution of food-grade sodium metabisulfite, at a pH >3.[23] The solution is circulated through the membranes, which are then individually packaged in oxygen-barrier plastic bags and vacuum sealed. If these preservation methods are not undertaken or hydration is not maintained, which is often the case during end-of-life disposal, the membranes will dry out, resulting in significantly reduced permeate flow.[24]

The cause of this extreme decrease in permeability has been attributed to the collapse of the pore structure of the polyester sulfone (PES)/polysulfone (PSf) membrane layer, which involves the shrinkage and volume reduction of the pores. As the water

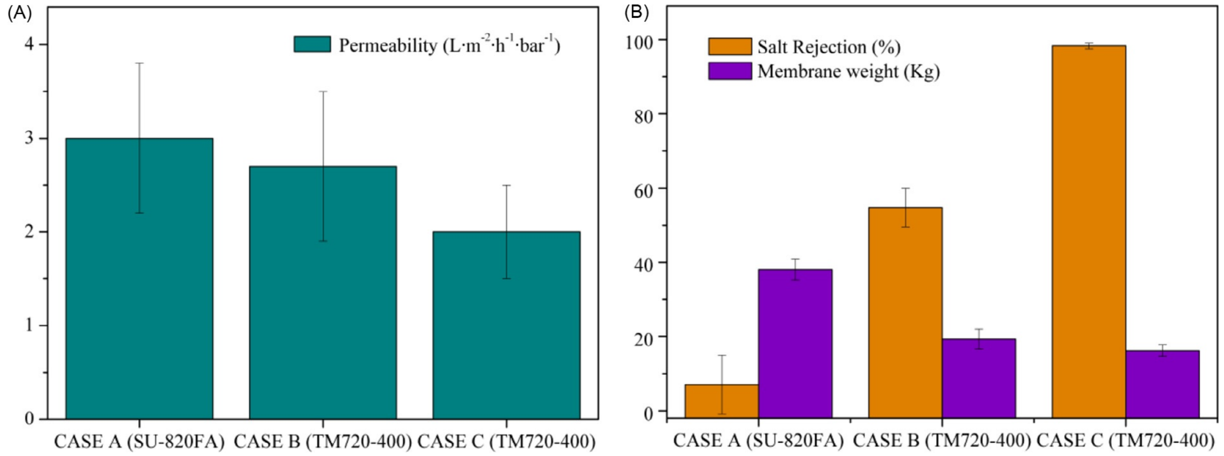


Fig. 3 Permeability, salt rejection coefficient, and weight of three cases of end-of-life membranes. Modified from Landaburu-Aguirre, J.; García-Pacheco, R.; Molina, S.; Rodríguez-Sáez, L.; Rabadán, J.; García-Calvo, E. Fouling prevention, preparing for re-use and membrane recycling. Towards circular economy in RO desalination. Desalination **2016**, *393*, 16–30.

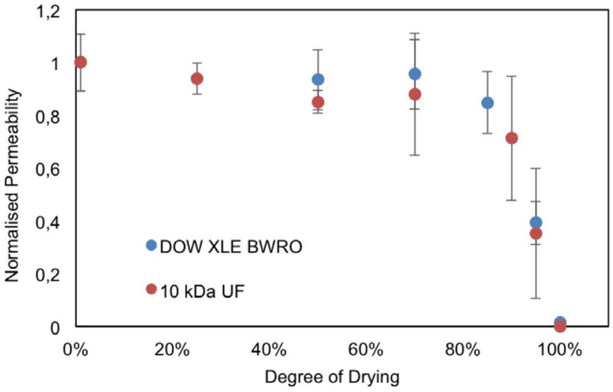


Fig. 4 Performance of membranes after varying levels of drying. Degree of drying defined as the percentage of water loss during drying, that is, 0% dry is fully hydrated and 100% dry is completely desiccated as measured by mass loss. Modified from Lawler, W. *Assessment of End-of-Life Opportunities for Reverse Osmosis Membranes*; The University of New South Wales: Kensington, NSW, 2015.

in the membrane pores evaporates, the pores collapse and form a denser structure.[25] This effect can be described by the Young–Laplace relationship:

$$\Delta P = 2\gamma r \cos\theta$$

where P is the force pulling the pores shut (Pa), γ is the surface tension (Nm^{-1}), r is the pore radius (m), and θ is the contact angle (°) between the liquid and the membrane material. The capillary pressure is directly proportional to the surface tension of the wetting liquid, and inversely proportional to the pore radius. If the swollen membrane modulus is lower than the exerted forces of the drying pores, the pores collapse and form a denser structure. As the membrane pores get smaller, the forces increase, and thus the pressure required to rewet the membrane pores increases.[26] As asymmetric membrane skin layer pores are significantly smaller than pores in the rest of the membrane, pore collapse is believed to be most predominant in the surface region.[27] This permeability loss is not recoverable through normal operation and is common between all RO membranes and tight PES/PSf UF membranes.[28]

A number of studies have investigated this effect and have concluded that pore collapse played a significant role in hydraulic performance loss.[27] This issue of permeability decrease due to drying has been recognized, but not quantified, and as such, a number of dry manufacturing techniques resulting in larger pore size have been developed. This larger pore size means that capillary forces are significantly decreased, resulting in a membrane that can be wetted and dried repetitively.[29] However, these considerations have been limited to cellulose acetate RO membranes, which are no longer commonly used. Membrane manufacturers are also aware of the negative effects of element drying, and note that it results in irreversible flux loss due to pore structure change in the PSf layer.[23]

A recent study investigated the mechanisms of pore collapse due to drying using a number of techniques including selective drying, synchrotron small-angle X-ray scattering analysis, scanning electron microscopy (SEM), atomic force microscopy, and rejection characterization, and also assessed the effectiveness of various rewetting techniques.[28] Fig. 4 shows how the permeability performance of RO and tight UF membranes degrades with drying.

The bulk of the permeability loss only occurs when 80% of the wetting water is removed from the membrane structure, indicating that only extreme drying leads to irreversible pore collapse. The study determined that drying had no impact on salt rejection for RO membranes. However, for UF membrane, drying caused an increase in protein and humic substance rejection, indicating a significant decrease in mean pore size due to pore collapse. Additionally, while tight UF membranes (10–30 kDa) lost up to 100% of initial permeability upon drying, 100 kDa membranes only lost ~50% of initial permeability, showing that pore collapse is dependent on initial mean pore size. After extensively testing a wide number of rewetting strategies, including those recommended by RO membrane manufacturers, the study showed that soaking the membrane in 50% w/w ethanol solution for over 15 min was the optimum method. Comparable performance recovery was also achieved by soaking in a solution of sodium lauryl sulfate for over 50 h. Total permeability recovery was never achieved on completely desiccated membranes, and many of the manufacturer-recommended methods, such as soaking in low-concentration HCl and HNO_3 solutions, did not result in significant performance recovery.

Fig. 5 shows the current storage of the end-of-life membranes in the desalination plants. Membranes are used to left drying at atmosphere conditions, to reduce their weight and the shipping and disposal cost. However, it is clear that maintaining membrane hydration throughout transport or maintenance is a priority; otherwise irreversible performance loss is expected to occur. If the modules are not properly stored with the intention of reusing them and are allowed to completely dry out, then the rewetting step will be a critical challenge, resulting in reduced performance and/or additional cost.

Main Alternatives for End-of-Life Membranes

According to the main pyramidal waste management principles of the European Directive 2008/98/EC on waste, preferred options such as material prevention, reuse, recycling, recovery, and disposal should be applied, in this priority order.[30] While Waste Management Directive is pyramidal, Landaburu et al.[13] proposed a new integral management scheme for RO membranes (Fig. 6). Following this idea, in a near future, new spiral wound RO configurations may be designed by the manufacturers to be recyclable and thus pointing the RO desalination industry toward a circular economy.[13] Prevention action is normally applied in the desalination plant by using antifouling membranes and optimizing the membrane use with pretreatment and cleaning cycles.[13] However, accumulation of end-of-life membrane is inevitable. Although direct reuse of old membranes without any additional treatment is obviously preferred, appropriate assessment of their current performance, further validation, and potential chemical cleaning protocols will be crucial in order to identify the optimal alternative routes.[11] In the following section, alternative options to end-of-life membrane disposal are described.

Reuse

In waste hierarchy, "reuse" includes checking, cleaning, or repairing recovery operations, by which products or components of products that have become waste are prepared so that they can be reused without any other preprocessing.[30] According to some studies, end-of-life RO membranes present similar performance to those of NF.[13,31] Based on desalination plant experiences (Sadyt and Valoriza Agua Cos.), aged membranes are often reused internally as "sacrificed" elements (placing them to the first or last position), in order to support the major fouling effect. Recently, Aqualia Co. has led the investigation in mechanical and chemical treatments to clean end-of-life RO membranes, at pilot scale during the Life-Remembrance project.[15] The main objective of the project was to recover RO membrane performance for further reuse by employing cleaning procedures without damaging the PA layer.[32] In this way, membranes were studied to be reused in the same desalination process where they came from or in other applications that need lower water quality such as urban tertiary wastewater treatment. In both cases, the industrial facilities were managed by Aqualia Co., demonstrating an example of centralized management of end-of-life membranes. Following this trend, the European project Life-Releach was initiated in 2014, aiming to reuse regenerated RO membrane in the treatment of landfill leachates.

Moreover, to date, Watersurplus, a US-based company, appears to be the only commercial supplier of second-hand RO, NF, and UF membrane elements. Watersurplus purchases, cleans and tests, repackages, and repurposes these elements at significant cost

Fig. 5 End-of-life membranes collected in a shipping container in a desalination plant. Pictures by (A) Neil Palmer, reproduced with authorization and (B) Pierre Le-Clech.

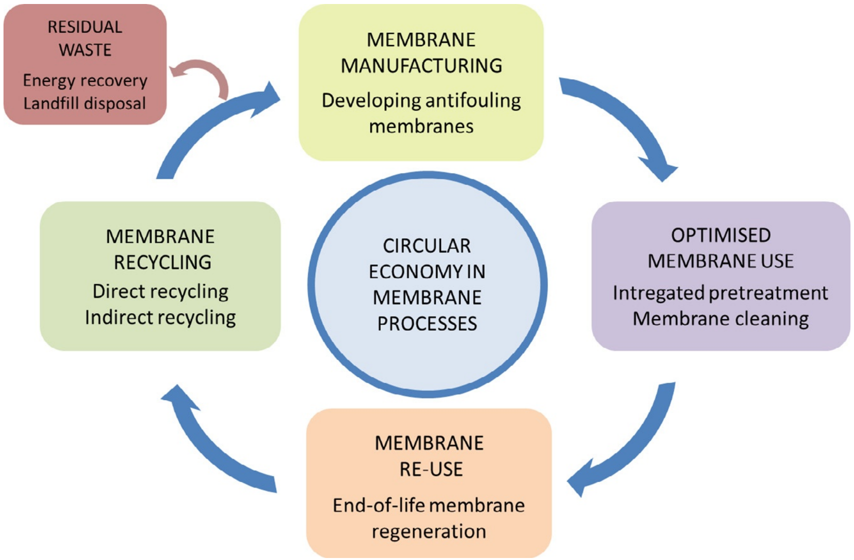


Fig. 6 Towards a circular economy in membranes used in desalination. From Landaburu-Aguirre, J.; García-Pacheco, R.; Molina, S.; Rodríguez-Sáez, L.; Rabadán, J.; García-Calvo, E. Fouling prevention, preparing for re-use and membrane recycling. Towards circular economy in RO desalination. *Desalination* **2016**, *393*, 16–30.

savings to the user. The unit cost ranges from \$150–\$400, with batches of up to 400 elements available to purchase.[26] By 2016, the company had acquired and reused over 25,000 surplus RO membrane elements that can be used in diverse applications such as power, oil and gas, mining, agriculture, industrial water reuse, and chemical manufacturing.[33]

Besides all of these examples and the growing interest for end-of-life RO membrane reuse, this option is not always possible due to the high membrane fouling or physical damage caused by abrasion of suspended particles. In these cases, membrane recycling becomes another potential strategy.

Recycling

According to the European Union Waste Framework Directive (2008), "recycling" relates to any recovery operation by which waste materials are reprocessed into products, materials, or substances whether for the original or other purposes. It includes the reprocessing of organic material, but does not include energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations.[30] Under the framework of membrane technology, this category can be divided into two recycling types: direct recycling and indirect recycling, depending on if recycled membranes conserve their original spiral wound structure or not.

Direct recycling

In the present context, direct recycling refers to the conversion of the end-of-life RO membranes through partial or complete degradation of the dense PA layer.[13] The relative vulnerability of the PA layer towards conventional oxidative agents has been widely studied in the context of aging/chemical degradation.[34–36] In case of direct recycling, PA oxidation is usually used as the recycling mechanism that changes the membrane morphology and performance. In fact, membrane direct recycling by chemical modification is gaining interest at academic and industrial level. Rodríguez et al. introduced the concept of transforming end-of-life membranes into UF membranes and their further use in wastewater treatment processes.[37,38] In this early work, sodium hypochlorite (NaOCl) and other strongly oxidative chemicals, such as hydrogen peroxide (H_2O_2), sodium dodecyl sulfate, and potassium permanganate (K_7MnO_4), were tested under different operating conditions (active recirculation versus passive immersion by soaking membranes) to degrade the active layer from the membrane. Among the chemical agent used, they identified K_7MnO_4 as the most successful one with an optimal dose of ~ 1000 mg L^{-1} for 1–2 h. The recycled membranes were then tested as a pretreatment prior to RO process removing up to 96% of the suspended solids. Although a high level of fouling was recorded during the filtration, a nearly complete recovery of the permeability was possible.[38] Following this recommendation, more recently Ambrosi and Tessaro used K_7MnO_4 to modify the end-of-life PA layer with a more controlled degradation.[39]

On the other hand, higher permeabilities of recycled membrane have been found by using higher exposure level (ppm h) of oxidant and using free chlorine as PA degradant at basic pH.[40–42] Lawler et al. demonstrated that the transformation of end-of-life RO membranes into UF membranes was possible due to the complete removal of the active PA layer. As an example, they reported an increase in permeability of 8.6-fold for the end-of-life Lenntech's CSM membrane after exposure to NaOCl at 300,000 ppm h. The membrane salt rejection capability was close to null, achieving NaCl rejection coefficients less than 1%.[41] Better control of the exposure time of the membrane to the chlorine agent could further lead the membrane transformation toward recycled NF

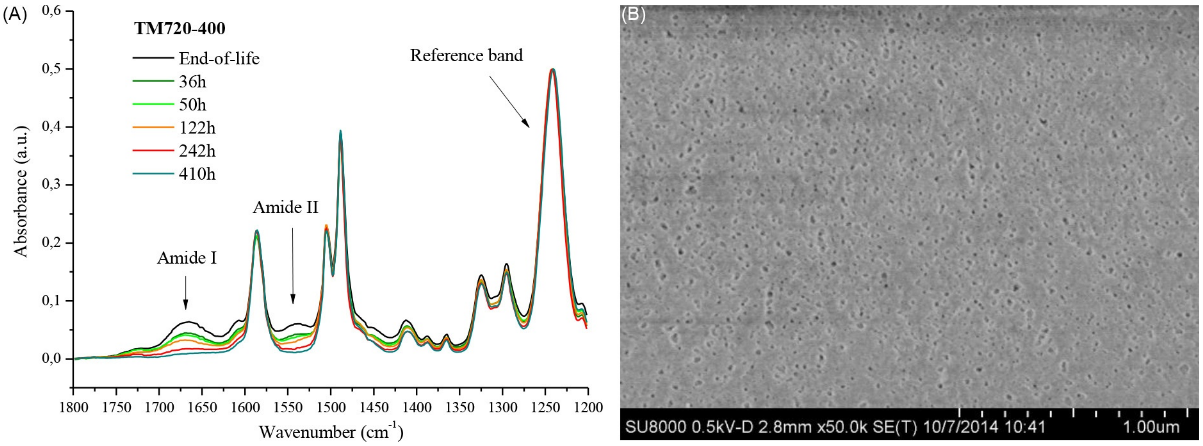


Fig. 7 (A) ATR-FTIR spectra of end-of-life TM720-400 membranes after different exposure times and (B) SEM micrograph of TM720-400 membrane exposed for 410 h. Conversion process in both cases was conducted by using 124 ppm free chlorine, pH >10, and passive immersion transformation method. Extracted from Molina, S.; García-Pacheco, R.; Rodríguez-Sáez, L.; García-Calvo, E.; Campos, E.; Zarzo, D.; et al. In *Transformation of End-of-Life RO Membranes Into Recycled NF and UF Membranes, Surface Characterization (15WC-51551)*, Proceedings of IDAWC15, San Diego, 30 August–4 Sept, 2015.

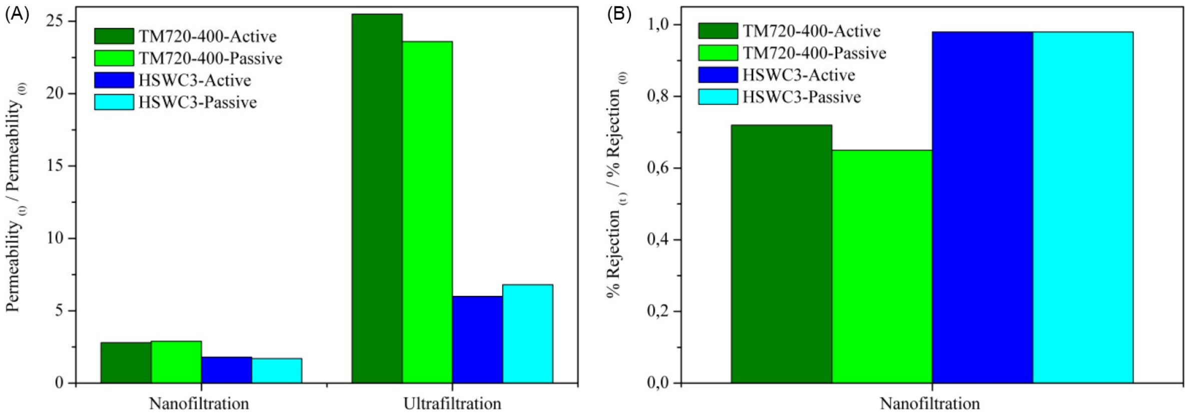


Fig. 8 (A) Normal permeability ($P_i/P_{\text{end-of-life}}$) and (B) normal salt rejection coefficient ($R_i/R_{\text{end-of-life}}$) of recycled NF and UF membranes by passive and active methods. Modified from García-Pacheco, R.; Rabadán, F. J.; Terrero, P.; Molina Martínez, S.; Campos, E.; et al. In *Life+13 Transfomem: A Recycling Example Within the Desalination World*, XI AEDyR International Congress, Valencia, 2016, VAL-112–16.

membranes. García-Pacheco et al.[42] used a mixed solution (synthetic BW) of monovalent, divalent, and low molecular organic compounds that help to identify the borderline condition between RO, NF, and UF properties. In this study, it was concluded that 50 h (reaching 6200 ppm h free chlorine) and 242 h (reaching 30,000 ppm h free chlorine) were required to convert, in most cases, end-of-life RO membranes into NF and UF membranes, respectively. In fact, in a parallel investigation, Molina et al.[43] demonstrated that, at these exposure levels of NaOCl, membrane surface significantly changes. Fig. 7(A) shows the attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra for TM720-400 model. All the spectra were normalized to band at 1240 cm^{-1}, of phenylene ether stretching vibration of the PSf support layer, which remains constant during the degradation of PA layer. The spectra from the end-of-life membrane show peaks at 1664 and 1542 cm^{-1}, corresponding to amide I and amide II bands, respectively, associated with C═O stretching and N—H plane bending. The peak at 1610 cm^{-1} is representative of the C═C stretching vibrations from the aromatic amide bonds.[11,36,44] Up to 50 h of exposure time, amide peaks were similar to the end-of-life membrane. However, the intensity of these peaks progressively reduced to reach non-detectable limits, when the exposure reached 242 and 410 h (>30.000 ppm h). The absence of peaks is due to the elimination of PA layer. In fact, further SEM micrograph analyses (Fig. 7B) that help to characterize membrane surface were conducted in four end-of-life RO commercial brands showing nanopores around 13 nm Feret diameter.

In both investigations (García-Pacheco et al. and Molina et al.), since low free chlorine concentration (124 ppm) was used, long exposure times were required to achieve UF-recycled membranes. Consequently, an industrial approach to more realistic exposure time was further investigated during the Life-Transfomem project. In this example, conversion of end-of-life 8″ RO modules is conducted following the exposure levels (ppm h) detected at laboratory scale, but using higher free chlorine concentration solution. Therefore the exposure time required for degradation is reduced. Moreover, the conversion methodologies (passive immersion and active recirculation) are under review for potential patenting.[45] Fig. 8 shows results of normal permeability

(Fig. 8A) and normal salt rejection coefficient (Fig. 8B) obtained after converting two end-of-life RO membrane models (TM 720–400, BW and HSWC3, SW) into NF and UF membranes using both methods.[46] In the case of conversion to NF membranes, permeability increased 1.5-fold with respect to the initial values, while the salt rejection capability slightly decreased. On the other hand, the conversion process to UF membrane resulted in complete degradation of the PA layer and consequently the membranes lost ion rejection capability. Indeed, free chlorine exposure of the end-of-life BW membranes achieved an increase of permeability up to 25-fold.[46] However, in case of SW RO membranes, the permeability increased only fivefold. This could be due to the high operation pressure (>60 bar) applied during the SW desalination process that provokes more compaction of the PSf pores, resulting in a final higher water resistance. In addition, variation in permeability might also be due to the intrinsic PSf characteristics that might vary among the different membrane models.[47,48]

As Fig. 8 shows, there is no significant variability between the passive (soaking membranes) and active (recirculation solution) conversion methods. However, end-of-life membrane conversion into UF-recycled membranes occurred more quickly using the active method (less ppm h is required). Nevertheless, circulation of the oxidant solution would require more energy and equipment cost than soaking membranes in a static reactor.

Indirect recycling

Indirect recycling relates to module deconstruction to reprocess the whole membrane or some sections into industrial products. Therefore, it would be an alternative for end-of-life membranes that cannot be directly recycled and for spent recycled membranes.

As discussed earlier, membranes are generally made of a number of polymeric materials. For example, RO membranes are thin-film composites including aromatic PA dense layer supported by microporous PSf inner layer and nonwoven polyester (PET) webbing. In addition, feed spacers and permeate spacers are made by polypropylene (PP) and PET, respectively. Acrylonitrile butadiene styrene (ABS) is used for the permeate tubes and end caps, and fiberglass for the outer casing, along with glued parts containing proprietary epoxy-like components.[49] As a result, each of those materials could be extracted and recycled (mechanically and/or chemically[13]).

Alternative indirect recycling options for the disposal of end-of-life modules have been previously studied and cover various options, from exotic fabric and decoration for clothing[50] to more realistic use as aggregate material in composite concrete and wood fillers.[13] PET permeate spacer and ABS permeate tube remain the most likely candidates to be recycled as these materials are only exposed to clean water. PET is widely and routinely recycled, especially to manufacturer drink containers. Therefore, this material could be separated and sent to a PET recycling plant. In case of PP feed spacer, the main challenge remains the high level of deposited fouling on the membrane and extensive cleaning would be required. Direct reuse of some of the membrane elements has also been reported. For example, sheets and spacers have been recycled as geotextiles in home gardens under a layer of gravel in order to maintain the position of decorative rocks and eliminate weed growth.[31] Additionally, potential agricultural applications for the spacers, including bird netting, wind breakers, or nets for lawn protection, have also been proposed.[49] The use of feed spacers and ABS caps could be particularly interesting in wastewater treatment as filler material of conventional trickling filter, to promote microbiological growth. Although no report on the recycling of the module fiberglass could be found, previous studies have investigated fiber-reinforced plastic composite recycling.[51,52] Even though landfill and incineration are the most commonly waste management route adopted for fiberglass,[53] it could also be recycled using physic-mechanical recycling method, converting it into a thermoset material.[54] Another possibility would be to use the inert granular material for the partial substitution of aggregates in cementitious mixtures.[51]

So far, only one business (MemRe GmbH Co., Germany) offers indirect recycling of end-of-life RO membranes. The company manages the transportation and labeling of end-of-life membranes, from the pickup on site until the recycling plant, and provides special services for radioactive contaminated membranes if requested. Indeed, the company provides the certificate of disposal to its customers, confirming conclusively the process, and completes the documentation requirements of customers, for example, regulators, official or governmental authorities, or the board of control.

Energy Recovery

Based on the concept of waste management hierarchy, the conversion of solid wastes with the controlled release of heat energy is another attractive opportunity for end-of-life products. The main categories of thermal processing commonly used in industry include incineration, pyrolysis or thermal processing in the absence of oxygen, gasification (i.e., partial combustion with limited air to produce syngas), and catalytic conversion to fuel oil.[55] Environmentally, gasification and pyrolysis offer advantages over simple incineration, as they produce fewer emissions, reduce waste residues, and increase energy recovery.[56] Most importantly, some of these processes can be applied to mixed plastic wastes, such as the combination of materials used in the manufacturing of membrane modules. Incineration of plastic solid waste can reduce the volume by 90%–99%, greatly reducing the strain on landfill. In addition, heat energy can be recovered and used for electricity generation or other heat-related processes.

Earlier consideration of using old membranes in thermal processes has been initiated with the study of the thermal decomposition of RO membranes.[49] As described earlier, the membrane components are comprised of synthetic polymers, with the exception of the fiberglass outer casing. The carbon content of the polymers ranges between 60% and 90% by mass for the major membrane components. A typical 8″ RO membrane element with 13.5 kg is therefore expected to contain approximately 9.1 kg of carbon, making it suitable for a number of thermal processing strategies. Moreover, with membrane module featuring an energy content equivalent to that of coal, energy recovery through incineration is an attractive option, resulting in the large reduction in waste volume and the generation of usable energy.[57] However, while current technology makes it possible to operate incineration plants with significantly reduced emissions, there is a large public and political resistance against incineration in some regions of the world.

Pyrolysis treatment is an alternative strategy for energy recovery, based on the use of plastics gasification to produce a syngas with high energy content. Pyrolysis features a number of advantages over traditional incineration, including the reduced air emissions and the production of a usable fuel product. Due to these advantages, this type of tertiary treatment of plastic waste is seen as one of the most sustainable solutions.[58] Syngas production is not a new process (traditionally based on coal as a feed product), and provides a promising energy recovery method for waste plastics.

A novel alternative is based on the use of old membrane components as a polymeric material source in electric arc furnace (EAF) steelmaking process. The use of waste plastics and rubbers has been extensively tested in recent years.[59] This method has been specifically tested with membrane components and the results show a similar benefit of their use, when compared to other waste materials tested.[28] A partial waste polymeric material substitute actually improves the EAF process through increased energy retention and promotion of foamy slag. There are, however, strict requirements for feed quality during this process and any type of contamination can lead to a negative impact on steel quality. Material deposited on the membrane surface and variations in the chemical makeup of the module lead to this process being viable, but complicated. As the industrial application of this process already utilizes the homogenous and ample material source of waste vehicle tires, the use of complex waste sources such as end-of-life membranes is not yet an attractive proposition.

Road Map for Better Management

Waste Policies-Product Stewardship

The constantly increasing amount of municipal and industrial wastes produced around the world has driven many governments to develop and implement a number of strategies to better manage the end-of-life fate of various items, including high-end products. As a result, a wide range of policies are now considered to target the disposal of specific waste materials, and it appears reasonable to seek legislated solutions for the fate of old membranes. In particular, the concept of product stewardship recently developed for electronic waste (e-waste) management is an interesting case study, from which a number of lessons could be considered for membrane modules.

Given their significant environmental impact, e-waste (i.e., computer, television, etc.) is now generally collected and recycled specifically by local municipalities and/or councils. Some of the suppliers have also developed their own recycling schemes but have generally failed to implement them globally due to the high economic impact of this effort. It would therefore appear that compulsory recycling schemes need to be implemented and that the responsibility of (and the costs associated with) the end-of-life product falls into the supplier hands rather than those of the local government.[60] This would undeniably result in an increase in the initial cost for the membrane purchase, but would warranty appropriate management of the product at the end of its life.

In a recent bill passed by the Australian Government,[61] a detailed framework is provided and allows the relevant stakeholders to develop specific product stewardship arrangements around three options: (1) voluntary, (2) coregulatory, or (3) mandatory arrangements, depending on the level of responsibility taken by the industry. More detailed considerations of these existing policies and how they could be applied towards membrane suppliers/users have been discussed in an Australian context.[11] In addition to the necessary consultation to be conducted between the various stakeholders, many remaining challenges are still to be addressed before implementation of a systematic approach for waste management of old membrane modules: In all proportions, the volume of membrane waste is still relatively small compared to other waste types (plastic bottle, e-waste, etc.), and the nature/contamination of the membrane waste is expected to significantly vary from sites to sites. Finally, the original location and the production frequency of this type of waste would also present logistic challenges for practical implementation.

Other documents, such as packaging covenant, can offer potentially useful pointers towards a more sustainable management for membrane waste.[62] National packaging covenants generally describe issues including the design of resource-efficient and more easily recyclable packaging, and considerations for increasing the recovery and recycling of used packaging and for reducing the incidence and impacts of packaging litter. Although it is difficult to imagine future design of membrane modules to be defined by those drivers only, those considerations could have a role to play to develop more sustainable products.

As mentioned previously, there is a growing interest in alternative management routes. Fig. 9 shows a roadmap of the various options currently considered.

Life Cycle Assessment of End-of-Life Options for RO Membranes

One of the primary considerations when selecting an end-of-life option for used membrane modules is its relative environmental impact. Life cycle assessment (LCA) can be used to quantity the impact of different manufacturing processes, and disposal options. LCA is a systematic tool that considers a wide range of inputs including the burden of raw material extraction and processing, energy consumption, and transportation.

Fig. 10 shows the life cycle of a membrane module from raw material extraction to end-of-life disposal and every relevant stage when performing an LCA. This tool has been increasingly used in the water treatment industry.[63]

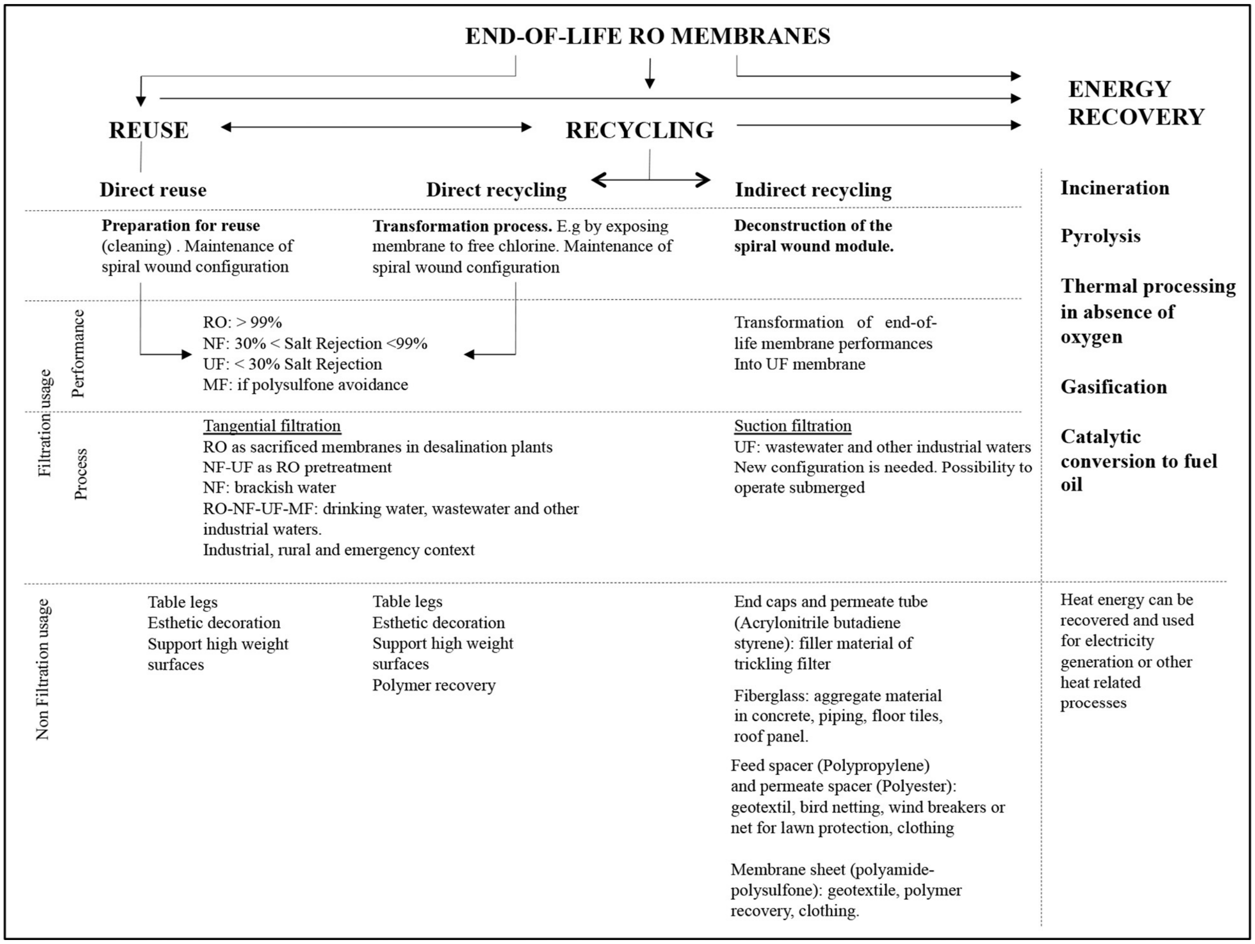


Fig. 9 Scheme of some alternative options for end-of-life membranes in terms of reuse and recycling, towards a circular economy.

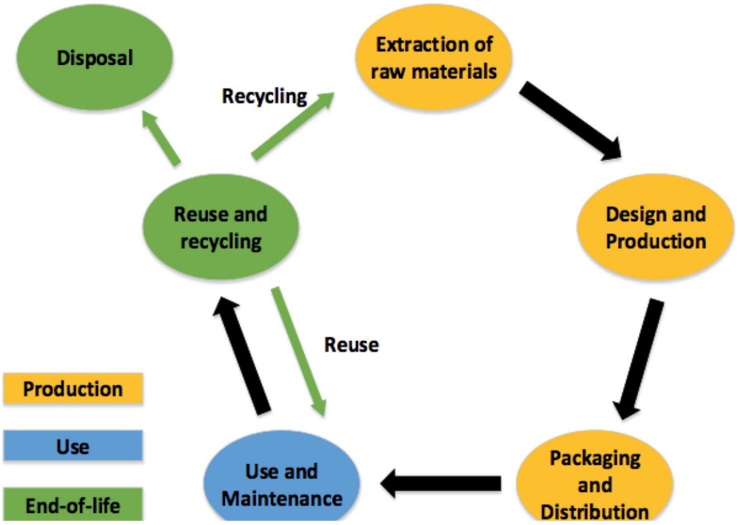


Fig. 10 Membrane life cycle. From Lawler, W.; Alvarez-Gaitan, J.; Leslie, G.; Le-Clech, P. Comparative life cycle assessment of end-of-life options for reverse osmosis membranes. *Desalination*, **2015**, *357*, 45–54.

An LCA follows a strict methodology outlined in ISO 14044/44,[64,65] and comprises four major steps: (1) goal and scope definition, which identifies the purpose and objectives of the study, including the objects and processes to be studied and their system boundaries; (2) life cycle inventory, which involves the systematic collection of all relevant inputs and outputs of all processes included within the system boundaries; (3) life cycle impact assessment (LCIA), where collected data is grouped and assigned to specific impact categories and characterized using a suitable LCIA model; and (4) life cycle interpretation, where the LCIA model is used to make conclusions and recommendations in the context of the original study goal.

A number of LCA studies have been completed on the production of potable water through treatment by RO and other membrane technologies.[66] It has been stated that the impact of RO membrane production and replacement is $<5\%$ of the overall process, per unit of water.[67,68] However, this only highlights high environmental burden of the desalination process and does not negate the potential benefits of an efficient end-of-life program for used RO membranes.

A recent study has built on this previous work by excluding the use phase of the membrane from the life cycle, therefore highlighting the impact of manufacturing and disposal.[69] The study, which was completed from an Australian geographical standpoint, uses an RO membrane module as the functional unit and compares all end-of-life options in terms of production offsets. For example, if a module is reused in a lower performance application, it partially offsets the manufacturing of a new module. The equivalent impact of manufacturing the different components of a standard 8″ RO membrane module can be seen in Fig. 11. The results include nine impact categories within the areas of climate change, resource depletion, human health and toxicity, and air pollution. This data can be used to highlight areas of the manufacturing process that can be potentially improved, and is critical in comparing different end-of-life options.

The end-of-life options that the study compares include incineration, syngas conversion, use as a coke substitute in EAF steelmaking, material recycling, direct RO reuse, and chemical conversion to UF membranes and then reuse. Fig. 12 shows the impact of these options relative to the impact of manufacturing the module. For example, -100% relative impact would indicate a complete offset of the production of the module. While nine impact categories were investigated, carbon dioxide-equivalent emissions (CO_2-e) and oil-equivalent consumption (oil-e) units are used to reflect climate change potential and nonrenewable resource depletion, respectively, which highlight key environmental issues.

The results of this study closely follow the expected results of the waste management hierarchy, with direct membrane reuse being the most favorable and landfill the least favorable options, in terms of CO_2-e emission and oil-e consumption. While the impact of landfill is relatively small due to the inert materials used in its construction, the primary environmental concern is the land required for disposal. In terms of diverting mass from landfill, incineration is the most favorable as it reduced the disposal mass by over 90%, with that remainder comprising of the residual silica from the fiberglass casing. Direct membrane reuse is the worst performer in this regard as the membrane still needs to be disposed of after the reuse period. These results are highly dependent on reuse life span and transportation distance, and a detailed sensitivity analysis can be found in the original work.[69] Material recycling is also a favorable option despite only 40% by weight of the module being suitable, with the remaining components requiring landfill disposal.

This type of LCA studies highlight the benefits of an organized program and encourage the development of a membrane disassembly recycling process and the use of recyclable components during manufacturing.[69] Additionally, the membrane manufacturing model can be directly applied in future LCA research involving RO desalination plants by replacing common simplified placeholder models for membrane construction and replacement.

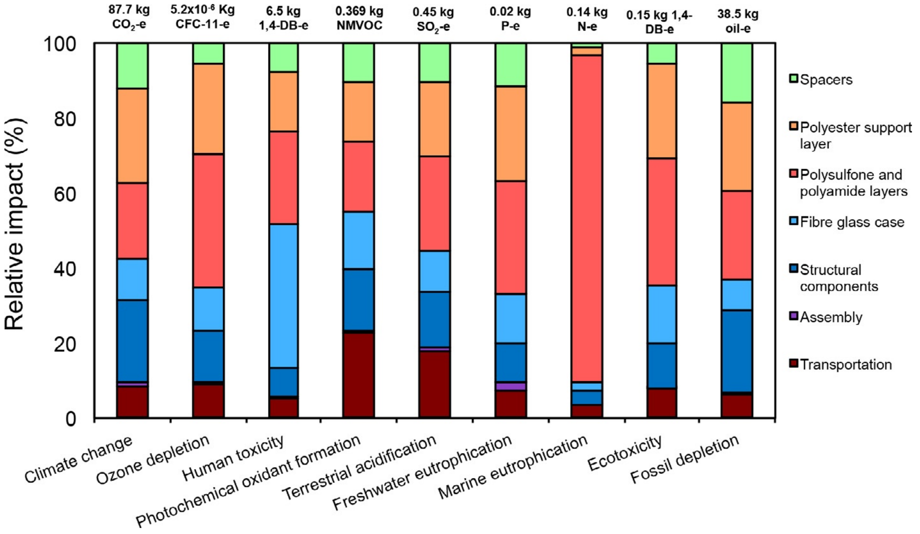


Fig. 11 Relative impact from different components during the manufacturing of one RO module. Values above bars are the total emissions for the impact category. From Lawler, W.; Alvarez-Gaitan, J.; Leslie, G.; Le-Clech, P. Comparative life cycle assessment of end-of-life options for reverse osmosis membranes. *Desalination*, **2015**, *357*, 45–54.

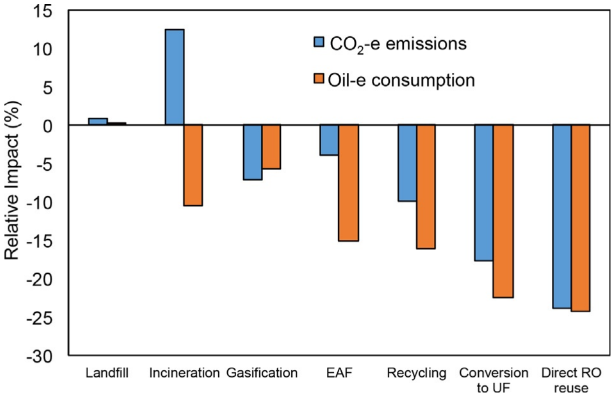


Fig. 12 Greenhouse gas emissions and resource depletion for the disposal of one RO membrane element. Results are displayed in terms of relative offset of membrane production. From Lawler, W.; Alvarez-Gaitan, J.; Leslie, G.; Le-Clech, P. Comparative life cycle assessment of end-of-life options for reverse osmosis membranes. *Desalination*, **2015**, *357*, 45–54.

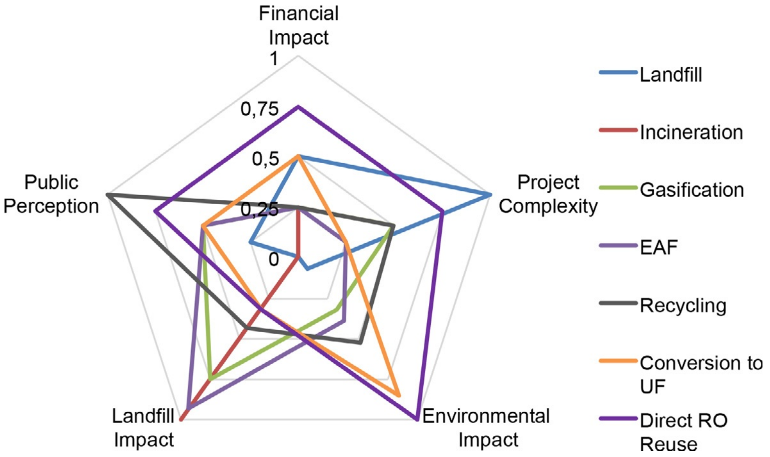


Fig. 13 Relative assessment score for end-of-life scenarios: (0) least favorable to (1) most favorable. Modified from Lawler, W. *Assessment of End-of-Life Opportunities for Reverse Osmosis Membranes*; The University of New South Wales: Kensington, NSW, 2015.

Decision-Making Tool for End-of-Life Membrane Users

Throughout recent years, options for end-of-life membranes have been assessed using a wide number of methods including financial viability, environmental impact, and technical feasibility. To bring this information together and to help select the optimum end-of-life options, a decision-making tool has been created.[28] This tool is called MemEOL and can be found online.[70]

The tool is based on a discrete multi-criteria decision analysis system (MCDA), which is a powerful method for modeling and solving problems with multiple inputs.[71] The strength of MCDA is that criteria measured in different units and both qualitative and quantitative information can be used.[72] Specifically, the quantitative results such as environmental impact from an LCA and the qualitative information such as public acceptance and project complexity can be combined in a single analysis. The specific MCDA method used is simple additive weighting, which is also known as the weighted sum method, and is a subset of multi-attribute utility theory.[73]The tool uses simple, non-overlapping criteria to assess the performance of the end-of-life alternatives for the used membranes. The criteria have been selected to reflect parameters significant to the user, and that facilitate comprehensive and meaningful assessment of the end-of-life options. The criteria include financial impact, public perception, project complexity, landfill impact, and environmental impact. During the development of this model the end-of-life options considered include landfill disposal, municipal incineration, gasification, use as a coke substitute in electric arc steelmaking furnaces (EAF), direct material recycling, chemical conversion to UF membranes, and direct reuse as RO membrane applications of lower performance requirements. The tool also takes user input in the form of membrane performance and the ranking of various parameters in order of importance for the specific end-of-life program being considered. Detailed discussion of the inputs and model can be found in the following works.[28,69]

Fig. 13 shows the simplified results from the model and allows for the comparison of various end-of-life options. A number of observations can be made, which will provide insight into the outcomes provided by the decision-making tool. Direct RO reuse is highly favorable in many of the considered categories, making this option preferable for a number of combinations of user input criteria rankings. Additionally, there are no assessment criteria in which the conversion to UF is preferable over direct RO reuse; therefore, it will only be recommended when direct reuse is not feasible, or presented as a secondary option. However, if the user indicates that physical damage is present, or the membranes are not within a usable performance range, the tool will assess alternative options. The scenarios of incineration, gasification, and EAF are highly favored if reduction in landfill waste is the user's priority. Apart from reduction of landfill waste, incineration has been shown to be the least favorable option. Sending the membranes to landfill is the option with the lowest project complexity, but is extremely unfavorable in all other categories.

This tool can help to promote better practices in the desalination industry by helping users to identify and select the optimum end-of-life options for their used RO membranes as the inputs and weighting of different criteria can be changed to address specific challenges.

Potential Markets Associated to Membrane Direct Recycling and Reuse

The constant growth of the RO technology together with the annual membrane replacement percentage (around 5%–20%) has created not only a nonstop accumulation of end-of-life RO membranes, but also a nonstop market of new RO elements. Already in 2004, replacements made up approximately 60% of the annual sales of RO/NF membrane.[74] Therefore, end-of-life RO membranes are available around the world and a high percentage of them are suitable to be transformed into spiral wound NF and UF membranes by direct recycling methods. Fig. 14 shows a potential business plan of a recycling end-of-life RO plant.

As Fig. 14 shows, the business plan is based on four main pillars: (i) the recycling RO plant, (ii) the potential clients that would be interested on purchasing the recycled membranes, (iii) stakeholders, and (iv) investors and shareholders, including the government.

Recycling RO Plant

Bearing in mind that, technically, membrane direct recycling is feasible, and with the expectation that the products obtained would be competitive in the existing membrane market, the success of the direct recycling process would depend on supply and demand. In Fig. 14, a recycling membrane plant is considered, which is expected to be managed by a company from waste, desalination, or manufacture membrane sectors. The recycling plant would have three main eco-innovative selling products: RO-, NF-, and UF-recycled membrane. These products could offer modularity, flexibility, smart monitoring, efficient treatment, and market diversification with lower cost. Although some research has been developed during the last decade, the recycled membrane plant would

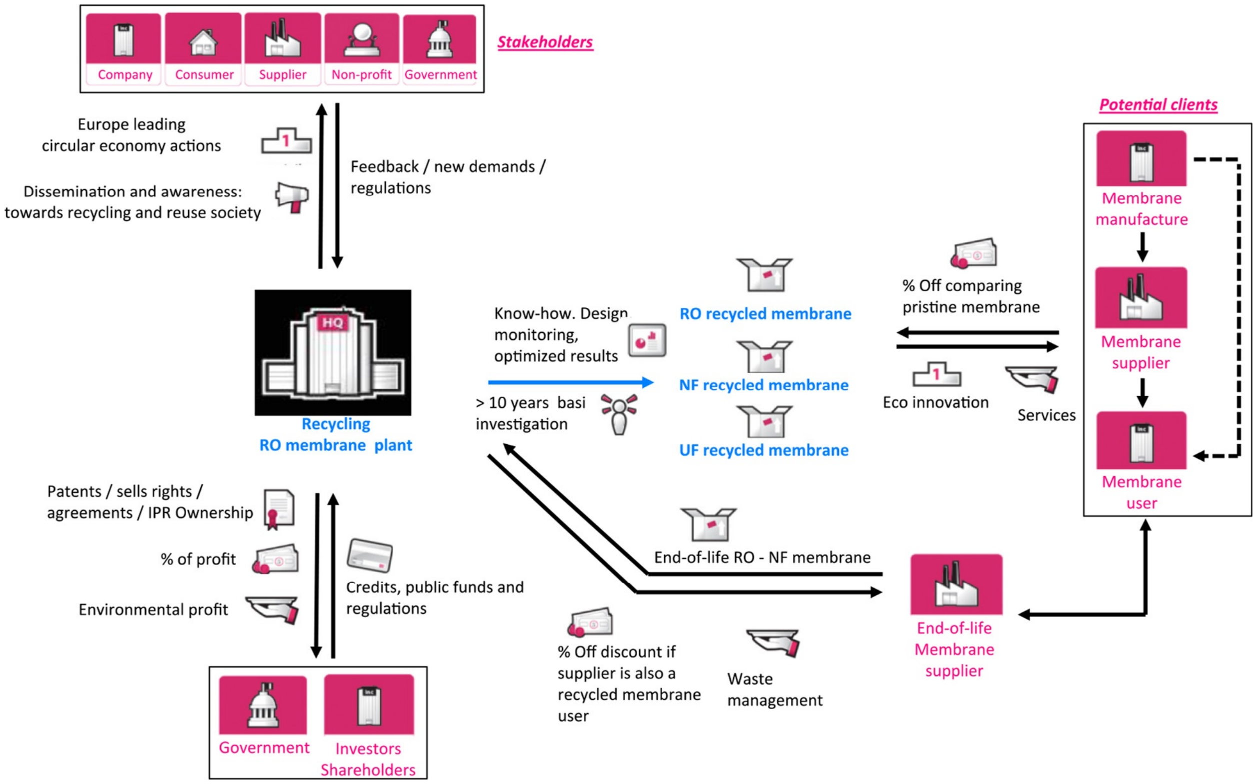


Fig. 14 Potential business plan for a recycling RO membrane plant (following Board of Innovation Tool).

improve laboratory and pilot operation conditions and would generate its own know-how for real scale, including patent rights and intellectual property right ownership.

Different business model scenarios could be proposed. On the one hand, a centralized business plan scenario may gain interest for membrane manufacture companies or waste manager companies. They could collect membranes from desalination plants and generate a stock of recycled membranes with diverse performance. On the other hand, the big desalination companies (Veolia, GE, Doosan, IDE, Sadyt, Acciona, etc.) that normally construct, manage, and maintain also other industrial plants like BW and wastewater plant could recycle their end-of-life RO membranes and further reuse them in their own industrial facilities (decentralized scenario).

Potential Clients

Potential customers have been identified as (i) membrane manufacturers, (ii) membrane suppliers, and (iii) membrane users. Membrane manufacturers produce their own membranes. However including recycled membranes as an eco-innovative brand in their catalog could increase their product diversification. Indeed, depending on the demand, membrane suppliers could acquire recycled module for their stocks in order to distribute them to the membrane users. Both manufacturers and suppliers could offer lower cost comparing to the conventional membranes due to the wide economic margin expected from the recycling process.

Membrane users can be grouped in two sectors: customers interested in long-term and short-term membranes. In the first case, old RO membranes (which still maintain RO performance) could be reused as sacrificed membranes in RO desalination plants, placing them in the first or the last position, according to the main membrane fouling tendency. In this scenario, 16%–30% of the membranes used could be second-hand membranes, thereby reducing the replacement cost and reducing the raw material needed for manufacturing new pristine modules. Moreover, for longer term applications, substitution of NF commercial membranes could be considered by recycled NF membranes to treat BW or in other industrial proposes. Finally, recycled UF membranes could potentially be reused as RO pretreatment in desalination process.

In addition, recycled membranes could have a potential use in decentralized wastewater treatment facilities. As an example, in Spain, nearly 6000 of over 8000 existing municipalities are small communities (<2000 equivalent inhabitants), which have wastewater treatment rates of less than 50%, and there is a lack of tertiary treatment facilities to treat this water. The implementation of advanced treatment facilities is often hindered due to economic reasons. Small communities do not benefit from the economy-of-scale effect and thus implantation and exploitation cost per habitant is higher, being most of the time unaffordable. Under this context, there is a potential market for compact and low-cost wastewater treatment facilities, where recycled membranes could be used.

The second group of membrane users could be classified as those demanding punctual treatment cases where the low cost of membranes makes their use feasible. In addition recycled membranes could be applied in cases where water quality is with high organic matter content and/or high salinity that provoke a rapid irreversible fouling that increases the membrane replacement rate. Industrial wastewater from landfill leaches, animal husbandry, textile, pharmaceutical, or food industry are examples of problematic waters. Recycled membranes could assert for temporary treatment solution by using mobile plants or by renting temporary systems.

Another potential sector identified as punctual users requesting low-cost membranes is international cooperation agencies to assess with drinking water at both levels: household treatment and conventional drinking water production and distribution, especially in case of emergency response. Common systems deployed for water production and distribution are normally robust systems with easy replacement parts and simple operating technology. Mainly, they consist in batch coagulation and disinfection or sand-active carbon pressure filtration with disinfection. However, this kind of system shows water quality limitation such as removal of salts, which is a concern in typhoon or tsunami emergencies due to the salinization of water resources. In fact, there is a market behind the emergency response to treat BW and SW using membranes: 3E (SETA), Aquamove MORO (Veolia Water), Emergency Service-Mobile Water Services (GE POWER & WATER), and Emergency SW 800 (Big Brand Water Filter). Moreover, military purchases for membranes used in mobile desalination (ROWPU) systems exceeded $15 million in 2004.[74]

It has already been recognized in literature that direct recycled end-of-life RO membranes have the potential to be used in low-cost humanitarian water treatment projects.[11] Moreover, preliminary studies conducted by Life-Transfomem consortium show that one recycled UF spiral wound module would be appropriate for few families according to the international standard recommendation (15 L per person × day[75]). Indeed, recycled membranes can achieve the maximum microbiological reduction (>4 Log_{10} reduction for bacteria and protozoa and >5 Log_{10} reduction for viruses) that WHO demands.[76]

Despite all the options summarized, it is expected that second-hand membranes will not be easily validated in high-risk applications such as potable water and water reuse in the pharmaceutical sector. Indeed, depending on the installed capacity of the desalination plant (especially in high-size plants), the reuse of recycled membrane would be considered in a distance time, when the zero risk could be guarantee.

Investors and Shareholders

In order to have a successful market penetration, the business model contemplates the key partnership of shareholders and investors that would inject money and resources. Further, financial funds and regulation from governments should be investigated in order to place the products into the market and to guaranty their sustainability thanks to the endorsement of the legislation.

Some legal actions could promote the usage of recycled membranes such as promoting an environmental tax-penalizing landfill option, implementation of subsidies for recycled membrane users, or credits with low interest for investments on recycling plants.

Stakeholders

Even though membrane recycling is demonstrated to be technically feasible, the wider application in industry and the market penetration is strongly dependent on overcoming further technical drawback, market competition, and social barriers.

Technical drawback

The main drawback expected for recycled membrane technology would be similar to conventional membranes, such as the energy required for the filtration process,[6] fouling,[77] cleaning, and concentrate stream management.[9]

Market competition

RO technology dominates the desalination field and its market is well established. 65% of the total capacity corresponds to RO membrane technology implementation.[20] However, new membrane models, featuring improved performance, such as higher permeability, are continuously implemented in the market. With RO module lifetime to be expected between 5 and 10 years for desalination, the recycled RO membranes would have to compete with the new commercial models. In fact, according to manufactures, TM720-400 or HWC3 models used in recycling membrane research are no longer being manufactured.

The successful implementation of NF mainly relies on its rejection capabilities, especially for divalent compounds. Even though NF process represents only the 2% of the installed desalination capacity worldwide for BW treatment,[20] it has numerous applications in other areas, especially for wastewater treatment, pharmaceutical and biotechnology, and food engineering.[78] Van der Bruggen identified the need to improve NF membranes such as the reduction of membrane fouling, increase in separation and rejection efficiency, improvement in membrane lifetime, and chemical resistance which are needed according to scientific community.[79] To achieve these improvements, diverse innovative methods in NF fabrication are being investigated such as (i) UV or photografting, (ii) electron beam irradiation, (iii) plasma grafting, and (iv) layer-by-layer methods.[78] However, thin-film composite NF membranes obtained through interfacial polymerization method are expected to remain the benchmark in development of NF membranes in the upcoming years.[78] This is the same methodology used to create RO membranes; therefore, end-of-life RO membrane recycled into NF would find a relative market niche, since they can support the NF membrane demand and can offer higher rejection properties than several commercial models available currently.

Nevertheless, the greatest implementation challenge is related to the UF membrane market. Spiral wound UF-recycled membranes have to compete with hollow fiber, tubular, and flat geometries. Between all, hollow fiber and spiral wound are still the most common used configurations for many industrial applications, such as milk and water filtration due to their low investment and energetic cost.[77] Improving antifouling properties of UF-recycled membranes would give them a value chain and reinforce their position in the market.

Polymeric membranes account for 80%–90% of the global treatment capacity[77]; however, ceramic membranes have been used extensively in the pharmaceutical, food and beverage, and industrial water treatment sectors, mainly due to their resistance to harsh operating and/or cleaning environments.[80] On the other hand, companies such as Veolia (CeraMem), Metawater, and Nanostone (CM-151) provide ceramic membranes. Indeed, the demand for ceramic membranes is continuously showing an upward trend, with an expected annualized growth of 12% between 2015 and 2020.[81] Therefore, they could also be high competitor for polymeric membranes such as the recycled UF membranes.

Social barriers

Besides the technical and market barriers, social acceptance and regulatory support are crucial in order to have an attractive and successful second-hand product in the market. To convince potential users, recycled membranes have to demonstrate several key capabilities, such as excellent removal, low prices, lower or similar energy consumption, and similar lifetimes as compared to the homologous RO, NF, and UF commercial membranes. On the other hand, health risk assessment should also be conducted and strict validation method should be applied in order to guaranty minimum risk of failure during the treatment process.

Future Work and Research Directions

This article has shown that alternative end-of-life RO membrane management routes to landfill disposal are feasible. However, the initial membrane performance of end-of-life RO membranes varies significantly depending on their fouling degree or damage level and therefore research on identifying end-of-life membrane management routes is still necessary. The weight of end-of-life membrane can be used as a good low-cost indicator of the fouling degree of the membrane; however, it is not accurate enough and further characterization methods are usually needed. In situ rejection characterization of single membranes, while in operation in the desalination plant, could be one potential solution. In addition, identification tools such as online MemEol can help to promote better practices in the desalination industry by helping users to identify and select the optimum end-of-life options for their used RO membranes.

Scientific articles published on membrane recycling show very promising results. However, the research regarding membrane recycling is relatively new and further studies are encouraged. The importance of proper storage of end-of-life membranes to maintain their properties has been figured out. Indeed, the feasibility of direct recycling membranes by using sodium hypochlorite has been demonstrated. However, new chemicals can be investigated for membrane transformation and also to improve antifouling properties of recycled membranes. In addition, indirect recycling methodologies can be considered as the next step to be taken after direct recycling, when recycled membranes exhaust their new life and their properties cannot be further restored. The deconstruction of the spiral wound modules to reuse plastic parts or the insertion of some plastic material in separate recycling routes is the main alternative evaluated. Moreover, LCA of potential alternative routes including energy recovery were evaluated. Conclusions show that direct membrane reuse is the most favorable and landfill the least favorable options, in terms of CO_2-e emission and oil-e consumption, while in terms of diverting mass from landfill, incineration is the most favorable as it reduced the disposal mass by over 90%.

Moreover, this article has shown the potential business model that could be followed based on four main parts:

(i) The membrane recycling entity as the center of the business plan.
(ii) Potential clients identified such as wastewater treatment plants and emergency response systems.
(iii) Shareholders and government, essential part that will invest not only in R&D but also for injecting money to further develop the recycling process and products.
(iv) Stakeholders/end users such as government and society that need to accept the product for its successful penetration into the market. In this way, a supportive regulatory framework is deemed necessary.

Recycled material to produce drinking water has to be approved and also politics incentives should encourage the membrane recycling and reuse procedures, for further successful implementation. In addition, some technical barriers have also been identified and therefore further full-scale monitoring of the recycled membranes should be still conducted. Membrane and transformation cost, effectiveness, durability, energy requirements, and maintenance should be investigated in more details. Indeed, since each sector has the conventional competitors, financial and economic studies should be completed.

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Paper III: scientific paper

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Transformation of end-of-life RO membranes into NF and UF membranes: Evaluation of membrane performance

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Surface transformation

ABSTRACT

Economic and environmental concerns demand the recycling and reuse of fouled, end-of-life, reverse osmosis (RO) membranes. Different dry stored coupons of commercial TM720-400 membranes were subjected to the chemical attack of NaOCl (124 ppm free chlorine), acetone solution (10,000 ppm) or N-methyl-2-pyrrolidone solution (10,000 ppm). The best permeability results were achieved with NaOCl solution and consequently it was used as the key reagent for further analysis. The effect of pH and membrane storage on the transformation process was evaluated. Membrane permeability and rejection coefficients were tested filtering synthetic brackish water containing NaCl (2,000 ppm), $MgSO_4$ (2,000 ppm) and dextrose (250 ppm). The basic pH showed the highest effect on the membranes performance therefore, experiments were carried out up to 410 h exposure time. The transforming process was repeated for five different commercial membrane brands, stored wet. Most of the transformed membranes achieved permeability and rejection like nanofiltration (NF) membranes up to 50 h exposure time and performed like ultrafiltration (UF) membranes after 242 h exposure time. It was observed that permeability and rejection coefficients were affected by the storage condition. This treatment may provide a cost effective and eco-friendly method of recycling end-of-life RO membrane process, at lab scale.

1. Introduction

One of the technical solutions to solve water scarcity is by using membrane technology, which allows obtaining fresh water from the major water sources. In fact, today reverse osmosis (RO) is the most widely used desalination technology globally [1] and aromatic polyamide-based (PA) composite membranes currently account for over 95% of existing RO desalination plants [2]. Reverse osmosis is a pressure-driven membrane process with a wide range of applications such as water purification, particularly, the desalination of brackish (BW) and sea water (SW) [3,4]. However, membrane technology suffers from the problem of performance decline caused by fouling [5] and despite many prevention strategies applied, fouling remains inevitable [6]. Fouling could block the pores and sometimes a fouling cake layer can be formed on the membrane surface [7]. As a consequence, the associated financial cost for m^3 of treated water increases significantly. In addition fouling is the main cause of the disposal of thousands of tones of RO membranes every year [8]. Generally, end-of-life membranes are handled according to the laws of each country and unfortunately, membranes usually end up in landfills.

According to the main pyramidal waste management principles of the European Directive 2008/98/EC on waste, prevention, preparing for re-use, recycling, recovery and disposal should be the priority order to be followed. Currently, desalination plants are operating in around 150 countries [9] and RO application in the worldwide industry processes is growing. Consequently, the number of disposed membranes is also increasing. Therefore, the recycling and reuse of end-of-life membranes should be a global environmental action. In fact, there are some studies that showed the potential of direct reuse (with no additional cleaning or treatment) [10]. Based on desalination plant experiences, changing the used membranes to the first position in the membrane tubes is another usual practice prior to be discarded. However, direct reuse is not always possible due to the high membrane fouling. Therefore, following waste management hierarchy, recycling of membrane modules should be the next step to be prioritized. Not-direct

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recycling strategies are being investigated and involve the deconstruction of the module. Examples of not-direct recycling are plastic combustion from the polymeric materials and material reuse like spacer and membrane sheet in not filtration processes [10]. Recently, National Centre of Excellence in Desalination from Australia (NCDA) has proposed to separate multiple layers and use them creatively as fabric and decoration for clothing and accessories [11]. More detail information about opportunities and strategies for end-of-life membranes were summarized by Lawler et al. [8].

Membrane direct recycling by chemical modification could be an interesting and innovative alternative that is gaining interest at academic and industrial level. Moreover, low polyamide tolerance of chemicals such as chlorine could be profited to change membrane morphology and performance. Membrane transformation can open new possibilities for end-of-life membranes rather than landfill disposal, prolonging the plastic material lifetime and the sustainability of the membranes processes. The aim of membrane direct recycling is to regenerate membranes able to compete with commercial membranes in terms of cost, effectiveness, durability, energy requirements and maintenance. Direct recycling strategies involve membrane regeneration and one of the techniques used is to employ a basic solution of sodium hypochlorite. This can allow to reinvest the membrane with characteristics similar to those possessed when first made (pristine reverse osmosis membrane) [12,13]. When the exposure level of chlorine is high, membrane performance can be transformed into different properties, creating new application membranes. In 2002, Rodríguez et al. introduced the concept of transforming end-of-life membranes into ultrafiltration membranes and their further reuse in wastewater treatment process [14,15]. They found that K_7MnO_4, was more successful chemical reagent for membrane transformation than NaOCl. However, the concentration range of chlorine used was low and it might have not been high enough for a significant transformation. Ambrosi and Tessaro [16] tried to recycle also end-of-life membranes by K_7MnO_4 but the resulting permeability of the transformed membranes were lower than those obtained employing high dose and exposure time of NaOCl [17,18]. Lawler et al. demonstrated that the transformation of end-of-life RO membranes to UF membranes was possible due to the complete removal of the active PA layer. An example of reported results is the end-of-life CSM RE8040-FE membrane case, which showed a significant increase in permeability ($>$ 8.6-fold) after 300,000 ppm h NaOCl exposure. Indeed, the membrane salt rejection capability was null, achieving NaCl rejection coefficients less than 1% [18]. In this work it was also demonstrated that dry membrane storage is detrimental to the success of the conversion process.

Research efforts have been focused on the end-of-life membrane transformation into recycled ultrafiltration membranes. However, controlling the exposure time of the membrane to the chlorine agent could further lead the membrane transformation towards recycled nanofiltration membranes [8]. Most of the previous studies reported the use of NaCl to evaluate changes in the membrane performance. Nevertheless, Ettori et al. used pretreated seawater for characterizing the aging process of RO membranes by NaClO [13]. To the best of our knowledge, there are no reports in the literature that use synthetic brackish water to evaluate transformed NF and UF membrane performance. Including mixed solutions containing inorganic salts such as NaCl and $MgSO_4$ and organic compounds could be crucial to find the border line conditions defining the transformation between ultrafiltration and nanofiltration membranes.

The main objective of this study is to examine at laboratory scale, the viability of recycling end-of-life RO membranes into nanofiltration and ultrafiltration membranes by a control exposure to NaOCl. A synthetic brackish water solution containing NaCl, $MgSO_4$ and dextrose were selected to conduct filtration tests. Membrane storage mode was also evaluated.

2. Experimental part

2.1. Materials and methods

2.1.1. Membrane and chemical reagents

All transformation assays were performed on several end-of-life polyamide RO membrane from 8″ diameter, spirally wound modules. Previously the membranes were used for treating, brackish water (BW) in case of the TM720-400 (Toray) and BW30 (Dow Filmtec) modules and sea water (SW) in case of TM820C-400 (Toray), SW30HRLE-440i (Dow Filmtec) and HSWC3 (Hydranautics). All membranes were conserved in Milli-Q water prior to be analysed, excepting some coupons of the TM720-400 module. In this case, membranes were conserved also under dry condition during two months prior to start the experiments. The membrane fouling was identified by autopsy and results are shown elsewhere [19]. All chemicals used in this study were purchased from Scharlab Lab (Spain). Reagent grade N-methyl-2-pyrrolidone (NMP), acetone, NaOCl (10%) were used for membrane regeneration. HCl (0.1 N) was used for pH adjustment and NaCl, $MgSO_4$ and dextrose were used for evaluating membrane rejection coefficients. Milli-Q water was used throughout the experiments.

2.2. Membrane transformation protocol

2.2.1. Preliminary analysis of membrane transformation potential

Dry stored membrane coupons of 216 cm^2 were cut from the TM720-400 end-of-life RO membrane in different places and hydrated in Milli-Q water for 24 h. Then, membranes were immersed (passive immersion) in solutions of either NaOCl (124 ± 8 ppm of free chlorine), 10,000 ppm NMP or 10,000 ppm acetone in sealed, opaque polypropylene plastic containers at room temperature (≈ 21 °C) for 0.08, 20 and 92 h. No agitation or pressure was applied in order to simulate the static conditions. Blank experiment involved the same protocol but exposing the membranes only to Milli-Q water. After the exposure times, the coupons were taken out of the containers and thoroughly rinsed with Milli-Q water until reaching Milli-Q pH. Membranes were conserved wet prior testing their water permeability according to the protocol described below (see Section 2.3).

2.2.2. Extended analysis of NaOCl-transformed membranes: PH effect

NaOCl was selected for further studies designed to optimize the transformation process. Dry stored coupons of TM720-400 membrane (the same size as above) were exposed to NaOCl transformation as described in Section 2.2.1, during 1, 20, 36, 50 and 122 h. Acid and neutral conditions were adjusted to pH-3 and pH-7 respectively, using 0.1 N HCl. For basic condition, no adjustment of pH was carried out (pH-10.5). The free chlorine concentration was analysed, prior and after membrane exposure, using a Pharo 100 Spectroquant spectrophotometer (Merck). After membrane exposure, the average chlorine depletion of the solutions was less than 10%, which is within the magnitude reported in the literature [20]. Basic pH modification condition was selected for further studies. In order to evaluate the reproducibility of the transformation process, five different brand models of end-of-life membranes stored in wet condition were evaluated: TM720-400 (BW), BW30 (BW), TM820-400 (SW), SW30HRLE-440i (SW) and HSWC3 (SW) membranes. In these cases, the exposure time series to NaOCl was 36, 50, 122, 242 and 410 h.

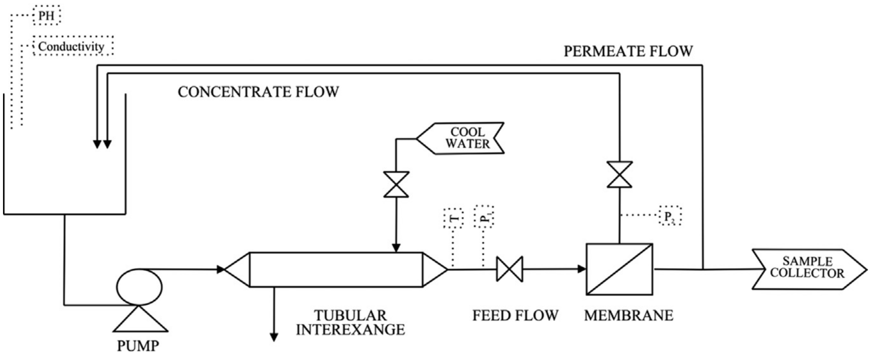

Fig. 1. Schematic diagram of the filtration setup.

2.3. Testing membrane performance

Three individual steps were carried out to find the difference between membrane permeability and rejection. The step-1 consisted in evaluating the end-of-life RO membranes performance in terms of permeability and rejection during filtration assays. The step-2 was based on the surface transformation of membrane in a chlorine solution (see Section 2.2). Finally, the step-3 consisted of the characterization of the transformed membranes using the same procedure as in the step-1. Steps-2 and -3 were repeated several times for the same membrane coupons until the exposure time series was completed.

A laboratory-scale cross-flow test system is shown in Fig. 1, with a high-pressure pump, a 25 L feed reservoir and a tubular heat exchanger with a temperature controller, was used in total recycle mode. The desired pressure and flow rate were achieved by adjusting the valve located after the membrane cell and the frequency pump regulator, respectively. Effective membrane filtration area (84 cm^2) was tested by loading the coupons into a flat-sheet stainless steel RO test cell, containing permeate and feed spacers from each original RO modules.

Milli-Q water and synthetic brackish water containing NaCl (2,000 ppm), $MgSO_4$ (2,000 ppm) and dextrose (250 ppm) were employed to test membrane performance. NaCl and $MgSO_4$ were chosen since they are the standard inorganic salts used by membrane manufacture for performances test. Dextrose was chosen as an organic solute since it is an uncharged, hydrophilic, low molecular weight compound (180.16 g mol^{-1}), that is retained at 90–100% by dense PA membranes and it is not absorbed by their surface [21]. All coupons were first compacted using total feed volume 5 L, flow rate 3.9 L min^{-1}, temperature 30 °C and at 15 bar transmembrane pressure (TMP). For the assays, the TMP was 5 bar and filtration tests were conducted maintaining the temperature at 30 °C and measuring the permeability and the rejection coefficients of the membranes. The permeability (P, L m^{-2} h^{-1} bar^{-1}), was calculated from the water flux measurements every 5 min, and the applied pressure. Permeate samples were returned to the feed tank to maintain the feed solute concentration. Salt rejection was calculated by measuring the conductivity of the feed (C_f) and the permeate (C_p) using a conductivity meter CM 35 (Crison Instrument, Barcelona) as expressed in Eq. (1). At least, six measurements of permeability and rejection were averaged for each representative data point for performance measurements.

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \cdot 100 \qquad (1)$$

After reaching the steady state condition for permeability and salt rejection (the experimental relative error was less than 5%), samples were taken from the feed and permeate for analysis. Individual ion rejection was determined by measuring the corresponding concentrations using an 861 advanced compact IC Metrohm ionic chromatograph. Organic compound (dextrose) rejection was determined by measuring the total organic carbon concentration using a TOC-V CSH Shimadzu device. The results were introduced into Eq. (1), where C_p and C_f now represent the concentrations of the corresponding analytes.

2.4. Membrane surface characterization

Some transformed membranes were further characterized for better understanding. The samples were dried at 110 °C for two days to remove moisture. Attenuated total reflectance–Fourier transform infrared (ATR–FTIR) spectroscopy using a Perkin-Elmer RX1 spectrometer was used to identify PA layer degradation. Scanning electron microscopy (SEM) using S-8000 Model (Hitachi) image device was also employed to examine the membranes surface.

3. Results and discussion

Initially, some preliminary tests were conducted with chemicals that could degrade the PA layer of the end-of-life PA RO

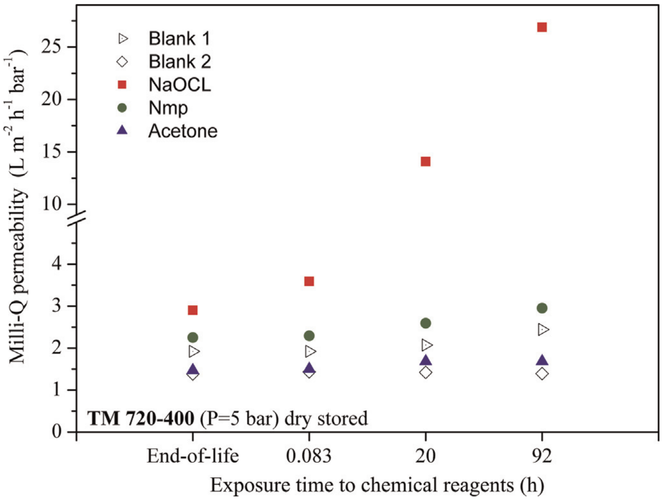

Fig. 2. Milli-Q permeability changes vs. exposure time of different chemical reagents (acetone, NMP, NaOCl). Membranes exposed to Milli-Q water are considered blanks.

membranes. The chemical reagents selected to used in transformation solution were NaOCl, which oxidizes the polyamide; NMP, which dissolves polyamide and acetone, which strips polyamide from membrane support layers. Fig. 2 shows the permeability for Milli-Q water achieved after the dry stored TM720-400 membranes coupons were exposed to these solutions. The longer the membranes were left immersed in the transformation agent, the better the permeability obtained. Since it was detected a 27% improvement (from 1.92 to 2.44 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$) in one of the blank samples after 92 h of Milli-Q exposure, a minimum of 30% increase permeability was considered as a significant effect. The improvement observed in the control samples might be due to several factors, including pore swelling and experimental error. Furthermore, acetone and NMP did not provoke substantial changes in Milli-Q membrane permeability. Therefore, it was observed that only the NaOCl treatment led to a noticeable increase in the Milli-Q water permeability: around 385% at 20 h (from 2.90 to 14.08 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$), and 827% at 92 h (from 2.90 to 26.90 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$). Then NaOCl was selected for further studies.

3.1. *Effect of NaOCl on dry stored TM720-400 membrane performance depending on the pH*

The chemistry of aqueous NaOCl solutions is largely dependent on pH. In water, NaOCl is totally dissociated, forming sodium hydroxide (NaOH) and hypochlorous acid (HOCl) which is in equilibrium with two other species, hypochlorite ($\mathrm{OCl^-}$) and chlorine gas ($\mathrm{Cl_2}$ (g)). For these reason, NaOCl membrane exposure was carried out at pH-3, pH-7 and pH-10.5.

3.1.1. *Permeability and salt rejection coefficients of transformed membranes*

To evaluate transformed membrane performance, filtering assays were conducted using synthetic brackish water. The average values of the physic and chemical quality parameters achieved in the brackish water solution are presented in Table 1. Fig. 3(a) and (b) shows the permeability and salt rejection percentage of five membranes tested: one for pH-3; one for pH-7 and three replicates for pH-10.5.

As Fig. 3 shows, prior to transformation process, the performance of all end-of-life membranes were similar. At pH-3 no significant change was found in permeability (less than 30% of increment). Since the main objective is the membrane transformation with higher permeability values, the experiments were stopped at 36 h exposure time. Similar results of this study have also been found [22,23]. However it has been widely reported in literature that at acid pH conditions the membrane permeability declines severely [24,25]. Controversial results can be explained due to the differences in the membrane material studied such as the origin of the PA membrane layer (commercial or tailor made). PA can be full aromatic, partial aromatic and functional modified PA layer. These all aforesaid conditions, could be produces different interaction with hypochlorite acid solution [26].

On the contrary to pH-3, pH-7 and pH-10.5 conditions showed significant performances changes on the transformed membranes. After low exposure time (1 h) at neutral and alkaline conditions the membranes permeability enhanced 3.7% (from 0.79 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$ to 0.82 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$) and 60.5% (from 0.81 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$ to 1.30 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$) respectively. Salt rejection percentage was kept almost constant at neutral pH (rise 3.8%, from 94.82% to 95.45%) and slight decreased at basic pH (drop 2%, from 92.57% to 90.75%). At low exposure level of $\mathrm{ClO^-}$ at pH-10.5, only the highly reactive end amine groups are chlorinated and the carboxylic group (R-COOH) turn to ($\mathrm{R\text{-}COO^-}$) groups in the linear part of crosslinked aromatic PA [25,26]. This pH condition let increase the hidrophility of the membrane surfaces and in consequence, exist less resistance to water passage through the membrane [25]. This fact has been observed also in other experimentation using NaOCl, where low chlorine exposure concentration [100–6,000 ppm h] was applied [23,27,28]. Results of these studies clearly address that the NaOCl is not only a good organic fouled membrane cleaner but also improves membrane performance.

Table 1
Average water quality parameters of the synthetic brackish water.

Conductivity (μm/cm)	6,225 ± 487	**$\mathrm{Cl^-}$ (ppm)**	1,273 ± 56	**$\mathrm{Na^+}$ (ppm)**	804 ± 42
pH	6.4 ± 0.3	**$\mathrm{SO_4{}^{2-}}$ (ppm)**	1,651 ± 102	**$\mathrm{Mg^{2+}}$ (ppm)**	409 ± 26

In both neutral and basic pH transformation conditions, after 36 h of membrane exposure time, the transformed membranes achieved the permeability rate of nanofiltration membranes (Table 2). In this case the transformation mechanism was based on the irreversible chlorine substitutions in aromatic rings formed through the Orton rearrangement of the amide N–Cl groups. Consequently, polyamide layer degradation occurred and the permeability of the transformed membranes increased, whilst the rejection coefficients decreased.

It is interesting to note that the effect of exposure time was dependent on the solution pH (Fig. 3). As an example, after 50 h of contact with chlorine solution at pH-7 the membrane showed a permeability of synthetic brackish water 3.6 times higher than the initial end-of-life values (from 0.79 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$ to 2.86 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$), whilst at basic pH the permeability was 11.7 times higher (from 0.81 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$ to 9.48 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$). This can be explained by the chemistry of aqueous NaOCl solutions. At basic pH the $\mathrm{ClO^-}$ is the main specie present in the solution (around 100% at $\mathrm{pH} > 10$) and at neutral pH the $\mathrm{ClO^-}$ is around 22% [20]. Therefore, the effect of $\mathrm{ClO^-}$ on the PA is more significant at basic pH. These results are in concordance with other works found in the literature and are reported as the most commons consequences of PA membranes exposure to hypochlorite ion [18,24,30].

At 122 h to NaOCl at basic pH, the initial permeability increased 15 times (from 0.81 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$ to 12.19 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$). Despite, the salt rejection capability decreased 95% (from 92.57% to 4.4%), the permeability range obtained did not clearly show ultrafiltration properties as reported other authors [17,18]. Consequently, further morphological study was performed. SEM analysis was used to examine changes in membrane topography. Fig. 4 shows images for TM720-400 membrane: pristine and membranes exposed to NaOCl during 122 h at each of the tested pH condition. Morphology of the exposed membranes was similar to the pristine surface and no pores were detected in any case, which could indicate that polyamide layer is still on the membrane. On the other hand, degradation of the PA layer was investigated by the ATR–FTIR spectroscopy (Fig. 4(f)). The spectra of the TM720-400 membrane surface shows that both end-of-life and transformed membranes had peaks at 1664 $\mathrm{cm^{-1}}$, 1542 $\mathrm{cm^{-1}}$ and 1610 $\mathrm{cm^{-1}}$. These wavenumbers corresponding to amide I and amide II bands and the C=C stretching vibrations from the aromatic amide bonds, respectively [20]. Despite the peaks signals were reduced in case of the transformed membranes, the PA layer is still on the surface. Therefore, in case of 122 h exposure time and 10.5 pH condition, SEM and ATR–FTIR results confirmed that the low percentage of salt rejection can not indicate properly the complete degradation of PA and the exposition to polysulfone layer therefore, morphological analysis are recommended to avoid misleading conclusions.

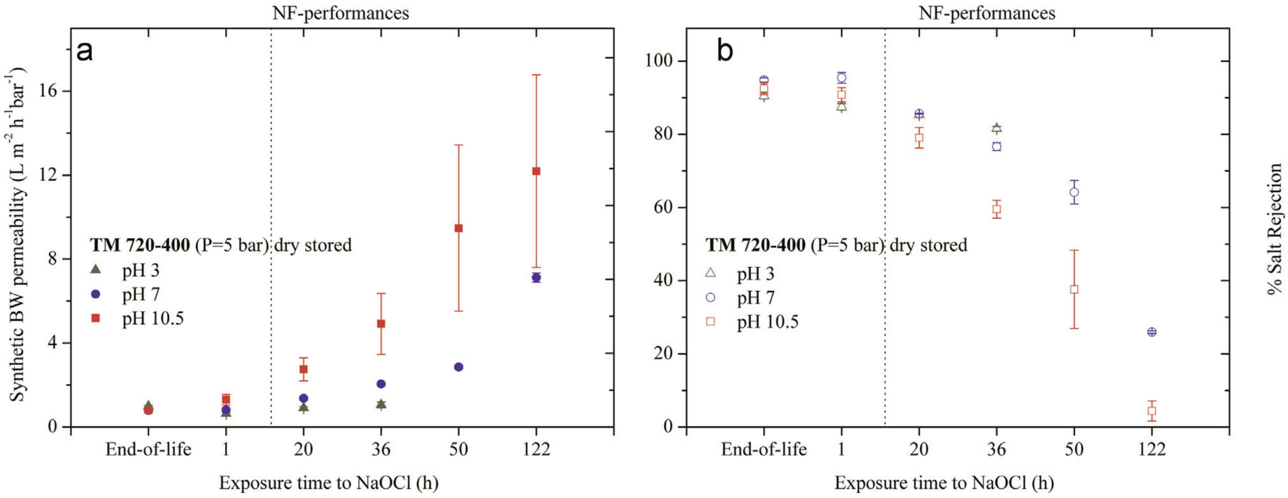

Fig. 3. Effect of pH transformation condition and exposure time to NaOCl: (a) permeability and (b) salt rejection percentage. In case of pH-10.5 transformation condition, it is showed that the average is obtained by repeating the experiments 3 times with 3 different membrane coupons (see Appendix A, Table A1).

Table 2
Typical polymeric membrane permeability and rejection data [29].

Membrane	*Reverse osmosis*	*Nanofiltration*	*Ultrafiltration*	*Microfiltration*
Permeability range L m^{-2} h^{-1} bar^{-1}	0.05–1.4	1.5–15	10–50	> 50
% Rejection	Low molecular compounds (amino acid) and monovalent ions	Low molecular compounds (sugar) and divalent ions	Colloidal and macro compounds	Bacteria and suspended particles

3.1.2. Rejection coefficients of mono/divalent ions and dextrose of transformed membranes

Previous studies focus on the effect of the chlorine solution to membrane performance, used only NaCl salt solution to evaluate membrane performance changes [17,18,31]. In addition, the rejection coefficient was often calculated by using only the conductivity measured at the feed and the permeate. In the present study, synthetic brackish water was used for more exhaustive membrane characterization to evaluate, not only monovalent rejection but also divalent and organic compound rejection. Consequently, the border line conditions between nanofiltration and ultrafiltration transformation could be identified. In fact, comparing Figs. 3 and 5, the salt rejection coefficient for the transformed membrane at pH-7 and 50 h exposure time was 64%. However, the single SO_4^{-2} rejection was 97%. The same behavior was observed when the membrane was transformed at pH-10.5, where the total salt rejection was 39% whilst the SO_4^{-2} rejection was 81%. The detection of successful SO_4^{-2} rejection coefficients indicates that the transformed membrane achieved nanofiltration performance. In fact, further characterization with dextrose (180 Da) showed that the transformed membrane had still capability to reject low molecular weight organic compounds. As an example, at 50 h exposure time at pH-7 and pH-10.5 the rejection coefficients were 71.4% and 43.9%, respectively. Indeed, at 122 h exposure time and pH-10.5, no rejection of dextrose was almost observed 2.9%, indicating that the transformed membrane rejection behaves as an ultrafiltration membrane.

As Fig. 5 denotes, divalent ions are rejected more efficiently than monovalent ions. This can be attributed to molecular size and charge of the membrane. It is well known that PA is an amphoteric and hydrophilic polymer which possess dissociable carboxylic groups [32]. As it has been reported in literature, chlorination process at the pH condition studied (pH-3, pH-7, and pH-10.5) should increase the negative charges on membrane surface [26,33,34]. Therefore we have assumed that transformed membranes had negative surface. The used synthetic brackish water for membrane characterization performance contains symmetric salts (NaCl and $MgSO_4$). Cl^- and SO_4^{-2} have the same charge sign as the membrane therefore, they are the dominant-ions (co-ions). Anions could be repelled by electrostatic repulsion mechanism due to the fixed negative charge density on the membrane surface [35], attributed to the deprotonation of carboxylic acid group and chloride ion attached on the membrane by transformation process [26,36]. Between Cl^- and SO_4^{-2} exists a co-ions competition that would explain minor rejection of Cl^-, which has less charge and higher mobility than SO_4^{-2}. Furthermore, stronger electrostatic repulsion results in higher ions rejection [37] which explain the best results SO_4^{-2}.

3.2. Reproducibility of membrane transformation process stored in wet condition

The reproducibility of the transformation process was evaluated by testing end-of-life membranes of 5 different module brands which were stored under wet condition. Specifications of each membrane model provided by manufactures and some information of the end-of-life membranes such as fouling level and initial Milli-Q permeability are summarized in Table 3. The transformation process was carried out using NaOCl at basic pH and following the same protocol as in Section 2.2. Testing membranes performance series (36, 50, 122, 242 and 410 h exposure time) were repeated three times for TM720-400, TM820C-400 and SW30HRLE-440i membranes, whilst only one series was done for HSWC3 and BW30 membranes. Fig. 6 and Table A2, show the results of the permeability and the rejection coefficients obtained with the transformed membranes. HSWC3 membrane showed different transformation behavior, which will be further discussed within this section.

At 50 h exposure time, the permeability of the synthetic brackish water ranged between 3.32 and 17.17 L h^{-1} m^{-2} bar^{-1}.

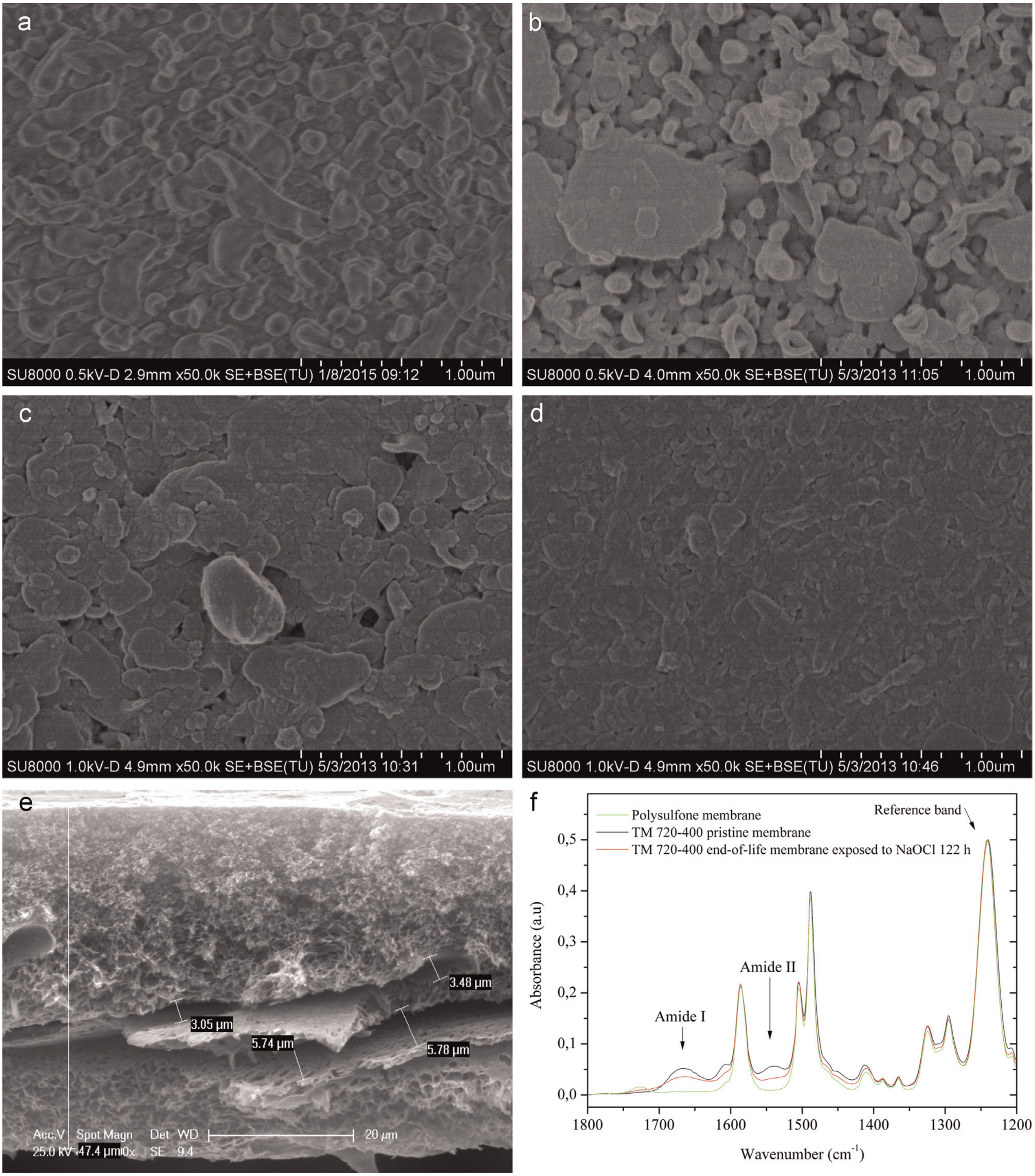

Fig. 4. Surface characterization of TM720-400 membrane (dry stored). SEM images of a pristine membrane (a), exposed membranes to NaOCl at 122 h at pH-3 (b), pH-7 (c) and pH-10.5 condition (d), cross section of end-of-life membrane (e) and ATR–FTIR spectra (f) for an end-of-life membrane, a transformed membrane and a pristine polysulfone membrane.

Therefore, all end-of-life RO membranes tested were transformed into nanofiltration membranes within the same transformation exposure time range. Earlier, some researchers discussed that it is possible to enhance permeability in detriment of rejection drop, controlling NaOCl exposure level [17,38]. Once membranes were transformed, all membranes showed similar performance in terms of rejection coefficients. The lowest rejection percentages were obtained using the transformed TM720-400 BW membranes. However, even at this case, the average values were still successful (45.8% Cl^-, 98.7% SO_4^{-2}, 59.4% Na^+, 87.3% Mg^{2+} whilst glucose rejection was up to 81.6%). Transformation process applied for end-of-life BW membranes let achieve higher permeability than in case of end-of-life SW membranes. This might be due to the origin of the polyamide layer and the process condition that the membranes suffered on its lifetime. Mostly, all the membranes showed an increased in permeability at 122 h exposure time, achieving values up to 34.44 L h^{-1} m^{-2} bar^{-1} (in case of the TM720-400 module). These values could be considered typical of UF

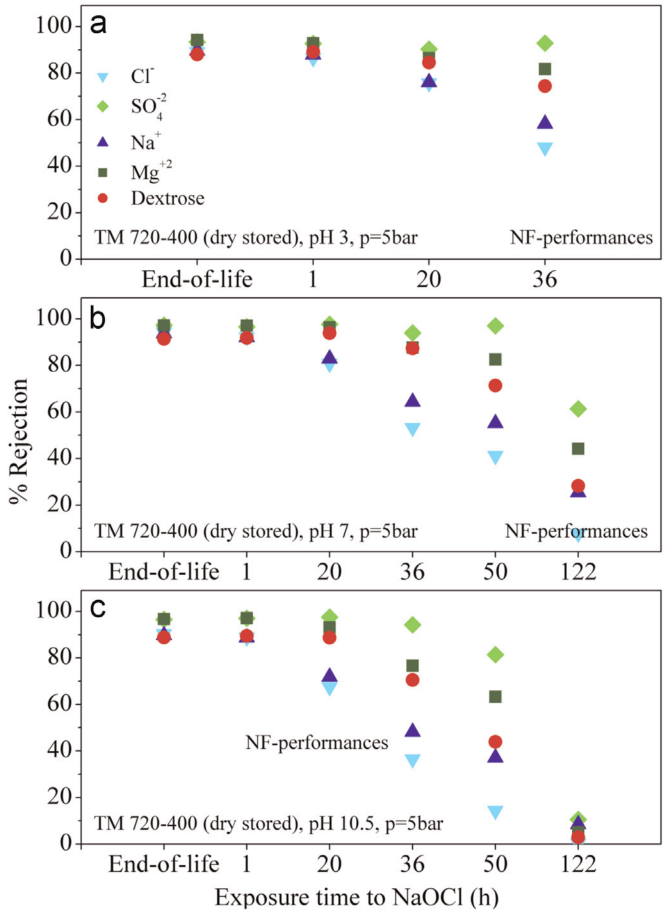

Fig. 5. Effect of pH transformation condition and exposure time to NaOCl on ions and dextrose rejection. In case of pH-10.5 transformation condition, it is shown that the average is obtained by repeating the experiments 3 times with 3 different membrane coupons (see Appendix A, Table A1).

membranes or a high permeable NF membrane (Table 2). It is interesting to note that divalent ions were still well rejected. In most of the cases, SO_4^{-2} and Mg^{2+} rejection was higher than 80% and 59%, respectively. For these reasons, 122 h exposure time could determinate the border line between the recycled nanofiltration and ultrafiltration membranes for all the membranes excepting for the HSWC3 module.

After applying 242 h exposure time, 3 over the 5 commercial membrane brands tested were transformed into UF membranes in terms of permeability. These were TM720-400 (BW), BW30 (BW), SW30HRLE-440i (SW). The permeability values achieved were ranged between 33.80 and 40.57 $L\,h^{-1}\,m^{-2}\,bar^{-1}$ (with a relative error less than 10%), whilst the individual rejection coefficients were lower than 17%. To ensure that the transformation into ultrafiltration membrane occurred, further morphological surface analyses were conducted. ATR–FTIR spectra showed that polyamide was removed completely and membranes revealed pores at the SEM micrographs with around 13 nm of ferret diameter [19]. In addition, at this transformation condition, TM820C-400 could be contemplated as a low permeable UF membrane. Longer exposure time than 242 h was employed to evaluate if the transformed membrane performance can further be affected by hypochlorite ion. Considering the average permeability of membranes and its standard deviation, results were similar (within the error range) after 242 h and 410 h in all the cases (excepting for HSWC3). This could indicate that for these 4 specific cases the commercial polysulfone were stable to long chlorine exposure in terms of permeability. Therefore, deeper studies should be conducted in order to confirm changes in the membrane texture and in the mechanical properties. These results are in concordance with other authors. Lawler et al. showed that transformed RO end-of-life membranes into UF membrane by exposure to NaOCl at 300,000 ppm h presented similar permeability than membranes exposed at higher ppm·h level [38]. Permeability stability has been also reported by Rouaix et al. using UF polysulfone membranes [39]. Even if a long exposure to sodium hypochlorite produced chain breaking in the polysulfone polymer, membrane permeability seemed to be poorly sensitive to such changes. However, permeability differences have been detected by the effect of NaOCl in other studies. Regula et al. summarized 34 published paper related on the action of hypochlorite on UF membranes [40].

Regarding HSWC3 membrane, it showed different behavior within the whole transformation process and after 242 h exposure time, the membrane performance was not equivalent to UF performance. Although it was exposed to the longest exposure time, the permeability was still within the nanofiltration range. Therefore, even the transformation procedure seems to work similarly for all the membranes when reaching the border line of NF membranes, the transformation towards UF membranes is more complex. This might be due to the type and degree of irreversible

Table 3
Manufacture specification and end-of-life membranes information.

Manufacture information of the spiral wound membrane						End-of-life membrane		
Commercial membrane brand	Membrane model	Active area, m^2	Permeate flow rate, m^3/d	Salt rejection, %	Maximum chlorine tolerance[a]	Treated water nature	Fouling level/ nature	Milli-Q P, $L\,h^{-1}\,m^{-2}\,bar^{-1}$
TORAY	TM720-400[b]	37	38.6	99.7	Not detectable	BW	Low/inorganic–organic	6.68 ± 0.75[c]
DOW™ FILMTEC™	BW30-400[b]	37	40	99.5	< 0.1 ppm	BW	High/inorganic–organic	6.76 ± 0.24
DOW™ FILMTEC™	SW30HRLE-440i[d]	41	31	99.80	< 0.1 ppm	SW	High/organic	2.15 ± 0.17[c]
TORAY	TM820C-400[d]	37	24.6	99.75	Not detectable	SW	High/inorganic	2.89 ± 0.14[c]
HYDRANAUTICS	HSWC3[d]	34	22.3	99.7	< 0.01 ppm	SW	High/inorganic–organic	2.19 ± 0.08

[a] Manufacture recommendation. The presence of free chlorine and other oxidizing agents will cause premature membrane failure. Since oxidation damage is not covered under warranty. It is strongly recommended to remove these oxidizing agents in feed water before operating RO system.

[b] Values are normalized to the following condition: 2,000 ppm NaCl, 15.5 bar applied pressure and 25 °C operating temperature.

[c] Average and standard deviation values of three different membrane coupons tested at lab scale.

[d] Values are normalized to the following condition: 32,000 ppm NaCl, 55 bar applied pressure and 25 °C operating temperature.

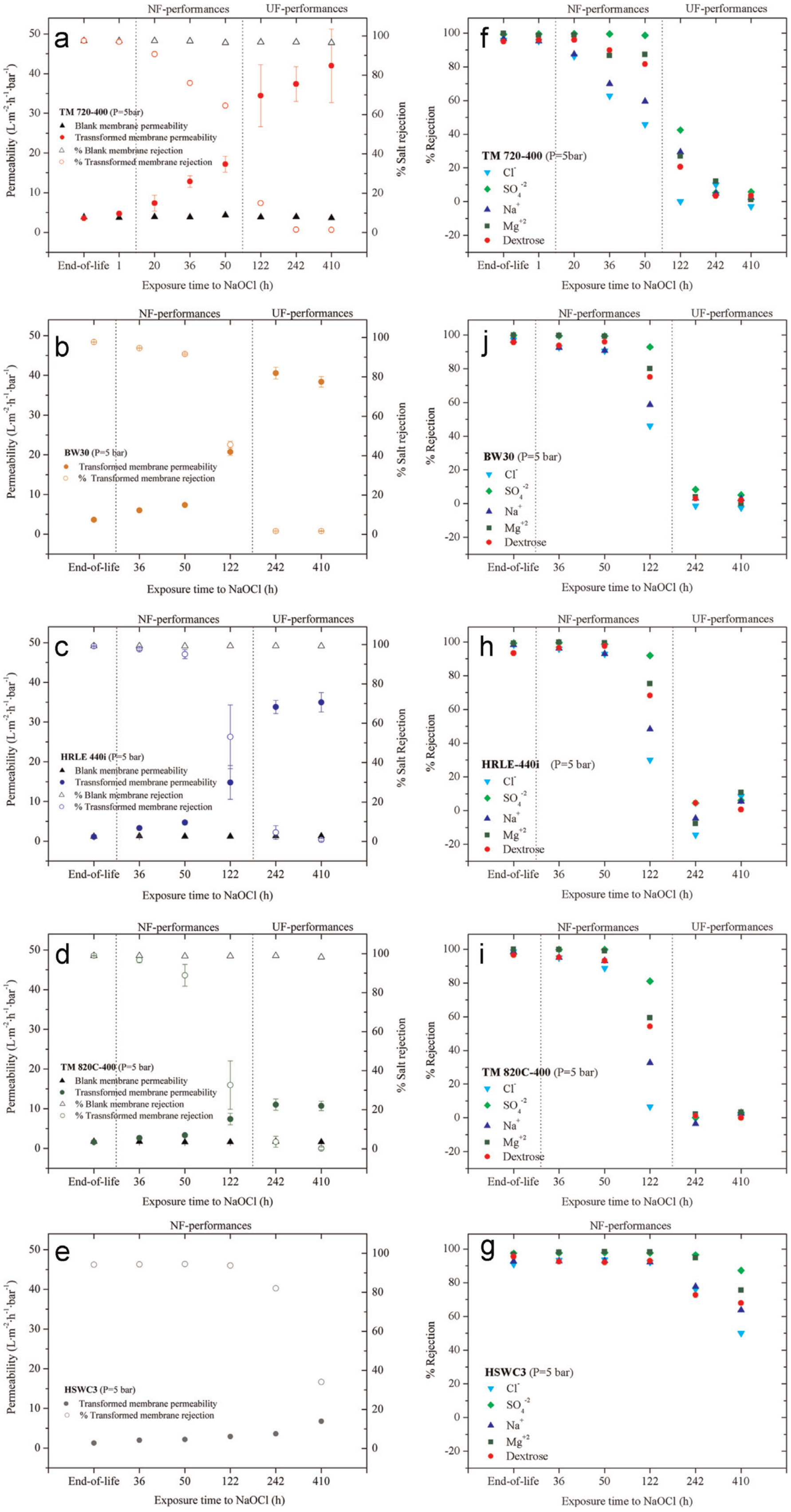

Fig. 6. End-of-life transformed membrane performances. Left column summarizes permeability and salt rejection (measured by conductivity). Right column summarizes ion and dextrose rejection. In case of TM720-400, SW30HRLE-440i and TM820C-400 membranes, it is shown that the average value is achieved by repeating in triplicate with 3 different membrane coupons (see Appendix A, Table A2).

fouling of the membranes. Severe surface irreversible fouling could inhibit the sodium hypochlorite attack to the polyamide layer being consequently, more difficult the access to the polysulfone layer.

3.3. End membrane conservation after industrial processes

Membrane conservation could be a challenge for transformation process. Noticeable differences in membrane performance were detected comparing same membrane TM720-400 stored at a dry atmosphere (Figs. 3 and 5) and stored in Milli-Q water (Fig. 6). Lawler et al. showed the importance of proper membrane storage in order to maintain hydraulic performance, as the dry membranes results in lower average permeability than the membranes that were stored wet. However, retaining rejection of NaCl was similar [18]. Despite reported results, it was observed that both permeability and rejection coefficient were affected by the storage condition, as it is observed in Figs. 5 and 6. For these reasons, to guarantee membrane transformation it is essential to keep the end-of-life membranes under wet condition after the industrial process.

4. Conclusions

According to the main pyramidal waste management principles on waste, membrane recycling should be considered as an environmental action to enhance the sustainability of membrane technology. Following the direct recycling strategy, the main aim of this study was to transform end-of-life RO membranes into recycled nanofiltration and ultrafiltration membranes at lab scale. The recycling methodology proposed is simple, reliable, inexpensive and valorises membranes that otherwise would be disposed of in landfills. Thus not only does this give a new lease of life to end-of-life membranes but also the environmental impacts associated with their disposal can be reduced.

At the preliminary study it was concluded that NaOCl was the most effective reagent to provoke substantial changes on the water permeability of the dry stored TM720-400 membranes. The applied other chemical like acetone and NMP did not provoke substantial changes in Milli-Q membrane permeability. This could be due to the selected concentration and the exposure time selected were not enough. Extended study was conducted using NaOCl solution at different pH (pH-3, pH-7 and pH-10.5). Indeed, the membrane transformation protocol at basic condition was one of the efficient to accomplish better permeability of end-of-life commercial membranes. Results revealed that using a mixed solution (synthetic brackish water) of monovalent, divalent and organic compounds let to identify the border line condition between reverse osmosis, nanofiltration and ultrafiltration properties after chlorine exposure. Nanofiltration properties were obtained when membranes were exposed to the chlorine solution for 36–122 h whilst at 242 h exposure, ultrafiltration properties were clearly achieved in most of the cases. HSWC3 membrane did not achieve ultrafiltration properties at any exposure time. Membrane polyamide surface, membrane fouling and transformation process could be considered as the main challenging variables that were under control. Beside, initial chemical cleaning could help to remove the fouling and let better interaction between polyamide and the hypochlorite ion. Therefore, fouling phenomena should be further studied in order to obtain standardization of the hydraulic performances after the transformation process.

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Appendix A

See Tables A1 and A2.

Table A1

Transformed membranes hydraulic performances and rejection percentage of the individual compounds contained in the synthetic brackish water for 5 membranes tested: one for pH-3 and pH-7 modification condition and three for pH-10.5. The chemical reagent used for transformation was NaOCl (124 ± 8 ppm free chlorine). These data are represented in Figs. 3 and 5.

Membrane and transformation pH		Exposure to NaOCl (h)	Synthetic brackish water Average P ± SD (L h^{-1} m^{-2} bar^{-1})		Salt rejection ± SD (%)		% Rejection of synthetic brackish water compounds				
							Cl^-	SO_4^{-2}	Na^+	Mg^{+2}	Dextrose
TM720-400 dry storage	**pH-3**[a]	End-of-life	0.99	± 0.04	90.47	± 0.78	90.3	94.6	89.8	95.1	90.1
		1	0.64	± 0.05	87.49	± 0.87	87.6	92.1	86.7	93	85.3
		20	0.91	± 0.06	85.31	± 0.40	83.8	91.4	83.9	91.2	85.3
		36	1.06	± 0.14	81.50	± 0.66	81.8	92.4	80.8	91.7	83.6
	pH-7[a]	End-of-life	0.79	± 0.03	94.82	± 0.06	94.3	97.3	93.8	97.2	91.4
		1	0.82	± 0.03	95.45	± 1.46	92.3	96.6	92.1	97.1	91.8
		20	1.37	± 0.07	85.62	± 0.10	80.8	97.7	82.9	96.4	93.9
		36	2.05	± 0.04	76.63	± 1.08	53.3	94	64.3	87.7	87.3
		50	2.86	± 0.09	64.19	± 3.21	41.2	97	55.1	82.6	71.4
		122	7.12	± 0.22	25.93	± 0.33	7.8	61.3	25.5	44.2	28.3
	pH-11[b]	End-of-life	0.81	± 0.12	92.57	± 1.72	90.3 ± 2.1	96.5 ± 0.4	89.7 ± 1.5	96.7 ± 0.8	88.8 ± 2.6
		1	1.30	± 0.25	90.75	± 1.91	88.9 ± 2.0	97.0 ± 0.7	88.7 ± 1.9	97.1 ± 0.2	89.5 ± 4.0
		20	2.75	± 0.55	79.04	± 2.82	67.5 ± 4.5	97.5 ± 0.7	71.9 ± 2.4	93.1 ± 1.5	88.7 ± 1.0
		36	4.91	± 1.45	59.55	± 2.43	36.5 ± 6.9	94.2 ± 5.2	48.2 ± 11.7	76.6 ± 8.1	70.5 ± 5.5
		50	9.48	± 3.96	39.27	± 7.26	14.4 ± 8.3	81.4 ± 14.3	37.1 ± 6.9	63.3 ± 8.9	43.9 ± 11.2
		122	12.19	± 4.59	4.40	± 2.72	0.3 ± 0.6	10.5 ± 4.9	8.5 ± 1.0	5.1 ± 0.9	29 1.6

[a] Only one coupon was tested,

[b] Three coupons were tested.

Table A2
Transformed membranes hydraulic performances and rejection percentage of single compounds contained in the synthetic brackish water, for 11 membranes tested. The chemical reagent used for transformation was NaOCl (124 ± 8 ppm free chlorine). These data are represented in Fig. 6.

Membrane	Exposure to NaOCl (h)	Synthetic brackish water Average P ± SD ($L\ h^{-1}\ m^{-2}\ bar^{-1}$)		Salt Rejection ± SD (%)		% Rejection of synthetic brackish water compounds				
						Cl^-	SO_4^{-2}	Na^+	Mg^{+2}	Dextrose
TM720-400 Wet storage[a]	End-of-life	3.56	± 0.11	97.49	± 0.25	95.7 ± 1.4	99.3 ± 0.5	96.6 ± 0.1	99.8 ± 0.1	95.0 ± 3.2
	1	4.71	± 0.25	96.85	± 0.50	95.3 ± 1.4	99.5 ± 0.1	95.3 ± 1.3	98.7 ± 1.8	95.9 ± 2.5
	20	7.37	± 2.03	90.64	± 0.56	86.2 ± 0.4	99.7 ± 0.0	87.4 ± 0.2	98.9 ± 0.1	96.0 ± 1.6
	36	12.82	± 1.45	75.96	± 4.44	62.7 ± 9.4	99.5 ± 0.1	69.9 ± 6.4	86.7 ± 12.6	89.9 ± 1.3
	50	17.17	± 2.02	64.49	± 5.67	45.8 ± 16.4	98.7 ± 0.7	59.4 ± 10.7	87.3 ± 5.7	81.6 ± 5.1
	122	34.44	± 7.79	14.96	± 13.72	0.0 ± 10.5	42.5 ± 36.7	29.4 ± 10.8	26.9 ± 31.7	20.6 ± 19.1
	242	37.38	± 4.37	1.51	± 0.66	-16.4 ± 47.0	6.2 ± 3.0	-0.4 ± 8.8	-16.2 ± 49.6	-14.1 ± 30.3
	410	41.98	± 9.26	1.40	± 0.85	13.8 ± 29.0	7.7 ± 3.8	5.6 ± 5.6	16.9 ± 27.2	17.1 ± 23.6
BW30 Wet storage[b]	End-of-life	3.63	± 0.16	97.68	± 0,11	97.0	99.8	96.7	99.8	95.7
	36	6.01	± 0.36	94.58	± 0,19	92.6	99.5	92.5	99.6	93.7
	50	7.37	± 0.24	91.59	± 0,38	90.6	99.4	90.7	99.2	95.9
	122	20.75	± 0.92	45.60	± 1,71	46.1	92.9	58.6	79.9	75.1
	242	40.57	± 1.49	1.68	± 0,27	-1.5	8.3	3.1	3.9	3.0
	410	38.37	± 1.34	1.66	± 0,09	-2.5	5.1	2.8	0.0	1.9
SW30HRLE-440I Wet storage[a]	End-of-life	1.13	± 0.25	99.22	± 0.20	98.4 ± 0.6	99.3 ± 0.7	98.3 ± 0.9	99.4 ± 0.7	93.4 ± 0.5
	36	3.32	± 0.40	97.65	± 0.57	95.9 ± 2.2	99.7 ± 0.1	96.3 ± 1.5	99.8 ± 0.1	96.6 ± 3.2
	50	4.72	± 0.54	95.08	± 2.32	92.9 ± 4.0	98.7 ± 1.8	93.0 ± 3.7	99.5 ± 0.3	97.6 ± 1.8
	122	14.80	± 4.25	53.08	± 16.17	30.1 ± 37.4	92.0 ± 12.1	48.3 ± 26.2	75.2 ± 21.9	68.3 ± 24.2
	242	33.80	± 1.68	4.56	± 3.45	-14.5 ± 19.9	4.5 ± 7.5	-4.7 ± 9.4	-7.8 ± 15.5	4.5 ± 3.0
	410	34.98	± 2.44	0.79	± 0.42	8.5 ± 10.1	6.0 ± 4.7	5.4 ± 5.2	10.7 ± 10.8	0.6 ± 0.7
TM820C Wet storage[a]	End-of-life	1.61	± 0.06	99.01	± 0.04	98.7 ± 0.1	97.2 ± 4.7	98.5 ± 0.2	100.0 ± 0.0	96.6 ± 0.9
	36	2.63	± 0.22	96.74	± 1.25	94.9 ± 2.7	99.9 ± 0.0	95.1 ± 2.5	99.8 ± 0.1	95.3 ± 2.1
	50	3.32	± 0.43	88.90	± 5.56	88.8 ± 1.2	99.9 ± 0.0	93.1 ± 5.9	99.0 ± 0.6	93.2 ± 5.0
	122	7.40	± 1.46	32.62	± 12.41	6.5 ± 14.6	81.1 ± 25.9	32.6 ± 16.9	59.3 ± 24.7	54.3 ± 30.5
	242	11.03	± 1.41	3.57	± 2.78	-0.6 ± 1.7	0.0 ± 1.1	-3.5 ± 3.8	2.1 ± 6.0	1.2 ± 1.8
	410	10.72	± 1.19	0.23	± 0.67	1.5 ± 11.1	3.2 ± 5.5	2.5 ± 3.9	3.3 ± 7.3	0.0 ± 0.3
HSWC3 Wet storage[b]	End-of-life	1.29	± 0.06	94.20	± 0.18	90.9	97.5	92.7	96.9	95.5
	36	2.00	± 0.07	94.34	± 0.21	93.3	97.7	92.8	98.1	92.6
	50	2.19	± 0.07	94.52	± 0.24	93.6	97.8	93.0	98.3	92.1
	122	2.93	± 0.13	93.78	± 0.22	92.1	97.7	92.1	98.2	93.0
	242	3.61	± 0.14	82.09	± 0.34	76.1	96.5	77.7	94.8	72.7
	410	6.78	± 0.16	34.09	± 0.56	50.1	87.3	63.7	75.6	67.9

[a] Three coupons were tested.
[b] Only one coupon was tested.

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Paper IV: congress proceeding

Molina, S., **García-Pacheco, R.**, Rodríguez-Sáez, L., García-Calvo, E., Campos, E., Zarzo, D., et al. Transformation of end-of-life RO membranes into recycled NF and UF membranes: surface characterization (15WC-51551). Previously published as part of The International Desalination Association (IDA) World Congress Proceedings, San Diego, California, USA 2015.

TRANSFORMATION OF END-OF-LIFE RO MEMBRANE INTO RECYCLED NF AND UF MEMBRANES, SURFACE CHARACTERIZATION

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Abstract

Energy consumption and membrane fouling represent some of the main concerns in membrane technology, since they increase the associated financial cost for m^3 of treated water. Because of the growth of reverse osmosis applications in industrial processes, not only economic but also environmental worries have started to demand the recycling and reuse of fouled, end-of-life, thin-film composite (TFC) reverse osmosis (RO) membranes. The present study, as part of the LIFE+ ENV/ES/000751 TRANSFOMEM European project, investigates the transformation of end-of-life membranes to be recycled as nanofiltration (NF) and ultrafiltration (UF) membranes. Such process is a simple, low energy, surface modification technique, based on polyamide chemical attack.

Initially, membrane fouling was identified by autopsy procedure which involves dissection of membranes, oxidative damage, and foulants collection for thermogravimetric (TGA), inductively coupled plasma mass spectrometric (ICP-MS) and microbiological tests. Pieces of such RO membranes were exposed to sodium hypochlorite (NaOCl) under basic pH condition up to 410 h. The resulting permeability was tested using Milli-Q water and a solution of poly(ethylene oxide)s (PEO) mixture with different molecular weights. Membrane-surface properties were also analyzed by scanning electron microscopy (SEM) including nanopores quantification after long exposure time to NaOCl, attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), contact angle and molecular weight cut-off (MWCO). Depending on the polyamide nature and membrane fouling, different exposure times were necessary to obtain nanofiltration and ultrafiltration membranes performances. For all the assays, NF-like properties were obtained and also for the majority of the cases UF-like properties were observed. This recovery process may provide a procedure of recycling end-of-life RO membranes as NF and UF membranes in order to reuse them and prolong their lifetime.

1. INTRODUCTION

World population is continually growing and it is expected to reach 9 billion in 2050. The need to increase the amount of consumer goods will involve a higher industrialization and water consumption. Therefore, the drinkable water necessity has become a global concern and governments struggle to keep this resource available to the whole population [1, 2]. With this purpose, in recent years numerous desalination plants have been built [3]. In 2016, the water production by desalination will exceed 38 billion m^3 per year, which is twofold the water produced by this process in 2008 [4].

Although conventional separation processes (filtration, distillation, evaporation, etc.) are still being considerably employed, most of the desalination plants built in the last two decades are based on the reverse osmosis technology, where semipermeable membranes are used. This is so because the reverse osmosis is the most energy-efficient technology for water desalination and the benchmark in comparison with any other technology [5, 6].

Spiral wound membrane module configuration is the most used in desalination plants because it contains a large membrane surface in small space, which allows a greater flexibility in the system design, an easy scaling and low replacement costs [7, 8]. Reverse osmosis membranes frequently used are thin film composite (TFC) polyamide membranes, which are formed by three layers: a non-woven polyester support, an asymmetric porous polysulfone (PSF) interlayer and a polyamide ultra-thin layer [9, 10].

Depending on the quality of water used and operation conditions, the RO modules have an average half-life from 5 to 10 years [11]. The major limitation of membrane processes is the formation of a fouling layer, which is produced as a consequence of the removal of dissolved matter and particles present in the feed stream. As a function of the fouling nature, it can be classified as inorganic fouling (precipitation of inorganic salts) or organic fouling (*biofouling*) (microorganisms and biological substances such as proteins or polysaccharides) [12-16]. Fouling phenomena can lead to a progressive loose of permeate flux. However, this fouling effect is often counterbalanced by increasing the pressure used in the process. This leads to an increase of energy consumption for the same volume of treated water and to a selectivity loss. Indeed, the cleaning operations would be more frequent and the membrane lifespan would decrease [17, 18].

Although many ways to mitigate fouling have been proposed, the fact is that after overcoming its lifespan, thousands of tons of RO membranes are deposited in landfills each year, which is the least environmentally favorable option according to the recent life-cycle assessment study [19]. The RO technology is more and more common and it is expected that the amount of membrane waste will rapidly increase, which has economic and environmental consequences. Therefore, solid waste, more specifically membrane waste, is the target of an increasing global concern and the object of study by the scientific community. In order to increase sustainability of RO membrane technology, Lawler et al.[20] described different strategies as follows:

1. Direct membrane reuse in the food processing, water and wastewater industries.
2. RO membranes transformation into porous membranes for direct reuse.
3. Material recycling, which involves the separation of all types of materials from the modules (propylene feed spacer, ABS caps, polyester permeate spacer, fiber glass, epoxy resin, etc.)
4. Combustion and carbonization for energy recovery.

The current work is framed in LIFE+ ENV/ES/000751 TRANSFOMEM European project. The aim of this project is to increase the sustainability of membranes for water treatment by improving their lifespan and reducing the environmental impact. Thus, the aim of this work was to outline methods for the conversion of end-of-life RO membranes into recycled NF and UF porous membranes. For this purpose, partial or complete removing of the dense polyamide active layer has been explored. This transformation process has been carried out exposing the membranes to a solution of sodium hypochlorite. The water flux and membrane selectivity of treated membranes were determined at different exposing time. The chemical composition of treated membranes and their fouling layers were analyzed by different spectroscopic techniques and the modified surface morphology was investigated by SEM and contact angle measurements.

2. MATERIALS AND METHODS

2.1 Membranes and chemical reagents

Experiments were performed on end-of-life, thin-film composite (TFC) polyamide RO membranes, which were taken out from spiral wound modules with diameter of 8". In order to get representative results, 5 membranes with several levels of organic and inorganic fouling were tested. These membranes had been used for water treatments for more than three years. The feed was brackish water (BW) in case of the TM 720-400 (Toray) and BW30 (Dow Filmtec) modules and sea water (SW) in case of TM 820C-400 (Toray), HRLE-440i (Dow Filmtec) and HSWC3 (Hydranautics).

Hydrochloric acid (HCl) and Nitric acid (HNO_3) of highest purity (TraceSELECT® Ultra products) from Sigma Aldrich were used in ICP analysis. Different analytical reagents purchased from Scharlab were used: sodium hypochlorite (NaOCl) was utilized for transformation of end-of-life membranes; sodium hydroxide (NaOH) and pyridine (C_5H_5N) were used in autopsy tests. Chromogenic coliform agar (CCA), CHROMagar pseudomonas, iron sulfite modified agar R2-A agar and malt extract agar No.1, acquired from Scharlab, were employed to conduct microbiological analysis.

Commercial polyethylene glycols (PEOs) purchased from Fluka with molecular weights from 10^3 to 10^5 Da, were selected to study the molecular weight cut-off in UF experiments of recycled membranes.

2.2 Membrane autopsy

Initially, the fouled membranes were identified by autopsy procedure, which involved dissection of membranes and visual inspection. Afterwards, fouling material was scraped off from the membrane surface and was dried in order to carry out thermogravimetric analysis (TGA), inductively coupled plasma mass spectrometry (ICP-MS) and microbiological tests.

2.2.1. Fujiwara analysis.

Membranes (4 cm^2) were cut and positioned in screwed test tubes. 10 mL of 10 M sodium hydroxide and equal amount of pyridine solution was added to the test tube, mixed in a vortex mixer during 10 s and placed in a water bath 90-95ºC for 2 min after sealing the test tubes. The test tubes were cooled and observed for any color change. Three samples were cut from each membrane for testing. Halogen damaged membrane samples and no damaged membrane samples were used as a positive (color change) and negative control (no color change) [21].

2.2.2 Thermogravimetric analysis (TGA) and inductively coupled plasma mass spectrometry (ICP-MS)

The thermogravimetric analysis (TGA) data of membrane fouling were recorded on a TGA Q500 analyzer under an oxidative (air) atmosphere with a heating rate of 5ºC/min from 45 to 800ºC.

The quantification of metals level in water samples was carried out to estimate inorganic element concentration of membrane fouling by using a quadrupole ICP-MS spectrometer device 7700x series from Agilent Technologies (Santa Clara, United States). The mass calibration of the ICP-MS instrument was tuned daily with a solution containing $1 \mu g\ L^{-1}$ of Ce, Co, Li, Mg, Tl and Y in 1% (v/v) HNO_3. Accurately weighed samples (50 mg) were digested with 4:1 ratio of trace metal analytical grade HNO_3:H_2O_2 (Fluka (St Louis, United States)) and then diluted in 100 ml of ultrapure water. Clear solutions obtained after digestion and dilution were analyzed by ICP-MS for inorganic element concentrations. Semi-quantitative results are given in relative percentage, which was calculated by dividing the metal detected mass by the total sample mass analyzed.

2.2.3 Bacteria detection and enumeration

For bacterial identification, fouling material samples of 36 cm^2 were aseptically scraped out and transferred to a sterile Pyrex flask with 100 mL of phosphate buffered saline solution (PBS buffer). Samples were mixed on a vortex mixer during 4 min. *E. coli*, total coliform, *pseudomona* and *clostridium* were detected following membrane filtration technique (Standard Methods: 9215 D) [22] and using their specific medium: chromogenic coliform agar (CCA), CHROMagar pseudomonas and iron sulfite modified agar respectively. Aerobic mesophilic bacterias, molds and yeasts were detected and enumerated following pour plate count technique (Standard Methods: 9215 B) [23]. R2-A agar and malt extract agar No.1 were employed respectively. When necessary, serial 10 fold dilutions were carried out to determine the number of bacteria per unit area of the membranes. Incubation time and temperature were specifically adjusted according to agar medium.

2.3 Membrane treatment protocol

Different exposure times of end-of-life membranes to sodium hypochlorite (NaOCl) were evaluated. The chlorine solutions were prepared by diluting a commercial sodium hypochlorite (10 %) with Milli-Q water to achieve 124±8 ppm of free chlorine. The free chlorine concentration was measured using a standard colorimetric method (4500-Cl G DPD) employing a Pharo 100 Spectroquant spectrophotometer (Merck). Two coupons of 216 cm^2 were cut from each membrane and conserved in Milli-Q water. Afterwards, they were immersed into the NaOCl solution and subjected to the attack by free chlorine for 36, 50, 122, 242 and 410 h under basic pH (>10), at room temperature (approximately 21°C) and without stirring in order to simulate static conditions. After these exposure times, the coupons were taken out of the containers and thoroughly washed with Milli-Q water until reaching the pure water pH. Membranes were stored in sealed plastic bags with water until they were used. One of the transformed coupons was used for membrane performance tests and the other one was employed to characterize the membrane surface properties.

2.4 Membrane performances: permeability and molecular weight cut-off determination.

A laboratory-scale cross-flow test system described previously [24], with an effective area of 5 x 10^{-4} m^2 and working at a transmembrane pressure of 3 bar, was used to carry out the permeability measurements of the transformed membranes. All membranes with three different exposure times to NaOCl were evaluated (122 h, 242 h and 410 h). These assays were performed initially using distilled water and then with an aqueous solution of PEOs. This feed solution contains PEOs of different molecular weight ranging from 10^3 to 10^5 g/mol, keeping the total concentration of 1g/L. The composition of PEOs used to prepare 10 L of the feed solution appears in Table 1.

The molecular weight cut-off (MWCO) is defined as this corresponding to a retention coefficient of 90%. It was determined from Size Exclusion Chromatography (SEC), which allows the estimation of the ideal retention coefficient for each membrane [25-27]. A PerkinElmer Series200 SEC device with a column from Polymer Labs (PL MIXED aquagel-OH) of nominal pore size 8 μm was used. Milli-Q water was used as the eluent with a flow rate of 1 mL/min. The calibration was carried out with narrow standards of PEO with molecular weights between 194 and 490,000 Da.

Table 1. Amount of PEOs used to prepare the feed solution

Molecular weight (g/mol)	Weight (g)	Molecular weight (g/mol)	Weight (g)
PEO-1000	1.2	PEO-8000	0.5
PEO-2000	0.8	PEO-10000	0.5
PEO-3000	0.5	PEO-20000	0.9
PEO-4000	0.3	PEO-35000	2.4
PEO-6000	0.5	PEO-100000	2.4

2.5 Membrane surface characterization

The surface morphology of both, starting and transformed membranes was characterized with different techniques in order to understand the relationships between the structure and composition of the skin layer with the membrane performances.

2.5.1 Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy

Membranes exposed to NaOCl were characterized by Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy using a Perkin-Elmer RX1 spectrometer equipped with an internal reflection element of diamond at an incident angle of 45°. An adequate pressure was applied on the membrane placed on the crystal surface. The spectra were recorded at a resolution of 2.0 cm^{-1} in the frequency region of 4000–650 cm^{-1}, with an average of 4 scans per sample. Previously the samples were dried at 110ºC to remove moisture for two days.

2.5.2 Contact angle

The static contact angles of membranes were determined with a KSV CAM200 instrument (KSV Instruments, USA) using the sessile drop technique. A film sample was fixed on a glass support, and 4.5 μL of Milli-Q water was placed on the membrane surface using a Hamilton syringe at room temperature. Ten measurements for two different pieces of the same dried membrane were acquired to get the average value. The experimental error was always lower than 2%.

2.5.3 Scanning electron microscopy (SEM)

Two imaging devices were used: XL30 ESEM Model (Phillips) and S-8000 Model (Hitachi). The first one was used to observe the cross section of the membranes. For this, the membranes were broken properly after being frozen into liquid nitrogen. The samples were dried and later were gold sputtered with a Sputter Coater Polaron SC7640 model to achieve 13–15 nm thickness prior to the SEM analysis. The second device (S-8000 Model (Hitachi)) was employed to examine the membranes surface. Afterwards, Digital Image Analysis (DIA) was used to determine the pore size distribution and the average pore diameter of converted membranes by ImageJ software (Java-based image processing program) [28].

3. RESULTS AND DISCUSSION

3.1. Membrane autopsy

The study of membranes by autopsy involves the entire destruction of the module and taking out the flat membranes for dissection. The membranes were unrolled in a dissection table and the samples were taken from diverse locations of the different flat sheets. TM 720-400 and HSWC3 membranes were facilitated by SADYT Company and were unrolled in IMDEA Water institute while Genesys International Company facilitated the rest of the membranes in coupons of 20 x 20 cm.

3.1.1 Fujiwara test

Fujiwara test was conducted to consider if the fouled membranes have been exposed initially to halogen compounds. In all the cases, Fujiwara tests were negative; therefore, surface damage due to halogens was not investigated prior to transformation assays. Therefore, polyamide degradation can be attributed just to the membrane transformation process applied in this study. However, it has to be mentioned that the surfaces analyzed were relative small ($4 \cdot 10^{-4}$ m^2) compared to membranes confined into commercial modules (37 m^2).

3.1.2 Thermogravimetric analysis (TGA) and inductively coupled plasma mass spectrometry (ICP-MS)

Thermogravimetric analyses (TGA) of the fouling materials were carried out under an oxidative atmosphere to obtain the percent composition of organic and inorganic fouling. Figure 1 shows the thermograms of the fouling membranes and their derivatives. The temperature of initial decomposition was detected between 175 and 240 °C, and this process occurred in several steps. Furthermore, while brackish water membranes (TM720-400 and BW30) and TM820C-400 membrane showed a char residue higher than 77%, the HRLE-440i and HSWC3 membranes exhibited a char residue lower than 34%.

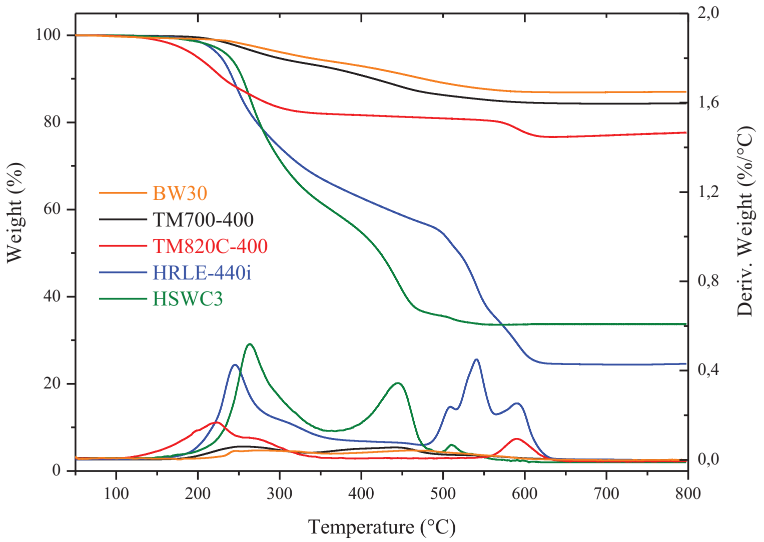

Figure 1. TGA curves of fouling materials (Heating rate 5 ºC/min from 45 to 800 ºC).

The percentage of organic and inorganic fouling of each membranes and the initial temperature of decomposition of each fouling are shown in Table 2.

Table 2. Percentage of organic and inorganic fouling and initial decomposition temperature of each fouling

Treated water	Membrane	T_d (ºC)[a]	% Inorganic fouling[b]	% Organic fouling[c]
BW	BW30	235	82.0	18.0
BW	TM720-400	210	84.3	15.7
SW	TM820C-400	175	77.0	23.0
SW	HRLE-440i	220	24.4	75.6
SW	HSWC3	240	33.7	66.3

[a] Onset temperature of initial weight loss.

[b] Char residue at 800 ºC ($R_{800ºC}$ (%)).

[c] 100% - $R_{800ºC}$ (%).

Fouling of HRLE-440i and HSWC3 membranes was over 66% organic matter, which is the most common category of fouling of RO membranes according to the review published by Genesys International [29]. Considering 150 elements autopsies, the results from that work revealed that, around 50% of membrane fouling was organic and the rest of inorganic foulants were distributed in 10.2% Fe_2O_3 and $CaSO_4$, 13.5% SiO_2, 3.8 Al_2O_3, 2.7% $CaPO_4$, 2.4% $CaCO_3$. The remaining inorganic elements (15%) were considered as other category.

In order to get a better understanding of the inorganic fouling, ICP-MS analyses were also performed. As Table 3 shows, aluminum, iron, potassium, phosphorus, silicon and magnesium were metals commonly detected. Membranes that had been used with brackish water (TM 720-400 and BW30) have higher relative percentage of aluminum, potassium and iron than the membranes used for treating seawater. Aluminum and iron are elements naturally present in many surface waters but they also could have been introduced in the filtration process by the use of flocculants like aluminum sulphate, ferrous sulphate or ferric chloride. The TM820C-400 membrane showed a specific fouling problem, probably related to quality of feed water. Manganese has been the main inorganic foulant found in this membrane (30%). Manganese salts are less frequently found than iron [29], however, some illustrative cases have been reported in literature. Concerning Mn fouling: Fernandez-Alvarez et al., reported about the autopsy of RO membranes after 8 years of operation treating seawater from Ceuta, Spain [30]. ICP-MS analysis has revealed a great variety of metals like Ba, Cr, Sr, V, Zn, Ni, including Mn. HRLE-440i membrane has the lowest inorganic percentage found among the 5 autopsies conducted. The most representative metallic elements were P, I and Na, which are elements naturally present in seawater [31]. Finally, the inorganic fouling of HSWC3 membrane is mainly due to Si, P, Fe and Al.

Table 3. Percentage of metals in the fouling, analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

Metals	**% ICP MS (m/m)**				
Elements	**BW30**	**TM 720-400**	**TM 820C-400**	**HRLE-440i**	**HSWC3**
Mn	0.06	0.01	***30.58***	0.17	0.01
Mg	3.68	0.32	***1.83***	0.68	0.55
Ca	1.95	0.08	***0.93***	0.53	N.D
K	***7.47***	***2.06***	0.19	0.27	0.29
P	1.02	0.66	0.32	***1.44***	***2.69***
Fe	***13.80***	***2.22***	0.19	0.36	***1.86***
Zn	0.04	N.D	0.14	N.D	N.D
Si	3.87	0.66	0.13	0.40	***6.17***
I	0.01	N.D	0.13	***1.55***	0.02
Co	N.D	N.D	0.11	N.D	0.05
Al	***32.20***	***10.53***	0.04	0.35	***1.59***
S	0.31	N.D	0.04	***1.93***	N.D
Mo	N.D	N.D	0.03	0.01	0.02
Na	1.29	0.10	0.03	***2.46***	N.D
Cr	0.17	0.03	0.02	0.15	0.24
Cu	0.03	N.D	0.02	0.01	0.01
Ni	0.02	N.D	0.01	0.01	0.03
Ti	0.47	0.11	N.D	0.03	0.02
Pb	N.D	N.D	N.D	N.D	N.D
B	0.02	0.01	N.D	0.01	0.08
As	N.D	N.D	N.D	N.D	N.D
V	0.05	0.01	N.D	N.D	0.01

3.1.3 Bacteria detection and enumeration

Biofouling matter was extracted from the end-of-life membranes in order to detect and enumerate bacteria yeasts and molds. Table 4 shows the estimated colony-forming unit detected by cm^2 of end-of-life membrane tested. All membranes show a biofilm on their surfaces since none of them did operate with sterile water. *E. coli* and *clostridium* bacteria were detected only in BW30 membrane. Very low concentrations of other coliforms bacteria were detected in the case of BW30, TM720-400 and HRLE-440i membranes. The colony forming unit (CFU) range of the microorganisms found was as following: *Pseudomona bacteria* 10^2-10^3 CFU/cm^2, yeast 10^2-10^4 CFU/cm^2, aerobic bacteria 10^3-10^4 CFU/cm^2 and molds, ranged between 10^4-10^5 CFU/cm^2. Mold population was the highest in all the membranes studied. All values can be considered as normal according with other works relating to membranes biofouling [29].

Table 4. Estimated colony-forming unit (CFU) bacteria in 1 cm^2 of end-of-life membranes tested

		Estimated CFU /cm^2						
Treated water	**Membranes**	***E. coli***	**Other coliforms**	***Clostridium***	***Pseudomona***	**Aerobic bacteria**	**Molds**	**Yeast**
BW	**BW30**	[0-1]	[10-10^2]	[10^3-10^4]	[10^2-10^3]	[10^3-10^4]	[10^3-10^4]	[10^2-10^3]
BW	**TM 720-400**	N.D	[0-1]	N.D	[10^2-10^3]	[10^4-10^5]	[10^4-10^5]	[10^3-10^4]
SW	**TM 820C-400**	N.D	N.D	N.D	[10^2-10^3]	[10^3-10^4]	[10^4-10^5]	[10^3-10^4]
SW	**HRLE-440i**	N.D	[1-10]	N.D	[10-10^2]	[10^3-10^4]	[10^4-10^5]	[10^3-10^4]
SW	**HSWC3**	N.D	N.D	N.D	[10^2-10^3]	[10^3-10^4]	[10^4-10^5]	[10^2-10^3]

3.2. Membrane performances: permeability and molecular weight cut-off determination.

As it has been found in a previous work conducted in our laboratory, an exposure time to NaOCl lower than 122 h leads to transform discarded RO membranes into nanofiltration membranes in terms of Milli-Q water, synthetic brackish water permeability, ions and dextrose rejection. However, higher treatment time allowed obtaining UF membranes, which will be analyzed in the current work.

Three membrane coupons, for each commercial brand, exposed to NaOCl during 122 h, 242 h and 410 h were evaluated. The membranes were tested in a laboratory UF cell as described in the experimental part. As an example, Figure 2 shows the Permeability (L·h^{-1}·m^{-2}·bar^{-1}) of distilled water vs. filtering time for TM720-400 and TM820C-400 membranes after they had been exposed to the oxidizing agent for the exposure time mentioned above.

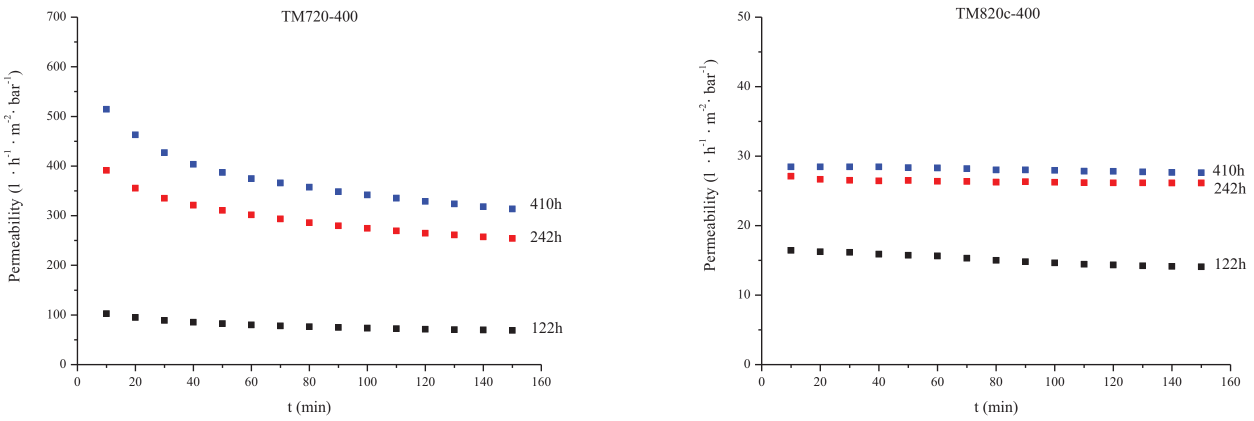

Figure 2. Permeability of transformed membranes (TM720-400 and TM820C-400) vs. filtering time using distilled water feed. Three exposure times to NaOCl (122 h, 242 h and 410 h) were considered.

As it can be observed in Figure 2, the permeability decreases with time until it reaches a plateau. This behavior is typical in UF porous membranes due to the compaction. This fact was more significant in brackish water membranes than in seawater membranes.

On the other hand, it can be noted that longer exposure time to NaOCl leads to a higher permeability because the active polyamide layer became more affected by the oxidizing agent. Further, a remarkable increase in permeability has been found for the membranes with exposure time longer than 122 h.

Table 5 shows the water and PEOs solution permeability values at steady state conditions for different transformed membranes. After a certain time (242 h), seawater membranes permeability (TM820C-400, HRLE-440i and HSWC3) has not increased significantly in any case (distilled water and PEO filtering tests). However, brackish water membranes have higher permeability than seawater membranes. This might be explained because the seawater membranes have been subjected to higher pressures during their lifetime than brackish water membranes. As a consequence, the seawater membranes should have suffered a greater compaction effect.

Fouling nature affects significantly the transformation process. Although, ICP-MS and microbiological analysis did not reveal high metal percentage concentration nor high population of microorganism (see above), the permeability of HSWC3 treated membrane is the lowest one. This could be due to several factors; firstly, some other types of microorganisms that have not been analyzed could also be present on the surface membrane. Indeed, these microorganisms could have generated an Extracellular Polymeric Substances (EPS) layer associated with a biofilm [32, 33]. Other explanation would be based on irreversible inorganic fouling attached onto the membrane that could not be removed completely.

Table 5. Permeability values and molecular weight cut-off for different transformed membranes.

Membrane		***Water Permeability*** **(l/hm^{2}bar)**	***PEOs solution Permeability*** **(l/hm^{2}bar)**	**MWCO , *R*=0.90 (g/mol)**
TM720400	122h	68.9	48.0	<1,000
	242h	253.9	83.9	8,900
	410h	313.5	85.5	22,400
TM820C-400	122h	14.1	13.8	<1,000
	242h	26.1	24.1	11,600
	410h	27.6	23.0	20,000
HRLE-440i	122h	15.1	6.8	-
	242h	79.2	47.9	19,000
	410h	79.5	48.5	37,800
HSWC3	122h	4.0	3.1	-
	242h	7.2	4.9	<1,000
	410h	13.4	8.1	16,000
BW30	122h	37.5	16.4	<1,000
	242h	128.1	41.2	1,900
	410h	236.0	60.5	10,100

The molecular weight cut-off (MWCO) was measured for all the five membranes plotting retention coefficients vs. molecular weight from analyzed permeate by SEC. The MWCO values have been listed in Table 5. Figure 3 shows retention curves for TM720-400 membrane. It can be observed that a higher exposure time to NaOCl causes a displacement of the retention curve towards higher molecular weight cut-off, which can be attributed to a higher degradation of polyamide layer after being exposed for a longer time to NaOCl. A similar behavior was observed for the rest of samples.

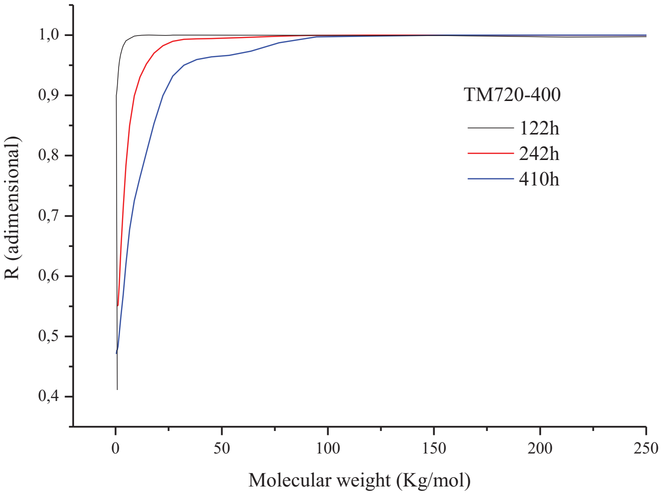

Figure 3. Retention curves of TM720-400 membrane (122h, 242h and 410h)

3.3. Membrane surface characterization

3.3.1 Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy

Degradation of the polyamide layer was investigated by the ATR-FTIR spectroscopy. In Figure 4, FTIR spectra for TM720-400 and HSWC3 membranes are shown. All the spectra were normalized to band at 1240 cm^{-1}, of phenylene ether stretching vibration of the polysulfone support layer, which remains constant during the degradation of polyamide layer.

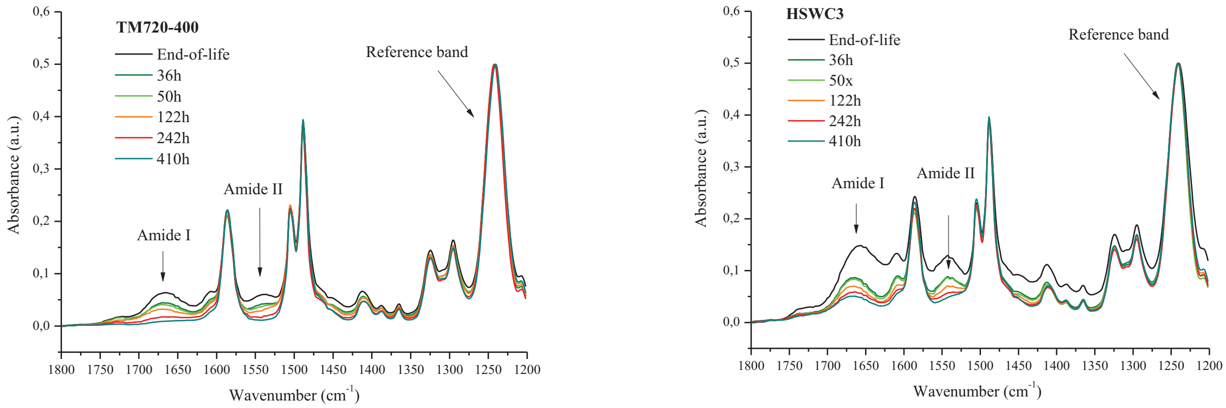

Figure 4. ATR-FTIR spectra of TM720-400 and HSWC3 membranes after different treatment time.

The spectra from the end-of-life membrane shows peaks at 1664 and 1542 cm^{-1}, corresponding to amide I and amide II bands, respectively associated with C=O stretching and N–H plane bending. The peak at 1610 cm^{-1} is representative of the C=C stretching vibrations from the aromatic amide bonds [20, 34, 35]. The intensity of these peaks progressively reduced and became nearly zero when the exposure time to

NaOCl reached 410 h, due to the elimination of polyamide layer. The same behavior was observed for the rest of samples, except for HSWC3 membrane, where the peaks (amide I and amide II) did not entirely disappear after exposure to hypochlorite.

3.3.2. Contact angle

The wettability of membranes was studied by contact angle measurement. The lower the contact angle the greater the tendency for water to wet the surface and the higher the hydrophilic character will be [36]. The contact angle values of end-of-life and transformed membranes are represented in Figure 5. The contact angles of end-of-life membranes were different from each other according to fouling nature. Generally, it was observed that membranes with inorganic fouling have lower contact angles than membranes with organic fouling. Moreover, when the fouling layer was removed after the first exposure hours, the contact angle values increased. In addition, as Figure 5 shows, the contact angle did not further vary after the membranes being exposed to the oxidizing agent for a longer time. This is probably due to similar hydrophilic character of the active layer and the porous layer.

Among the membranes studied, HSWC3 showed the most hydrophobic character after being exposed to NaOCl, showing contact angle values around 78-80º. The rest of membranes presented higher hydrophilic character because their contact angle values were around 66-68º.

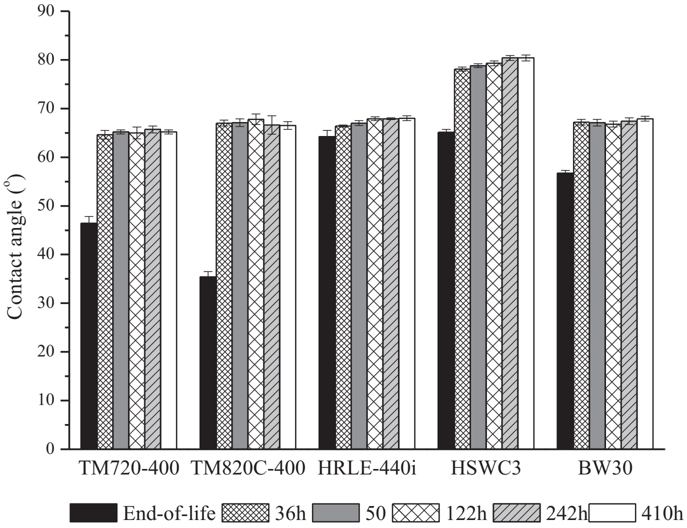

Figure 5. Contact angles of end-of-life and transformed membranes

Lawler et al.[37], have found contact angle values around 70º for RO membranes exposed to NaOCl solution of 300,000 ppm·h. Other authors have found that the wettability increases when lower chlorine concentration was employed [38-40]. Van Thanh Do et al. indicated that both trends in wettability might be explained by two competitive effects of N-chlorination of amide groups and hydrolysis processes. The incorporation of chlorine atoms on the membrane surface can cause an increase in hydrophobicity and inhibition of membrane wetting. However, an increase in carboxylic/ hydroxyl functional groups leads to an increase of the membrane hydrophilic character.[41, 42]

3.3.3. Scanning electron microscopy (SEM)

The SEM micrographs of the cross-section and surface of TM720-400 and HSWC3 membranes are shown in Figure 6.

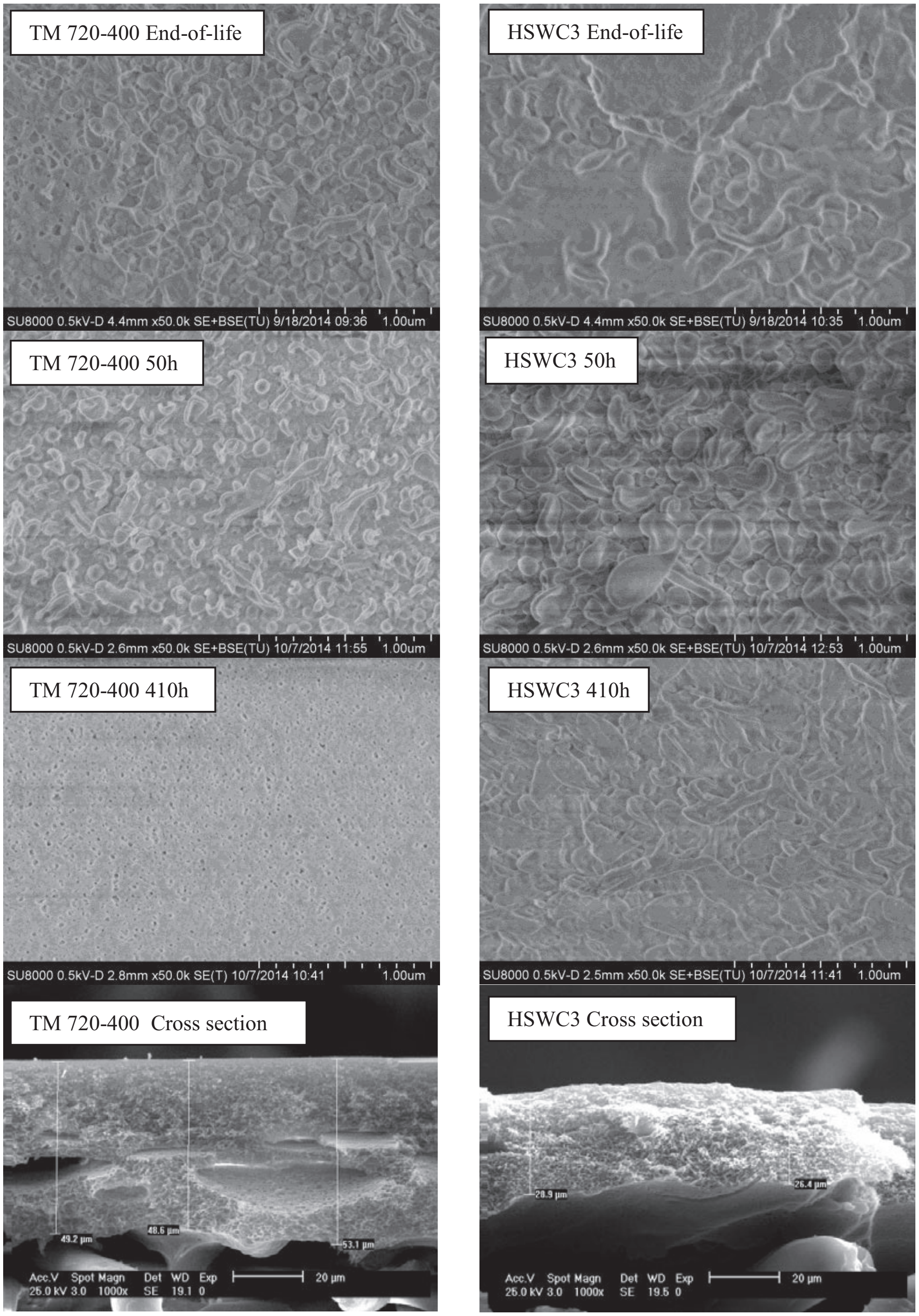

Figure 6. Scanning Electron Microscopy (SEM) micrographs of TM720-400 and HSWC3 membranes: End-of-life membranes, transformed membranes after 50h and 410h and cross sections

SEM micrographs of the membrane surface were taken to verify the appearance of pores after the treatment with the NaOCl. Before the NaOCl exposure, the end-of-life membranes were totally covered by a fouling layer. After, as it can be seen in Figure 6, the surface morphology of the membranes has changed with increasing time of exposure to NaOCl. In HSWC3 membrane, the pores hardly began to be detectable after 410 h. However, in the rest of the membranes clean porous surfaces were obtained. As an example, the TM720-400 membrane is shown in Figure 6 after 410 h exposure time to hypochlorite.

On the other hand, the cross-section micrographs allow observing the membrane porous structure which contains some macrovoids. The most significant difference perceived was the thickness. In general, brackish water membranes (TM720-400 and BW30) have almost double thickness than seawater membranes (TM820C-400, HRLE-440i and HSWC3). This difference in thickness may be due to difference in membrane compaction since brackish water membranes have been subjected to less pressure than the seawater membranes.

3.3.4 Digital Image Analysis

The surface SEM micrographs of the membranes exposed during 410 h were studied by Digital Image Analysis. The analytical procedure and the statistical processing reported in [24] were followed, in order to obtain the average diameter distribution and the pore sizes.[43-45]

Feret Diameter (d_F) is a tool commonly used to measure the pore size and it is directly related to the molecules size that can be retained by the membrane. Therefore, when the d_F increases, the rejection capability of the membrane decreases. Table 6 shows the d_F values calculated from SEM micrographs of membrane surfaces.

Table 6. Feret diameter values for membranes exposed to NaOCl during 410 h

Membrane	$d_{F,medio}$ (nm)
TM720-400	12.9 ± 6.1
TM820C-400	12.8 ± 5.9
HRLE-440i	14.2 ± 6.9
HSWC3	-
BW30	11.9 ± 5.8

The treated TM720-400 and TM820C-400 membranes have similar d_F and analogous MWCO from 22400 to 22000 g/mol. However, the TM720-400 membrane may have greater industrial interest because the permeability is around ten-fold higher. Another membrane to be highlighted is the transformed BW30 membrane because it has a high permeability and the highest rejection capability (10100 g/mol) because the d_F is the lowest of the entire series. Finally, the transformed HRLE-440i membrane has the highest d_F, which leads to the greater value of MWCO (37800 g/mol), and it shows the rejection ability of an ultrafiltration membrane.

Unfortunately, the analysis of the image surface of HSWC3 membrane could not be made because the pores were not visible after 410 h treatment. This result is consistent with the FTIR-ATR data obtained for this membrane, where bands from the polyamide active layer are still detectable even after 410 h treatment into the oxidizing solution. Apparently, NaOCl could not react with the polyamide layer due to the inorganic fouling layer, and consequently, permeability and surface lie still within the nanofiltration properties.

In order to reach a deeper understanding of the pore size distribution, histograms from the image processing were built, and they are displayed in Figure 7. As can be seen the data are adjusted in all cases to a Gaussian distribution.

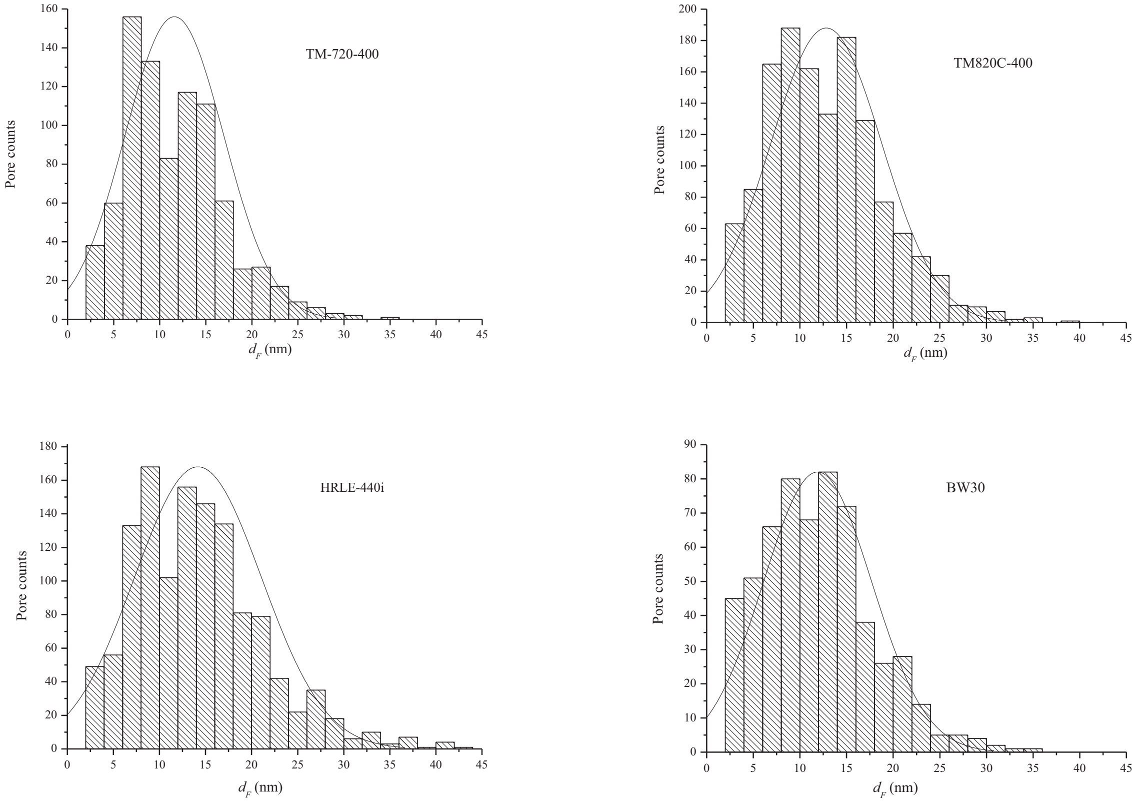

Figure 7. Histograms and pore diameter size distributions for analyzed membranes

4. CONCLUSIONS

End-of-life RO membranes were efficiently transformed into NF and UF membranes by exposing to NaOCl solution (passive immersion). It was also possible to determine the kind of fouling present in each membrane by their autopsy, where it is important to perform an initial good membrane surface characterization.

Studies on permeation and MWCO measurements permit to conclude that when the exposure time increases, the permeate flux and the MWCO increase. The existence of pores in the membranes after 410 h of exposing to oxidizing agent was confirmed by SEM micrographs of surface-membrane. The degradation of the polyamide active layer has been also followed by ATR-FTIR. The intensity of amide I and amide II peaks was progressively reduced and nearly vanished when the exposure time to the oxidizing solution increased to 410 h. The degradation of this active layer leads to the appearance of porous polysulfone structure as shown in SEM micrographs.

From Digital Image Analysis, *Feret diameter* of surface-membrane micrographs was measured; these results were consistent with MWCO values obtained, i.e. the higher the Feret diameter the greater the MWCO of the membrane.

The process outlined here allows a new usage of end-of-life membranes and the environmental impacts associated with their disposal can be reduced.

Future research planned by our group include fouling studies with proteins and cleaning cycle tests of recovered membranes in order to reach a next step of TRANSFOMEM project: pilot scale.

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LIFE+13 TRANSFOMEM: un ejemplo de reciclaje en el mundo de la desalación

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Resumen:

Las membranas de ósmosis inversa están constituidas por una serie de materiales muy duraderos, en su mayoría polímeros como poliamida, polisulfona, polipropileno, poliéster, acrilonitrilo butadieno estireno y fibra de vidrio. Sin embargo, la membrana en su conjunto tiene una vida útil que depende de muchos factores. A día de hoy cuando las propiedades filtrantes de las membranas se ven reducidas se declaran inservibles, se envían a vertederos y se reponen por elementos nuevos.

El proyecto LIFE TRANSFOMEM investiga distintas formas de reciclaje de membranas para obtener membranas de nanofiltración y ultrafiltración competitivas con respecto a las membranas comerciales, en términos de: permeabilidad, rechazo, tiempo de vida y ciclos de limpieza. Se ha caracterizado el ensuciamiento de las membranas y se han determinado las condiciones de transformación de las membranas mediante dos metodologías: pasiva (sumergiendo las membranas en una solución de transformación) y activa (a través de la recirculación de la solución de transformación). Los resultados obtenidos empleando modelos diferentes de membranas procedentes de distintas desaladoras (agua de mar y salobre) con distinto tipo de ensuciamiento (orgánico e inorgánico), permiten observar que el proceso de transformación es más eficiente si se realiza con membranas empleadas en procesos de desalinización de agua salobre. Estas convierten sus propiedades de ósmosis inversa, en propiedades que se ajustan al rango de las membranas de nanofiltración y ultrafiltración. Por otro lado, las membranas que fueron destinadas al tratamiento de agua de mar, aunque soportan altos niveles de exposición al hipoclorito de sodio, también pueden ser transformadas. No obstante los valores de permeabilidad obtenidos son inferiores. A pesar de que el proceso de transformación está vinculado al grado de ensuciamiento de las membranas, se ha observado que el ensuciamiento orgánico o inorgánico de características arcillosas, no impide el proceso de transformación, pudiendo reciclar las membranas sin aplicar ciclos de limpieza previos.

Abstract:

Commonly reverse osmosis (RO) membranes are made of long-term polymeric materials such as polyamide, polysulfone, polypropylene, polyester, acrylonitrile butadiene styrene and fiberglass. However, membrane operating lifespan depends on a lot of factors. Nowadays, when membranes performance is reduced, they became a waste. Therefore, end-of-life membranes use to be disposed in landfill and new membranes modules are replaced in the desalination plants.

Life Transfomem Project is investigating on end-of-life RO membranes recycling at pilot scale. It is aimed to demonstrate the viability of transforming end-of-life membranes into competitive nanofiltration (NF) and ultrafiltration (UF) membranes, in terms of: permeability, rejection coefficients, lifespan and cleaning cycling. Initially, membrane fouling has been identified. Therefore, it has been figured out the transformation condition by two different types of transformation process. In the first, called passive transformation, the membranes are immersed in a sodium hypochlorite solution. The second mode, active transformation, forces the solution to circulate in the membranes. It has been employed different end-of-life RO membranes models (brackish water and seawater designs) with diverse fouling (organic and inorganic). Results let observe that the transformation process is more efficient if it is applied in end-of-life membranes, which were treating brackish water in their operating life. In other hand, seawater RO membranes, although resist to higher exposure level of free chlorine, they also transform their properties into NF and UF performance range. In all cases, recycling process is linked to the membranes fouling level. Nevertheless, it has been observed that organic fouling and clay fouling (inorganic) does not interfere in the transformation process, being possible to recycling membranes with no previous cleaning cycles.

1 INTRODUCCIÓN

1.1 Problemática ambiental

Dentro de la consolidada tecnología de las membranas de ósmosis inversa, la gestión de los módulos agotados es a día de hoy un reto muy importante que hay que afrontar para cumplir con los términos de desarrollo sostenible. Las membranas están constituidas por una serie de materiales muy duraderos, en su mayoría polímeros como poliamida, polisulfona, polipropileno, poliéster, fibra de vidrio, etc. Sin embargo, la vida útil de las membranas depende de muchos factores principalmente relacionados con la calidad del agua a tratar, las sustancias químicas empleadas en el pretratamiento y las condiciones de proceso de filtración. Desafortunadamente, a día de hoy estos materiales una vez se declaran inservibles para el proceso industrial perecen en vertederos. Algunos estudios estiman que en España anualmente el número de membranas de ósmosis inversa desechadas ascendería a más de 80,000 y a nivel mundial la cifra podría ascender a más de 800,000 unidades. En definitiva, grandes toneladas de plásticos (>14,000 Toneladas a nivel mundial) con un gran potencial para posibles usos son desechadas anualmente [1]. De acuerdo con la Directiva 2008/98/EC sobre residuos, la eliminación de los módulos inservibles de membranas en los vertederos es la última de las opciones dentro de la jerarquía de gestión (prevención, preparación para la reutilización , reciclado, otro tipo de valoración y eliminación).

1.2 Antecedentes

Lawler et al. [2], realizó recientemente un estudio de análisis de ciclo de vida de distintas opciones de gestión de las membranas residuos, para evaluar su impacto ambiental. Las opciones contempladas fueron: el vertedero, la incineración, la gasificación, la recuperación energética, el reciclaje directo (convirtiendo las propiedades de las membranas a ultrafiltración) y reutilización directa en procesos de ósmosis inversa. El estudio demostró que la reutilización directa es la opción ambiental más favorable, mientras que la deposición de las membranas en el vertedero es la peor opción. Iniciativas de reciclaje directo se han llevado a cabo desde el año 2002 de mano de la Universidad de las Palmas de Gran Canaria [3,4], quienes mostraron que el K_7MnO_4 es un compuesto favorable para la transformación de membranas desechadas de ósmosis inversa en ultrafiltración e introdujeron este concepto por primera vez. A estas experiencias, le siguieron más estudios a escala laboratorio empleando tanto soluciones de K_7MnO_4 [5], como de hipoclorito de sodio [6,7]. Además algunos de los estudios han tratado de controlar la concentración y el tiempo de exposición para poder transformar las membranas desechadas tanto a membranas de nanofiltración como a membranas de ultrafiltración [8,9].

El interés de España por ofrecer opciones alternativas al envió de membranas a vertedero es firme y varios han sido los proyectos financiados recientemente y soportados por grandes empresas de desalación. En 2011, la empresa española Aqualia lideró el proyecto de demostración piloto Life-Remembrane, para recuperación de membranas de ósmosis inversa desechadas (sin perder sus propiedades de alta capacidad de rechazo) [10]. Desde 2014, en el proyecto Life-Transfomem, IMDEA Agua junto con las empresas SADYT y VALORIZA Agua, se investiga distintas formas de reciclaje de membranas desechadas (en varios pilotos) para su transformación en membranas de nanofiltración y ultrafiltración empleando NaOCl. Por último, recientemente en 2016 dio comienzo el proyecto nacional INREMEM, cuyo objetivo es el reciclaje de membranas deterioradas de ósmosis inversa (a escala laboratorio) para estudiar su viabilidad en 5 técnicas diferentes: i) biomembranas (BM) para tratar aguas superficiales, ii) biorreactores de membrana (BRM) para tratamiento de aguas residuales, iii) ósmosis directa (FO) para tratamiento de aguas residuales, iv) electrodiálisis (ED) para regeneración de disoluciones osmóticas y v) destilación por membrana (MD) para regeneración de disoluciones osmóticas.

2 OBJETIVOS

El objetivo del presente trabajo es demostrar la viabilidad técnica de la transformación de membranas desechadas de ósmosis inversa a membranas de nanofiltración y ultrafiltración, a escala piloto mediante dos metodologías de transformación, activa y pasiva.

3 METODOLOGÍA

3.1 Membranas y reactivos

Se recopilan membranas de ósmosis inversa desechadas que en su vida útil estuvieron tratando agua de mar y agua salobre. Se cuenta con modelos de hydranautics (HSWC3), Dow (BW30 XFR-400734i) y Toray (TM720-400, SU 820-FA, SU-720F y SU-720L). Se emplean reactivos químicos tales como NaOH, SDS y HCL, para realizar limpiezas convencionales previas a las transformaciones; NaOCL 170 g/L de cloro libre y $NaHSO_3$ en el proceso de transformación para controlar la degradación e inhibición de la poliamida, respectivamente.

3.2 Caracterización de las propiedades filtrantes de las membranas

Las membranas se conservan en una disolución de bisulfito de sodio entre 500-1000 mg/L. Previo a la caracterización de las propiedades filtrantes, se pesan las membranas en húmedo, tras 60 min en posición vertical. Se comprueban la permeabilidad y los coeficientes de rechazo de sales, de iones monovalentes, divalentes y de materia orgánica empleando un agua natural, salobre y pretratada (filtración por arena) con una conductividad media de 10-11 mS/cm (agua salobre). Se emplea un caudal de recirculación de 7500 L/h, 20-25 ºC y 15 bar de presión de transmembrana. Este proceso se realiza como etapa previa a la transformación y se repite al finalizar la exposición de las membranas ante el hipoclorito de sodio, para evaluar el estado inicial de las membranas y el grado de transformación (a nanofiltración o a ultrafiltración) respectivamente. Una vez caracterizadas las membranas se vuelven a conservar en bisulfito de sodio.

Los valores más característicos son la permeabilidad de la membrana, es decir la cantidad de agua que atraviesa la membrana por unidad de superficie y tiempo en función de la presión de transmembrana aplicada (Ecuación 1) y los coeficiente de rechazo en sales y en iones, calculado a través de los valores de conductividad medidos o concentración media, medidos la corriente de permeado y de influente (Ecuación 2).

$$Permeabilidad_{(L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1})} = \frac{Q_{(p)}}{S\cdot P} \quad (1) \qquad \%\mathrm{R} = (1 - \frac{C_p}{C_f}\cdot 100) \quad (2)$$

3.3 Protocolo de limpieza

Se ha establecido un protocolo de limpiezas de membranas según literatura existente [11], aplicando 2 horas de limpieza básica (0.1$\%_m$ NaOH y 0,03$\%_m$ SDS) y 2 horas de limpieza ácida (0,5 $\%_m$ HCL). Las limpiezas se realizan en el mismo equipo de caracterización de las propiedades filtrantes, empleando un caudal de circulación de 6000 L/h. Se aplica como paso previo a las transformaciones activas, puesto que el arrastre de ensuciamiento durante el proceso de transformación podría dañar de forma mecánica (por abrasión) la superficie de las membranas. En el casos de las transformaciones pasivas, se realiza para comparar los resultados de membranas transformadas con y sin limpieza previa.

3.4 Protocolo de transformación activa y pasiva

Aprovechando la sensibilidad de la poliamida al cloro libre, se emplea hipoclorito de sodio para degradar de forma controlada la capa selectiva de las membranas de ósmosis deterioradas. Se combinaron pares de membranas limpias y sucias de varios modelos y plantas para estudiar si el ensuciamiento sobre la membrana afecta al proceso de transformación. Se escogieron dos niveles de exposición en base a la experiencia de los autores a escala laboratorio [9]. El nivel moderado se usó para la transformación a nanofiltración y el nivel alto para la transformación a ultrafiltración.

En el caso de la transformación pasiva, se ponen en contacto las membranas en un depósito con disolución de hipoclorito de sodio el tiempo requerido para cumplir el nivel de exposición fijado (ppm·h). En el caso de la transformación activa, se hace circular la solución de hipoclorito de sodio a través de las membranas a temperatura ambiente, con una presión máxima de 2 bar y con un caudal de recirculación de 6000 L/h (similar al que suele realizarse en las limpiezas).

3.5 Caracterización de la superficie de las membranas: desechadas y transformadas

3.5.1 Autopsia de membranas

Se realiza la apertura de los módulos de membranas en una mesa específica adaptada con una radial para corte de fibra de vidrio y un soporte plegable. Se extraen tanto la fibra de vidrio como los conectores de influente y rechazo y se desenrollan las láminas del tubo del permeado facilitando su inspección y toma de muestras. Se realiza una inspección visual sobre el estado de las líneas de pegamento, la integridad del tubo de permeado, de la carcasa, de los laterales, de los espaciadores y de las láminas filtrantes. Se observa la uniformidad de la distribución del ensuciamiento y las deposiciones (orgánicas-coloidales) y precipitación de sales. Se inspecciona el color del ensuciamiento, el espesor, su consistencia y si se desprende olor.

3.5.2 Análisis termogravimétrico (TGA)

El análisis termogravimétrico del ensuciamiento se realiza en una termobalanza modelo TGA Q500, bajo una atmósfera oxidante (aire). La muestra se somete a un aumento de temperatura desde 45ºC a 800ºC a una velocidad de 10ºC/min. Así, la materia orgánica se degrada y queda un residuo que es la fracción inorgánica. Teniendo en cuenta el peso inicial de la muestra y del residuo (parte inorgánica), por diferencia de pesada se obtiene el porcentaje de parte orgánica.

3.5.3 Espectrometría de masas con plasma de acoplamiento inductivo (ICP Masas)

La cuantificación de metales se llevó a cabo mediante el espectrofotómetro quadrupolo ICP-MS 7700 x series de Aligent Technologies. Las masas se calibran de forma diaria con 1 µg/L de Ce, Co, Li, Mg, Tl y Y en 1% (v/v) de HNO_3. 50 mg de muestra de ensuciamiento es digerido en una solución con HNO3:H_2O_2 (4:1) y después diluidas en 10 mL de agua Milli-Q. Tras la digestión y la correspondiente dilución se realiza un análisis semi-quantitativo del ICP.

3.5.4 Caracterización de la superficie de membranas transformadas a ultrafiltración

Las membranas se han caracterizado para identificar la presencia de la capa superficial de poliamida. La superficie de las membranas fueron examinadas mediante Microscopía Electrónica de Barrido (SEM) usando un microscopio modelo S-8000 (Hitachi) y a través de la técnica de espectroscopía infarroja por transformada de Fourier (ATR-FTIR) empleando un espectrómetro Perkin-Elmer RX1 equipado con un elemento de reflexión interna de diamante con un ángulo de incidencia de 45º.

4 RESULTADOS

4.1 Caracterización de las membranas desechadas

4.1.1 Propiedades filtrantes de las membranas: permeabilidad y coeficientes de rechazo

En la Tabla 1 se recogen los distintos modelos de membranas, el número disponible, su procedencia y el peso húmedo (tras 60 min drenando en posición vertical). El peso medio de las membranas nuevas (7) SU-720F es de 14,6 kg, mientras que el peso medio de 75 membranas sucias húmedas es de 22 kg, la mediana y moda son de 17 Kg. Sin embargo se detectaron pesos mínimos de 15 kg y máximos de 42 Kg.

Tabla 1. Membranas desechadas de OI, peso medio y desviación estándar.

Código	Membrana	Procedencia	Tipo agua	Peso$_{medio}$(Kg)	±(sd)	Nº módulos
0	HSWC3*	IDAM Carboneras	Mar	16,8	0,2	4
1	HSWC3*	Sta. Cruz de Tenerife	Mar	17,0	0,4	6
2	SU-820FA	Cuevas del Almanzora (pilotos)	salobre	38,0	2,8	6
3	TM720-400*	Atabal (Acuasur)	salobre	19,2	2,8	6
4	BW30XFR-400/34i*	Atabal (Acuasur)	salobre	18,8	0,4	3
5	SU-720F	Desconocido	salobre	15,2	0,2	2
6ª	TM720-400	Codeur	salobre	40,3	0,9	6
6b	TM720-400	Codeur	salobre	16,6	1,1	24
7	SU-720F	Cocón Águilas	salobre	14,6	0,4	4
8	SU-720L	Cocón Águilas	salobre	16,0	0,0	1
9	TM720-400	Desconocido	salobre	16,2	1,6	17

En la Figura 1 se muestran los resultados de coeficientes de rechazo de iones monovalentes y divalentes, obtenidos en la caracterización inicial de las membranas. En 5 de 9 casos analizados, las membranas desechadas presentaban un rechazo inicial en sales aceptable, obteniendo coeficientes >94,9% en cualquiera de los iones analizados. Así, una vez limpias, estas membranas podrían ser apropiadas para ser reutilizadas en procesos de OI menos exigentes. Por otra parte, estas mismas membranas se podrían transformar a membranas de nanofiltración.

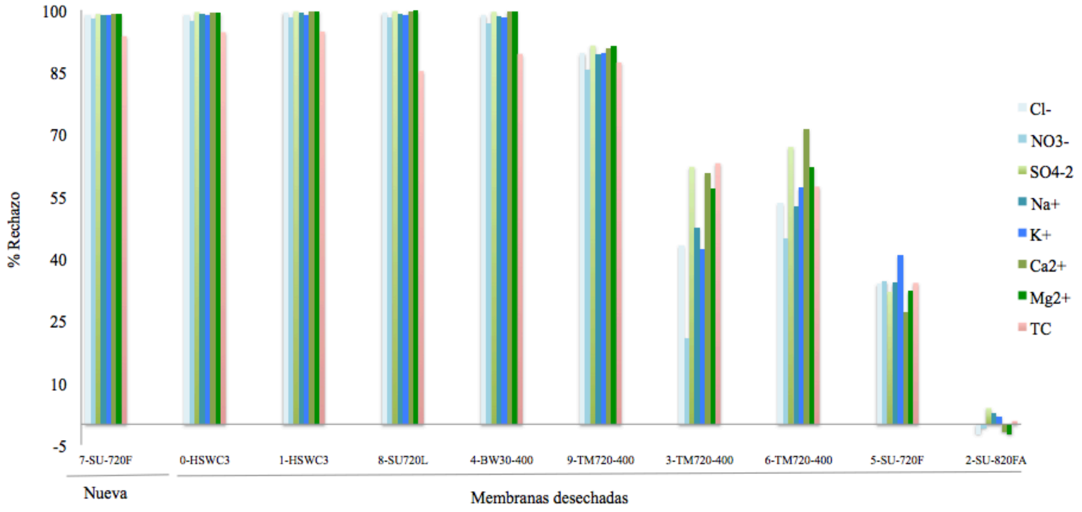


Figura 1. Porcentajes de rechazo obtenidos de iones monovalentes, divalentes.

Por otro lado, se observa que existe una correlación entre el peso de las membranas desechadas (Tabla 1) y su capacidad de rechazo. Cuando el peso de las membranas es superior a 35 kg, los coeficientes de rechazo son inferiores al 70%, llegando a ser nulos en el caso de la membrana SU-820FA. Además, el flujo de permeado aumenta entre 1,5 y 2,5 veces en relación los valores de fábrica. En 4 de los 9 casos estudiados se observa un alto nivel de deterioro. Estas membranas podrán ser recicladas directamente a membranas de ultrafiltración. Dentro de este grupo se encuentran las membranas que más pesaron, aunque los valores oscilan desde 16 kg hasta 40 kg.

4.1.2 Autopsia de membranas: caracterización de ensuciamiento

Análisis termogravimétrico (TGA)

Los resultados de la TGA (Figura 2) indican que la mayor parte de las membranas analizadas (44%) tienen un ensuciamiento de naturaleza inorgánica. Según la inspección visual realizada en las autopsias, 3 membranas de 3 desaladoras distintas presentaron una costra salina sobre los espaciadores: (2) SU-820 FA, (3) TM720-400 y (6) TM 720-400. Estas membranas, como se observó en la Tabla 1, presentan un peso elevado (en dos de los casos por encima del valor de la media). Además, hay membranas de agua de pozo que presentan un ensuciamiento visual arcilloso, (9) TM720-400, y que no exhiben sales precipitadas. En 2 de 9 casos (22%), las membranas presentan mayor porcentaje de ensuciamiento orgánico. Los modelos HSWC3 (agua de mar), a simple vista presentan bajo nivel de ensuciamiento y en el caso de las membranas procedentes de Tenerife ni siquiera se logró recoger depósito sobre la membrana.

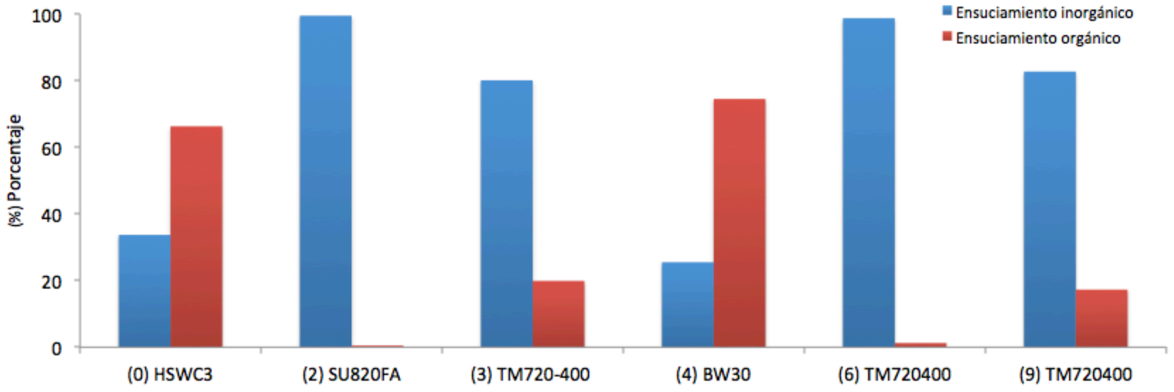


Figura 2. Porcentaje de ensuciamiento orgánico e inorgánico de las membranas desechadas.

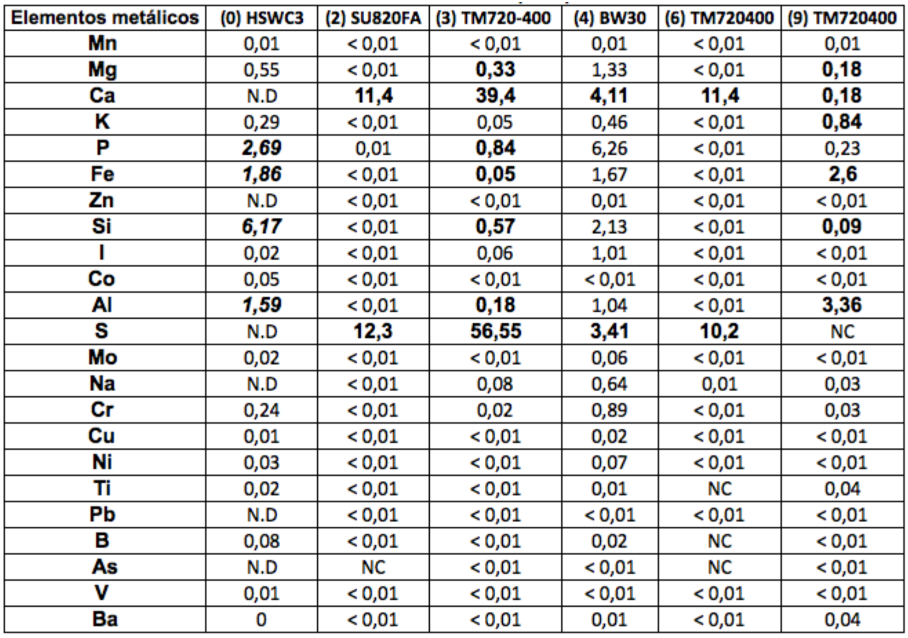
Espectrometría de masas con plasma de acoplamiento inductivo, ICP Masas

El ICP permite identificar el contenido en metales de la parte inorgánica del ensuciamiento detectado. Los resultados corresponden por tanto al porcentaje respecto a la masa total de la muestra (Tabla 2), lo que explica que los coeficientes sean en muchas ocasiones tan bajos.

Aquellas membranas que trataron agua de pozo y que visualmente presentan una costra de sal precipitada sobre el espaciador de influente de las membranas tienen un mayor contenido en calcio (Ca) y el azufre (S). La sal precipitada del modelo (3) TM720-400 puede tener sulfato de calcio. Por otro lado, los modelos (2) SU820-FA y (6) TM 720-400 podrían tener carbonato como componente principal (el carbono no se detecta en el ICP), dado el bajo porcentaje detectado en calcio, magnesio, azufre, bario o silicio; elementos que suelen aparecer en el *scaling.* Por otro lado, el modelo (9) TM720-400, que presentaba ensuciamiento coloidal tiene mayor contenido en potasio (K), hierro (Fe), Silicio (Si) y aluminio (Al), típico del ensuciamiento coloidal de las matrices arcillosas.

En el caso de las membranas que trataron agua de mar presentan elementos metálicos tales como el Magnesio (Mg), potasio (K), fósforo (P), hierro (Fe), yodo (I) y el aluminio (Al).

Tabla 2. Resultados del porcentaje elemental de la fracción inorgánica del ensuciamiento.



Elementos metálicos	**(0) HSWC3**	**(2) SU820FA**	**(3) TM720-400**	**(4) BW30**	**(6) TM720400**	**(9) TM720400**
Mn	0,01	< 0,01	< 0,01	0,01	< 0,01	0,01
Mg	0,55	< 0,01	**0,33**	1,33	< 0,01	**0,18**
Ca	N.D	**11,4**	**39,4**	**4,11**	**11,4**	**0,18**
K	0,29	< 0,01	0,05	0,46	< 0,01	**0,84**
P	***2,69***	0,01	**0,84**	6,26	< 0,01	0,23
Fe	***1,86***	< 0,01	**0,05**	1,67	< 0,01	**2,6**
Zn	N.D	< 0,01	< 0,01	0,01	< 0,01	< 0,01
Si	***6,17***	< 0,01	**0,57**	2,13	< 0,01	**0,09**
I	0,02	< 0,01	0,06	1,01	< 0,01	< 0,01
Co	0,05	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01
Al	***1,59***	< 0,01	**0,18**	1,04	< 0,01	**3,36**
S	N.D	**12,3**	**56,55**	**3,41**	**10,2**	NC
Mo	0,02	< 0,01	< 0,01	0,06	< 0,01	< 0,01
Na	N.D	< 0,01	0,08	0,64	0,01	0,03
Cr	0,24	< 0,01	0,02	0,89	< 0,01	0,03
Cu	0,01	< 0,01	< 0,01	0,02	< 0,01	< 0,01
Ni	0,03	< 0,01	< 0,01	0,07	< 0,01	< 0,01
Ti	0,02	< 0,01	< 0,01	0,01	NC	0,04
Pb	N.D	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01
B	0,08	< 0,01	< 0,01	0,02	NC	< 0,01
As	N.D	NC	< 0,01	< 0,01	NC	< 0,01
V	0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01
Ba	0	< 0,01	< 0,01	0,01	< 0,01	0,04

4.2 Caracterización de las membranas transformadas

4.2.1 Propiedades filtrantes. Comparativa entre la transformación pasiva y activa

En la Figura 3 se muestran los resultados relativos de permeabilidad (Figura 3 izq.) y coeficiente de rechazo en sales (Figura 3 drcha.) de varios modelos de membranas (agua de mar y salobre) transformadas a través de la metodología activa y pasiva respecto a los valores iniciales (previos a la transformación).

A la vista de los resultados, las dos metodologías permiten realizar cambios similares en las propiedades de las membranas, no existiendo diferencias significativas en términos de permeabilidad y rechazo. En el caso de la transformación a nanofiltración, las membranas aumentan alrededor de 1,5 veces su permeabilidad inicial, mientras que la capacidad de rechazo disminuye levemente. En el caso de la transformación a ultrafiltración, las membranas de agua salobre aumentan hasta 25 veces su permeabilidad con respecto a los valores iniciales. Sin embargo, en el caso de las membrana de agua de mar (HSWC3), a pesar de eliminar la capacidad de rechazo en sales de las membranas, la permeabilidad solamente aumenta hasta 5 veces con respecto a los valores iniciales. Una de las hipótesis planteadas es que las membranas que tratan agua de mar, al estar sometidas a fuertes presiones (alrededor de 60 bar) se compactan notablemente y, a pesar de eliminar la capa de poliamida, siguen ofreciendo gran resistencia al paso del agua. Otras hipótesis se centran en el bioensuciamiento relacionado con sustancias poliméricas extracelulares (EPS) o con la propia naturaleza de la polisulfona. No obstante, no se han realizados estudios para confirmar ninguna de estas dos últimas afirmaciones.

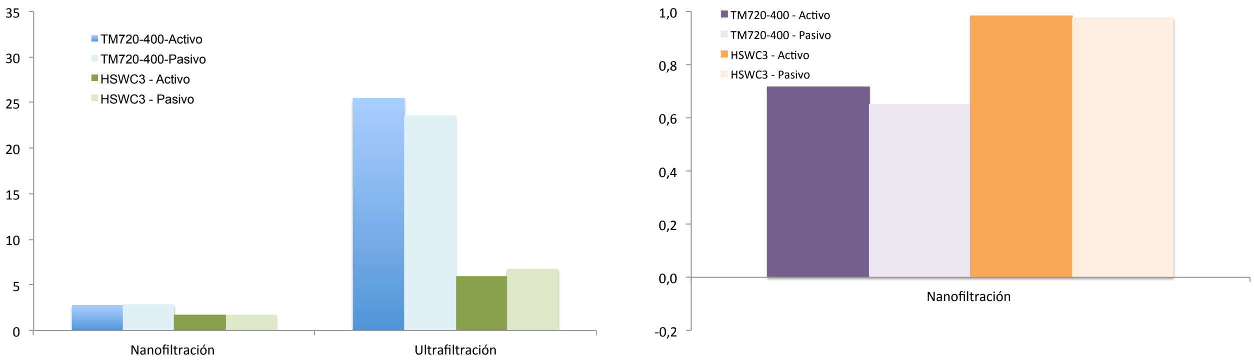


Figura 3. Comparativa de las propiedades filtrantes de los modelos TM720-400 (agua salobre) y HSWC3 (agua de mar) transformados de forma pasiva y activa.

4.2.2 ¿Afecta el ensuciamiento al proceso de transformación?

El ensuciamiento de las membranas afecta al estado inicial en el que se encuentran las mismas. Algunas membranas que inicialmente presentaban coeficientes de rechazos altos, no mostraron diferencias significativas entre haber operado en distintas desaladoras o haber sufrido un tratamiento de limpieza previo al proceso de transformación. Este es el caso del modelo HSWC3 procedente de la desaladora de agua de mar de Carboneras y de Tenerife. Dentro de las membranas procedentes de la misma desaladora (modelos HSWC3 y TM720-400), tampoco hay diferencia significativa entre realizar o no una limpiar previa a la transformación.

4.2.3 Caracterización de las membranas transformadas a ultrafiltración

Microscopía electrónica de barrido (SEM)

Se han realizado algunas analíticas de verificación para corroborar la existencia de poros en los casos de haber transformado las membranas desechadas a membranas de ultrafiltración. En la Figura 4 se muestra la membrana SU-720F transformada de forma pasiva. Como ya se verificó en trabajos anteriores de los autores a escala laboratorio [8], se detectan presencia de nanoporos en la superficie de la membranas. En consecuencia, se confirma la eliminación completa de la poliamida, quedando expuesta la polisulfona como superficie filtrante. Esto se repite en el resto de membranas transformadas.

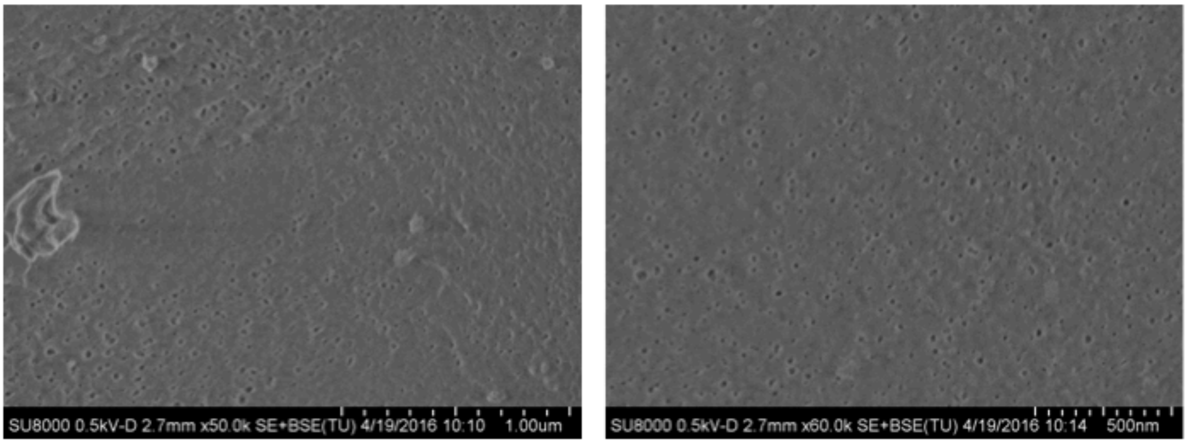


Figura 4. Micrografía de SEM del modelo SU-720F a distintas escalas.

Espectroscopía Infrarroja (ATR)

En la Figura 5 (izquierda) , se muestran todos los espectros de ATR-FTIR en absorbancia obtenidos para cada membrana desechada. Para interpretar fácilmente los resultados es necesario compararlos con los espectros de la poliamida y la polisulfona de membranas nuevas (Figura 5 drcha.). Todos los espectros presentados están normalizados con respecto a la banda de referencia de polisulfona (1240 cm^{-1}). Los espectros de las membranas de OI sucias y nueva muestran señales a 1664 y 1542 cm^{-1}, que se corresponden a las bandas amida I y amida II, respectivamente y que se asocian al movimiento de extensión del enlace C=O y al movimiento de flexión del enlace N-H. La señal situada a 1610 cm^{-1} es representativa de las vibraciones de tensión de los enlaces C=C aromáticos de las amidas. Tras la transformación a membranas de ultrafiltración, se observa en la que estas señales de amida I y II no aparecen tal y como ocurre en el espectro de la polisulfona.

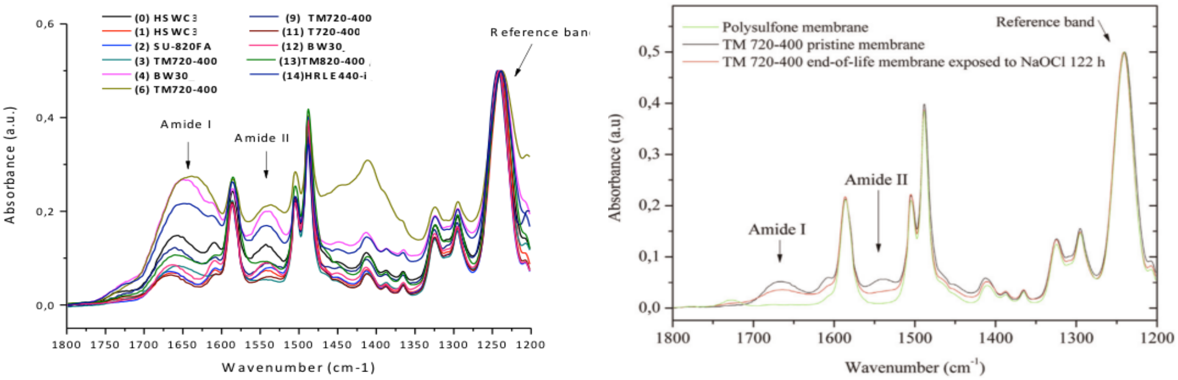


Figura 5. Espectros de absorbancia de las membranas desechadas (izq) y de membranas nuevas (drcha.).

5 CONCLUSIONES

La desalación genera un residuo constante de membranas desechadas que tienen un potencial de reciclaje y reutilización dentro de los procesos de filtración. Sin embargo a día de hoy no hay soluciones industriales que se ocupen de una gestión distinta al envió de dichas membranas al vertedero.

La pesada de las membranas desechadas, así como la caracterización de la permeabilidad y los coeficientes de rechazo, empleando agua con contenido en sales tanto monovalentes como divalentes, son indicadores efectivos y no agresivos, para determinar el estado inicial de las membranas desechadas, e indican qué transformación es la apropiada (ninguna, nanofiltración o ultrafiltración). A la vista de los resultados obtenidos, el reciclaje directo (manteniendo la configuración de enrollamiento en espiral) de membranas de ósmosis inversa, a escala piloto, utilizando disoluciones de hipoclorito de sodio concentradas, es técnicamente posible tanto a través de técnicas pasivas como activas. En función del nivel de exposición (ppm·h) de las membranas al agente reactivo, se consigue degradar parcialmente la poliamida (membranas de nanofiltración) o totalmente (membranas de ultrafiltración).

6 AGRADECIMIENTOS

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Paper VII: patent

Proceso de transformación de membranas de poliamida con enrollamiento en espiral que han agotado su vida útil en membranes de utilidad industrial. In English: Transformation of spiral wound polyamide membranes after its industrial lifespan. Spanish Patent P201630931, 08 July 2016.

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INVENCIÓN LABORAL:	[✓]
CONTRATO:	[ ]
SUCESIÓN:	[ ]
PORCENTAJE DE TITULARIDAD:	050,00 %
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CÓDIGO PAÍS:	ES
NIF/NIE/PASAPORTE:	G84912732
CNAE:	
PYME:	
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PROVINCIA:	28 MADRID
CÓDIGO POSTAL:	28805
PAÍS RESIDENCIA:	España
CÓDIGO PAÍS:	ES
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CORREO ELECTRÓNICO:	
PERSONA DE CONTACTO:	
MODO DE OBTENCIÓN DEL DERECHO:	
INVENCIÓN LABORAL:	[✓]
CONTRATO:	[ ]
SUCESIÓN:	[ ]
PORCENTAJE DE TITULARIDAD:	050,00 %
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NIF/NIE/PASAPORTE:	74535387-T
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NIF/NIE/PASAPORTE:	74680967-J
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NIF/NIE/PASAPORTE:	10174706-N

(7) TÍTULO DE LA INVENCIÓN:	PROCESO DE TRANSFORMACIÓN DE MEMBRANAS DE POLIAMIDA CON ENROLLAMIENTO EN ESPIRAL QUE HAN AGOTADO SU VIDA ÚTIL EN MEMBRANAS DE UTILIDAD INDUSTRIAL

(8) PETICIÓN DE INFORME SOBRE EL ESTADO DE LA TÉCNICA:

SI	[✓]
NO	[ ]

(9) SOLICITA LA INCLUSIÓN EN EL PROCEDIMIENTO ACELERADO DE CONCESIÓN

SI	[✓]
NO	[ ]

(10) EFECTUADO DEPÓSITO DE MATERÍA BIOLÓGICA:

SI	[ ]
NO	[✓]

(11) DEPÓSITO:

REFERENCIA DE IDENTIFICACIÓN:	
INSTITUCIÓN DE DEPÓSITO:	
NÚMERO DE DEPÓSITO:	
ACCESIBILIDAD RESTRINGIDA A UN EXPERTO (ART. 45.1. B):	

(12) DECLARACIONES RELATIVAS A LA LISTA DE SECUENCIAS:

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LA LISTA DE SECUENCIAS EN FORMATO PDF Y ASCII SON IDENTICOS	[ ]

(13) EXPOSICIONES OFICIALES:

LUGAR:	
FECHA:	

(14) DECLARACIONES DE PRIORIDAD:

PAÍS DE ORIGEN:	
CÓDIGO PAÍS:	
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OTROS (Aparecerán detallados):	
(17) EL SOLICITANTE SE ACOGE AL APLAZAMIENTO DE PAGO DE TASA PREVISTO EN EL ART. 162 DE LA LEY 11/1986 DE PATENTES, DECLARA: BAJO JURAMIENTO O PROMESA SER CIERTOS TODOS LOS DATOS QUE FIGURAN EN LA DOCUMENTACIÓN ADJUNTA:	[ ]
DOC COPIA DNI:	[ ] N.º de páginas:
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DOC COPIA LIBRO DE FAMILIA:	[ ] N.º de páginas:
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(19) FIRMA:	
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LUGAR DE FIRMA:	MADRID
FECHA DE FIRMA:	08 Julio 2016

MINISTERIO
DE INDUSTRIA, ENERGÍA
Y TURISMO

Oficina Española
de Patentes y Marcas

AGENTE: María Isabel Lehmann Novo
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Madrid, a 16 de septiembre de 2016

Continuación de Procedimiento de la solicitud de Patente Nacional 201630931

La Oficina Española de Patentes y Marcas (OEPM) le notifica, en relación con la tramitación de su solicitud de patente 201630931, que dicha solicitud ha superado el examen previsto en los artículos 31 de la Ley 11/1986, de Patentes y 17 de su Reglamento de Ejecución (RD 2245/1986).

Esta notificación se publicará en el Boletín Oficial de la Propiedad Industrial (BOPI) en fecha 22/09/2016. El BOPI puede consultarse en la Web de la OEPM.

Si desea que su solicitud se retire y no sea publicada, deberá comunicarlo por escrito a la mayor brevedad en el Registro de la OEPM, preferentemente a través del formulario **3587X** disponible al efecto en la página web (www.oepm.es).

Atentamente,

Gemma Esteban

Fdo.: Gemma Esteban García
Técnico/a Superior Examinador/a

PROCESO DE TRANSFORMACIÓN DE MEMBRANAS DE POLIAMIDA CON ENROLLAMIENTO EN ESPIRAL QUE HAN AGOTADO SU VIDA ÚTIL EN MEMBRANAS DE UTILIDAD INDUSTRIAL

CAMPO DE LA INVENCIÓN

La presente invención se refiere al reciclaje de membranas de poliamida con enrollamiento en espiral que han agotado su período de vida útil.

ANTECEDENTES DE LA INVENCIÓN

La desalación mediante membranas de poliamida con enrollamiento en espiral se ha consolidado en la última década como una tecnología madura y muy asentada en el mercado internacional. De hecho, la tecnología de la ósmosis inversa ocupa el 65% de los procesos de desalación.

Las membranas están constituidas por una serie de materiales muy duraderos, en su mayoría polímeros como poliamida, polisulfona, polipropileno, poliéster, fibra de vidrio, etc. Sin embargo, las membranas tienen una vida útil limitada, cuya duración depende de muchos factores, principalmente relacionados con la calidad del agua a tratar, las sustancias químicas empleadas en el pretratamiento y las condiciones de proceso de filtración. De hecho, aunque muchos fabricantes aconsejan su reposición después de 3-7 años de uso, existen plantas que extienden la vida de sus membranas mucho más tiempo. No obstante, antes o después, la membrana pierde sus propiedades respecto a la permeabilidad del agua y a su capacidad de rechazar sales y materia orgánica. Una vez que dichas propiedades decaen, la cuestión a resolver es qué se hace con ellas.

Debe tenerse en cuenta al respecto que según datos de junio de 2015 ofrecidos por la Asociación Internacional de desalación (IDA)[1], en el mundo hay instaladas más de 18,400 plantas de desalación en 150 países, que suman una capacidad de agua desalada de más de 86,8 Hm^3/día, de los cuales alrededor de 56,4 Hm^3/día son obtenidos mediante membranas de ósmosis inversa y cerca de 1.7 Hm^3/día son obtenidos mediante membranas de nanofiltración. En ambos casos se trata de membranas de poliamida con enrollamiento en espiral. En España, la Asociación Española de Desalación y Reutilización (AEDYR) tiene registradas 711 plantas de desalación con una capacidad total instalada de 5,4 Hm^3/día. También existen pequeñas plantas privadas (con una capacidad inferior a 500 m^3/día) que incrementan la cifra total a aproximadamente 950 instalaciones. En términos generales, se considera que para generar 1.000 m^3 agua desalada se necesitan alrededor de 100 módulos de membrana con enrollamiento en espiral (cilindros de 1 m de longitud y 20 cm de diámetro). Haciendo un simple cálculo podemos observar que a día de hoy la suma de módulos de ósmosis inversa instalados en el mundo podría ascender a 5,6 millones de unidades. Si consideramos una tasa de reposición anual del 15% y el peso medio de las membranas desechadas (22 Kg), más de 80.000 módulos de membranas (>1000 Tn) se desechan en España al año. Mundialmente la cifra asciende a más de 840.000 módulos. Puesto que actualmente las membranas desechadas son almacenadas en vertederos, si consideramos las cifras anteriores, probablemente más de 14.000 toneladas al año de material plástico estén siendo depositadas en los vertederos.

Hoy en día hay desaladoras que tratan de aprovechar al máximo sus membranas, por ejemplo, cambiándolas de posición dentro de los tubos de presión. Sin embargo, una vez agotadas las posibilidades y los ciclos de limpieza, las membranas inevitablemente acaban siendo depositadas en vertederos.

El objetivo general de la presente invención es paliar en cierta medida esta situación e intentar reciclar o reutilizar dichas membranas desechadas para diferentes usos, entre los que podemos mencionar:

- Membranas de sacrificio (membranas recicladas pero con propiedades similares a las comerciales). Dentro de los tubos de presión que conforman los bastidores del proceso de ósmosis, la primera membrana es la que más sufre ensuciamiento orgánico y la última la que más sufre el ensuciamiento inorgánico. Por tanto si en lugar de emplear membranas nuevas se emplean membranas recicladas, el coste de reposición será menor.
- Ablandamiento de agua salobre (membranas de nanofiltración recicladas).
- Pretratamiento del agua antes de entrar al proceso de ósmosis inversa. Tanto las membranas de nanofiltración y ultrafiltración recicladas podrían emplearse como pretratamiento para mejorar la calidad del agua antes de someterla al proceso de ósmosis. Aunque en España no es una práctica habitual, internacionalmente en las

desaladoras de nueva construcción sí se está empleando (con membranas comerciales).

- Tratamiento de agua residual. Las membranas recicladas podrían emplearse en la regeneración de agua residual para su posterior reutilización. En función de la calidad de agua deseable se podría emplear membranas de ósmosis, nanofiltración o ultrafiltración recicladas.

A nivel de investigación existen algunas iniciativas de reciclaje. Rodríguez et al. [1,2], investigaron sobre la transformación de membranas desechadas de ósmosis inversa exponiéndolas a distintos agentes oxidantes como hipoclorito de sodio, peróxido de hidrógeno y permanganato potásico, siendo este último el más favorable en las condiciones empleadas. Fruto de este trabajo y considerando los niveles de exposición usados, los investigadores determinaron que el mejor agente de transformación es el permanganato potásico.

En el documento WO 2004/069392 [3] se describe un proceso para reconvertir membranas de ósmosis inversa obsoletas procedentes de plantas de desalinización de aguas o plantas similares, para su posterior utilización como filtros en el rango de la microfiltración en otro tipo de plantas de tratamiento como por ejemplo depuradoras de aguas residuales. El proceso consiste en la eliminación de la capa activa de la membrana, mediante el empleo de un producto decapante adecuado que no perjudique la capa microporosa de la membrana. El agente químico empleado en la transformación fue el permanganato potásico.

Por otro lado, en investigaciones posteriores se determinó que son las disoluciones básicas, concentradas de cloro libre las más favorables para eliminar la capa de poliamida de la membrana (capa fundamental en el proceso de ósmosis inversa ya que es la que ejerce como barrera selectiva al paso de iones). El agente comúnmente empleado es el hipoclorito de sodio.

Algunos autores han establecido el nivel de exposición adecuado para la transformación de las membranas de ósmosis inversa a ultrafiltración [4,5]. El grupo de tecnología de membranas de IMDEA Agua ha conseguido determinar también las condiciones límite necesarias para la transformación a membranas de nanofiltración y ultrafiltración [6,7].

En concreto, en el documento [7] se revelan concentraciones de hipoclorito de sodio y tiempos de exposición para la transformación de membranas de ósmosis inversa desechada en membranas de nanofiltración y ultrafiltración a escala laboratorio. Específicamente, se trabajó con una concentración de 124 ppm de hipoclorito de sodio y unos tiempos de exposición específicos: 50 h para transformar las propiedades a nanofiltración y 242 h para ultrafiltración. Ahora bien, los tiempos de exposición mencionados en [7] son demasiado largos para ser escalables a nivel industrial, por lo que los inventores continuaron explorando concentraciones y tiempos de exposición. Los rangos de transformación obtenidos se muestran en el presente documento.

El motivo por el cual el uso de hipoclorito de sodio (NaOCl) es más comúnmente empleado para la modificación y degradación de las membranas de poliamida reside en su poder oxidante. En disolución acuosa, el NaOCl se disocia totalmente formando hidróxido de sodio (NaOH) y ácido hipocloroso (HOCl). Este último está en equilibrio con otras dos especies: el ión hipoclorito (OCl^-) y el cloro gas ($Cl_{2\,(g)}$) [13]. Las especies HOCl y OCl^- son comúnmente denominadas cloro libre y aumentan o disminuye su concentración en función de si el pH es ácido o básico, respectivamente. A pH básico (>10), la mayor especie presente es OCl^- (99,7%) [8]. Hay abundante literatura entorno a la degradación de la poliamida mediante ataque de cloro y aunque en algunos casos existe controversia, se acepta comúnmente que es un proceso complejo. Las variaciones en los rendimientos de filtración de las membranas expuestas a cloro libre están atribuidas a cambios estructurales específicos en la capa activa de las membranas, la poliamida [11]. Estos cambios estructurales dependen en gran medida de la composición de la poliamida, del proceso de preparación de la misma, del tipo de poliamida (aromática o lineal), del grado de entrecruzamiento [14] y además de la concentración del cloro, el pH y el tiempo de exposición al que se sometan las membranas. Generalmente, las disoluciones ácidas de cloro (HOCl como especie dominante) provocan una disminución de la capacidad de rechazo y de la permeabilidad de las membranas, mientras que las disoluciones básicas (ClO^- como especie dominante) disminuyen la capacidad de rechazo pero permiten aumentar la permeabilidad de la membrana.

Algunos autores describen diversos posibles mecanismos de alteración de la poliamida mediante el ataque de cloro [9, 10, 12, 14]. En la Figura 1 se muestra en términos generales en qué consisten estos mecanismos. Por un lado puede darse una reacción de activación reversible del grupo amida de cadena lineal, para formar una *N*-Cloroamida, que consiste en una sustitución formal del átomo de hidrógeno por un átomo de cloro. En este caso, el enlace original amida puede llegar a restablecerse en condiciones básicas sin pérdida de propiedades de la poliamida. Por otro lado, las cadenas aromáticas pueden reaccionar con el del producto intermedio, *N*-cloroamida (-O=C-N-Cl), o con otros cloros de la disolución, a través de una reacción irreversible en el anillo aromático (Transposición de Orton). Finalmente se produce una reacción en cadena provocando la desfragmentación de la cadena de poliamida y generándose diversos subproductos tales como anillos de benceno cloro sustituidos, derivados de la quinona u otros grupos de oxidación.

SUMARIO DE LA INVENCIÓN

La invención proporciona un proceso de transformación de una membrana de poliamida con enrollamiento en espiral, con al menos una capa selectiva de poliamida, desechada por haber agotado su vida útil en una membrana reciclada de nanofiltración cuya permeabilidad sea mayor a la de la membrana desechada y cuyo rechazo en sales divalentes sea > 30% o en una membrana reciclada de ultrafiltración cuya permeabilidad sea mayor a la de la membrana desechada y cuyo rechazo en sales divalentes sea <30%. El proceso comprende la exposición de dicha membrana de poliamida con enrollamiento en espiral desechada a una disolución de un compuesto con una concentración de cloro libre superior a 100 ppm a un nivel de exposición igual o superior a 1.000 ppm·h y puede llevarse a cabo estando dicha disolución en reposo cuando está en contacto con la membrana desechada (proceso de transformación pasiva) o bien haciendo recircular dicha disolución a través de la membrana para favorecer el contacto entre la disolución y la superficie de la membrana (proceso de transformación activa).

En el caso de membranas utilizadas en su vida útil para tratar agua salobre de pozos, el nivel de exposición está comprendido entre 1.000 y 100.000 ppm·h (transformación pasiva) o entre 1.000 y 50.000 ppm·h (transformación activa). Si la membrana desechada tiene un coeficiente de rechazo de sales menor del 90%, el nivel de exposición está comprendido entre 1.000 y 60.000 ppm·h (transformación pasiva) o entre 1.000 y 35.000 ppm·h (transformación activa), obteniéndose una membrana reciclada de nanofiltración en el rango 1.000 - 15.000 ppm·h en ambos procesos y una membrana reciclada de ultrafiltración en el rango 10.000 - 60.000 ppm·h (transformación pasiva) o en el rango 10.000 – 35.000 ppm·h (transformación activa). Si la membrana desechada tiene un coeficiente de rechazo de sales mayor o igual al 90%, el nivel de exposición está comprendido entre 2.000 y 100.000 ppm·h (transformación pasiva) o entre 2.000 y 50.000 ppm·h (transformación activa), obteniéndose una membrana reciclada de nanofiltración en el rango 2.000 - 25.000 ppm·h en ambos procesos y una membrana reciclada de ultrafiltración en el rango 15.000 - 100.000 ppm·h (transformación pasiva) o en el rango 15.000 y 50.000 ppm·h (transformación activa).

En el caso de membranas utilizadas en su vida útil para tratar agua de mar, el nivel de exposición está comprendido entre 2.500 y 400.000 ppm·h (transformación pasiva) o entre 2.500 y 100.000 ppm·h (transformación activa). Si la membrana desechada tiene un coeficiente de rechazo de sales menor del 90%, el nivel de exposición está comprendido entre 2.500 y 200.000 ppm·h (transformación pasiva) o entre 2.500 y 50.000 ppm·h (transformación activa), obteniéndose una membrana reciclada de nanofiltración en el rango 2.500 – 100.000 ppm·h (transformación pasiva) o en el rango 2.500 y 30.000 ppm·h (transformación activa) y una membrana reciclada de ultrafiltración en el rango 20.000 - 200.000 ppm·h (transformación pasiva) o en el rango 20.000 y 50.000 ppm·h (transformación activa). Si la membrana desechada tiene un coeficiente de rechazo de sales mayor o igual al 90%, el nivel de exposición está comprendido entre 3.500 y 400.000 ppm·h (transformación pasiva) o entre 3.500 y 100.000 ppm·h (transformación activa), obteniéndose una membrana reciclada de nanofiltración en el rango 3.500 - 150.000 ppm·h (transformación pasiva) o en el rango 3.500-35.000 ppm·h (transformación activa) y una membrana reciclada de ultrafiltración en el rango 30.000 - 400.000 ppm·h (transformación pasiva) o entre 30.000 y 100.000 ppm·h (transformación activa).

Además, utilizando un nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada a dicha disolución comprendido entre 400.000 ppm·h y 2.000.000 ppm·h, se obtiene como membrana transformada una membrana de ultrafiltración con una permeabilidad mayor a la de la membrana desechada y una capacidad de rechazo de materia orgánica propia de una membrana transformada de ultrafiltración.

El proceso de transformación pasiva se lleva a cabo mediante los siguientes pasos:

a) disponer la membrana de poliamida con enrollamiento en espiral desechada en un depósito;

b) introducir en el depósito una disolución de un compuesto (tal como el hipoclorito de sodio) con una determinada concentración de cloro libre mediante un flujo dirigido perpendicularmente al eje de la membrana de poliamida con enrollamiento en espiral desechada hasta recubrirla completamente;

c) hacer circular dicha disolución a través de la membrana de poliamida con enrollamiento en espiral desechada un tiempo predeterminado para liberar el aire contenido en ella;

d) exponer la membrana de poliamida con enrollamiento en espiral desechada a una disolución de dicho compuesto durante el tiempo correspondiente al nivel de exposición deseado, computado desde el final del paso anterior, estando dicha disolución en reposo.

e) retirar dicha disolución del depósito e introducir en él una disolución de un agente inhibidor de cloro libre (tal como el bisulfito sódico) para parar la reacción de transformación.

El proceso de transformación activa se lleva a cabo mediante los siguientes pasos:

a) disponer la membrana de poliamida con enrollamiento en espiral desechada en el interior de un tubo de presión;

b) hacer circular por el tubo de presión una disolución de un compuesto (tal como el hipoclorito de sodio) con una determinada concentración de cloro libre durante el tiempo correspondiente al nivel de exposición deseado de forma que se favorezca el contacto entre la disolución y la superficie de la membrana;

c) retirar dicha disolución del tubo de presión e introducir en él una disolución de un agente inhibidor de cloro libre (tal como el bisulfito sódico) para parar la reacción de transformación.

En una realización el compuesto utilizado en el proceso es hipoclorito de sodio.

Otras características y ventajas de la presente invención se desprenderán de la descripción detallada que sigue de realizaciones ilustrativas de su objeto en relación con las figuras que se acompañan.

BREVE DESCRIPCIÓN DE LAS FIGURAS

La Figura 1 muestra mecanismos conocidos de degradación de la poliamida mediante OCl^- [12].

La Figura 2a muestra tres vistas esquemáticas en perspectiva de una instalación para llevar a cabo el procedimiento de transformación pasiva de la invención y la Figura 2b es un diagrama de una instalación para llevar a cabo el procedimiento de transformación activa de la invención.

Las Figuras 3a y 3b son diagramas que muestran los valores de la permeabilidad de varias muestras de membranas recicladas utilizando el procedimiento de transformación pasiva de la invención. Las membranas tipo 1 corresponden a membranas que en su vida útil estuvieron tratando agua salobre y las membranas de tipo 2 corresponden a membranas que en su vida útil estuvieron tratando agua de mar. Las membranas desechadas han sido obtenidas utilizando disoluciones de hipoclorito sódico con cuatro concentraciones de cloro libre (124, 1.240, 6.200 y 12.400 ppm cloro libre) y distintos tiempos de exposición con objeto de someter las membranas desechadas a tres niveles fijos de exposición (6.200, 30.000 y 300.000 ppm·h). Además, a efectos de comparación, se muestra el valor de la permeabilidad de los dos tipos de membranas desechadas (Eol, iniciales de "End of Life").

Las Figuras 4a, 4b son diagramas que muestran los valores de los coeficientes de rechazo en sales de las mismas membranas recicladas a las que se refieren las Figuras 3a y 3b.

Las Figuras 5a y 5b son diagramas que muestran los valores de la permeabilidad y de los coeficientes de rechazo de varias muestras de membranas recicladas utilizando el procedimiento de transformación pasiva de la invención. Han sido obtenidas transformando membranas de ósmosis inversa desechadas, con distinto ensuciamiento, utilizando disoluciones de hipoclorito sódico con un nivel de exposición de cloro libre moderado (6.556 y 12.601 ppm·h). Algunas muestras son de tipo 1 (agua salobre) y otras son de tipo 2 (agua de mar).

Las Figuras 6a y 6b son diagramas que muestran los valores de la permeabilidad y de los coeficientes de rechazo de varias muestras de membranas recicladas de poliamida con enrollamiento en espiral, utilizando el procedimiento de transformación pasiva de la invención. En concreto en este ejemplo, han sido obtenidas transformando membranas de ósmosis inversa desechadas, con distinto ensuciamiento, utilizando disoluciones de hipoclorito sódico con un nivel de exposición de cloro libre alto (90.917, 369.267 y 660.867 ppm·h). Algunas muestras son de tipo 1 (agua salobre) y otras son de tipo 2 (agua de mar).

Las Figuras 7a y 7b son diagramas que muestran resultados de permeabilidad y coeficientes de rechazo obtenidos utilizando el procedimiento de transformación activa de la invención.

Las Figuras 8a y 8b son diagramas que muestran comparativamente los resultados medios de los coeficientes de rechazo de iones monovalentes y divalentes de una membrana desechada y de membranas transformadas a partir de membranas desechadas procedentes de la misma desaladora utilizando un procedimiento activo y un procedimiento pasivo de transformación con dos niveles de exposición de cloro libre.

DESCRIPCIÓN DETALLADA DE LA INVENCIÓN

El objetivo de la presente invención es conseguir un procedimiento de transformación de membranas de poliamida con enrollamiento en espiral desechadas en membranas recicladas que sean viables industrialmente y, en particular, membranas recicladas de nanofiltración (NF) cuya permeabilidad sea mayor a la de la membrana desechada y cuyo rechazo en sales divalentes sea > 30% o en una membrana reciclada de ultrafiltración cuya permeabilidad sea mayor a la de la membrana desechada y cuyo rechazo en sales divalentes sea <30%.

Preferentemente, las membranas recicladas de nanofiltración tienen una permeabilidad mayor de 1,5 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ y las membranas recicladas de ultrafiltración una permeabilidad mayor de 4 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$.

Los inventores han encontrado que ese resultado puede obtenerse exponiendo las membranas de poliamida con enrollamiento en espiral desechadas a una disolución de un compuesto (tal como el hipoclorito sódico) con una determinada concentración de cloro libre combinando adecuadamente la concentración de cloro libre (ppm) y el tiempo de exposición (h) o, lo que es lo mismo, sometiendo a las membranas de poliamida con enrollamiento en espiral desechadas a un nivel de exposición (ppm·h) preestablecido. El efecto del nivel de exposición de la membrana al cloro libre, a pH básico, depende fundamentalmente de los dos factores: concentración de cloro libre y tiempo de exposición. Por otra parte, la transformación de las membranas desechadas puede llevarse a cabo de manera pasiva o activa.

Transformación pasiva

Dicha exposición puede llevarse a cabo de la manera ilustrada en la Figura 2a en la que las membranas de poliamida con enrollamiento en espiral desechadas 11 con configuración en espiral dispuestas en un carrusel 13 se colocan en el interior de un depósito 15 que se llena con una disolución de hipoclorito sódico procedente de un tanque de almacenamiento. Inicialmente la disolución se recircula de forma perpendicular al eje de las membranas de poliamida con enrollamiento en espiral desechadas 11. Una vez que el depósito 15 está lleno, se hace circular la disolución a través de ellas unos minutos para liberar el aire. Una vez terminado el tiempo de exposición programado se vacía el depósito 15 (llevando la disolución de hipoclorito sódico al tanque de almacenamiento), aprovechando así la disolución para más membranas. A continuación se llena el depósito (que todavía contiene las membranas) con una disolución con un agente reductor del cloro libre como es el bisulfito de sodio, para detener la reacción de transformación de las membranas. Este procedimiento puede repetirse para otro conjunto de membranas.

Las Figuras 3a, 3b y 4a, 4b se refieren a ensayos realizados con dos tipos de membranas de ósmosis inversa (que como ya se ha indicado son membranas de poliamida con enrollamiento en espiral), siendo la Membrana tipo 1 una membrana de la firma Toray® modelo TM 720-400 (BW) utilizada para desalinizar agua de pozo y la Membrana tipo 2 una membrana de la firma Hydranautics® modelo HSWC3 (SW) utilizada para desalinizar agua de mar. Esas Figuras ilustran combinaciones apropiadas para transformar membranas de ósmosis inversa desechadas en membranas de nanofiltración o en membranas de ultrafiltración. En el caso de la Membrana tipo 1 se deduce que, tras la exposición al cloro libre a un nivel de 6.200 ppm·h, la membrana transformada tiene unas propiedades dentro del rango de la nanofiltración (ver Figura 3a), similares a las de membranas comerciales tales como los modelos NF90 y NF270 de la firma comercial Dow Filmtec. En todos los modelos probados de tipo 1, a partir de 30.000 ppm·h las membranas recicladas adquirieron propiedades dentro del rango de la ultrafiltración.

En el caso de la Membrana tipo 2 (ver Figura 3b), muestran mayor resistencia al ataque del cloro libre, dando lugar a membranas recicladas de nanofiltración con niveles inferiores a 300.000 ppm·h y a membranas con propiedades de ultrafiltración, tras un nivel de exposición de 300.000 ppm·h, aunque con una permeabilidad baja (en cualquiera de los niveles de exposición probados, se obtiene mucha mayor permeabilidad en las membranas tipo 1 que en las membranas tipo 2).

No obstante, y aunque no se muestra en ninguna figura, se realizó el mismo estudio con otros modelos dentro de las membranas tipo 2, permitiendo concluir que existe una diferencia de resistencia de la poliamida al ataque del cloro entre distintos modelos de membranas del tipo 2. A continuación se expone un ejemplo experimental empleando un nivel de exposición de 30.000 ppm·h y usando una disolución de 124 ppm de cloro libre. En estas condiciones se obtuvieron membranas recicladas de ultrafiltración en el caso de modelos de agua de mar como SW30 y TM820C, mientras que el modelo HSWC3, como se ha mencionado anteriormente, mantuvo valores de nanofiltración.

Respecto a los efectos de la concentración y tiempo para un nivel de exposición fijo, se ha demostrado que las concentraciones bajas y tiempos de exposiciones muy largos, la degradación de la poliamida tienen mayor efecto. Empleando como ejemplo igualmente la dosis de 30.000 ppm·h, membranas del tipo 2 como el modelo SW30 presentaron capacidad de rechazo en sales entre 20-68% al emplear disoluciones de transformación con las siguientes concentraciones: 1.240, 6.200 y 12.400 ppm, mientras que con la disolución poco concentrada (124 ppm) la capacidad de rechazo de sales fue <5%.

Las Figuras 5a y 5b se refieren a ensayos realizados con membranas de tipo 1 y de tipo 2. En la Figura 5a coexisten membranas del tipo 1 (las TM1, TM2, TM3, TM4 del modelo TM 720-400 con distinto grado de ensuciamiento) y del tipo 2 (las HSWC3 1 y 2 con distinto grado de ensuciamiento). Los resultados corroboran la diferencia de sensibilidad al cloro libre entre las membranas tipo 1 y tipo 2. Las membranas tipo 1 que inicialmente mantienen propiedades de ósmosis inversa, adquieren propiedades de nanofiltración empleando disoluciones con un rango bajo-moderado de cloro libre (entre 6.556 y 12.601 ppm·h de cloro libre). Sin embargo cuando las membranas de tipo 1 inicialmente están deterioradas (coeficientes de rechazo de sales inferiores al 65%) se transforman directamente a membranas de ultrafiltración tras 12.601 ppm·h de exposición al cloro libre (debido a la pérdida de la capacidad de rechazar sales).

Por otro lado, del análisis de las Figuras 5a y 5b, se corrobora que las membranas del tipo 2 son más resistentes al ataque del cloro, ya que con niveles bajos-moderados, se deduce que ese nivel de exposición parece no afectar significativamente a las propiedades de membranas de ósmosis inversa utilizadas para desalar agua de mar, si bien esas membranas recuperadas podrían reinsertarse en procesos de ósmosis inversa, empleándose como membranas de sacrificio si se llegaran a colocar en la primera y/o la última posición dentro de los tubos de presión de las plantas de desalinización.

Las Figuras 6a y 6b son diagramas que muestran los valores de la permeabilidad y de los coeficientes de rechazo de varias membranas recicladas utilizando el procedimiento de transformación pasiva. En ambas Figuras coexisten membranas del tipo 1 (las TM 5 y TM 6 del modelo TM720-400 y las SU 1 y SU 2 del Modelo SU-720F) y tipo 2 (las HSWC3 2 y HSWC3 3). Analizando esas Figuras se deduce que las membranas desechadas de tipo 1 se transforman a membranas de ultrafiltración empleando un rango alto de cloro libre (entre 90.917 y 660.867 ppm·h). Por otro lado, se deduce que la transformación de membranas de tipo 2 a membranas de ultrafiltración es viable empleando un rango de nivel de exposición entre 369.267 y 660.867 ppm·h ya que se elimina completamente la poliamida. Se ha realizado experimentación hasta 2.000.000 ppm·h de cloro libre y se ha observado que aunque la permeabilidad de las membranas aumenta considerablemente (en el caso de membranas de tipo 1 se superan los 50 $L \cdot h^{-2} \cdot m^{-2} \cdot bar^{-1}$), se sigue manteniendo la capacidad de rechazo típica de las membranas de ultrafiltración.

Por último, fruto de otras investigaciones realizadas por los inventores, se ha detectado que es posible transformar las propiedades de las membranas desechadas a nanofiltración con una muy alta capacidad de rechazo, empleando un nivel de exposición inferior a los 6.200 ppm·h mostrados en la Figura 3a y 3b. Las muestras de membranas empleadas inicialmente tenían coeficientes de rechazo en sales superiores al 90%. Así modelos de membrana tipo 1 (agua salobre) perciben cambios en sus propiedades a los 2.500 ppm·h (duplican su permeabilidad y reducen sus coeficientes de rechazo en sales mixtas medidas por la conductividad, en más de 3 puntos de porcentaje). Por otro lado, en las membranas de tipo 2 se observan cambios sustanciales a partir de 4.000 ppm·h (se duplica la permeabilidad y el porcentaje de rechazo en sales se reduce más de un 2%).

Transformación activa

En la transformación activa, la exposición de las membranas de poliamida con enrollamiento en espiral desechadas a una disolución de un compuesto con una determinada concentración de cloro libre (tal como el hipoclorito de sodio) se lleva a cabo de la manera ilustrada en la Figura 2b en la que una membrana de poliamida con enrollamiento en espiral desechada 21 con configuración en espiral se coloca en el interior de un tubo de presión 22, por el que se hace circular dicha disolución desde el depósito de almacenamiento 24 gracias a la bomba 23. La disolución se recircula de forma paralela al eje de la membrana de poliamida con enrollamiento en espiral desechada 21. Para mantener durante toda la transformación la concentración de cloro libre deseada en la disolución, el sistema dispone de una bomba dosificadora 27 para la dosificación en continuo de la concentración deseada de cloro libre. Una vez terminado el tiempo de exposición programado se paraliza el bombeo y se conserva en el depósito 24 la disolución para futuras transformaciones. A continuación se desplaza el volumen residual bombeando agua de aclarado desde el depósito 25 que se envía al depósito 26 para su tratamiento y neutralización antes de su vertido con compuesto apropiado suministrado por la bomba dosificadora 29. Este desplazamiento puede realizarse mediante la bomba 23 o con otra bomba instalada para tal fin. Posteriormente se recircula agua de aclarado desde el depósito 25 con un agente reductor del cloro libre (tal como el bisulfito de sodio) suministrado por la bomba dosificadora 28 como medida de seguridad para detener la reacción de transformación de la membrana 21. Esta recirculación puede realizarse mediante la bomba 23 o con otra bomba instalada para tal fin. Este procedimiento se puede realizar para la transformación simultánea de una o más membranas.

En la Figura 7a coexisten membranas del tipo 1 (las TM7, TM8 del modelo TM 720-400 de la misma desaladora y mismo grado de ensuciamiento) y del tipo 2 (las HSWC3 5 y 6 de la misma desaladora y mismo tipo de ensuciamiento). Los resultados indican que no existe una diferencia significativa entre la transformación activa y pasiva para la obtención de membranas de nanofiltración y ultrafiltración en el caso de las membranas de tipo 1. Sin embargo en el caso de las membranas de tipo 2 la transformación requiere menores niveles de exposición. En el caso de las membranas HSWC3 se obtienen valores de nanofiltración recirculando una disolución de hipoclorito de sodio durante 23.400 ppm·h y se obtienen membranas de ultrafiltración tras valores de 42.500 ppm·h. Igualmente que ocurre en la transformación pasiva, se mantiene la diferencia de sensibilidad al cloro libre entre las membranas tipo 1 y tipo 2. La utilidad industrial de las membranas transformadas de forma activa es la misma que las transformadas de forma pasiva.

Las Figuras 8a y 8b muestran comparativamente los resultados medios de los coeficientes de rechazo de iones monovalentes y divalentes de membranas tipo 1, procedentes de una misma desaladora y transformadas con el procedimiento de transformación activa (Fig. 8a) y con el procedimiento de transformación pasiva (Fig. 8b) utilizando una disolución de hipoclorito de sodio de similar concentración. En esas Figuras, se utiliza el código Des para indicar los resultados de la membrana desechada y los códigos NF1 y NF2 para indicar los resultados obtenidos con transformaciones realizadas con unas concentraciones de, respectivamente, 6.500 ppm·h y 15.000 ppm·h. Como se deduce de dichas Figuras se obtienen resultados similares en ambos tipos de transformación. La permeabilidad media de las membranas transformadas aumenta con respecto a los valores de las membranas desechadas 1,5 y 2,8 veces, para los niveles de exposición 1 y 2 respectivamente. En todos los casos los coeficientes de iones divalentes superan el valor de 30%.

Aunque se ha descrito la presente invención en conexión con varias realizaciones, puede apreciarse a partir de la descripción que pueden hacerse varias combinaciones de elementos, variaciones o mejoras en ellas y que están dentro del alcance de la invención definido en las reivindicaciones adjuntas.

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REIVINDICACIONES

1. Proceso de transformación de una membrana de poliamida con enrollamiento en espiral desechada (11, 21) por haber agotado su vida útil en una membrana reciclada de nanofiltración cuya permeabilidad sea mayor a la de la membrana desechada y cuyo rechazo en sales divalentes sea > 30% o en una membrana reciclada de ultrafiltración cuya permeabilidad sea mayor a la de la membrana desechada y cuyo rechazo en sales divalentes sea <30%, teniendo la membrana de poliamida con enrollamiento en espiral desechada (11, 21) al menos una capa selectiva de poliamida, comprendiendo el proceso de transformación un paso de exposición de dicha membrana de poliamida con enrollamiento en espiral desechada (11, 21) a una disolución de un compuesto con una determinada concentración de cloro libre durante un tiempo determinado, caracterizado porque:

- dicha concentración de cloro libre es superior a 100 ppm;
- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11, 21) a dicha disolución es igual o superior a 1.000 ppm·h.

2. Proceso según la reivindicación 1, en el que la membrana reciclada de nanofiltración tiene una permeabilidad mayor de 1,5 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ y la membrana reciclada de ultrafiltración tiene una permeabilidad mayor de 4 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$.

3. Proceso según cualquiera de las reivindicaciones 1-2, en el que el paso de exposición de dicha membrana de poliamida con enrollamiento en espiral desechada (11) se lleva a cabo estando dicha disolución de cloro libre en reposo.

4. Proceso según la reivindicación 3, en el que:

- la membrana de poliamida con enrollamiento en espiral desechada (11) fue utilizada durante su vida útil para tratar agua salobre de pozos;
- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 1.000 y 100.000 ppm·h.

5. Proceso según la reivindicación 4, en el que:

- la membrana de poliamida con enrollamiento en espiral desechada (11) tiene un coeficiente de rechazo menor del 90%;
- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 1.000 y 60.000 ppm·h.

6. Proceso según la reivindicación 5, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 1.000 y 15.000;
- la membrana transformada es una membrana reciclada de nanofiltración.

7. Proceso según la reivindicación 5, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 10.000 y 60.000 ppm·h;
- la membrana transformada es una membrana reciclada de ultrafiltración.

8. Proceso según la reivindicación 4, en el que:

- la membrana de poliamida con enrollamiento en espiral desechada (11) tiene un coeficiente de rechazo igual o mayor que el 90%;
- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 2.000 y 100.000 ppm·h.

9. Proceso según la reivindicación 8, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) desechada a dicha disolución está comprendido entre 2.000 y 25.000 ppm·h;
- la membrana transformada es una membrana reciclada de nanofiltración.

10. Proceso según la reivindicación 8, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 15.000 y 100.000 ppm·h;
- la membrana transformada es una membrana reciclada de ultrafiltración.

11. Proceso según la reivindicación 3, en el que:

- la membrana de poliamida con enrollamiento en espiral desechada (11) fue utilizada durante su vida útil para tratar agua de mar;
- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 2.500 y 400.000 ppm·h.

12. Proceso según la reivindicación 11, en el que:

- la membrana de poliamida con enrollamiento en espiral desechada (11) tiene un coeficiente de rechazo menor del 90%;
- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 2.500 y 200.000 ppm·h.

13. Proceso según la reivindicación 12, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 2.500 y 100.000 ppm·h;
- la membrana transformada es una membrana reciclada de nanofiltración.

14. Proceso según la reivindicación 12, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 20.000 y 200.000 ppm·h;
- la membrana transformada es una membrana reciclada de ultrafiltración.

15. Proceso según la reivindicación 11, en el que:

- la membrana de poliamida con enrollamiento en espiral desechada (11) tiene un coeficiente de rechazo igual o mayor que el 90%;
- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 3.500 y 400.000 ppm·h.

16. Proceso según la reivindicación 15, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 3.500 y 150.000 ppm·h;
- la membrana transformada es una membrana reciclada de nanofiltración.

17. Proceso según la reivindicación 15, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 30.000 y 400.000 ppm·h;
- la membrana transformada es una membrana reciclada de ultrafiltración.

18. Proceso según la reivindicación 3, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (11) a dicha disolución está comprendido entre 400.000 ppm·h y 2.000.000 ppm·h;

- la membrana transformada es una membrana reciclada de ultrafiltración con una permeabilidad mayor a la de la membrana desechada.

19. Proceso según cualquiera de las reivindicaciones 1-2, en el que el paso de exposición de dicha membrana de poliamida con enrollamiento en espiral desechada (21) se lleva a cabo haciendo recircular dicha disolución a través de la membrana para favorecer el contacto entre la disolución y la superficie de la membrana.

20. Proceso según la reivindicación 19, en el que:

- la membrana de poliamida con enrollamiento en espiral desechada (21) fue utilizada durante su vida útil para tratar agua salobre de pozos;

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (21) a dicha disolución está comprendido entre 1.000 y 50.000 ppm·h.

21. Proceso según la reivindicación 20, en el que:

- la membrana de poliamida con enrollamiento en espiral desechada (21) tiene un coeficiente de rechazo menor del 90%;

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (21) a dicha disolución está comprendido entre 1.000 y 35.000 ppm·h.

22. Proceso según la reivindicación 21, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (21) a dicha disolución está comprendido entre 1.000 y 15.000;

- la membrana transformada es una membrana reciclada de nanofiltración.

23. Proceso según la reivindicación 21, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (21) a dicha disolución está comprendido entre 10.000 y 35.000 ppm·h;

- la membrana transformada es una membrana reciclada de ultrafiltración.

24. Proceso según la reivindicación 20, en el que:

- la membrana de poliamida con enrollamiento en espiral desechada (21) tiene un coeficiente de rechazo igual o mayor que el 90%;

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (21) a dicha disolución está comprendido entre 2.000 y 50.000 ppm·h.

25. Proceso según la reivindicación 24, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral (21) desechada a dicha disolución está comprendido entre 2.000 y 25.000 ppm·h;

- la membrana transformada es una membrana reciclada de nanofiltración.

26. Proceso según la reivindicación 24, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (21) a dicha disolución está comprendido entre 15.000 y 50.000 ppm·h;

- la membrana transformada es una membrana reciclada de ultrafiltración.

27. Proceso según la reivindicación 19, en el que:

- la membrana de poliamida con enrollamiento en espiral desechada (21) fue utilizada durante su vida útil para tratar agua de mar;

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (21) a dicha disolución está comprendido entre 2.500 y 100.000 ppm·h.

28. Proceso según la reivindicación 27, en el que:

- la membrana de poliamida con enrollamiento en espiral desechada (21) tiene un coeficiente de rechazo menor del 90%;

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (21) a dicha disolución está comprendido entre 2.500 y 50.000 ppm·h.

29. Proceso según la reivindicación 28, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (21) a dicha disolución está comprendido entre 2.500 y 30.000 ppm·h;

- la membrana transformada es una membrana reciclada de nanofiltración.

30. Proceso según la reivindicación 28, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (21) a dicha disolución está comprendido entre 20.000 y 50.000 ppm·h;

- la membrana transformada es una membrana reciclada de ultrafiltración.

31. Proceso según la reivindicación 27, en el que:

- la membrana de poliamida con enrollamiento en espiral desechada (21) tiene un coeficiente de rechazo igual o mayor que el 90%;

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (21) a dicha disolución está comprendido entre 3.500 y 100.000 ppm·h.

32. Proceso según la reivindicación 31, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (21) a dicha disolución está comprendido entre 3.500 y 35.000 ppm·h;

- la membrana transformada es una membrana reciclada de nanofiltración.

33. Proceso según la reivindicación 30, en el que:

- el nivel de exposición de la membrana de poliamida con enrollamiento en espiral desechada (21) a dicha disolución está comprendido entre 30.000 y 100.000 ppm·h;

- la membrana transformada es una membrana reciclada de ultrafiltración.

34. Proceso según cualquiera de las reivindicaciones 3-18 que comprende los siguientes pasos:

a) disponer la membrana de poliamida con enrollamiento en espiral desechada (11) en un depósito (15);

b) introducir en el depósito (15) una disolución de un compuesto con una determinada concentración de cloro libre mediante un flujo dirigido perpendicularmente al eje de la membrana de poliamida con enrollamiento en espiral desechada (11) hasta recubrirla completamente;

c) hacer circular dicha disolución a través de la membrana de poliamida con enrollamiento en espiral desechada (11) un tiempo predeterminado para liberar el aire contenido en ella;

d) exponer la membrana de poliamida con enrollamiento en espiral desechada (11) a una disolución de dicho compuesto durante el tiempo correspondiente al nivel de exposición deseado, computado desde el final del paso anterior, estando dicha disolución en reposo;

e) retirar dicha disolución del depósito (15) e introducir en él una disolución de un agente inhibidor de cloro libre para parar la reacción de transformación.

35. Proceso según cualquiera de las reivindicaciones 19-33 que comprende los siguientes pasos:

a) disponer la membrana de poliamida con enrollamiento en espiral desechada (21) en el interior de un tubo de presión (22);

b) hacer circular por el tubo de presión (22) una disolución de un compuesto con una determinada concentración de cloro libre durante el tiempo correspondiente al nivel de exposición deseado;

c) retirar dicha disolución del tubo de presión (22) e introducir en él una disolución de un agente inhibidor de cloro libre para parar la reacción de transformación.

36. Proceso según cualquiera de las reivindicaciones 34 y 35 en el que dicho compuesto es hipoclorito de sodio.

37. Proceso según cualquiera de las reivindicaciones 34 y 35 en el que dicho agente inhibidor de cloro libre es una disolución de bisulfito sódico.

RESUMEN

Proceso de transformación de membranas de poliamida con enrollamiento en espiral que han agotado su vida útil en membranas de utilidad industrial. El proceso comprende la exposición de una membrana de poliamida con enrollamiento en espiral desechada (11,21) tras ser utilizada en un proceso industrial, tal como la desalinización de agua salobre de pozos o la desalación de agua de mar, a una disolución de un compuesto con una concentración de cloro libre superior a 100 ppm a un nivel de exposición igual o superior a 1.000 ppm·h, estando dicha disolución o bien en reposo o bien en recirculación para mantener constante la concentración de cloro libre. Se obtienen membranas recicladas de nanofiltración o ultrafiltración con una permeabilidad mayor a la de la membrana desechada y con un rechazo en sales divalentes mayor del 30% y menor de 30%, respectivamente.

Fig. 2a

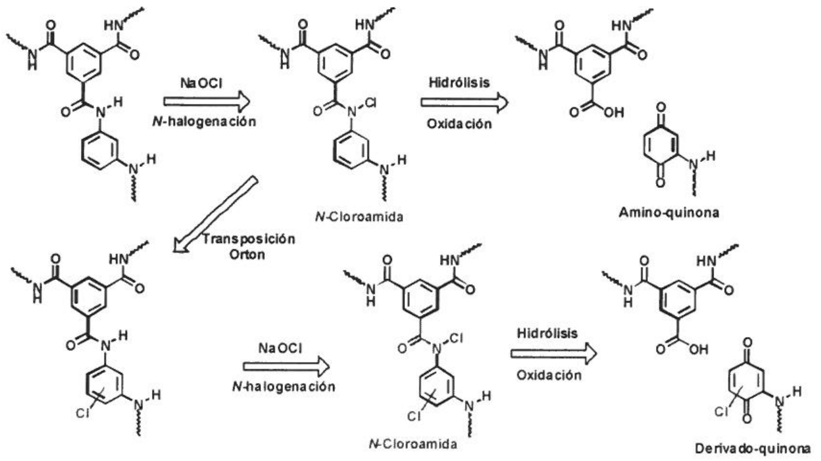


FIG. 1

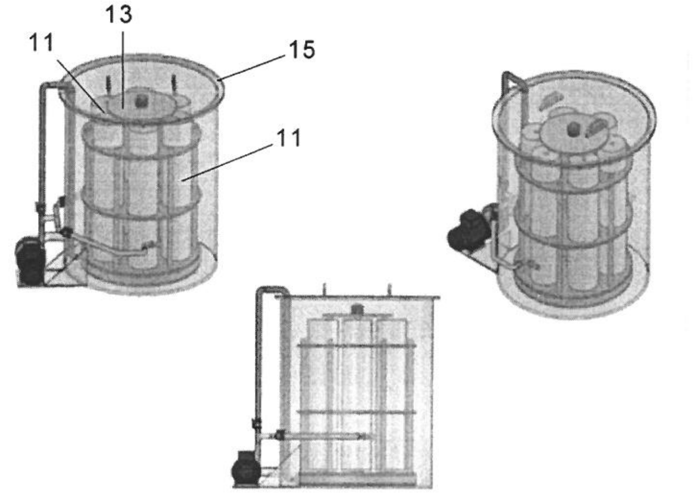


FIG. 2a

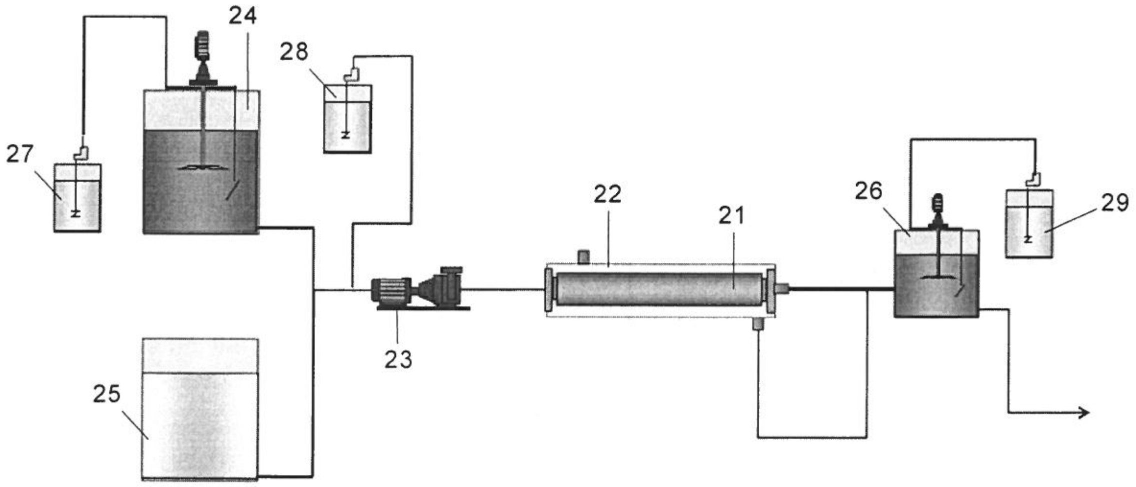
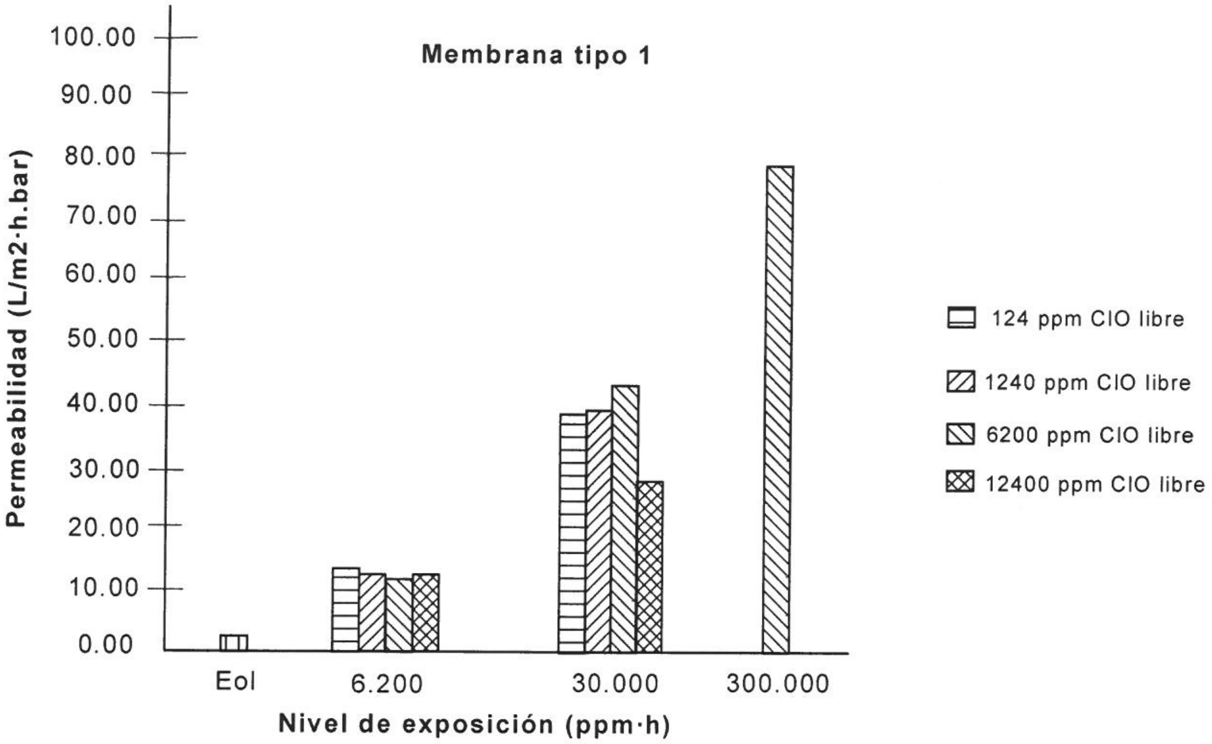
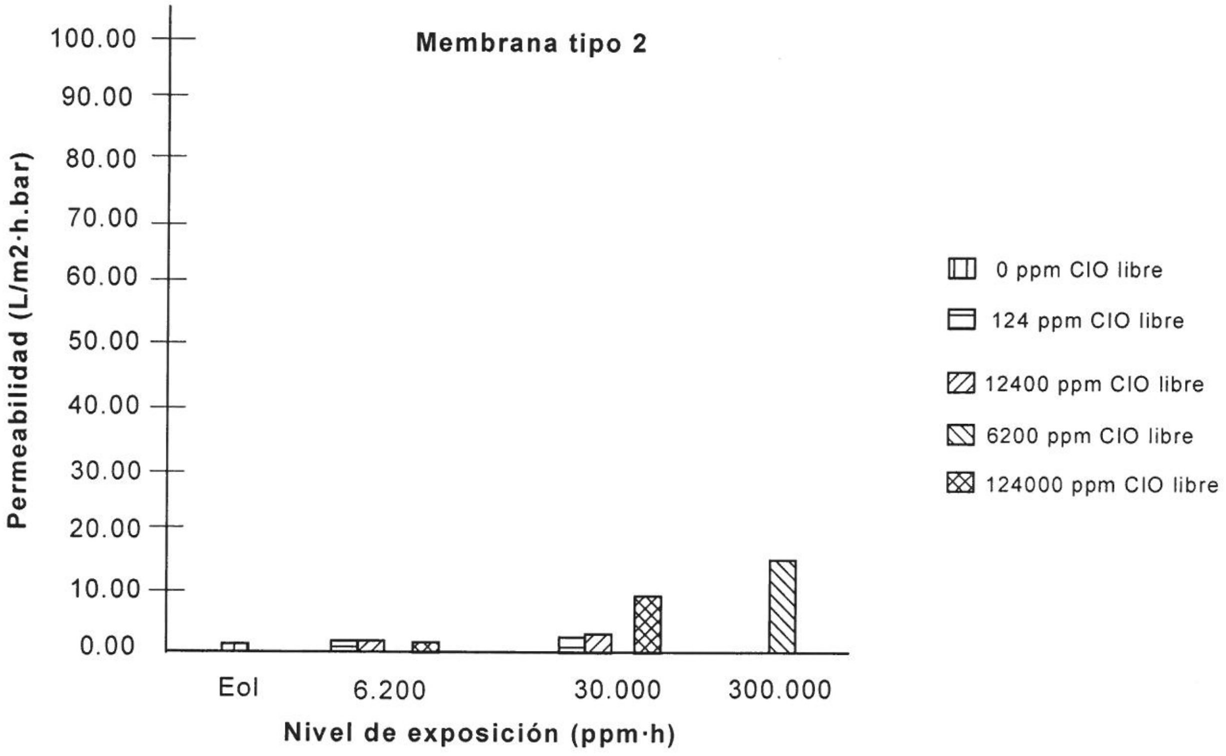


FIG. 2b



Membrana tipo 1
Permeabilidad (L/m2·h.bar)
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
EoI
6.200
30.000
300.000
Nivel de exposición (ppm·h)
124 ppm ClO libre
1240 ppm ClO libre
6200 ppm ClO libre
12400 ppm ClO libre

FIG. 3a



Membrana tipo 2
Permeabilidad (L/m2·h.bar)
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
EoI
6.200
30.000
300.000
Nivel de exposición (ppm·h)
0 ppm ClO libre
124 ppm ClO libre
12400 ppm ClO libre
6200 ppm ClO libre
124000 ppm ClO libre

FIG. 3b

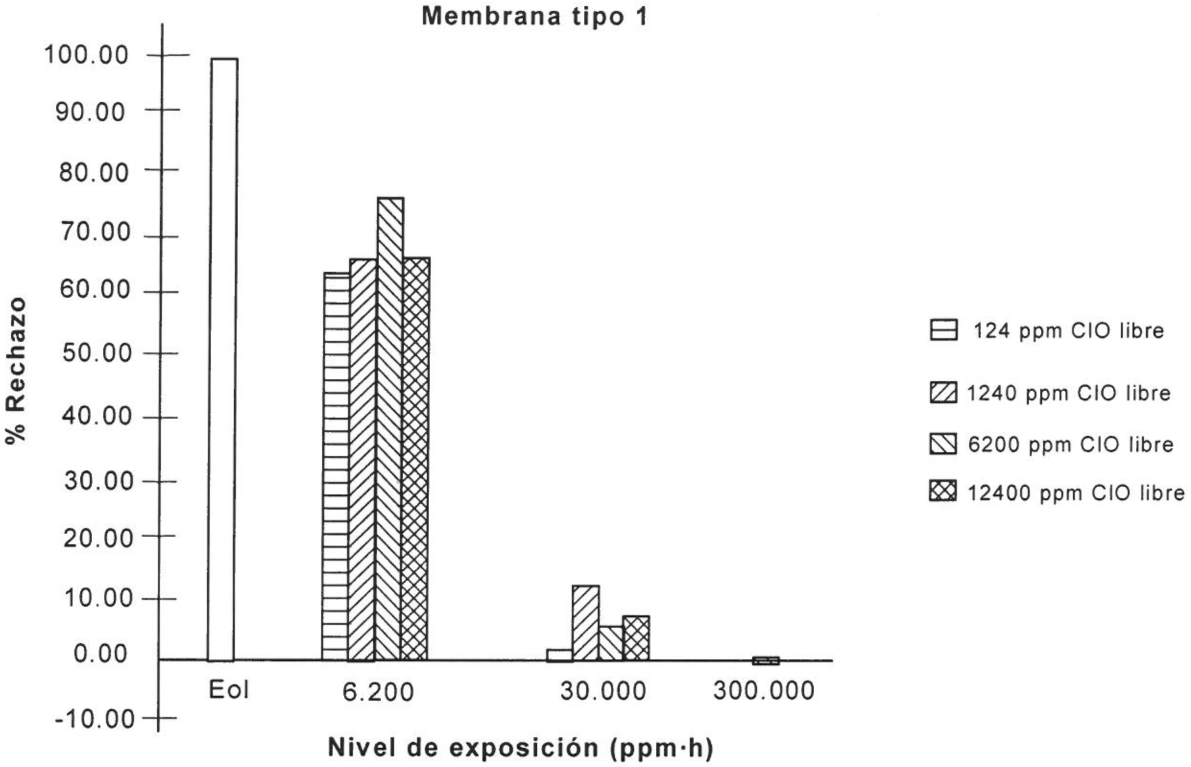

Membrana tipo 1
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
% Rechazo
Eol
6.200
30.000
300.000
Nivel de exposición (ppm·h)
124 ppm ClO libre
1240 ppm ClO libre
6200 ppm ClO libre
12400 ppm ClO libre

FIG. 4a

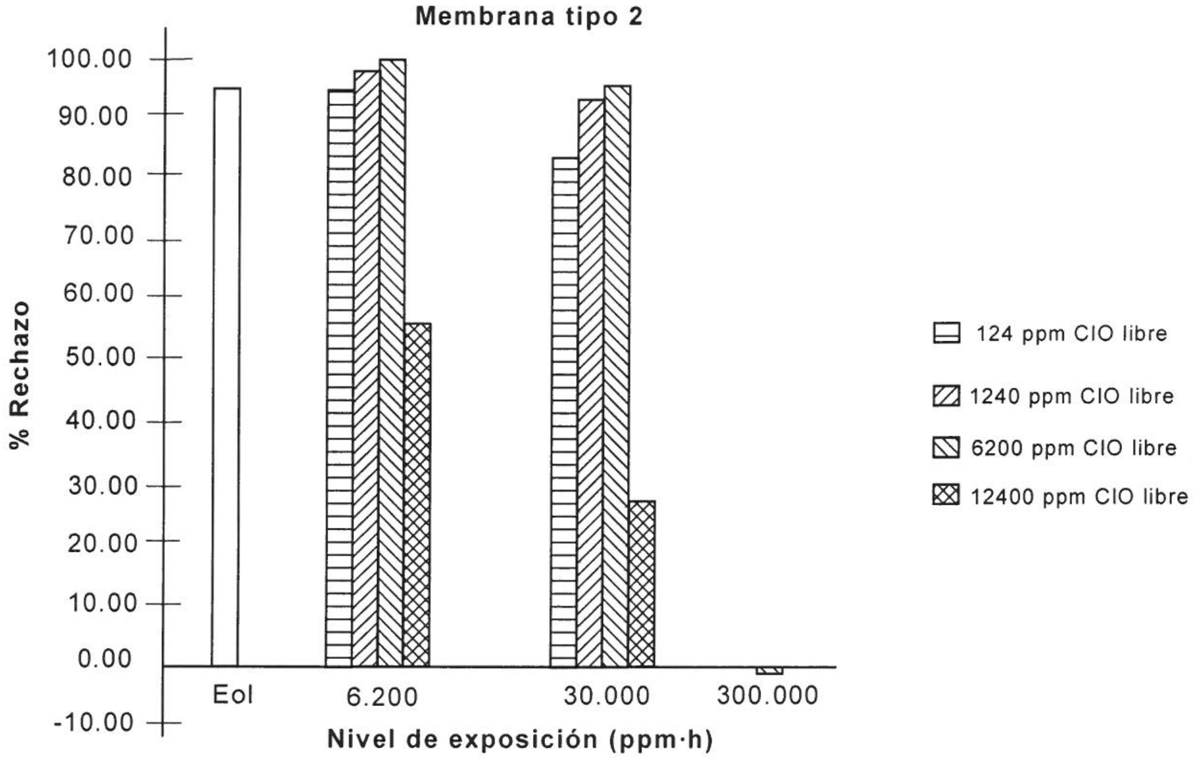

Membrana tipo 2
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
% Rechazo
Eol
6.200
30.000
300.000
Nivel de exposición (ppm·h)
124 ppm ClO libre
1240 ppm ClO libre
6200 ppm ClO libre
12400 ppm ClO libre

FIG. 4b

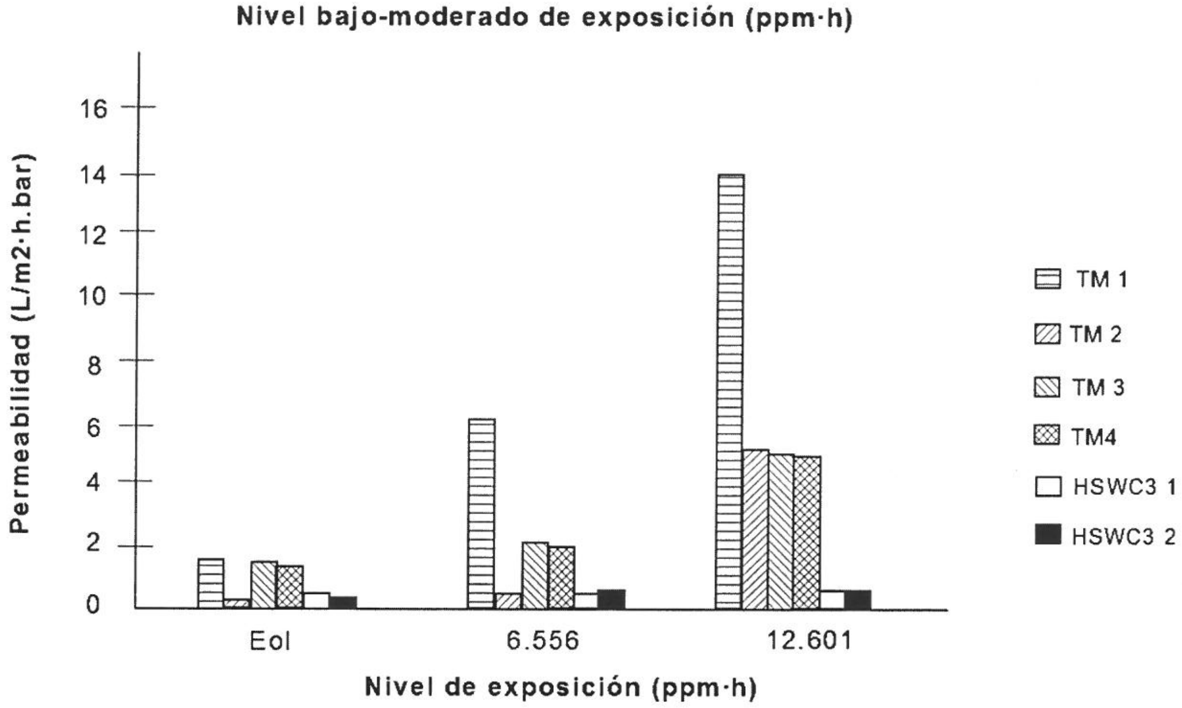

Nivel bajo-moderado de exposición (ppm·h)
Permeabilidad (L/m2·h.bar)
16
14
12
10
8
6
4
2
0
Eol
6.556
12.601
Nivel de exposición (ppm·h)
▤ TM 1
▨ TM 2
▧ TM 3
▩ TM4
☐ HSWC3 1
■ HSWC3 2

FIG. 5a

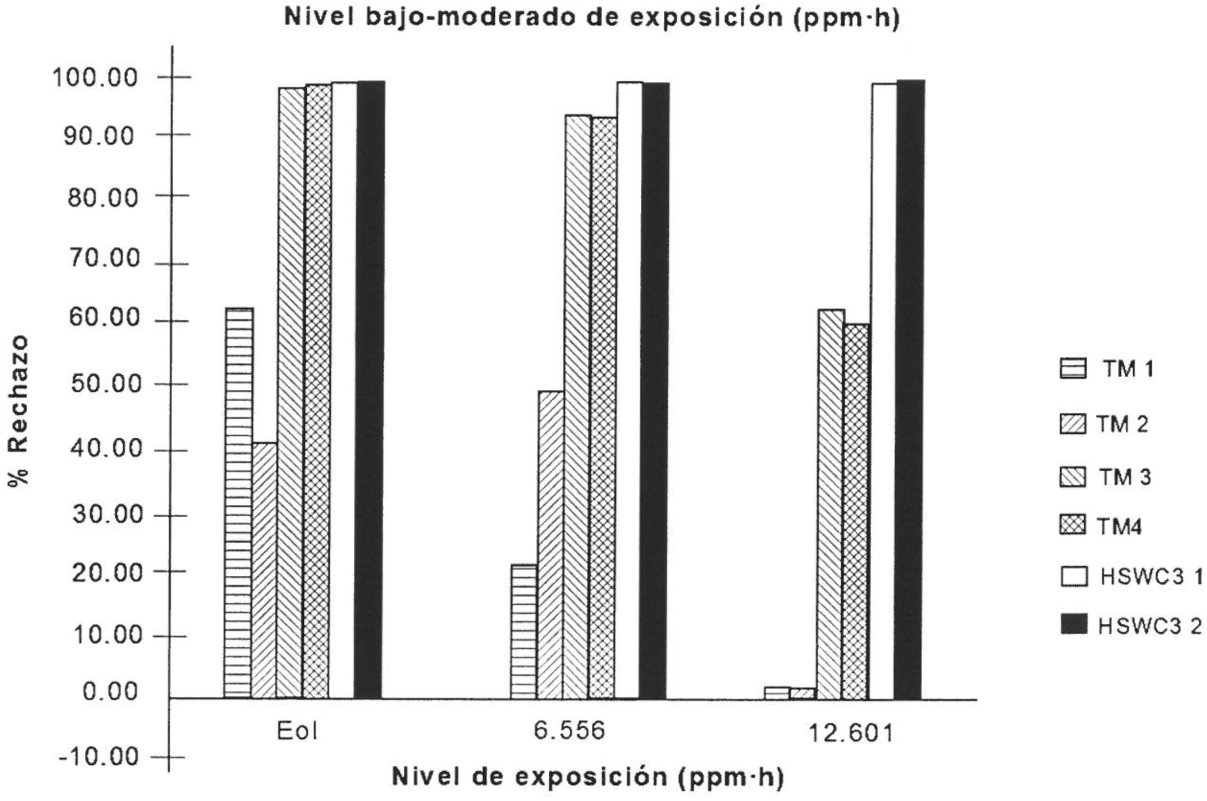

Nivel bajo-moderado de exposición (ppm·h)
% Rechazo
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
Eol
6.556
12.601
Nivel de exposición (ppm·h)
▤ TM 1
▨ TM 2
▧ TM 3
▩ TM4
☐ HSWC3 1
■ HSWC3 2

FIG. 5b

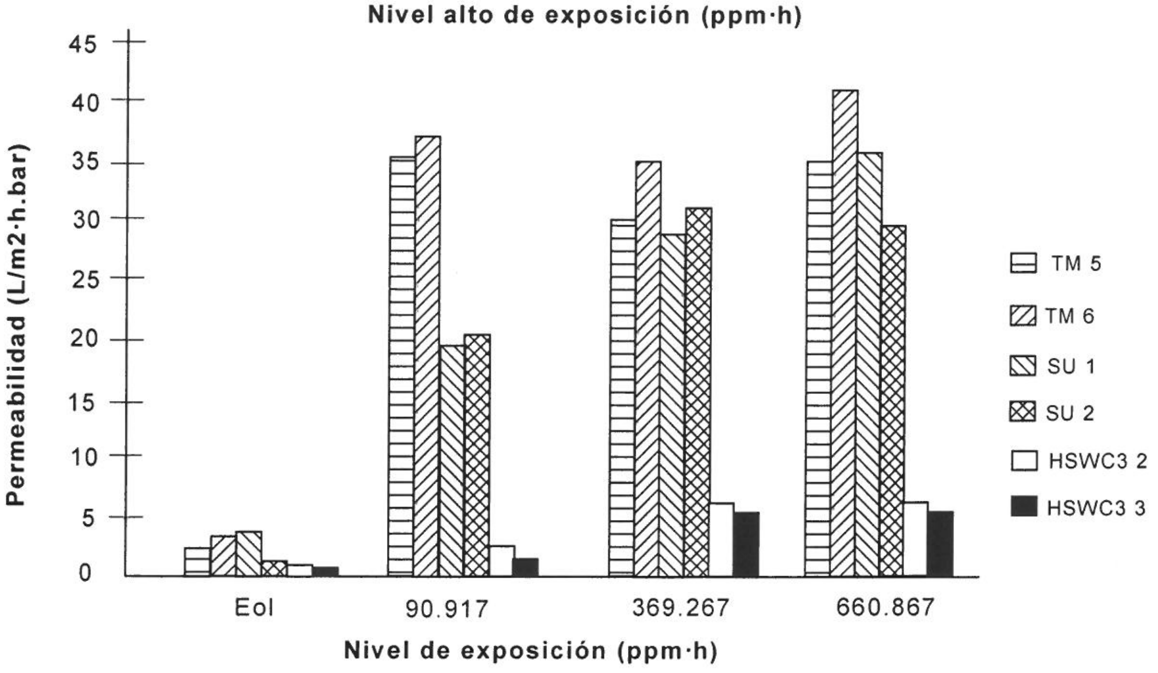

Nivel alto de exposición (ppm·h)
Permeabilidad (L/m2·h.bar)
45
40
35
30
25
20
15
10
5
0
Eol
90.917
369.267
660.867
Nivel de exposición (ppm·h)
TM 5
TM 6
SU 1
SU 2
HSWC3 2
HSWC3 3

FIG. 6a

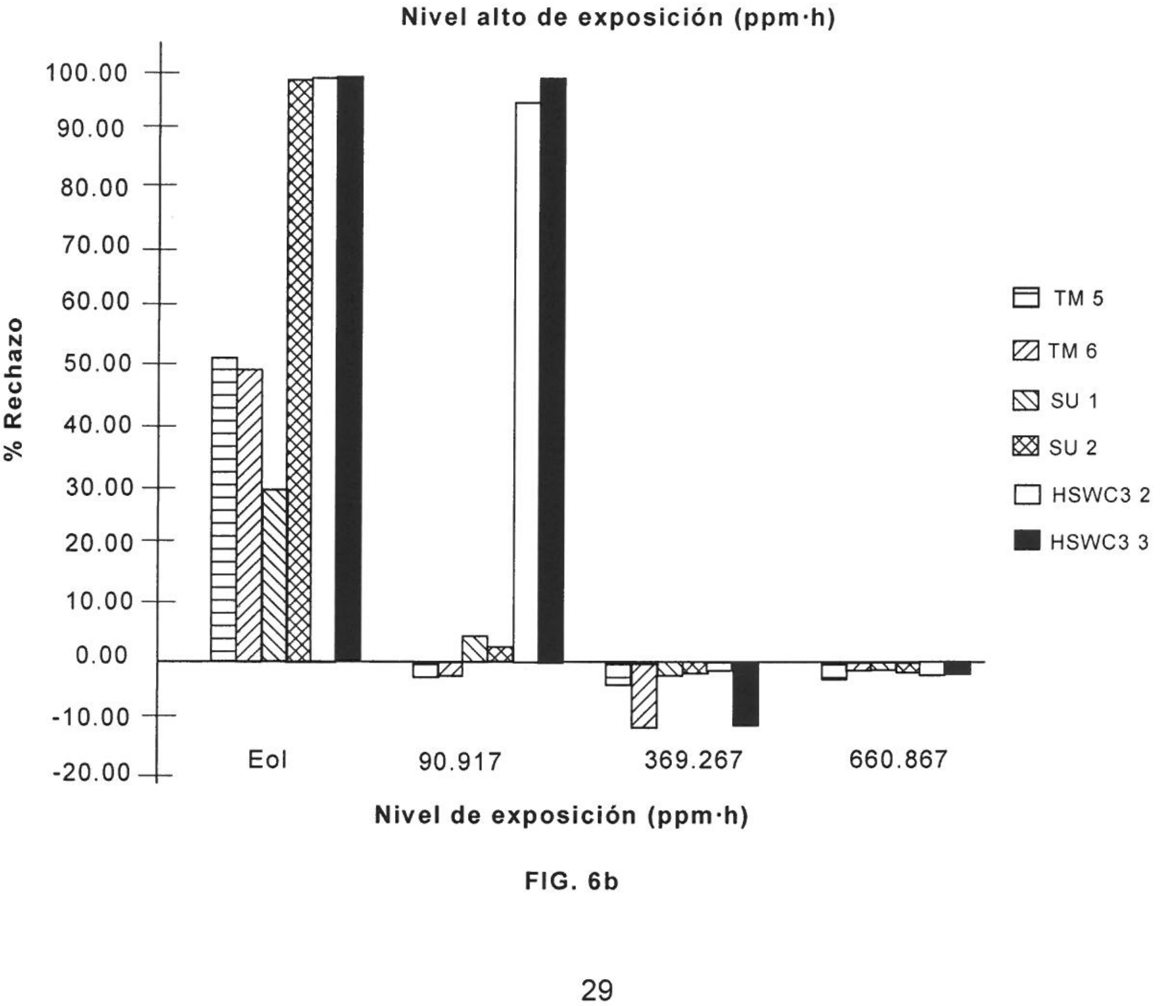

Nivel alto de exposición (ppm·h)
% Rechazo
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
-20.00
Eol
90.917
369.267
660.867
Nivel de exposición (ppm·h)
TM 5
TM 6
SU 1
SU 2
HSWC3 2
HSWC3 3

FIG. 6b

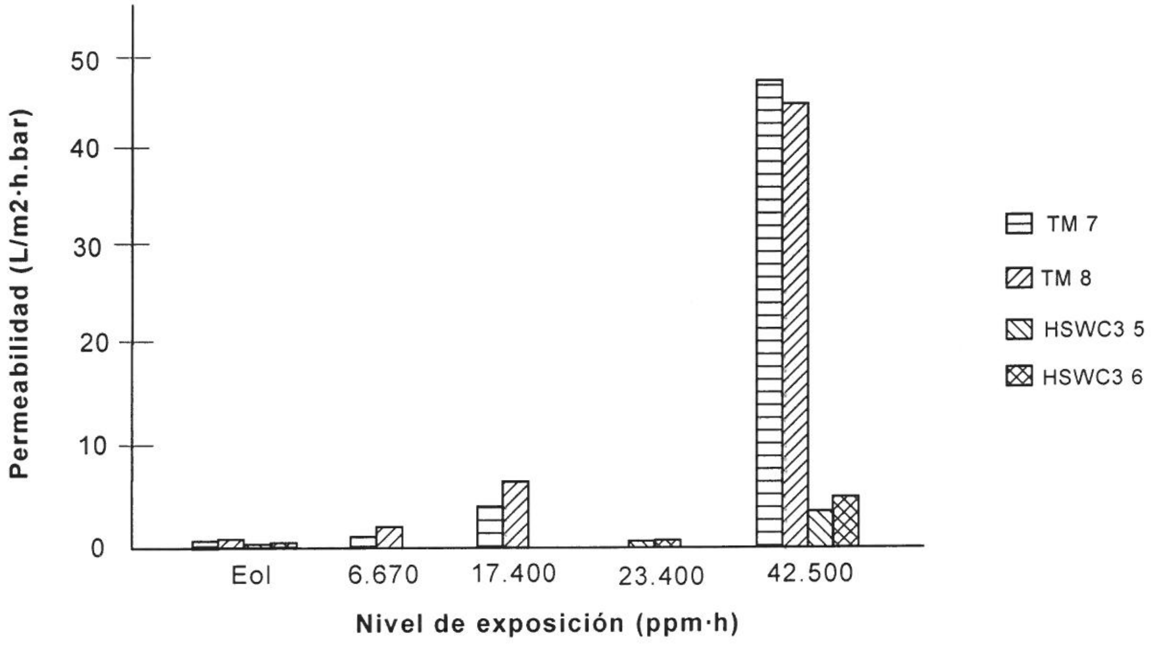

Permeabilidad (L/m2·h.bar)
50
40
30
20
10
0
Eol
6.670
17.400
23.400
42.500
Nivel de exposición (ppm·h)
TM 7
TM 8
HSWC3 5
HSWC3 6

FIG. 7a

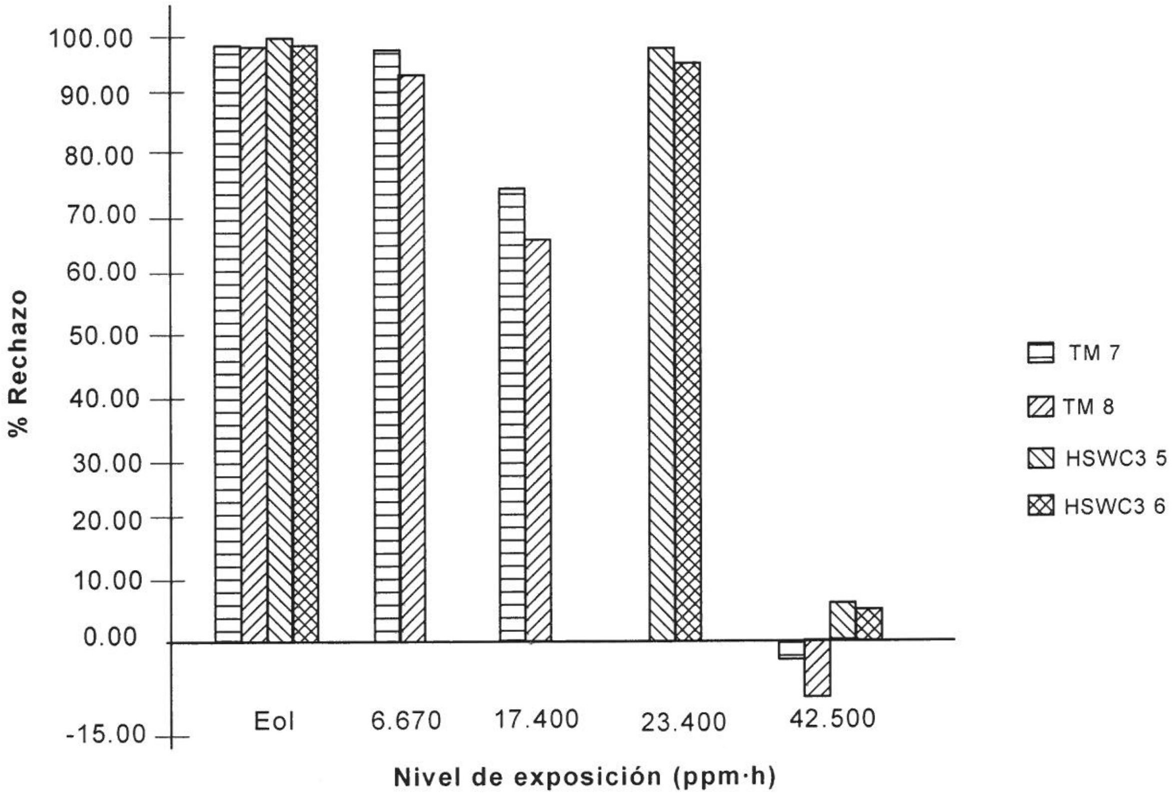

% Rechazo
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
-15.00
Eol
6.670
17.400
23.400
42.500
Nivel de exposición (ppm·h)
TM 7
TM 8
HSWC3 5
HSWC3 6

FIG. 7b

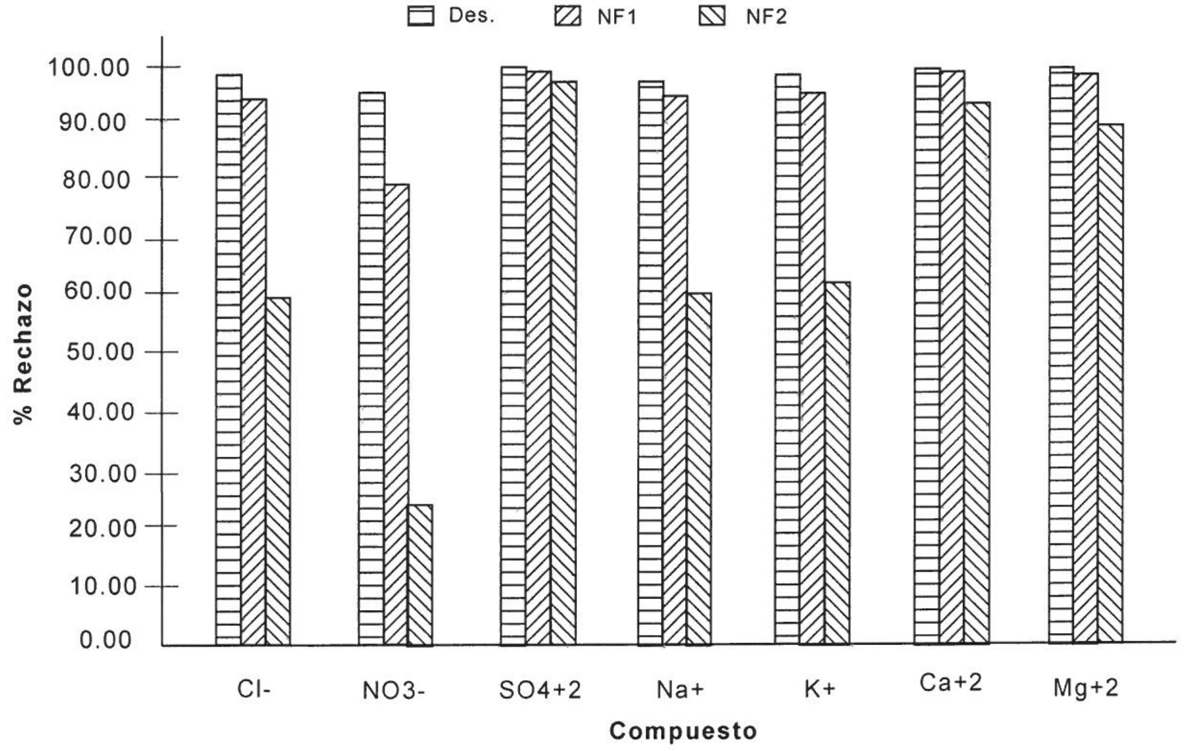

Des.
NF1
NF2
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
% Rechazo
Cl-
NO3-
SO4+2
Na+
K+
Ca+2
Mg+2
Compuesto

FIG. 8a

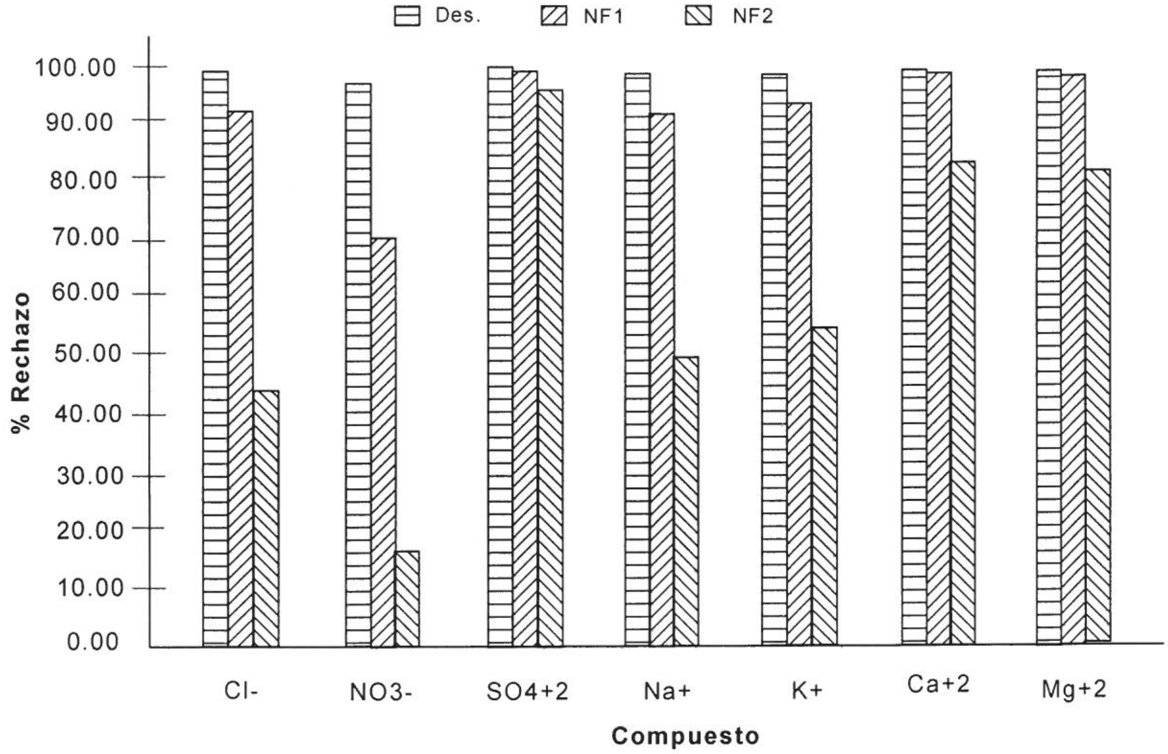

Des.
NF1
NF2
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
% Rechazo
Cl-
NO3-
SO4+2
Na+
K+
Ca+2
Mg+2
Compuesto

FIG. 8b