DOCTORAL THESIS

Implementation of Recycled Ultrafiltration Membranes in Membrane Bioreactor (MBR) for Wastewater Treatment

Towards Circular Economy in Membrane Technology

Hydrology and Management of Water Resources Doctoral Program

Laura Rodríguez Sáez 2024

Universidad de Alcalá

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Programa de Doctorado en Hidrología y Gestión de los Recursos Hídricos

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Implementation of Recycled Ultrafiltration Membranes in Membrane Bioreactor (MBR) for Wastewater Treatment: Towards Circular Economy in Membrane Technology.

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Alcalá de Henares, 2024

A mi familia

Funding and scientific support

INREMEM (Innovation in Membrane Recycling, Ref. CTM2015-65348-C2-1-R, **INREMEM 2.0** (Hybrid wastewater treatments based on recycled membranes with the objective of zero liquid discharge (ZLD), Ref. RTI2018-096042-B-C21; Both supported by Spanish Ministry of Science and Innovation (MCI), State Research Agency (AEI), and co-financed by the European Regional Development Fund (ERDF). **nanoCLEAN** (Quantification, treatment and environmental impact of micronanoplastics in WWTPs), PID2019-111519RA-I00 financed by MICIU/AEI /10.13039/501100011033; **EMERGING** (Plastisphere in urban wastewaters: Membrane based hybrid systems for water reuse and sludge recycling). Grant PID2022-143233OB-I00 financed by MICIU/AEI /10.13039/501100011033 and FEDER, UE; **μNanoCare** (Quantification of micronanoplastics in reclaimed water and agricultural ecosystems. Environmental risk assessment) Grant RTC2019-007261-5 financed by MICIU/AEI /10.13039/501100011033. **TRANSFOMEM** (Transformation of disposed reverse osmosis membranes into recycled ultra-and nanofiltration membranes, Ref. LIFE+ ENV/ES/000751. This Project received funding from the European Union LIFE Programme Under Grant Agreement Number LIFE13 ENV/ES/000751. **CLEANCM project** "Control and elimination of chemical and biological risks in water cycle" (REACT-UE resources of the Madrid Operational Program 2014-2020, in the line of action of R&D projects in response to COVID 19), whose objective is the study of methodologies to evaluate and eliminate biological risks (with SARS-CoV-2 as a model) and chemicals in different real matrices of the water cycle: wastewater, reclaimed water and groundwater. Project is funded by Comunidad de Madrid and the European Union, through the European Regional Development Fund (ERDF) Union "A way of making Europe", funded as part of the Union's response to the COVID-19 pandemic. Action funded through the agreement between the Community of Madrid (Regional Board of Education, Universities, Science and Spokesperson´s Office) and the IMDEA Water Foundation for the direct granting of a grant of 1,135,000.00 euros to finance the performance of actions in the field of research on SARS-CoV-2 and the COVID-19 disease financed with REACT-EU resources from the European Regional Development Fund.

Also, I want to thank to ICTS "NANBIOSIS", more specifically to the Confocal Microscopy Service: Ciber in Bioengineering, Biomaterials & Nanomedicine (CIBERBNN) at the Alcala University (CAI Medicine Biology).

Likewise, I would like to express my sincere gratitude to the Institute of Polymer Science and Technology of the Spanish National Research Council (ICTP-CSIC), for the close collaboration maintained during these years. Also, I want to thank to the Natural Resources and Renewable Energies Laboratory (NRRE) of Chemical Process Engineering Research Institute (CPERI) in Centre for Research and Technology-Hellas" (CERTH), Greece, for hosting me in their institutions, where a considerable part of the presented study was conducted. Lastly, the support from the University of Alcalá and IMDEA Water are particularly acknowledged.

Agradecimientos

Esta tesis ha sido un trabajo largo y complejo en el que han participado y ayudado, directa o indirectamente, muchas personas. Debido a su inestimable ayuda, siento la necesidad de agradecérselo.

En primer lugar, quisiera dar mi agradecimiento a IMDEA Agua, no solo por haberme dado la oportunidad de desarrollar este trabajo sino, también, por todos los años vividos (y trabajados) en el centro y por todo el apoyo recibido. Especialmente, quiero dar las gracias a mis directoras de tesis, Junkal y Serena, porque sin ellas (por muchos motivos) esta tesis no habría sido posible. Gracias por vuestro apoyo y confianza en momentos en los que ni siquiera yo confiaba. Gracias también a mi tutor, Eloy, por darme esta gran oportunidad.

Quiero agradecer además a Raquel, ya que ella fue la clave para el inicio de mis andaduras en IMDEA y la persona que, con su gran trabajo, ha inspirado en gran parte esta tesis.

Así mismo, quisiera agradecer su tiempo y paciencia (y amistad) a todas las personas que me acogieron en mi estancia en CERTH, Grecia. En especial a Sotiris, que me enseñó gran parte de lo que en este trabajo se presenta y al Profesor Anastasios J. Karabelas por permitirme realizar esa estancia que me llenó de conocimiento y vivencias.

También quisiera agradecer a todo el grupo de Tecnología de Membranas de IMDEA, en especial a Jorge que aportó sus conocimientos al presente trabajo. Pero, por supuesto, a todos los que están y estuvieron en este grupo de membranas como Amaia, Helena e Imane por todo el tiempo compartido entre oficina y laboratorios y, especialmente, a Anamary, por compartir despacho, viajes, tiempo y confidencias.

A todos los compañeros y excompañeros de IMDEA Agua, con los que he compartido grandes momentos tanto dentro como fuera del centro, por hacer del instituto un lugar más agradable en el que trabajar. En especial quiero agradecer a gente a la que, sobre todo, puedo llamar amiga. Gloria, Mabel, habéis sido mi sustento aquí. Juana y José Ángel, gracias por vuestra paciencia infinita y por estar siempre dispuestos a escuchar. A mi Carola y a mi Bei, gracias por estar ahí siempre, para escucharme y ayudarme. Virtu y

Raffa, gracias por vuestro gran apoyo en momentos oscuros. A Pepis, Diego, Cova, Amaya, Patri, Jesús, Angélica, Juanma, Ana, Blanca, MA, Gloria, Rubén, Alberto… (seguro que me dejo a alguien…) porque sin vosotros este camino hubiese sido mucho más árido.

Pero, además, una tesis expande sus largos brazos llegando y envolviendo a la vida fuera del centro durante mucho tiempo. Por lo que mis amigos y familia se merecen igualmente un hondo agradecimiento. Cris, no tengo palabras para agradecerte estar ahí sin importar qué, cómo ni cuándo. Ire, gracias por ser mi apoyo siempre. Edu y Noni, gracias por nuestras tardes que se hacen noches juntos, me han dado el aire necesario para seguir adelante durante este tiempo. Carmen y José, gracias por acogerme como una más de la familia. Gracias a Juanjo, Gabri, Pepe, Alfon, José Ángel, Diego, Miguel, Isa, Olalla, Caty, Pablo, Alfredo, Cris, Ine, Sonsi, Iván, Olga (seguro que me dejo a alguien, me perdonáis) por seguir ahí sin importar los años, con las tonterías de siempre que me han dado (y me dan) la vida.

Gracias a los amigos que recientemente han aparecido en mi vida (En Torrejón… ¡Quién me lo iba a decir!) que me han acompañado en estos años tan duros, por unas cosas o por otras.

Gracias a mi familia, sin ellos no habría podido seguir adelante todos estos años, que han tenido luces y sombras, por diversos motivos. Gracias también a esa parte de familia más reciente que han acompañado y ayudado en la etapa más difícil de mi vida. Gracias por hacerme sentir una más desde el primer día.

Si hay alguien que ha pasado estos años tan duros a mi lado aguantando carros y carretas ese has sido tú, Sergio. Es imposible plasmar en palabras lo agradecida que estoy por tu apoyo. Gracias.

Para terminar, quiero agradecer a mis abuelos, Luis y Carmen, por cuidarme, apoyarme y ayudarme siempre. Soy quien soy gracias a vosotros. Os quiero. Y, por último, quiero agradecerle TODO a la persona más importante, sin la que ni esta tesis, ni ninguna otra cosa, habría sido posible. Mamá, te quiero. ¡GRACIAS!

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Abbreviations

ABS	Acrylonitrile butadiene styrene
AFM	Atomic force microscope
aMBR	Aerobic membrane bioreactor
ANOVA	Analysis of variance
ATR–FTIR	Attenuated total reflectance–Fourier transform infrared spectroscopy
BOD_5	Biological Oxygen Demand
BRM	Biorreactor de membrana
BSA	Bovine serum albumin
CA	Catechol
CAGR	Compound annual growth rate
CAPEX	Capital expenditure
CAS	Conventional activated sludge
c-MF	Commercial microfiltration
COD	Chemical oxygen demand
cSWW	Concentrated synthetic wastewater
DCMD	Direct contact membrane distillation
DIA	Digital image analysis
DO	Dissolved oxygen
ED	Electrodialysis
EDX	Energy dispersive X-Ray
EIB	European Investment Bank
EoL	End of Life
EPS	Extracellular polymeric substances
FRR	Flux recovery ratio

FS	Flat sheet
HF	Hollow fiber
HRT	Hydraulic retention time
LCA	Life Cycle Assessment
MBfR	Membrane biofilm reactor
MBR	Membrane bioreactor
MC	Microcystin
MF	Microfiltration
MLR	Multiple linear regressions
MLSS	Mixed liquor suspended solids
mr-UF	Modified recycled ultrafiltration membrane
MWCO	Molecular weight Cut Off
NF	Nanofiltration
OI	Ósmosis inversa
OPEX	Operational expenditure
PA	Polyamide
PC	Polycarbonate
PDA	Polydopamine
PEG	Polyethylene glycols
PEI	Polyethylenimine
PES	Polysulfone/poly(ether sulfone)
PET	Polyester
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Poly(viny1idene fluoride)
RIS	Resistance in series model

RO	Reverse osmosis
r-UF	Recycled ultrafiltration
SDG	Sustainable development goals
SEC	Specific energy consumption
SEM	Scanning electron microscopy
SMP	Soluble microbial products
SRT	Solid retention time
SWW	Synthetic wastewater
TFC	Thin film composite
TMP	Transmembrane pressure
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorous
UF	Ultrafiltration
UN	United Nations
UNICEF	United Nations International Children's Emergency Fund
WCA	Water contact angle
WHO	World Health Organization
XPS	X-ray photoelectron spectroscopy

Symbols

μ	Dynamic viscosity (Pa.s)
A	Membrane effective area (m^2)
DF	Degrees of freedom
F_{value}	Fisher test calculated value
$F_{tabulated}$	Fisher test critical value
h	Time (hours)
J	Flux ($L \cdot m^{-2} \cdot h^{-1}$)
L	Membrane permeability ($L \cdot m^{-2} \cdot h^{-1}$ bar^{-1})
$L_{average}$	Average permeability ($L \cdot m^{-2} \cdot h^{-1}$ bar^{-1})
L_i	Individual permeability ($L \cdot m^{-2} \cdot h^{-1}$ bar^{-1})
L_r	Relative permeability
L_S	Membrane permeability at certain time ($L \cdot m^{-2} \cdot h^{-1}$ bar^{-1})
PRESS	Prediction residual sum of squares
p-value	Probability
Q	Membranes permeate flow ($L.h^{-1}$)
Q^2	Response variation percentage predicted by the model
R	Resistance (m^{-1})
R^2	Coefficient of determination
R^2adj	Adjusted coefficient of determination
R_a	Arithmetic average of absolute values of surface height deviations (nm)
R_c	Cake Layer Resistance (m^{-1})
$R_{c(ir)}$	Cake Layer Irreversible Resistance (m^{-1})
$R_{c(rev)}$	Cake Layer Reversible Resistance (m^{-1})
R_f	Fouling Resistance (m^{-1})

R_{ir}	Irreversible Resistance (m^{-1})
R_m	Membrane Resistance (m^{-1})
R_{pb}	Pore Blocking Resistance (m^{-1})
R_q	Root mean square average of height deviation (nm)
R_{rev}	Reversible Resistance (m^{-1})
R_T	Total Resistance (m^{-1})
S	Membrane surface (m^2)
SS	Sum of squares
t	Time (h)
T	Temperature (ºC)
TMP	Transmembrane Pressure (Pa)
W	Permeate weight (g)
ρ	Solution density (g/L)

I. Resumen

La escasez de agua potable y la falta de acceso a un sistema de saneamiento adecuado es un problema instalado a nivel global que, además, se ha visto agravado en las últimas décadas debido al exponencial aumento de la población mundial y, por supuesto, al cambio climático. Así mismo, la contaminación de las masas de agua es un problema añadido que, paralelamente, se ha ido agravando a pesar del incremento y mejora en los esfuerzos para la conservación del medio ambiente y, por ende, del agua. Esta situación, ha hecho necesario la implantación de normativa y el desarrollo de tecnología específica que ayuden a mitigar este escenario.

Muchos tratamientos convencionales se han desarrollado a lo largo de los años con bastante éxito para atajar estas situaciones. Uno de los sistemas más exitoso y, por tanto, más empleado en el tratamiento de agua ha sido la tecnología de membranas. Aunque, a priori, pueden ser sistemas más caros de implementar que otros sistemas, las membranas poseen gran versatilidad en cuanto a sus aplicaciones además de proporcionar una alta calidad de agua tratada. En concreto, la desalación de agua de mar mediante el uso de membranas de ósmosis inversa (OI) produjo una revolución en el acceso al agua potable. Otro sistema destacable de tratamiento de agua residual, tanto residual como industrial basado en membranas serían los sistemas de biorreactor de membranas (BRM) que presentan importantes ventajas frente a los tratamientos convencionales. Sin embargo, como cualquier proceso científico y tecnológico, estos tratamientos también presentan algunas desventajas. En concreto, debido al ensuciamiento y deterioro de las membranas usadas en estos procesos a lo largo del tiempo, estas deben ser sustituidas aumentando así los costes de operación. No solo eso, sino que, además, estas membranas debido a su composición plástica y a la complejidad de su estructura son difíciles de reciclar y, normalmente, acaban siendo depositadas en vertederos o siendo incineradas aumentando la generación de residuos y produciendo contaminación en el medio ambiente. Además, esta forma de gestión de las membranas desechadas choca frontalmente con los principios establecidos tanto por la normativa de la Unión Europea como con los propios principios de la Economía Circular en los que se basa. Debido a esta situación, muchos de los estudios científicos en los últimos tiempos en el campo de la tecnología de membranas se han

centrado en la mitigación la tasa de reposición de las membranas mediante distintos mecanismos.

La presente tesis doctoral se centra en el uso de membranas recicladas de ultrafiltración (r-UF) obtenidas a partir de membranas desechadas de OI, que se usaron previamente para desalar agua de mar o tratar agua contaminada, mediante el reciclaje indirecto de las mismas. De esta forma se les da una nueva vida útil, en este caso como membranas de ultrafiltración en otro tipo de sistemas concretamente en BRM. Se propone así, siguiendo los principios de la Economía Circular, obtener membranas recicladas que sean medioambientalmente sostenibles a la vez que se reduce también el nivel de inversión económica, consumo de materias primas y de energía que requeriría la producción de nuevas membranas. Todo ello, lleva aparejado una reducción de emisiones de gases de efecto invernadero asociadas tanto a la fabricación como al transporte y almacenaje de las membranas nuevas como la generación de membranas desechadas que se convierten en un residuo que, normalmente, acaba en vertedero o siendo incinerado.

Para ello, lo primero que se realizó fue una prueba de concepto para averiguar si estas membranas podían ser sometidas a las condiciones de trabajo de un BRM. Se comparó su funcionamiento con una membrana de microfiltración (MF) en términos de calidad de permeado, permeabilidad y ensuciamiento obteniendo resultados prometedores comparables a los obtenidos con la membrana comercial. De esta forma se determinó que estas membranas recicladas eran aptas para ser usadas en un BRM.

A continuación, se realizó una modificación de la superficie de las membranas recicladas a nivel laboratorio. Se buscaba una modificación que mejorase la resistencia de la membrana reciclada al ensuciamiento y alargar así la vida útil de estas membranas. En esta experimentación además se realizó un diseño estadístico experimental para analizar no solo los factores de la modificación y las respuestas estudiadas, en este caso permeabilidad y recuperación del ensuciamiento, sino la relación entre los factores de la modificación. Se observó que, en efecto, la interacción entre los factores afectaba a la modificación y por tanto a las respuestas estudiadas. Así mismo, se determinaron las condiciones para una modificación óptima.

Por último, se realizó la validación de las membranas recicladas mediante una experimentación más larga en un BRM. Se estudió el comportamiento de la membrana reciclada y la membrana reciclada modificada usando las condiciones de modificación óptimas encontradas en la experimentación anterior. Así mismo, se estudiaron dos membranas comerciales de UF con similares características a las membranas recicladas para poder comparar el rendimiento en condiciones de trabajo similares. Los resultados alcanzados fueron muy alentadores ya que la membrana reciclada y la membrana modificada se comportaron de forma muy similar a las membranas comerciales respecto a la calidad de agua obtenida. Además, la membrana reciclada, sin necesidad de modificación, mostró un comportamiento excelente, especialmente a nivel de ensuciamiento. Se realizó también una extensiva caracterización de las membranas donde se observó que efectivamente la membrana reciclada no presentaba bacterias adheridas en superficie. Adicionalmente, esta membrana presentaba niveles de cloro en su superficie más altos de que el resto de las membranas estudiadas con lo que se concluyó que las características adquiridas por esta membrana a lo largo del proceso de reciclaje le conferían una intrínseca resistencia al ensuciamiento, haciéndola óptima para trabajar en este tipo de ambientes.

En conclusión, la presente tesis doctoral muestra una innovadora metodología que permite el reciclaje indirecto de las membranas de OI al final de su vida útil para su uso como membranas de UF en BRM demostrando la viabilidad técnica de las membranas obtenidas para este tipo de sistemas. Así mismo, este trabajo de investigación pretende así contribuir a mitigar el problema de la generación de residuos y los costes de operación relacionados con el tratamiento de agua siguiendo las directrices de la Economía Circular.

II. Abstract

Drinking water scarcity and the lack of access to an adequate sanitation system is a global problem that has also been worsened in the last decades due to the exponential increase of world's population and climate change. Likewise, water bodies contamination is a further problem that has also gotten worse despite the increasing efforts to preserve the environment and, therefore, water. This mentioned situation evidences the necessity of the implementation of regulations and the development of specific technology that may help mitigating this scenario.

Numerous conventional treatments have been successfully developed over the years to address these situations. Membrane technology has emerged as one of the most successful and widely used water treatment systems. Even though membrane systems may present higher implementation costs compared to other technologies, they offer significant versatility in their applications and deliver high-quality treated water. Specifically, seawater desalination using reverse osmosis (RO) membranes transformed the access to drinking water. Moreover, other remarkable membrane-based wastewater treatment systems are membrane bioreactor (MBR) systems that present notable advantages over conventional treatments for the treatment of both urban and industrial wastewater. However, like any scientific and technological process, these treatments also present some drawbacks. Concretely, due to fouling and deterioration of the membranes used in these processes over time, they must be replaced, increasing operating costs. Not only that, but these membranes, due to their plastic composition and the complexity of their structure, are quite complex to be recycled and, consequently, they usually end up being landfilled or incinerated, increasing both waste generation and pollution. In addition, these discarded membrane management alternatives confront with both principles established by European Union regulations and Circular Economy. Given this abovementioned situation, many of the recent scientific studies in the field of membrane technology have been focused on mitigating the replacement rate of membranes through different mechanisms.

This doctoral thesis focuses on the use of recycled ultrafiltration membranes (r-UF) obtained from discarded RO membranes that were used

for seawater desalination and contaminated water treatment by means of indirect recycling. In this way, these recycled membranes are available to be used again as ultrafiltration membranes in other water treatment systems, specifically in MBR systems. Following the principles of the Circular Economy, it is thus proposed to obtain recycled membranes that are environmentally sustainable, while also reducing economic investment, raw material consumption, energy usage, and greenhouse gas emissions associated with the manufacturing, transport, and storage of new membranes. Additionally, r-UF membrane adoption contributes to a reduction in discarded membranes that would otherwise become landfill waste or require incineration.

Firstly, a proof-of-concept study was carried out to assess if these membranes could be subjected to MBR working conditions. To this end, its operation performance was compared to a microfiltration (MF) commercial membrane in terms of permeate quality, permeability and fouling behavior. Promising results were obtained, comparable to those achieved with the commercial membrane. Hence, it was determined that the recycled membranes were suitable for their use in MBRs.

Subsequently, a laboratory scale membrane surface modification was conducted. It was intended to improve the fouling behavior of the recycled membranes and consequently to extend the lifespan of these membranes. In this research, a statistical design of experiments was developed to analyze not only the factors of the modification and the responses studied, in this case permeability and recovery from fouling, but also the interactions between the factors studied during the modification. It was observed that, in fact, the interaction between the factors affected significantly the modification and, therefore, the responses studied. Likewise, the conditions for an optimal modification were determined.

Finally, a longer experimentation was conducted to assess the validation of the recycled membranes in MBR. The behavior of the recycled membrane and the modified recycled membrane was studied using the modification identified as optimal in the previous experimentation. Also, two commercial UF membranes with similar characteristics to the recycled membranes were studied to compare the performance during similar working conditions. The obtained results were very encouraging since the recycled membrane and the modified membrane behaved in a very similar way to commercial membranes in terms of water quality. Further, the recycled membrane without the need of further modification showed an excellent performance, especially in terms of fouling. Additionally, an extensive characterization of the membranes was performed. It was observed that, indeed, the recycled membrane did not present bacteria attached to its surface. In addition, this membrane exhibited higher levels of chlorine on its surface than the other studied membranes. Therefore, it was concluded that the characteristics acquired by this membrane throughout the recycling process gave it an intrinsic anti-biofouling character, making it optimal for working in this type of environment.

In conclusion, the present doctoral thesis shows an innovative methodology that allows the indirect recycling of End of Life (EoL) RO membranes for their use as UF membranes in MBR, demonstrating the technical feasibility of the membranes obtained for this type of systems. Likewise, this research work aims to contribute mitigating the problem of waste generation and the operating costs related to water treatment following the guidelines of the Circular Economy.

III. List of publications

This thesis is based on the publication cited below. Each scientific paper corresponds to a chapter of the present work:

Scientific paper 1 (published) as chapter 3

L. Rodríguez-Sáez, S.I. Patsios, J. Senán-Salinas, J. Landaburu-Aguirre, S. Molina, E. García-Calvo. A Novel Application of Recycled Ultrafiltration Membranes in an Aerobic Membrane Bioreactor (aMBR): A Proof-of-Concept Study. Membranes (2022) 12 (2), 218. https://doi.org/10.3390/membranes12020218.

Scientific paper 2 (published) as chapter 4

L. Rodríguez-Sáez, J. Landaburu-Aguirre, S. Molina, M.C. García-Payo, E. García-Calvo. Study of surface modification of recycled ultrafiltration membranes using statistical design of experiments. Surfaces and Interfaces (2021) 23, 100978. https://doi.org/10.1016/j.surfin.2021.100978.

Scientific paper 3 (published) as chapter 5

L. Rodríguez-Sáez, J. Landaburu-Aguirre, E. García-Calvo, S. Molina. Application of recycled ultrafiltration membranes in an aerobic membrane bioreactor (aMBR): A validation study. Membranes. Membranes (2024) 14 (7), 149. https://doi.org/10.3390/membranes14070149

IV. Other contributions

The research conducted during this Thesis has resulted in the following communications in conferences and international research stays:

Communication in conferences

Oral communications

L. Rodríguez-Sáez, J. Landaburu-Aguirre, E. García-Calvo, S. Molina. Application of recycled ultrafiltration membranes in an aerobic membrane bioreactor (aMBR): A validation study. **Euromembrane** 8-13 September 2024**,** Prague.

Posters

L. Rodríguez-Sáez; J. Landaburu-Aguirre; S. Molina; M.C. García-Payo; E. García-Calvo, Study of surface modification of recycled membranes using statistical design of experiments. **ICOM 2020**, International Congress on Membranes & Membrane Processes. Online. 7-11 December.

L. Rodríguez-Sáez; S.I. Patsios; J. Landaburu-Aguirre; S. Molina; E. García-Calvo; A.J. Karabelas. Use of recycled ultrafiltration membrane for aerobic membrane bioreactor. **ICOM 2020**, International Congress on Membranes & Membrane Processes. Online. 7-11 December.

L. Rodríguez-Sáez; J. Landaburu-Aguirre; S. Molina; E. García-Calvo, Antibiofouling surface modification of recycled reverse osmosis membranes for membrane bioreactors. **Euromembrane**. 9-13 July 2018. Valencia (Spain).

Research stay

Dates	01/02/2019-31/05/2019
Host supervisor	Prof. Anastasios J. Karabelas
Department	Natural Resources and Renewable Energies Laboratory (NRRE)
Institution	Centre for Research and Technology - Hellas. chemical Process and Energy Resources Institute (CERTH/CEPERI)
City, Country	Thessaloniki, Greece
Publication	L. Rodríguez-Sáez, S.I. Patsios, J. Senán-Salinas, J. Landaburu-Aguirre, S. Molina, E. García-Calvo, A Novel Application of Recycled Ultrafiltration Membranes in an Aerobic Membrane Bioreactor (aMBR): A Proof-of-Concept Study, Membranes (2022). 12 (2), 218. https://doi.org/10.3390/membranes12020218

Other scientific contribution closely related to the topic of the thesis is summarized below.

Scientific publications

S. Molina; H. Ocaña-Biedma; L. Rodríguez-Sáez; J. Landaburu-Aguirre. Experimental Evaluation of the Process Performance of MF and UF Membranes for the Removal of Nanoplastics. Membranes (2023) 13 (7), 683. https://doi.org/10.3390/membranes13070683

R. García-Pacheco; J. Landaburu-Aguirre; A. Ortiz de Lejarazu; L. Rodríguez-Sáez; S. Molina; T. Ransome; E. García-Calvo. Free chlorine exposure dose (ppm·h) and its impact on RO membranes ageing and recycling potential. Desalination 457 (2019) 133–143. https://doi.org/10.1016/j.desal.2019.01.030

S. Molina; J. Landaburu-Aguirre; L. Rodríguez-Sáez; R. García- Pacheco; J. García de la Campa; E. García-Calvo. Effect of sodium hypochlorite exposure on polysulfone recycled UF membranes and their surface characterization. Polymer Degradation and Stability 150 (2018) 46 - 56. https://doi.org/10.1016/j.polymdegradstab.2018.02.012

J. Landaburu-Aguirre; R. García-Pacheco; S. Molina; L. Rodríguez- Sáez; J. Rabadán; E. García- Calvo. Fouling prevention, preparing for re-use and membrane recycling. Towards circular economy in RO desalination. Desalination. 393 (2016) 16 - 30. https://doi.org/10.1016/j.desal.2016.04.002

R. García-Pacheco; J. Landaburu-Aguirre; S. Molina; L. Rodríguez- Sáez; S. B. Teli; E. García-Calvo. Transformation of end-of-life RO membranes into NF and UF membranes: Evaluation of membrane performance. Journal Membrane Science. 495 (2015) 305 - 315. https://doi.org/10.1016/j.memsci.2015.08.025

Industrial and intellectual property

Proceso de transformación de membranas de poliamida con enrollamiento en espiral que han agotado su vida útil en membranas de utilidad industrial. ES2589151 A1. **Inventors/authors/obtainers:** Elena Campos Pozuelo; Patricia Terrero Rodríguez; Domingo Zarzo Martínez; Francisco José Molina Serrano; Mercedes Calzada Garzón; Raquel García Pacheco; Serena Molina; Laura Rodríguez Sáez; Francisco Javier Rabadán; Junkal Landaburu Aguirre; Amaia Ortiz de Lejarazu Larrañaga; Eloy García Calvo. **Entity holder of rights:** IMDEA WATER. **Nº of application:** 201630931. Country of inscription: Spain, Community of Madrid Date of register: 08/07/2016

Communications in conferences

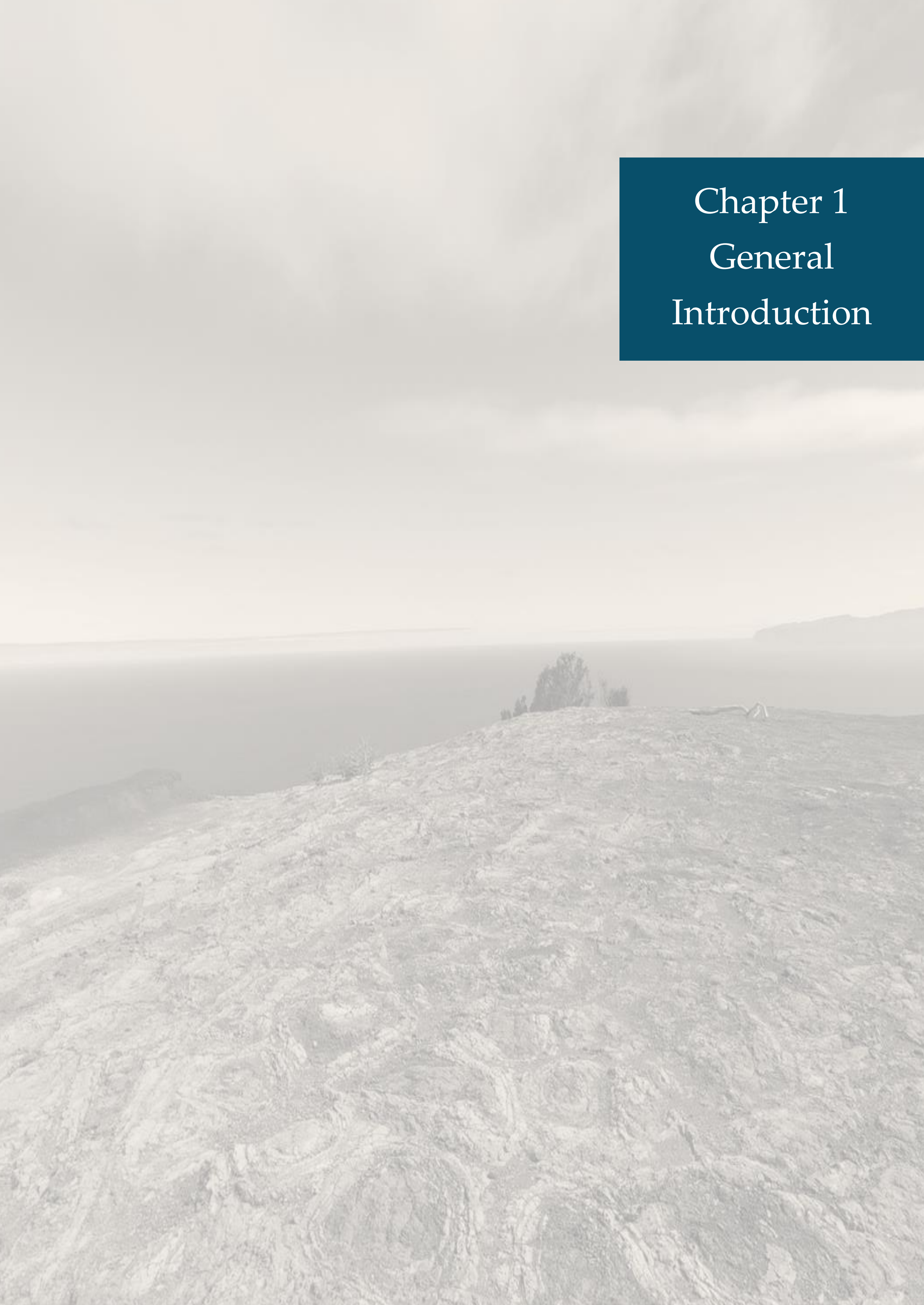
R. García-Pacheco; J. Rabadán; P. Terrero; S. Molina; D. Martínez; E. Campos-Pozuelo; F. Molina; L. Rodríguez-Sáez; A. Ortiz de Lejarazu Aguirre; J. Landaburu-Aguirre; D. Zarzo; E. García-Calvo. "LIFE+13

TRANSFOMEM: un ejemplo de reciclaje en el mundo de la desalación **XI Congreso Internacional de AEDYR** 2016 Valencia, Valencian Community, Spain.

S. Molina; R. García-Pacheco; L. Rodríguez-Sáez; E. García Calvo; E. Campos-Pozuelo; D. Zarzo; J. González de la Campa; J. de Abajo González. "Transformation of end-of-life RO membrane into recycled NF and UF membranes, surface characterization. **IDA - The International Desalination Association World Congress on Desalination and Water Reuse 2015**. San Diego, United States of America.

Chapter 1

General Introduction



1. Introduction

1.1. Water accessibility

At least half of the world's population faces critical water scarcity at some point over the course of a year [1]. Even though 75% of the planet's surface is covered by water, less than 3 % is available for us (Figure 1) [2].

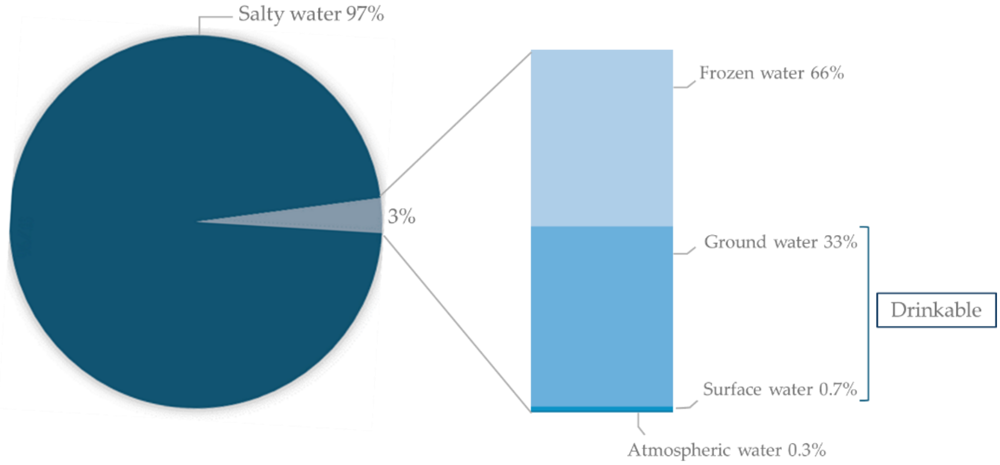


Figure 1. Water distribution

The 2030 Agenda for Sustainable Development aims to ensure availability and sustainable management of water and sanitation for all (SDG 6) including specific targets for the universal access to safe drinking water and sanitation, paying special attention to the needs of women and girls and those in vulnerable situations. Another important part of this goal is to improve water quality worldwide. This involves reducing pollution, stopping illegal dumping and limiting the release of harmful chemicals and materials into water sources. Additionally, the aim is to cut the amount of untreated wastewater in half and significantly increase recycling and the safe reuse of water on a global scale [3]. However, according to the World Health Organization (WHO) and the United Nations International Children's

Emergency Fund (UNICEF), none of the SDG regions are expected to achieve universal access to water by 2030 [4]. Additionally, by 2050, freshwater demand is expected to increase between 20 to 30% [5].

In the view of the above issues, to manage the current situation several factors need to be taken into consideration for the development of strategies to cope with freshwater requirements (Figure 2). A necessary feature in this regard is that Governments and Institutions orient their policies and strategies to a common main goal: to achieve universal access to clean water [6]. However, one of the most important obstacles still is the financial resources to cover the needed changes. The budget for this purpose has been identified to be insufficient for 75% of the countries [7]. Additionally, environmental vicissitudes due to global climate change and the extreme events related to this matter need to be urgently considered. Furthermore, it is clear that strong regulation, active policies and effective management are needed to succeed [8,9]. However, conventional water providing plans like surface water diversion and water related infrastructure can face geographic and climate issues apart from, occasionally, public discomfort.

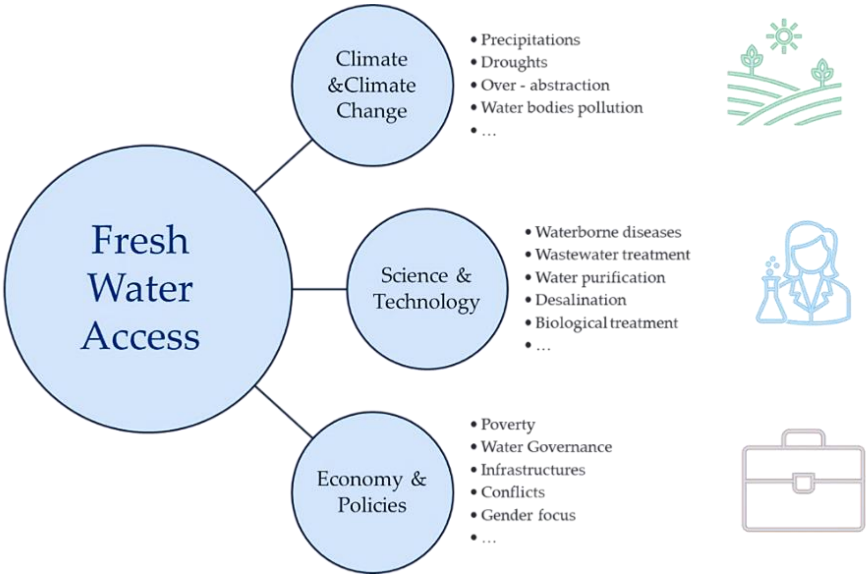


Figure 2. Fresh water access affecting factors and strategies

Fortunately, there is a growing interest related to innovative water sources that could provide long-term water supply security. These unconventional resources comprehend, for instance, reuse of water provided by wastewater treatment plants or desalination technology that grants safe drinking water. Therefore, collaboration with the scientific community is essential to conduct further research in these technologies aiming to minimize the global water access problem. Innovation and continuous scientific and technological development are crucial for ensuring the access to safe water.

1.2. Wastewater treatment

According to the European Investment Bank (EIB), around 380 billion m^3 of municipal wastewater is generated annually and this amount is expected to grow by 51% by 2050 [10]. Regarding wastewater management, it is estimated that high-income countries treat around 70% of wastewater streams, 38% is treated in upper middle-income countries and 28% in lower middle-income countries. However, for low-income countries wastewater treatment capacity drops drastically, reaching only 8%. Therefore, it is estimated that around 80% wastewaters produced around the world is directly discharged into the environment with no sufficient or efficient treatment [11]. Moreover, according to the United Nations (UN), only 11 % of treated wastewater is reused [12]. Nevertheless, the reuse of treated wastewater is considered to be an important resource that could improve water masses quality and ecosystem health while providing an alternative source of freshwater for human use and subsequently reducing struggle for conventional water supplies [13,14].

Nonetheless, according to the European Commission, Spain is failing to accomplish the requirements imposed by the European Directive for Wastewater treatment (Directive 91/271/EEC). The Directive requires to treat all the urban wastewater before discharge into the natural environment. Recent agreements between the European Council and Parliament have expanded the directive's scope to include agglomerations with a population equivalent (p.e.) of 2,000 or more [15].

According to Spanish Government, more than 500 municipalities still do not reach the quality standards imposed by the European Directive

(Directive 91/271/CEE). Specifically, around 21.5% of the municipalities bigger than 2,000 p.e. do not reach the Directive requirements. Also, Spain has more than 8,000 municipalities which 72% of them have less than 2,000 p.e. where the situation is even worse [16]. Wastewater treatment for big metropolises has been prioritized over the years and, therefore, for small settlements wastewater management remains quite challenging. In general, wastewater facilities imply elevated implementation and operational expenditures (CAPEX and OPEX) that these small and dispersed settlements cannot afford.

On the other hand, the Spanish Government, aligned with the Circular Economy Strategy, have developed a ten-point action plan to be achieved by 2030 which is part of a broader strategy related to the Recovery, Transformation, and Resilience Plan (PRTR) This mentioned plan recognizes needs such as improving the efficiency of water use, reduce water consume for households and industrial and technological process, development of water policy instruments, etc. Specifically, this document establishes the important goal of reaching a 10% improvement in water reuse efficiency by 2030. Also, in 2021, a National Plan for Wastewater Treatment, Sanitation, Efficiency, Savings and Reuse (DSEAR) Plan was ratified. Some of the main aims of this DSEAR Plan are the improvement of sanitation issues and wastewater treatment in all urban settlements, to promote measures to reduce plastic pollution or to implement the state of the art scientific and technological innovations for water and wastewater treatment facilities [17].

The given global and local scenario is the confirmation that technological innovation and the adoption of advanced processes is the key to overcome wastewater treatment issues. Moreover, following the Circular Economy path, in a global situation where world´s population is still growing and natural resources are more limited every day, water treatment technology is a necessary tool to enhance not only water access and quality but resource recovery from wastewater.

Essentially, the wastewater treatment process normally involves successive steps: i) pre-treatment including to remove large suspended or floating solids; ii) primary treatment that aims to remove organic and inorganic solids using physicochemical and chemical processes such as sedimentation, coagulation, flocculation and flotation; iii) secondary treatment that oxidate dissolved organic matter using chemical and biological treatments and iv) tertiary treatment where physical and chemical processes as oxidation, carbon activated, filtration, ozonation, etc. are employed to adequate and sanitize the treated water depending on its final use [18].

Consequently, there is a wide range of water treatments adaptable for every specific need such as physicochemical and/ or biological treatments, electrochemical processes or membrane technology-based systems depending on wastewater stream properties and the destiny of the treated effluent. Even though traditional treatments are still used due to its simplicity and lower implementation and maintenance costs, advanced technologies, such as membrane technology, could retain not only solids and nutrients as phosphorous and nitrogen, but they can also eliminate pathogens. Due to the exceptional water quality achievable, membrane technology has been effectively implemented for tertiary treatment. Considering the current quality standards for effluents from membrane processes coupled with the growing interest in recovering valuable compounds from wastewater streams, membrane-based systems have garnered extensive significance in recent times [19]. Moreover during the last decades, membranes have been actively implemented as part of secondary treatments presenting an efficient performance that complements and/or improves the conventional activated sludge processes coping with flow and composition fluctuations in the wastewater stream [20,21].

1.3. Membrane Technology

A membrane is defined as a physical semipermeable barrier that allows to separate two different phases and permit the selective transport through it. Transport through membrane can be merely physical but also can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient (Figure **3**).

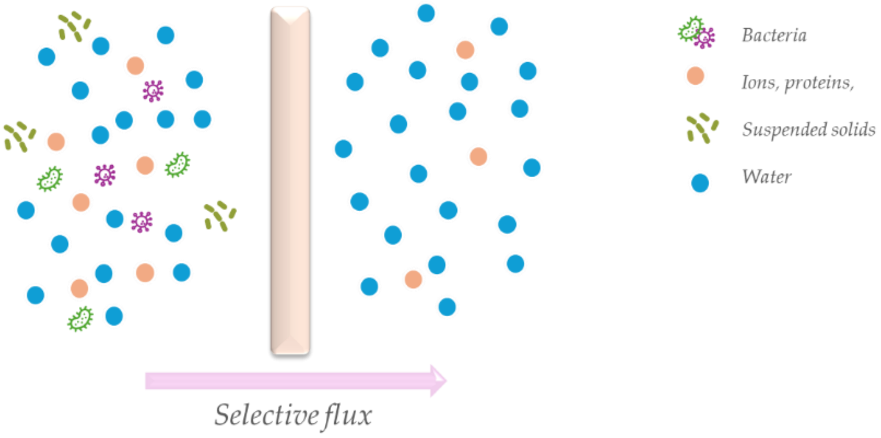


Figure 3. Membrane performance outline

Membrane-based technology is a very mature and extensively employed technology, due to its versatility and high removal efficiency, for numerous varieties of technical, medical and industrial processes including drinking water production, wastewater treatment or desalination [22–26].

There is an extensive diversity of membrane classification regarding diverse membrane properties such as membrane structure, membrane configuration or driving force (Figure 4). Regarding membrane material, membranes can be categorized into polymeric or organic membranes and inorganic membranes. Polymeric membranes are widely used because their fabrication is relatively easy and economical and permits a wide range of membrane pore sizes. Most used polymers on membrane manufacturing are cellulose acetate, polytetrafluoroethylene (PTFE), poly(vinylidene fluoride) (PVDF), polypropylene (PP), polyethylene (PE), polycarbonate (PC), polysulfone/poly(ether sulfone) (PES) and polyamide (PA). However, polymeric membranes present certain limitations related to pH and temperature range, chlorine tolerance, etc. On the other hand, inorganic membranes present higher mechanical strength and chemical and thermal stability, tolerating more extreme performance conditions. Some materials used on inorganic membranes manufacturing are borosilicate glass, pyrolyzed carbon, zirconia/stainless steel, or zirconia/carbon. However, they are also fragile, and their manufacturing is expensive compared to the polymeric membranes. [27,28].

Membranes are assembled into membrane modules which present different configurations:

- *Tubular modules.* Due to their large internal diameters, are adequate to treat streams that contain large particles. However, these tubular membranes need large floor space to operate.
- *Hollow fiber*. This module configuration endures higher backpressure. Also, these modules have higher surface area/volume.
- *Flat sheet*. This is a configuration where a flat sheet membrane is attached to both sides of a flat plate forming a sandwich-like module with spacers in between. This configuration allows an easier cleaning and maintenance.
- *Spiral wound*. These modules are formed of two flat membrane sheets which are separated by a spacer, where the active membrane sides face away forming and envelope-like configuration. Also, these membrane envelopes are separated by feed spacers and are attached to a permeate tube where the permeate is collected. The main advantage of these modules is that they present high surface area/volume ratio.

As Figure 4 shows, membranes can also be classified according to the type of driving force required for the separation to occur. Generally, pressure driven membranes are the most employed membrane for a variety of membrane systems. Concerning pressure driven membranes, separation is achieved by applying external pressure to overcome the hydraulic resistance of the membrane, pushing in this way a fluid through the membrane. This process selectively allows certain substances to pass while others are retained, primarily based on differences in particle size, charge, or chemical characteristics. In Table 1 the more important membrane characteristics of the pressure driven membranes such as membrane structure, separation principles, membrane permeability or work pressure are shown. As Table 1 shows, when the membrane pore size is bigger, the hydraulic resistance of the membrane will be smaller, and consequently, the external pressure required will also be smaller. Usually, pressure driven membranes are classified as high-pressure membranes (reverse osmosis (RO) and nanofiltration (NF) membranes) and low-pressure membranes (ultrafiltration (UF) and microfiltration (MF)), according its exclusion sizes and working pressure [28,29]

MF and UF membranes present a porous structure, retaining components due to sieving mechanism. Then, for these membranes the separation mechanism depends on membrane pore size and molecular weight cut-off (MWCO). NF and RO membranes present both porous and dense layer forming an asymmetric composite structure. For NF membranes, separation mechanism is due not only to a sieving effect, but it is also affected by electrostatic interactions. However, for RO membranes the separation principle is based on the solubility and mobility of the solutes. [30,31]

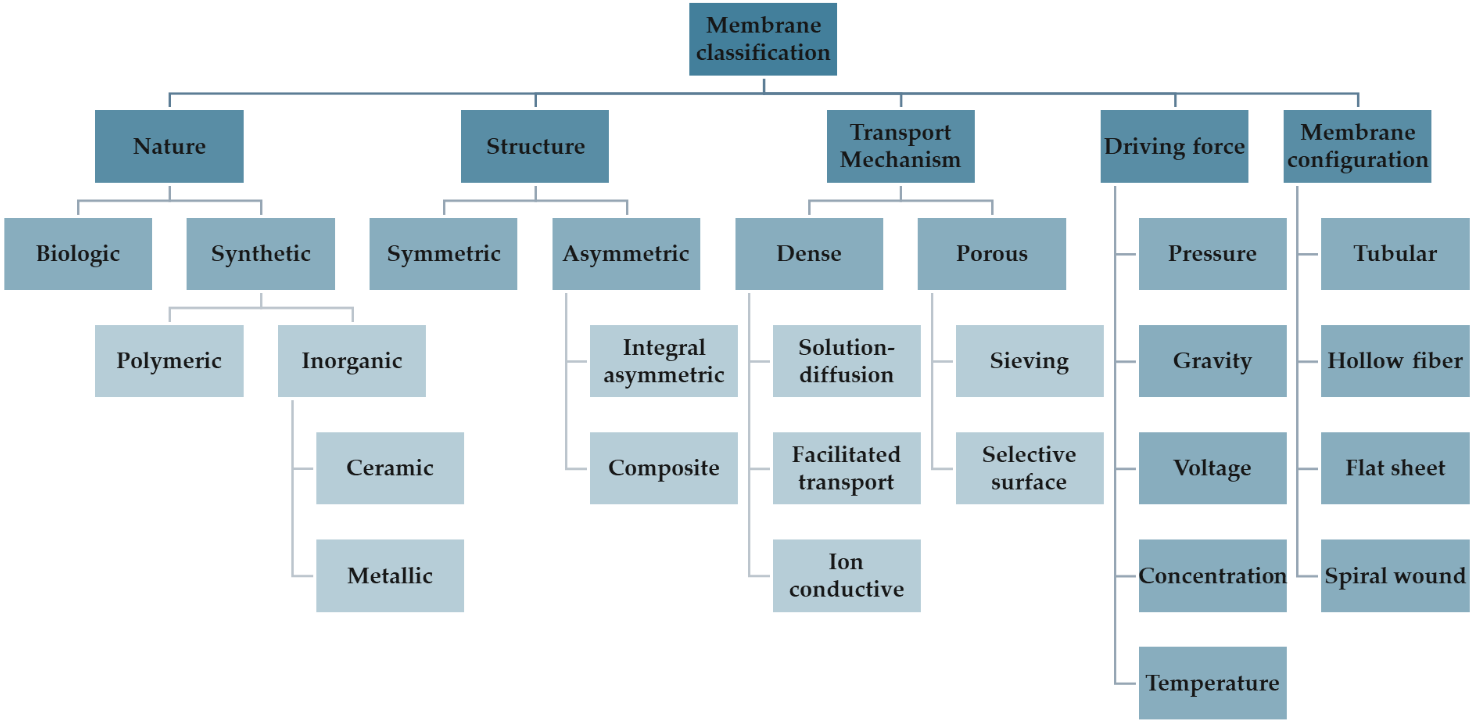


Figure 4. General membrane classification

Table 1. Pressure driven membranes

[30–33]

	Structures	**Separation principle**	**Thickness (μm)**	**Pressure difference**	**Hydraulic permeability (L m^{-2} h^{-1}bar^{-1})**	**Pore size**	**Rejection capacity**
MF	Porous symmetric; or asymmetric	Sieving	10-150	0.1-2	> 1000	0.1-10 μm	Suspended solids, bacteria
UF	Porous asymmetric	Sieving	150-250	1-10	10-1000	0.01-0.1 μm	Macromolecules, bacteria, virus, proteins, polysaccharides
NF	Asymmetric composite	Sieving and charge effect	150	10-25	1.5-30	0.001-0.01 μm	Mono-di and oligosaccharides, polyvalent ions, bacteria, viruses
RO	Asymmetric composite	Solubility and mobility	150	15-80	0.05-1.5	<0.001 μm	Monovalent ions

1.3.1. Membrane bioreactor systems

Membrane bioreactor systems (MBR) could be defined as hybrid processes that combine biological treatment along with pressure driven membrane (MF and UF membranes) for wastewater treatment [34].

Traditionally, one of the most used secondary wastewater treatment is conventional activated sludge (CAS) consisting in the removal of soluble organics compounds using several microbial processes such as aerobic biological oxidation, nitrification–denitrification, etc. [35]. However, the use of MBR systems instead of CAS offers various advantages. The use of membranes allows the MBR to operate at higher volumetric loading rates than CAS systems, leading also to smaller space requirements for the facilities because it eliminates the need of other processes encountered in conventional wastewater treatment facilities like secondary clarification or tertiary filtration (Figure 5) [36,37]. In addition, MBR provides higher removal efficiency regarding pollutants, nutrients, microorganisms and suspended solids due to the use of membranes [38,39].

Depending on membrane configuration, MBR may be categorized as follows: a) submerged; b) external submerged; and c) side stream MBR (Figure 6). As Figure 6 shows, in both submerged configurations, membranes are directly placed on a sludge tank. However, on the side stream configuration, membranes are placed outside the biological tank and mixed liquor is pumped into the membrane system [40].

Submerged configuration is widely used due to its simpler configuration and, in general terms, lower overall costs. The side stream configuration presents higher energy consumption imputable to the additional pumping needs. In fact, energy saving for the use of submerged MBR is between 10 to 25 times compared to the use of side stream MBR systems [40–42].

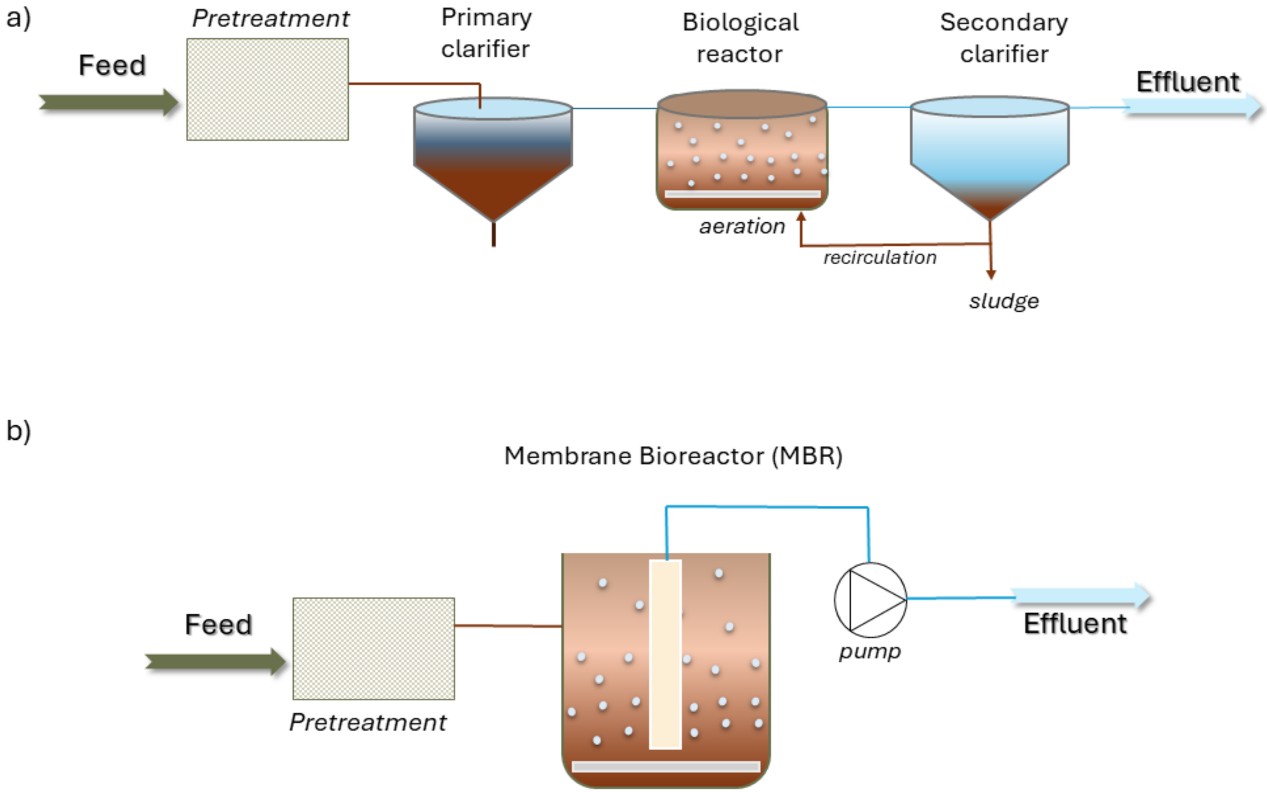


Figure 5. a) Conventional Activated sludge. b) Membrane bioreactor

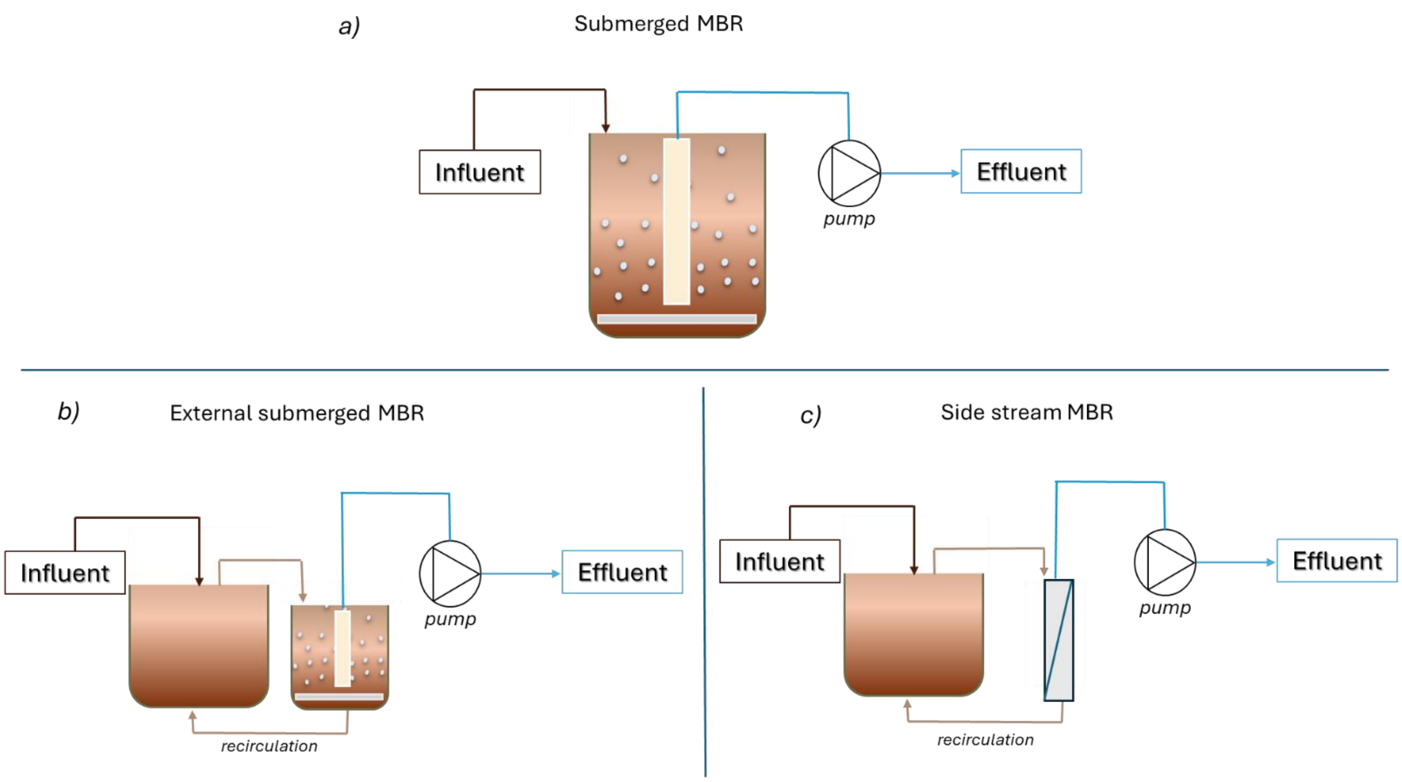


Figure 6. Types of MBR system depending on membrane configuration. a) Submerged MBR; b) External submerged MBR; c) Side stream MBR

Diverse types of membranes are used for MBR systems. Depending on the intrinsic membrane configuration, membranes used for these processes are a) flat sheet (FS); b) hollow fiber (HF) and c) tubular membranes. Membranes configurated as FS and HF are the most used on submerged MBR systems while tubular membranes are often placed into vessels for their use on side stream configuration [43] (Figure 7).

Figure 7. Flat sheet microfiltration cartridge. b) Hollow fiber ultrafiltration module.

The estimation of installed membranes in MBR facilities are around 60% of HF membranes and 30% of FS membranes. According to membrane pore size, most of HF membranes are UF membranes while the commercial FS membranes might be UF or MF membranes [37,44].

Due to its different configuration HF and FS membranes may present different advantages and drawbacks. HF membranes are particularly affected by braiding caused by long fiber and/or hair. Also, sludge could be accumulated especially around the lower part of the membrane module reducing water and air flow. However, HF membranes present higher active area than FS membranes. Also, during membrane operation, HF may have relaxation and/or backflushing periods. On the other hand, FS membranes are more robust and less prone to suffer from braiding. However, fouling tends to accumulate between membrane plates and could block the space between modules forming the membrane rack. During its operation, FS commercial membranes, normally, cannot be backflushed and, also, present higher aeration requirements (Table 2) [37,45].

Table 2. Advantages & disadvantages depending on membrane configuration

	Flat sheet membrane	**Hollow fiber membrane**
Advantages	Robust Simple system and process control Handy manual cleaning Low frequency of cleaning	Back flushing High specific surface area Lower aeration requirements Possibility of automatic cleaning
Disadvantages	Less active area per m^3 No backflushing Higher aeration requirements	More susceptible to clogging No manual cleaning More complex system Poor turbulence promotion

Polymeric membranes are the most common membranes used in MBR systems. Regarding membrane material, most used polymers in MBR membranes manufacturing are: i) PVDF; ii) PES; iii) PE and iv) PP. Approximately, half of the membrane modules implemented on MBR systems are made of PVDF, followed by PES and PE membranes [46].

1.4. Membrane fouling

Even though membrane technology is widely used due to all its advantages, it also presents some significant obstacles. The main drawbacks related to membrane performance, that at the same time increases the OPEX, have been identified to be energy consumption, membrane fouling and membrane replacement rate [47–50].

Membrane fouling may be defined as the deposition and accumulation of organic, inorganic and biological substances affecting the membrane pores and surface, which increases the hydraulic resistance of the membrane, affecting membrane performance [51]. As Figure 8 shows, there are different type of membrane fouling mechanisms [45,52]:

- Cake layer formation: foulants remain on the membrane surface creating a layer.
- Pore blocking: partial or total blocking of the pores, depending on if the pore is completely obstructed by foulants or not.
- Internal pore blocking: foulants smaller than the pores partially block the pore canal narrowing them.
- A combination of them.

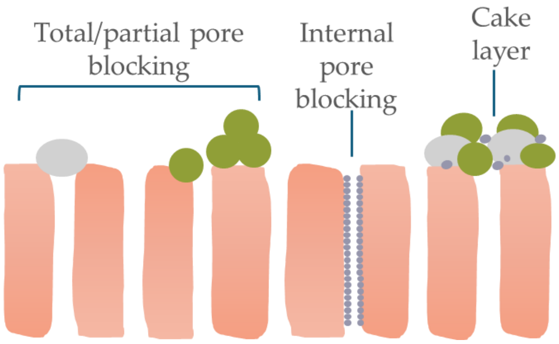


Figure 8 Fouling mechanisms

Depending on the type of foulants involved in the fouling formation process, fouling may be classified as [53,54]:

- Inorganic fouling due to deposition of minerals, salts, oxide, etc.
- Organic fouling due to the deposition/adsorption of proteins, polysaccharides, etc.
- Colloidal fouling due to particle deposition.
- Biofouling, which consists of microorganisms placed on the membrane surface.

Even though MBR system is well known as an effective wastewater treatment process, this technology still faces some difficulties that need to be encountered. Membrane fouling is, in fact, one of the major problems that a MBR system faces [55,56].

The fouling affecting MBR systems could be classified as biofouling, organic fouling and inorganic fouling [57]. Biofouling is primarily caused by bacteria and the products they generate, such as soluble microbial products (SMP) and extracellular polymeric substances (EPS) [58]. Biofouling represents the most significant type of fouling affecting membranes in MBR systems [59–61]. Organic and inorganic fouling found in MBR systems is produced by the organic and inorganic compounds present in the treated wastewater such as humic and fulvic type substances, proteins and polysaccharides and salt molecules [62,63]. Membrane fouling increases the need of chemicals consumption due to membrane cleaning and, eventually, creates the necessity of membrane replacement, which considerably increases MBR OPEX [52,56]. Moreover, whilst the energy required for regular MBR operation is around 0.5 to 1 kWh/m^3 (estimated for full-scale facilities), the transmembrane pressure (TMP) increase due to biofouling increases the energy consumption by 30%-70% [64].

On the other hand, as Figure 9 shows, several parameters influence fouling development in MBR systems such as membrane type and configuration, foulant characteristics, temperature, aeration, mass ratio, hydrodynamic conditions, maintenance or cleaning strategies [64]. Table 3 summarizes some of the operational parameters that can be controlled to mitigate fouling in MBR systems. However, almost inevitably, fouling normally occurs and detailed membrane cleaning procedures should be established. Basic standard cleaning procedures implemented are a) mechanical cleaning including backflushing, bubbling cleaning or ultrasonic cleaning; or aeration; b) chemical cleaning using acid/based cleaning, anti-scaling products or surfactants; c) biological cleaning controlling such as quorum sensing or enzymatic disruption or d) electrical-based cleaning strategies like electro-coagulation and electrophoresis [65–68].

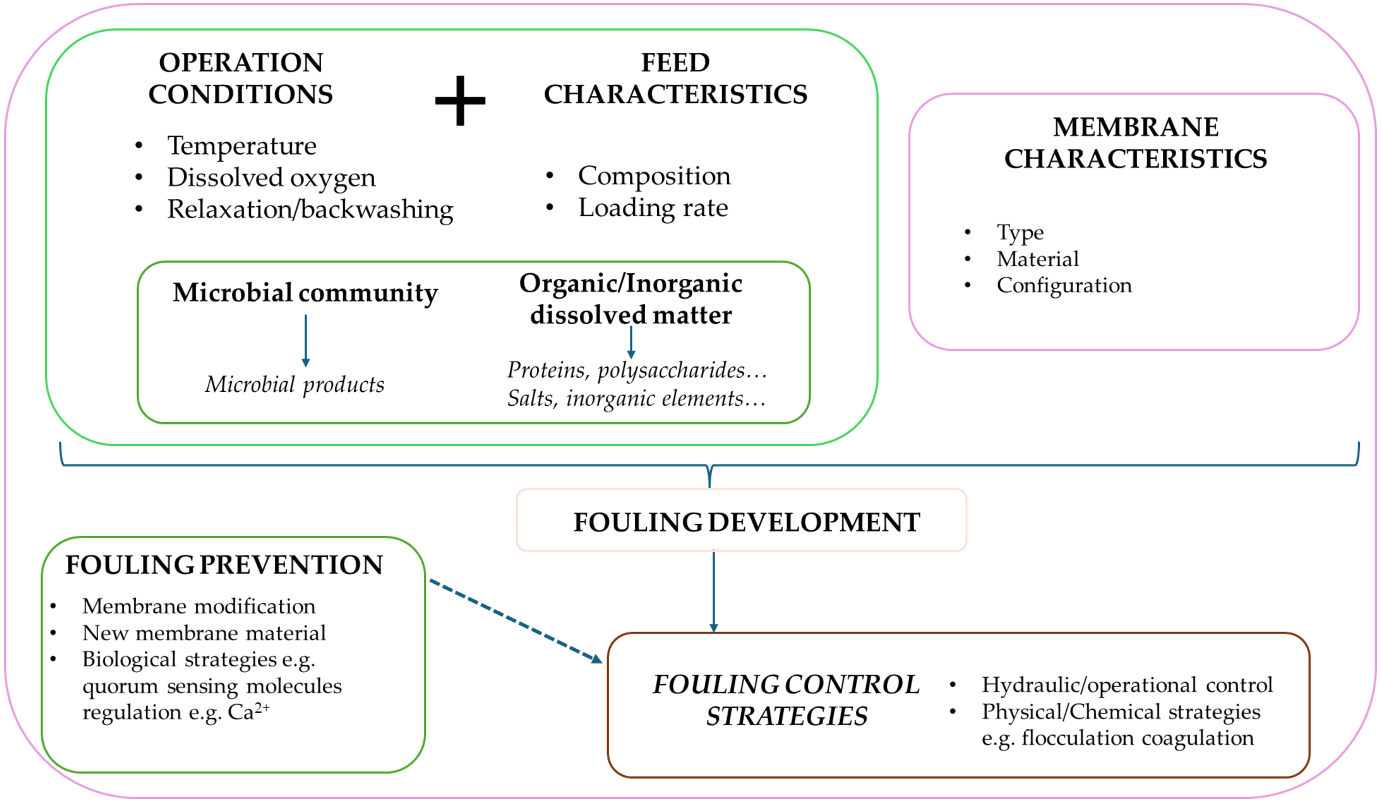


Figure 9. MBR fouling affecting factors

Table 3. Some of the most studied strategies mitigate fouling in MBR
(adapted from [57])

Hydraulic control	**Chemical control**	**Biological control**
• HRT ↓: Sludge viscosity ↑ • Aeration ↑: permeability ↑ cake removing efficiency ↑ cake resistance ↓ • Periodical backwashing: flux↑ total fouling resistance ↓ • Low flux operation; sustainable operation	• Powdered activated carbon: EPS↓ Irremovable fouling ↓ • Flocculation/coagulation: organic matter ↓ • Chemically enhanced backwashing: fouling removal	• SRT↑: bounded EPS↓ SMP ↓ • MLSS ↓: permeate flux ↑ cake layer fouling ↓ • F/M ratio ↓: fouling resistance ↓ • Filamentous bacteria ↓: bound EPS ↓

Membrane fouling is a complex process influenced by the interplay of membrane properties and foulants characteristics (Figure 10). The interactions between the membrane and foulants can be electrostatic and non-electrostatic (hydrophobic, acid-based) or a combination of them [54,69,70]. Additionally, as mentioned above, PES is one of the most used polymers for membrane manufacturing due to its several advantages (wide range of pH and temperature and chemical and mechanical resistance). However because of its hydrophobicity this polymer is, intrinsically, more prone to fouling [71]. Because of this, among the large volume of ongoing research focused on fouling mitigation strategies, the assessment of novel low-cost membranes and membrane surface modification methods have gain importance during the last few years [72–75]. Some specific examples are exhibited on Table 4.

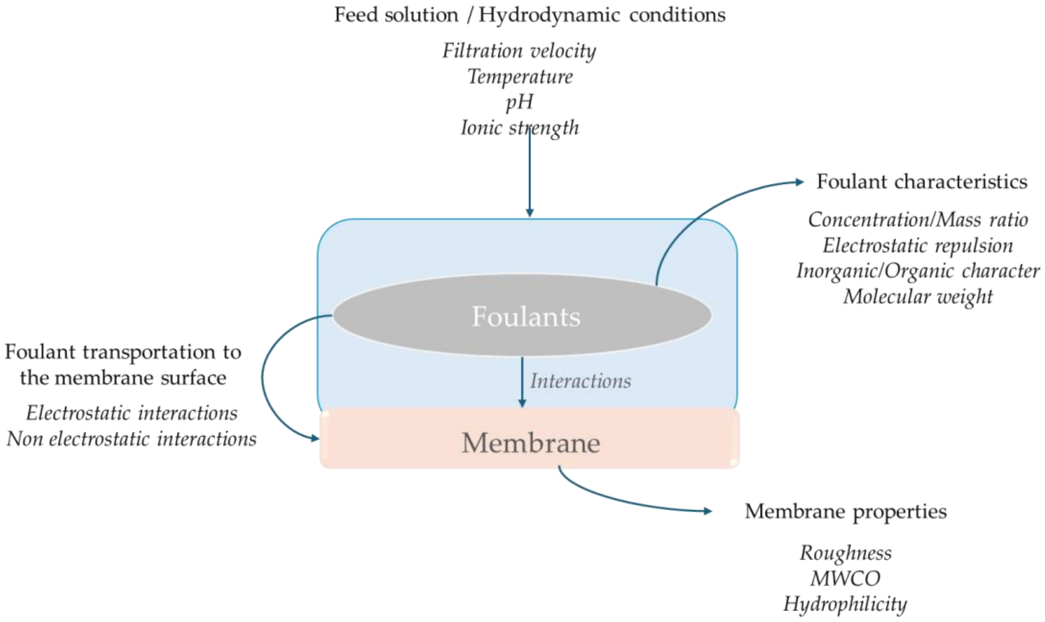


Figure 10. Membrane fouling interactions

Table 4. Surface modifications for polymeric membranes

Surface modifier	**Base polymer**	**Effect**	
Chitosan interfacial polymerization	PA membrane	↑ hydrophilicity ↓ roughness ↓ fouling	[83]
Silver-PEGylated dendrimer nanocomposite membranes	TFC membrane	↑ hydrophilicity ↓ fouling protein / bacteria	[84]
Carboxymethyl chitosan/Fe_3O_4	PES membrane	↑ FRR ↓fouling resistance ↑pure water flux	[85]
Multi-walled carbon nanotubes (MWCNTs) with carboxylic groups (MWCNTsCOOH) and MWCNTs with polyethylene glycol groups (MWCNTs-PEG)	PES membranes	↑ hydrophilicity ↓flux ↑ permeability	[86]
Adsorption-crosslinking process of poly(vinyl alcohol) (PVA)	PES membrane	↑ hydrophilicity ↓ flux ↑ FRR	[87]
Nano-sized alumina (Al_2O_3)	PES membrane	↓ flux decline ↓fouling ↓membrane performance mitigation	[88]
Non-ionic surfactants Triton® X-100 and Pluronic® F108	PES membrane	↑hydrophilic ↓foulants' adsorption	[89]
Electrostatic self-assembly of polyethyleneimine (PEI)	PA membrane	↑fouling resistance ↑ hydrophilicity ↑fouling resistance and the ↑ surface hydrophilicity	[90]
Tripolyphosphate-crosslinked chitosan (TPP-CS)	PES membrane	↑ hydrophilicity ↑ permeability	[91]
Polydopamine (PDA) deposition followed by poly(ethylene imine) (PEI) grafting	PES membrane	↑ Salt rejection ↓ pure water flux	[81]
Co-deposition of catechol (CCh) and PEI	PP membrane	↑Antibacterial ↑antifouling BSA	[92]

There exist multiple membrane modification techniques. However, in general terms, this process could be classified as [71] (Figure 11):

- Bulk modification of polymer prior to membrane preparation. The chemical modification of polymers is usually focused on providing the membrane an antibiofouling character.
- Surface modification after membrane preparation. The surface of the membrane is modified to improve membrane hydrophilicity and enhance water permeability and resistance to fouling using techniques as:
  - Membrane coating: simple surface modification that can be conducted under mild conditions. The coating process involves depositing a thin layer on the membrane surface, usually by immersing the membrane in a coating solution (dip coating). These coatings are linked to the membrane through weak interactions so it may be gradually wash away.
  - Membrane grafting: this modification of membrane surface involves the chemical attachment of compounds by covalent bonds making the modification more stable and enduring.
- Polymer blending: This technique combines two or more polymeric materials or inorganic nanoparticles in a casting solution producing a membrane with tailored properties.

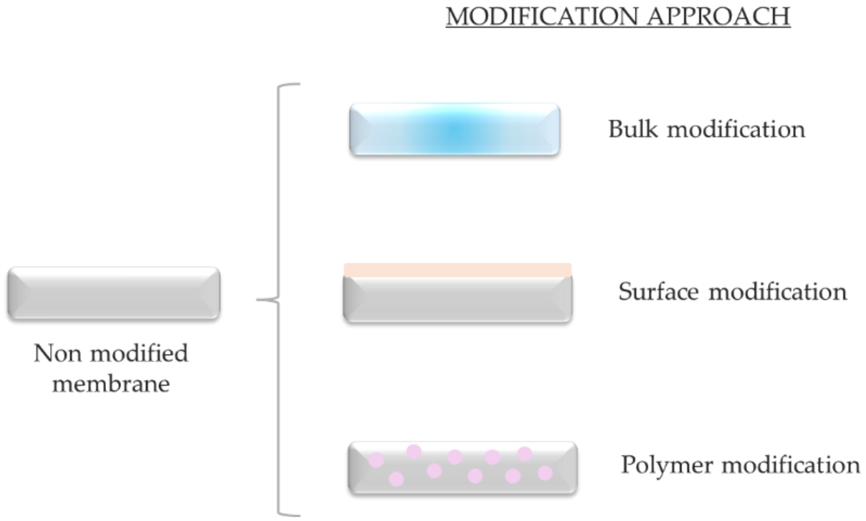


Figure 11. Membrane modification outline
(based on [71])

Coating procedure has been pointed out as preferred surface modification process because its i) simplicity; ii) reproducibility; iii) environmentally friendly behavior and iv) cost effectiveness [76,77]. Particularly, dip-coating is a simple, yet effective, method for modifying membrane surface.

Several studies have investigated the modification of membrane surfaces using various compounds and/or particles to enhance hydrophilicity and reduce fouling agent adsorption. These modifications often employ chemical compounds like i) polyethylene glycols (PEG´s) [78]; ii) nanoparticles [79]; iii) polyaniline [80] or iv) novel bio-inspired materials like polydopamine (PDA) [81,82].

However, eventually, membrane fouling occurs, and membrane replacement is needed. Generally, considering that membrane lifespan for MBR membranes is between 5 to 10 years, membrane replacement rate contributes to increase OPEX by 10-12% in MBR systems [93,94].

Besides the implementation of fouling prevention and mitigation strategies such as pretreatment, cleaning strategies and membrane modification, more recent trends must also be considered. To cite an instance, the use of recycled membranes may be an interesting cost-effective alternative to be used for membrane replacement in MBR systems instead of using brand new membranes [95].

1.5. EoL RO desalination membranes management

1.5.1. Desalination

For many years now, brackish and sea water desalination using membrane technology have been extensively used. It has been specially developed at geographical regions and/or industrial and technological processes where there exist a lack of water [96,97]. Desalination demand has continued to increase over the years, due to the freshwater scarcity, to fulfill water demand [98]. Desalination membrane systems usually consist on RO, NF and also electrodialysis (ED) membranes or a combination of these membranes with UF and/or MF membranes that are normally used as a pretreatment [99].

1.5.2. Reverse Osmosis membranes

Reverse Osmosis facilities represent the wider implemented technology among desalination technology installed worldwide, producing the 69% of the total desalinated water [99]. These RO desalination systems achieve extraordinary permeate quality presenting lower CAPEX and OPEX compared with other desalination methods [100]. Currently, total production of desalinated water using RO technology is estimated to be between 90 to 125 million m^3 day^{-1} [98,101]. According to economic forecasts, the growth of RO desalination is expected to increase significantly. The compound annual growth rate (CAGR) is currently estimated to be around 7.5%, but it is projected to reach over 12% by 2033 [102,103]. Moreover, the trend in installed desalination capacity over the last decades shows an increasing rate, expected to exceed 200 million m^3 per day by 2030 [104].

At the moment, most used commercial membranes for desalination processes are polymeric thin film composite (TFC) membranes in a spiral-wound configuration (Figure 12) [105,106]. Most RO membranes used are PA-TFC membranes [107,108]. Additionally, these membranes present an active polyamide (PA) layer (~0.2 µm), a porous layer made of polysulfone (PSF) (~40 µm) and another layer of polyester (PET) (~ 100 µm) that works as a mechanical support for the mentioned layers (Figure 13) [95,109].

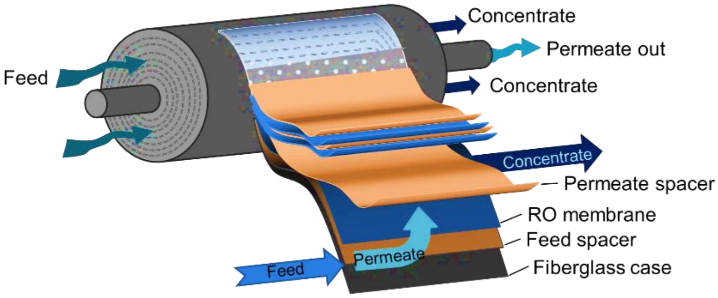


Figure 12. Spiral wound RO commercial module.

From S. Molina [110]

Figure 13. Schematic representation of a TFC-PA RO membrane layer composition and structure

The RO modules, additionally to the membrane itself, present other components such as spacers, permeate collector, fiberglass case, etc. made of polymeric compounds (e.g. polypropylene (PP), polyester (PET), acrylonitrile butadiene styrene (ABS), or glass fiber (Figure 14) [95,111].

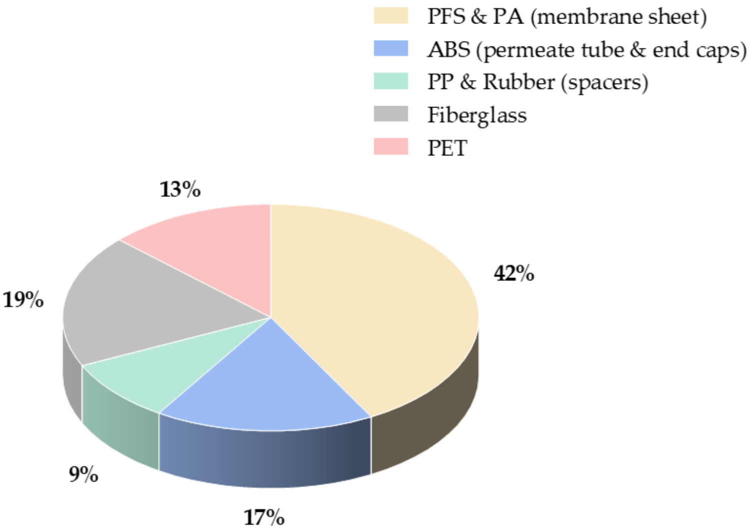


Figure 14. Membrane module components

However, the miscellaneous composition of the membrane modules makes them difficult to be managed properly using some other routes than landfill disposal or incineration.

1.5.3. End of Life (EoL) membranes management: membrane recycling

Life span of RO membranes is generally estimated to be between 5 to 10 years [95]. Related to this, the estimated annual membrane replacement rate is 20 % in the case of sea water desalination and 5% of RO membranes for brackish water desalination [112]. Most of the countries manage the disposal of EoL membranes according to their own legislation, which generally implies that most of the EoL membrane modules end up in landfills following the conventional model of linear economy [113]. It is expected that, by 2055, more than 30,000 tons of EoL-RO membranes will be generated and placed into landfills worldwide [114].

However, this management option directly collides with the European Union principles associated with Circular Economy [115–117]. This includes the collision with the European Green Deal developed by the European Commission that remarks as priorities to reduce water pollution, to boost water reuse, improving waste management and avoiding, as much as possible, disposal in landfills [6,118,119]. Additionally, current landfill disposal tendency also elevates the greenhouse emissions, causes disturbing odors and generates visual impacts [120]. Also, it is important to remark that membrane landfill disposals produce a loss of energy and materials that could be used as a resource, diminishing raw materials extraction [121].

Related to EoL RO membranes management, several alternative scenarios to landfill disposal have been considered in academia concluding that landfill disposal was the least environmentally friendly option [111]. As Table 5 shows, the selection of the most suitable management alternative will depend, basically, on the state of the EoL RO membrane and its possibilities of recovery (Figure 15):

- Direct reuse: membrane module remains intact. It seeks to recover permeability and rejection capacity of the RO membrane performing a chemical cleaning and avoiding the damage of the PA active layer [122]. However, when membranes exhibit further physical damage and/or deterioration of the membrane characteristics like salt rejection, they are not suitable for direct reuse, and consequently, alternatives such as membrane recycling must be considered [95](Figure 16).
- Direct recycling: consists in a total or partial elimination of the active PA layer of the EoL RO membranes using oxidizing agents such as NaClO [113,123]. The module remains intact, maintaining the original configuration. Depending on the exposure dose, the membranes obtained will exhibit properties

like NF membranes (1,000-150,000 ppm·h) or UF membranes (10,000-400,000 ppm·h) [123,124] (Figure 16).

- Indirect recycling: When neither direct reuse or direct recycling procedure is possible due to the condition of the EoL RO membrane, the module must be disassembled, and all components are managed separately. Once the membrane flat sheet is extracted from the spiral wound module, it is exposed to the oxidant agent to gain UF-like or NF-like properties, depending on the expected use for the recycled membrane. Extracting the membrane from the module adds versatility to the possible uses of the recycled membrane. Additionally, a variety of membrane modifications could be conducted to optimize the recycled membrane for its new application [125].
- Energy recovery: When none of the abovementioned alternatives is suitable, energy recovery steps up as an alternative to landfill disposal. According to various Life Cycle Assessment (LCA) studies energy recovery, present less environmental impact than landfill disposal [126].
- Landfill disposal: Despite the above mentioned options, landfill disposal still is the most common EoL RO membrane management alternative currently conducted, producing several worrying environmental impacts including greenhouse emissions, toxics leachates or odors and visual impact [120,127].

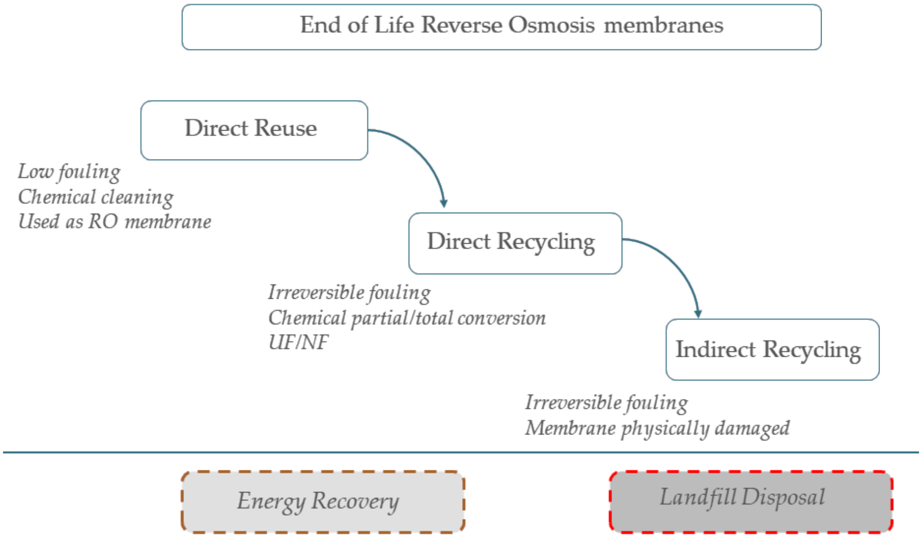


Figure 15. EoL RO membranes management alternatives

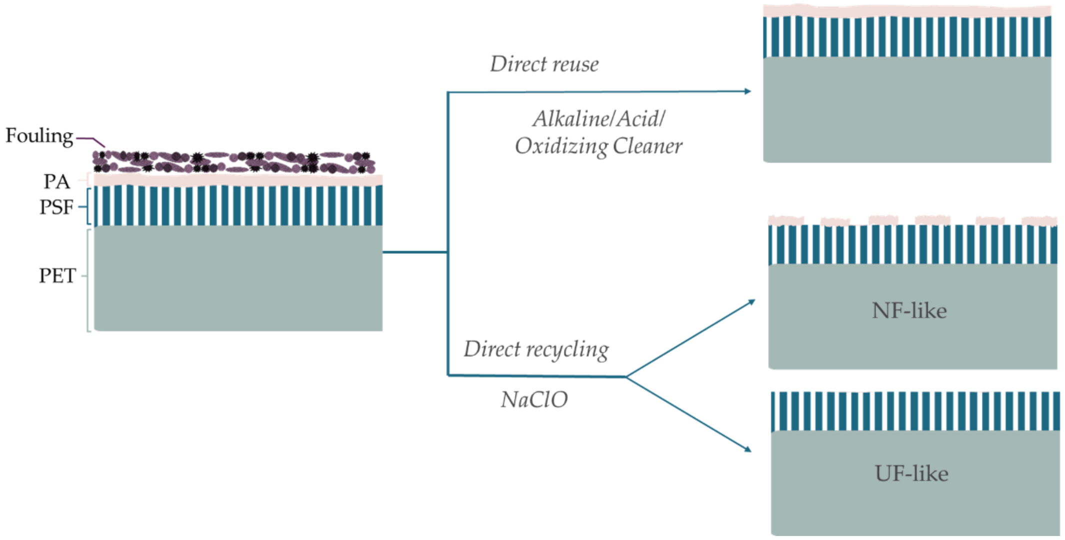


Figure 16. Difference between EoL Ro membrane direct reuse and direct recycling

Table 5. Principal characteristics for EoL RO membrane reuse and recycling processes (Based on [95])

	Direct Reuse	**Direct Recycling**	**Indirect recycling**
	Membrane use for the same/similar process.	Membranes chemical conversion obtaining different type of membranes	Disassembling the modules to obtain separate material for different applications
EoL membrane properties	Salt rejection coefficient (R) > 99%,	Salt rejection coefficient (R) > 99% and low fouling (module weight <25 kg)	High fouling (module weight >25 kg)
Process	Chemical cleaning	Partial/total elimination of PA layer to UF and NF membranes respectively	Individual management of flat sheet membranes and other module components by disassembling the EoL RO module
Strengths	Reduce waste; Extend life span; Lower investment	Reduce waste, new membranes adapted to different processes and needs.	Obtaining materials avoiding the fabrication of new ones and the consume of raw materials
Limitations	Salt rejection and permeability could be diminished	Complex process Not all membranes could benefit from this process	Complex process, obtained material application could be complex due to the lost and/or damage of component properties

1.5.4. Use of indirect recycled membranes

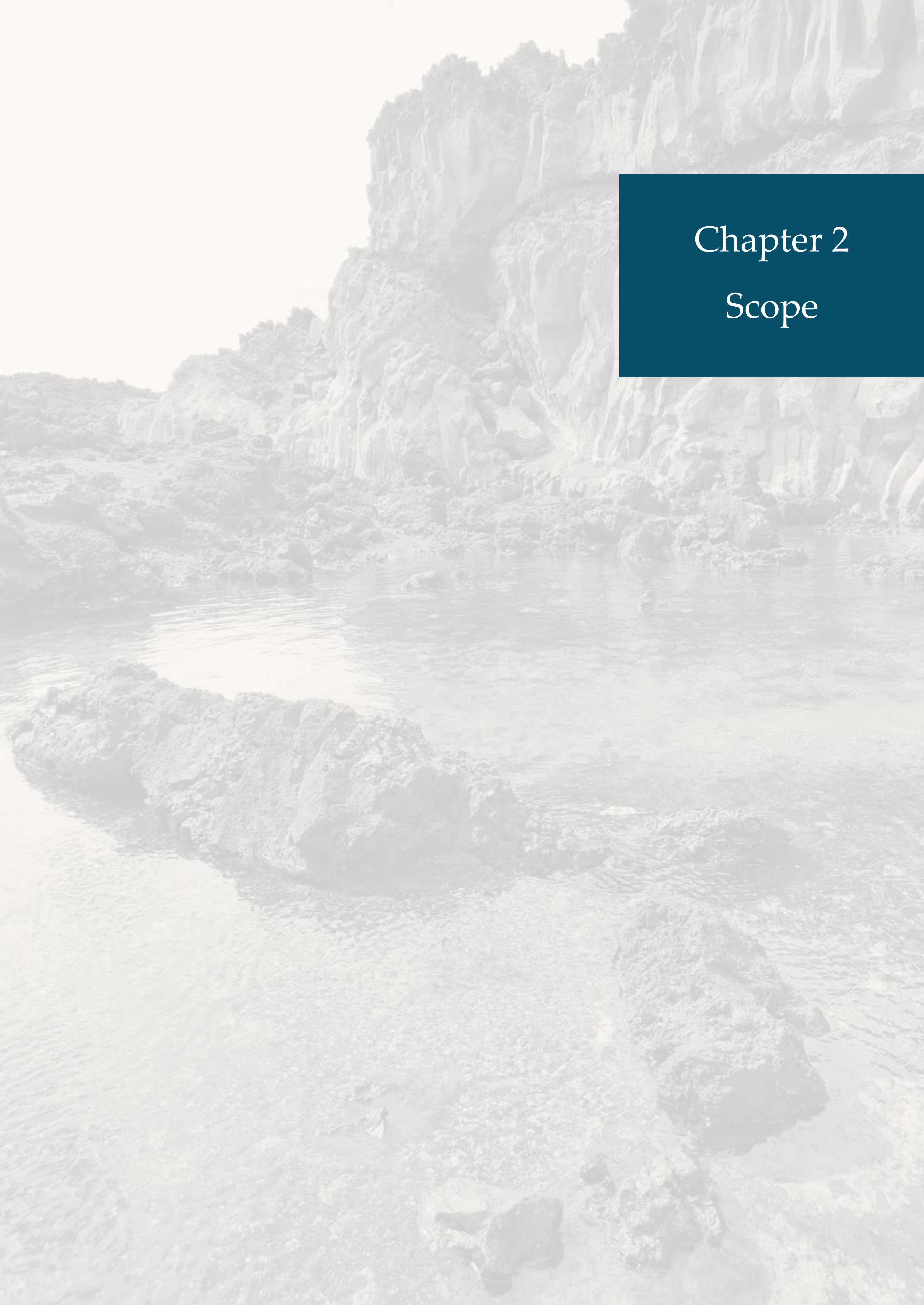
In the last few years, a promising trend of research based on indirectly recycled ultrafiltration membranes (r-UF) that come from EoL RO membranes were developed. These indirect recycled membranes have been successfully used in several membrane processes. J. Morón-López et al., addressed the challenge of cyanotoxin release during water treatment, developing a novel biological system utilizing recycled membranes coming from EoL RO membranes for the removal of microcystins (MC). They developed a recycled-Membrane Biofilm Reactor (R-MBfR) that consisted of MC degrading biofilms placed on the surface of recycled membranes. This study showed that the recycled system not only effectively removes MC but also mitigates the environmental impact of RO membrane waste by extending their functional lifespan [128]. J. Contreras et al. reused internal components of EoL RO modules, including membranes and spacers. These components were repurposed by applying a nanofibrous layer of PVDF through electrospinning on top of the recycled membrane once the polyamide layer is completely eliminated. This newly created material was then utilized in direct contact membrane distillation (DCMD) for brine desalination [129]. In addition, A. Lejarazu-Larrañaga et al., conducted the indirect recycling of EoL RO modules obtaining recycled membrane and spacers that were pre-conditioned using NaClO. Their use was evaluated in two applications: (i) as membrane support for the fabrication of anion exchange membranes and (ii) as polypropylene components for assembling an electrodialysis stack, respectively [125].

Additionally to this, some recent studies of a comparative LCA have been developed. Senán-Salinas et al. entailed a LCA and cost-effectiveness analysis of the recycled membranes compared to the commercial membranes having into consideration as a primordial factor, among others, the permeability of the recycled membranes [117].

In the view of the above issues, the hypothesis of the current research arises as: i) Recycled membranes performance could be comparable with commercial MBR membranes. In this way, they may be considered as an interesting alternative for membrane replacement in MBR systems instead of using brand new membranes; ii) Additionally, membrane surface modification could be an interesting methodology to enhance recycled membrane performance improving its antibiofouling character; iii) For long term operations in MBR systems, both recycled and modified recycled membranes could be successfully implemented.

Chapter 2

Scope



2. Justification of the thesis

This doctoral thesis follows the path of the previous studies carried out by Membrane Technology Research Group at IMDEA Water, regarding the development of a methodology for the recycling of EoL RO membranes for its transformation into NF and UF membranes by direct recycling [130]. These recycled membranes were also tested to validate theirs performance at real-site pilot scale for different applications [131]. However, even though direct recycling is an excellent alternative to landfill disposal or incineration, due to the membrane deterioration extent it is not always possible. Given this scenario, indirect recycling presents itself as an interesting alternative for EoL membranes management [95].

Indirect recycling involves disassembling the membrane module, allowing the individual management of its components. This approach not only enables to separately handle the plastic parts and membranes but also provides the opportunity to reassemble these components in new configurations for their use in different membrane systems. As a result, indirect recycling represents an innovative strategy that supports the transition toward a Circular Economy.

2.1. Research objectives and thesis outline

Giving the abovementioned, the main objective of the present thesis is to validate the use of r-UF coming from EoL RO membranes for its use in submerged aerobic membrane bioreactors (aMBR) in a flat sheet membrane configuration. The following chapters have been organized according to the following sub-objectives addressed during the present work:

Chapter 3: Proof of concept study *(Research developed during a research stay in Centre for Research and Technology Hellas (CERTH), Greece)*

- To assess if r-UF membrane were suitable for working in an aMBR.
- To test r-UF membrane performance.

- To compare r-UF membrane performance to a commercial MF membrane performance in similar working conditions.
- To conduct a preliminary economic assessment of the membrane recycling process compared to the commercial membrane fabrication.

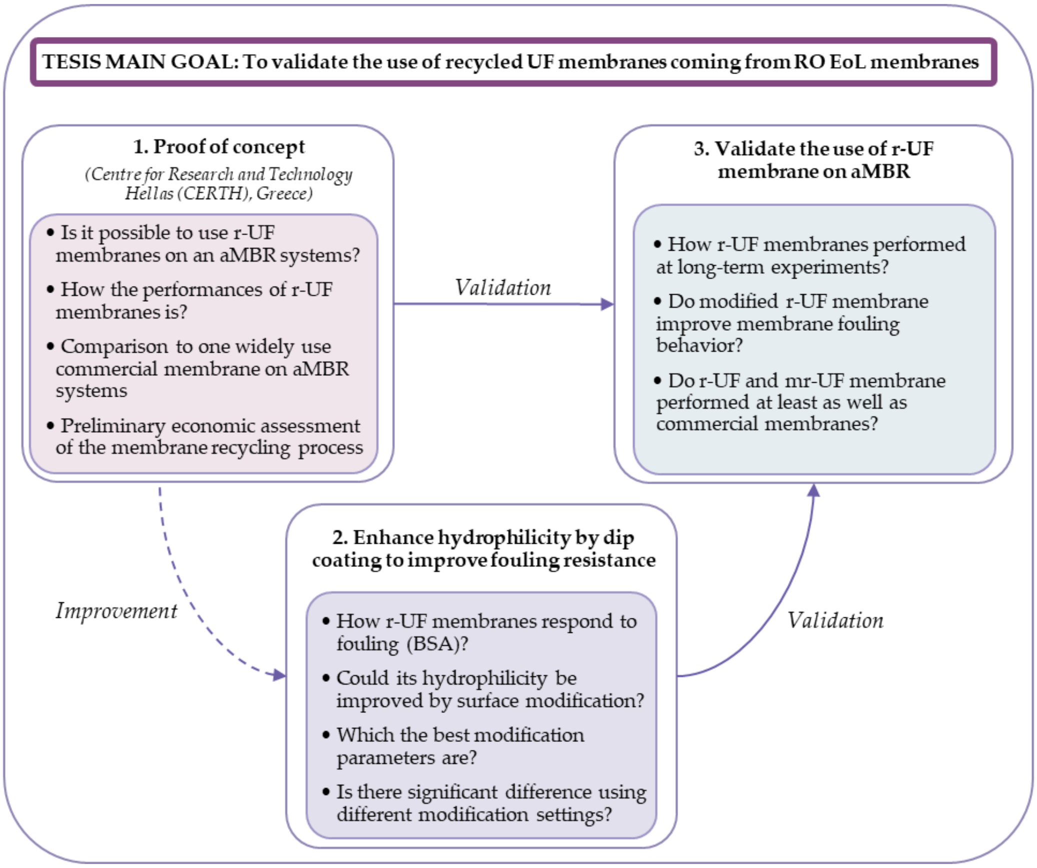
Chapter 4: Recycled membrane surface modification.

- To evaluate if surface modification could be performed in r-UF membrane.
- To improve the hydrophilicity and fouling resistance of r-UF membrane.
- To assess the optimum parameters for membrane modification.
- To study the interaction between the modification factors.

Chapter 5: Validation study.

- To assess if r-UF membrane and modified recycled membrane (mr- UF) were suitable for long-term working periods in MBR.
- To compare the performance of recycled membranes to the performance of commercial UF membranes.
- To evaluate permeate quality, membrane permeability and membrane fouling behavior in recycled MBR systems.

The research framework is represented in Figure 17.



TESIS MAIN GOAL: To validate the use of recycled UF membranes coming from RO EoL membranes

1. Proof of concept

(Centre for Research and Technology Hellas (CERTH), Greece)

- Is it possible to use r-UF membranes on an aMBR systems?
- How the performances of r-UF membranes is?
- Comparison to one widely use commercial membrane on aMBR systems
- Preliminary economic assessment of the membrane recycling process

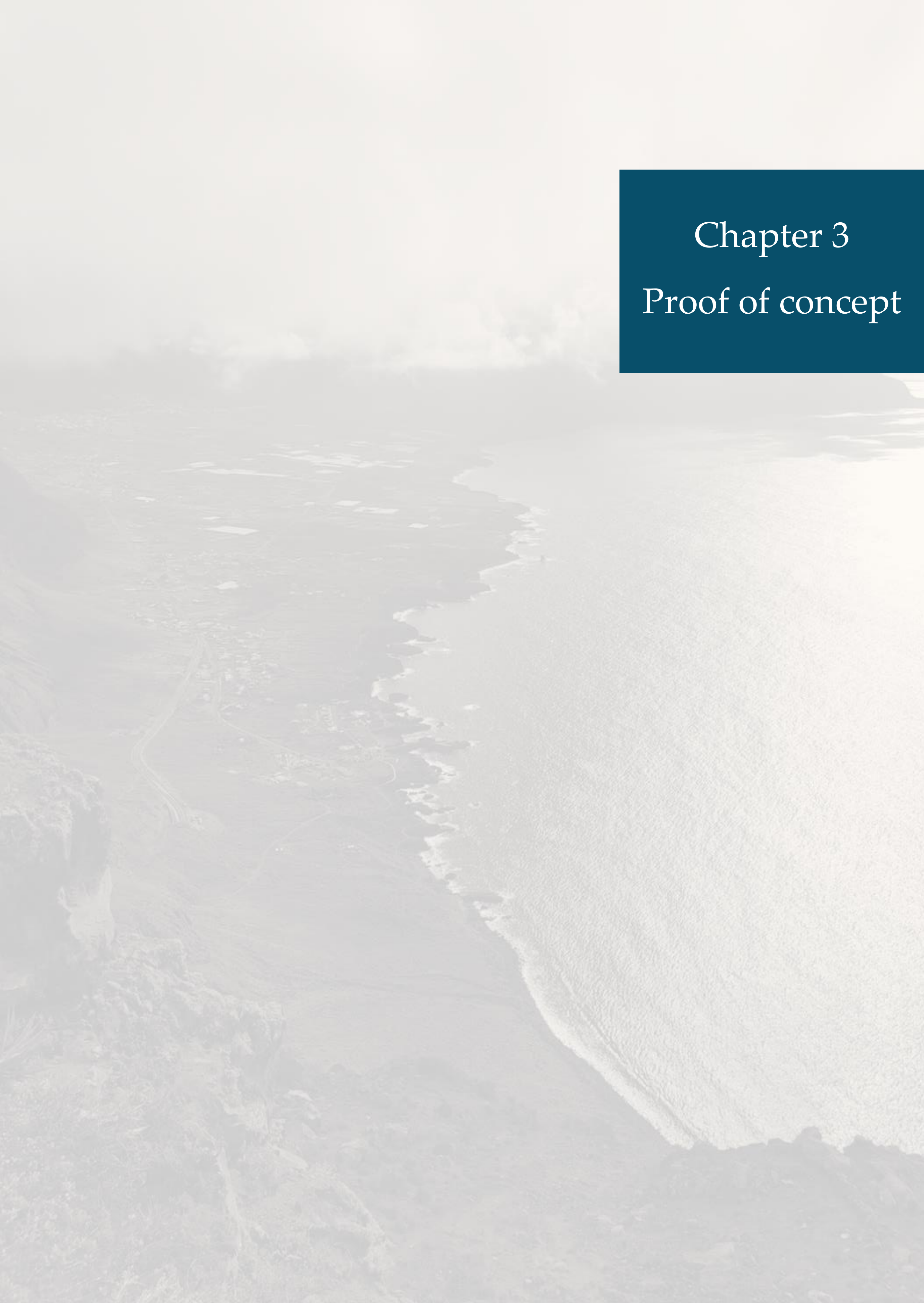
2. Enhance hydrophilicity by dip coating to improve fouling resistance

- How r-UF membranes respond to fouling (BSA)?
- Could its hydrophilicity be improved by surface modification?
- Which the best modification parameters are?
- Is there significant difference using different modification settings?

3. Validate the use of r-UF membrane on aMBR

- How r-UF membranes performed at long-term experiments?
- Do modified r-UF membrane improve membrane fouling behavior?
- Do r-UF and mr-UF membrane performed at least as well as commercial membranes?

Figure 17. Research framework of the thesis



Chapter 3

Proof of concept

membranes

MDPI

Article

A Novel Application of Recycled Ultrafiltration Membranes in an Aerobic Membrane Bioreactor (aMBR): A Proof-of-Concept Study

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Abstract: The use of recycled ultrafiltration (r-UF) membranes, originating from end-of-life reverse osmosis membranes, as submerged flat-sheet membranes in an aerobic membrane bioreactor (aMBR) system is described herein for the first time. A feasibility study of this new approach was performed in a laboratory-scale aMBR system. The r-UF membrane performance was evaluated in terms of permeability, fouling behavior, and permeate quality using a widely used commercial flat sheet microfiltration membrane (c-MF) as a reference. Tests were conducted under steady-flux operation (at 12 and 14 $L \cdot m^{-2} \cdot h^{-1}$) and a variable trans-membrane pressure. Synthetic wastewater simulating urban wastewater characteristics with approx. 0.4–0.5 g/L COD concentration was used as the feed. The obtained results showed that the rejection performance of the r-UF membrane was similar to the performance of the commercial flat sheet microfiltration membrane (c-MF) under comparable operating conditions. Moreover, concerning fouling behavior, the r-UF membrane exhibited higher fouling resistance compared with the c-MF membrane, although the permeability decline rate was lower. Both membranes had comparable fouling mechanisms behavior, with cake layer fouling resistance accounting for approx. 60% of the total fouling resistance. Finally, a preliminary economic assessment pointed out the potential competitiveness of using r-UF membranes for aMBRs (5.9–10.9 $EUR \cdot m^{-2}$) and the scaling-up challenges toward industrial applications.

Keywords: membrane bioreactor (MBR); recycled ultrafiltration membrane; circular economy; recycling; cost analysis

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Citation: Rodríguez-Sáez, L.; Patsios, S.I.; Senán-Salinas, J.; Landaburu-Aguirre, J.; Molina, S.; García-Calvo, E. A Novel Application of Recycled Ultrafiltration Membranes in an Aerobic Membrane Bioreactor (aMBR): A Proof-of-Concept Study. *Membranes* **2022**, *12*, 218. https://doi.org/10.3390/membranes12020218

Academic Editor: Cristiana Boi

Received: 29 December 2021
Accepted: 8 February 2022
Published: 14 February 2022

1. Introduction

During the last few decades, membrane bioreactors (MBRs) for wastewater treatment have gained increasing significance. The installed capacity in 2019 was estimated at over 2×10^7 m^3 per day, including medium- and high-capacity treatment plants [1]. The trend is also positive when economic data are considered. The global market of MBR reached EUR 2.5 billion in 2019 and it is expected to reach EUR 3.5 billion by 2024 [2]. The main reason for this economic growth is the notable advantages of MBRs compared with the conventional activated sludge (CAS) process. The use of membranes for treated effluent separation allows for the MBR to operate at higher volumetric loading rates than CAS systems, leading also to smaller space requirements for the facilities. In addition, an MBR provides higher removal efficiency regarding pollutants, nutrients, microorganisms, and suspended solids due to the use of membranes.

3. Proof of concept

The current chapter presents a proof-of-concept study (Scientific Paper 1), aiming to evaluate the feasibility of using recycled ultrafiltration membranes (r-UF), obtained from EoL RO membranes, as submerged flat-sheet membranes in an aerobic MBR (aMBR) system. The process performance of the r-UF membranes has been evaluated in terms of i) membrane permeability, ii) resulting permeate quality. and iii) membrane fouling behavior. Furthermore, a preliminary cost analysis of the use of r-UF membranes is discussed, to get an insight on the economic feasibility of the proposed application.

3.1. Materials and Methods

3.1.1. Chemicals

The chemicals used for the preparation of synthetic urban wastewater were glucose ($C_6H_{12}O_6$) D(+) glucose anhydrous, extra pure, Ph Eur, BP, USP (Sigma-Aldrich; Baden-Württemberg, Germany); meat peptone (Sigma-Aldrich; Baden-Württemberg, Germany); urea (Urea, ACS reagent grade, Sigma-Aldrich; Baden-Württemberg, Germany); sodium chloride (NaCl reagent grade, ACS, ISO, Reag. Ph Eur, Sigma-Aldrich; Baden- Württemberg, Germany); sodium bicarbonate ($NaHCO_3$, extra pure, Pharmpure®, Ph Eur, BP, USP, Sigma-Aldrich; Baden-Württemberg, Germany); di-potassium hydrogen phosphate anhydrous (K_2HPO_4 for analysis, ExpertQ®, ACS, Reag. Ph Eur, Sigma-Aldrich; Baden-Württemberg, Germany); calcium chloride dihydrate ($CaCl_2.2H_2O$ powder, for analysis, ExpertQ®, ACS, Sigma-Aldrich; Baden-Württemberg, Germany); magnesium sulfate heptahydrate ($MgSO_4.7H_2O$ for analysis, ExpertQ®, ACS, Reag. Ph Eur Sigma- Aldrich, Baden-Württemberg, Germany); and iron (III) chloride hexahydrate, ($FeCl_3.6H_2O$ ACS reagent 97%, Sigma Aldrich, Baden-Württemberg, Germany). The chemicals used for the membrane recycling process and membrane cleaning were sodium hypochlorite (NaOCl 10% w/v, Scharlab; Barcelona, Spain) and ethanol (96% EPR Ph.Eur. Sigma-Aldrich; Baden-Württemberg, Germany). Samples and solutions were prepared using Milli-Q water.

3.1.2. Membranes: description and characterization

The performance of a r-UF membrane was evaluated in terms of i) membrane permeability, ii) permeate quality, and iii) membrane fouling behavior. A c-MF membrane (Table 6), widely used in MBR systems, was also employed as a reference membrane to set the performance benchmarks for the evaluation of the r-UF membrane performance. The c-MF was selected for its widely application on MBR plants in Spain [44].

As Figure 18 shows, the r-UF membranes were obtained by eliminating the polyamide (PA) layer of EoL RO membranes by means of exposure to a NaClO dose of 800,000 ppm·h according to the procedure proposed by García-Pacheco et al. [113]. Membrane transformation was conducted on the whole module at a pilot scale [131]. The recycling process was performed by conducting a passive transformation by immersing the entire modules into the NaOCl solution to chemical attack the membrane surface to eliminate the polyamide layer. Then, the module was disassembled to obtain the membrane samples used in the present study. Coupons (0.06 m^2 area) of the r-UF membrane (12 nm nominal pore size) were used in this study.

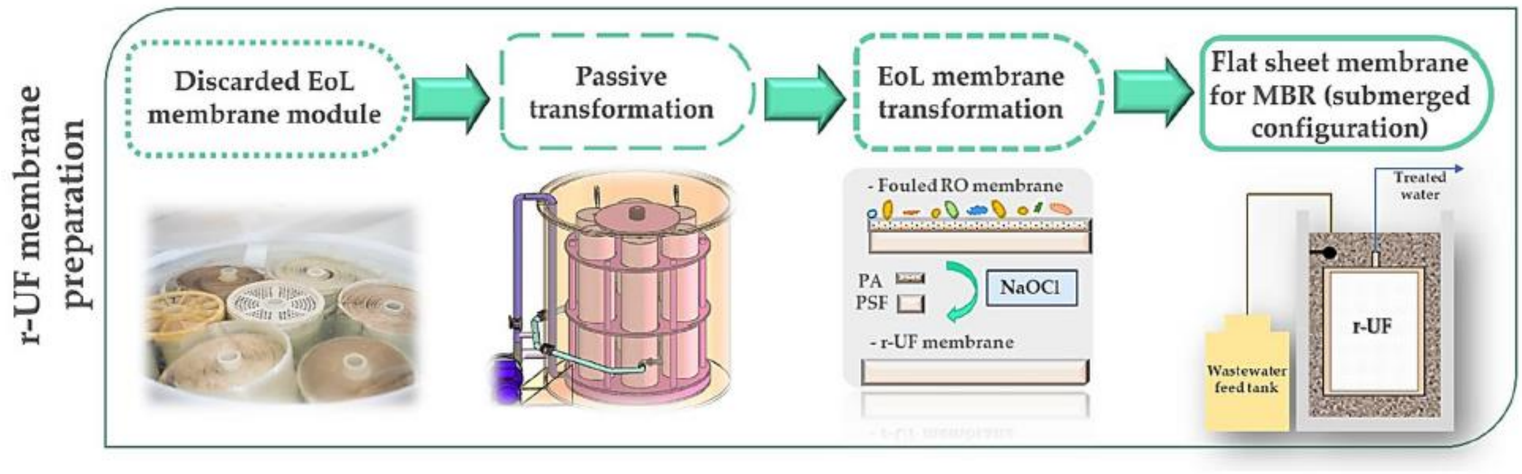


Figure 18. r-UF membrane preparation flow chart

Table 6. Commercial microfiltration (c-MF) membrane technical data

	Membrane Material	Nominal Permeability (20 °C)	Nominal Pore Size	Effective Membrane Area	R_a	R_q	Contact angle
c-MF	Chlorinated polyethylene	1,300 L $m^{-2} h^{-1} bar^{-1}$	0.4 μm	0.11 m^2	184 ± 21 nm	234 ± 26 nm	104 [132]°
r-UF	PES	255 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$	12 nm	0.11 m^2	4.7 ± 0.6 nm [133]	6.3 ± 1.2 nm [133]	68° [134]

3.1.3. Experimental set-up

The experiments were performed in a lab-scale aerobic MBR system that allowed for continuous operation. The MBR tank volume was approx. 18 L and a flat sheet membrane module with an effective membrane area of 0.11 m^2 in a submerged configuration were employed. A piston pump (Fluid Metering Inc.; Syosset, NY, USA) was used for constant flux operation, whereas a pressure transducer recorded the temporal evolution of the TMP. A pH meter with an integrated temperature sensor (713-type pH meter, Metrohm Ltd.; Herisau, Switzerland) was used to monitor the pH and temperature of the bioreactor. The laboratory-scale aMBR was built and set in operation at the Natural Resources and Renewable Energies Laboratory (NRRE) of the Chemical Processes and Energy Resources Institute (CPERI/CERTH; Thessaloniki, Greece). Details of the construction and characteristics of the aMBR unit can be found elsewhere [135].

The membranes were tested in the aMBR unit using synthetic wastewater (SWW) simulating urban wastewater, with an approximate COD concentration of 0.4–0.5 g/L. The synthetic wastewater feed was selected, instead of real municipal wastewater, to minimize the fluctuations in the parameters of the feed and render the operating conditions of the aMBR steady and reproducible regarding its feed characteristics. The feed stream was made by diluting a 50-times-concentrated cSWW with tap water. To avoid early contamination and spoilage, concentrated SWW was pasteurized by placing it in an oven at 50-60 ºC for 5-6 hours. The concentrated SWW composition was as follows: 300 mg/L $C_6H_{12}O_6$; 100 mg/l peptone; 30 g/L CH_4N_2; 28 mg/L K_2HPO_4; 7 mg/L NaCl; 4 g/L $CaCl_2$; 2 mg/L $MgSO_4$; 2 mg/L $FeCl_3.6H_2O$ and 150 mg/L $NaHCO_3$. Initial sludge inoculum was obtained from the Municipal Wastewater Treatment Plant of Thessaloniki. To assess the MBR performance, the transmembrane pressure (TMP), pH and temperature data were monitored and stored daily. The MBR feed and permeate were analyzed twice a week, together with the characterization of the mixed liquor properties. The mixed liquor suspended solids (MLSS), dissolved oxygen (DO), biochemical oxygen demand (BOD_5), and chemical oxygen demand (COD) were determined based on APHA Standard Methods procedures [136]. TP and TN were determined colorimetrically (UV-1700 Spectrophotometer, Shimadzu Co.; Kyoto, Japan) based on DIN 38405 D9

(N- NO_3) and DIN EN ISO 6878 (P-PO_4) methods, respectively, after sample digestion using sulfuric acid/peroxydisulfate and alkaline potassium persulfate. TOC was measured using a TOC analyzer (TOC-5000A, Shimadzu Co.; Kyoto, Japan). DO concentration in the bioreactor was measured by an oxygen probe (Z921, Consort). MLSS were measured via filtration on a Whatman GF/A microfiber glass filter (1.6 μm nominal pore size).

A steady-flux (J, $L \cdot m^{-2} \cdot h^{-1}$) operation and variable TMP were selected to evaluate the membrane filtration performance. The steady-flux operation was achieved by employing a positive displacement (piston) pump (FMI—piston metering pumps), which can retain a steady volumetric flow rate, regardless of the pumping pressure (i.e., TMP). Two different flux values were employed for each membrane, i.e., 12 and 14 $L \cdot m^{-2} \cdot h^{-1}$, to evaluate the performance of the r-UF membrane under at least two different filtration conditions to increase the validity of the drawn conclusions. These flux values were lower compared with the flux values of commercial MBR systems (i.e., 20–30 $L \cdot m^{-2} \cdot h^{-1}$) to avoid operation close to the critical flux values. The critical flux value is defined as the highest initial flux where the TMP values remain rather stable [137], and it is suggested that submerged membranes of MBR systems should operate in the subcritical flux region [138]. Membrane operation was set on cycles of 8 minutes of suction followed by 2 minutes of relaxation. The laboratory-scale aMBR unit was operated at a hydraulic retention time (HRT) of 7 h. Except for the samples necessary for analyses and monitoring, no biomass was wasted from the reactor during the operation for days 1–25 (resulting in a sludge retention time SRT = ∞), whereas for days 26–41, 60 mL/d of mixed liquor (SRT = 233 days) were wasted. Regular measurements of pH, EC, and DO and MLSS concentrations were performed during the whole 41-day experiment to ascertain that the MBR operated under the same operating conditions, achieving pseudo-steady-state conditions. The average values and the SD of the aforementioned measurements were as follows: pH = 7.83 ± 0.18, EC = 942.5 ± 42.4 μS/cm, DO = 1.29 ± 0.24 mg/L, and MLSS = 5.06 ± 0.96 g/L. The low SD of the measurements denoted that the MBR operated under pseudo-steady-state conditions. The permeability decline rate was estimated for different periods with linear regression models. The basic package of R software v.4 was used for the static assessment [139].

The initial experimental goal for each operating stage was to operate under the selected operating parameters for at least a week (7 days). However, after the first operating stage Ia, the duration of the following stages was increased to gather more data (e.g., for stage Ib) and/or to further study the sudden TMP increase between days 5 and 6 during stage IIb). Therefore, after a start-up period of 20 days, when the biomass was acclimatized to the operating conditions, the laboratory-scale aMBR plant operated for a total period of 41 days. During the first operating period (period I), the c-MF membrane was used, i.e., (Ia) c-MF (7 days, 12 $L \cdot m^{-2} \cdot h^{-1}$) and (Ib) c-MF (15 days, 14 $L \cdot m^{-2} \cdot h^{-1}$); whereas, during the second operating period (period II), the r-UF membrane was used, i.e., (IIa) r-UF (10 days, 12 $L \cdot m^{-2} \cdot h^{-1}$) and (IIb) r-UF (9 days, 14 $L \cdot m^{-2} \cdot h^{-1}$). The c-MF and the r-UF were meticulously mechanically cleaned between stages Ia and Ib, and between stages IIa and IIb, respectively. For the mechanical cleaning, membranes were first rinsed with tap water. Then, the membranes were, again, rinsed with tap water for one minute on each side. Then, using a wet sponge each side was vertically and horizontally cleaned. Finally, the membranes were immersed in a tank with tap water with aeration for 5 more minutes

3.1.4. Membrane fouling analysis

Membrane fouling at the end of each membrane operating period (i.e., after stages Ib and IIb) was analyzed using a resistance-in-series model proposed by Di Bella et al. to assess the relative importance of pore blocking and cake layer formation on both membranes [140]. A schematic representation of the different resistances to permeation affecting the membrane performance can be seen in Figure 19.

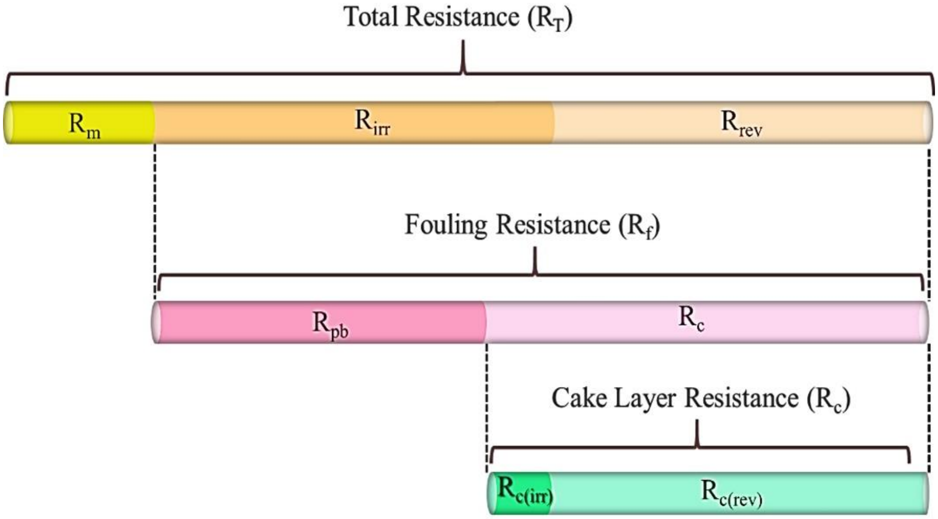


Figure 19. The role of fouling mechanisms in a membrane bioreactor. Modified from Di Bella et al. by specifying the two types of cake layer resistances

[141]

The various filtration resistances during MBR operation can be described using Darcy's law (Equation (1)), as follows:

$$R = \frac{TMP}{\mu \times J} \tag{1}$$

Here R is the resistance to permeation (m^{-1}); TMP is transmembrane pressure (Pa); μ (Pa.s) is the permeate's dynamic viscosity (water viscosity at 20ºC); and J is the permeate flux ($m^3 \cdot m^{-2} \cdot s^{-1}$). Further, the membrane resistance R_m (m^{-1}) is the original resistance that a pristine membrane presents during clean water filtration (Equation (2)):

$$R_m = \frac{TMP_{H2O}}{\mu \times J} \tag{2}$$

The total resistance, R_T (m^{-1}), is defined as the sum of three different resistances, at the end of each membrane operating period Ib and IIb (Equation (3)):

$$R_T = R_m + R_{c\,(rev)} + R_{c(ir)} + R_{pb} \tag{3}$$

where $R_{c\,(rev)}$ (m^{-1}) represents the reversible fraction of the cake layer resistance that is removable during relaxation or backwashing. $R_{c(ir)}$ (m^{-1}) corresponds to the irreversible fraction of the cake layer resistance that cannot be removed during relaxation or backwashing. R_{pb} indicates the fraction of the fouling affecting membrane pores. Fouling resistance (R_f; (m^{-1})) is defined as the total resistance due to fouling excluding the membrane resistance R_m (Equation (4)).

$$R_f = R_{c(rev)} + R_{c(ir)} + R_{pb} \tag{4}$$

3.1.5. *Preliminary economic assessment*

To evaluate the economic potential of recycling EoL RO membranes to MBR submerged flat-sheet UF membranes, the cost of producing r-UF MBR membranes (EUR·m^2) was analyzed. Figure 20 shows the processes considered (i.e., the system boundaries) when conducting the cost analysis of the EoL RO recycling into r-UF MBR membranes.

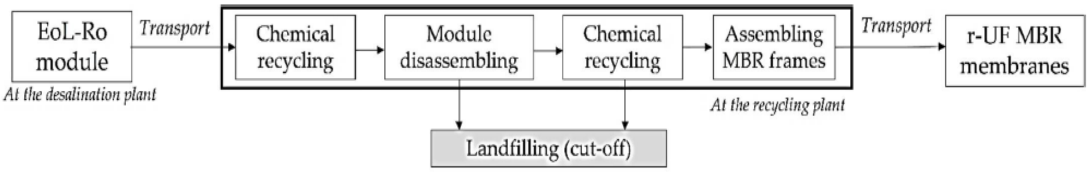


Figure 20. System boundaries of the economic analysis of r-UF membrane production process

The costs of Eol-RO collection and the transformation into UF were adopted from Senán-Salinas et al. [142]. The modules disassembling was analyzed in Lawler et al. [111]. Finally, the adaptation of EoL-RO membrane sheets into MBR flat sheets frames was conducted considering five different commercial and standardized MBR frames [37].

3.2. Results and discussion

3.2.1. *Characterization of the studied membranes: permeability and pore size*

Membrane permeability and pore size are two of the main membrane properties that affect membrane performance and the technological niche of a UF membrane for aMBR. To illustrate the state of the art of commercial membranes and identify the technological position of the studied r-UF membranes, Figure 21 summarizes the values of the clean water permeability versus the nominal pore size of the commercial membranes and the recycled ones.

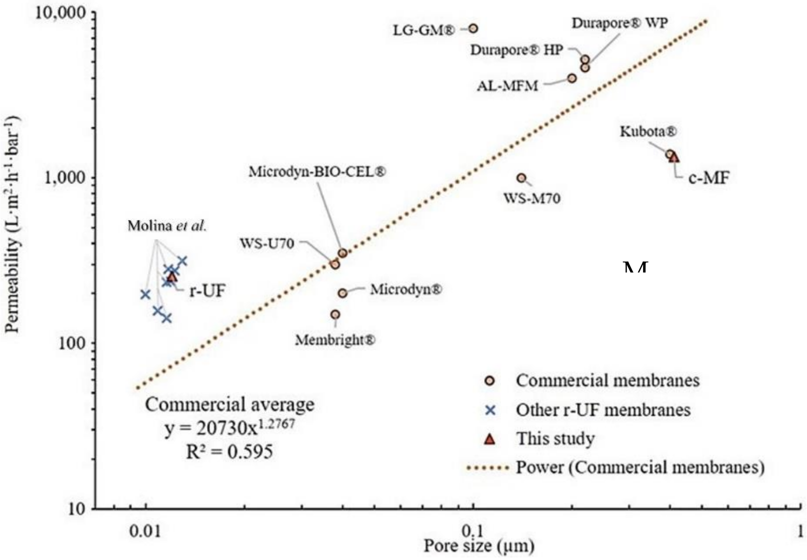


Figure 21. Membrane permeability for clean water according to pore size for commercial membranes and the membrane used in the present study according to Judd et al. and Molina et al.

Sources: Judd and Molina et al. [37,134].

The obtained permeability (L; $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) for the r-UF membrane was 255±4 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$. This permeability value is in accordance with the average permeability range of various UF commercial membranes (i.e. 200-300 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) (Figure 21). Furthermore, the results summarized in Figure

21 provide evidence of the strong non-linear relationship (R^2 =0.595) between the pore size and the permeability of UF and MF commercial flat sheet aMBR membranes. Even though the r-UF membrane presents a pore size that is much smaller than the pore size usually found among the commercial ones, the permeability values are in the same range of the UF commercial membranes (i.e., 200-300 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$).

3.2.2. Performance efficiency of the lab-scale aMBR unit

3.2.2.1. Permeate quality

Regarding the permeate quality, Table **7** shows the obtained results for the analyzed parameters of the permeate.

TOC, COD and BOD_5 average removal values for the r-UF MBR were higher than 98.9 ± 0.3% and up to 99.7 ± 0.1%. The organic matter removal efficiency of the c-MF MBR was equally high, i.e., higher than 98.2 ± 0.2%, during the whole operation. Moreover, turbidity values obtained with the r- UF membrane were very low, i.e., 0.04 ± 0.02 NTU during stage IIa and 0.01 ± 0.05 NTU during stage IIb. Taking Spanish legislation into consideration, the turbidity values obtained were consistent with the stricter requirements for treated wastewater reuse [143]. The turbidity values of the c-MF permeate were also quite low (i.e., 0.14 ± 0.01 NTU during stage Ia and 0.29 ± 0.32 NTU during stage Ib). However, the average values of the c-MF turbidity were statistically higher than the values of the r-UF. Another statistically significant difference in the average values concerning the permeate quality was the TOC concentration. Although the TOC concentration of the effluent was very low during all operating stages, the average values of the r-UF MBR permeate were slightly lower compared with the respective values of the c-MF. Overall, the permeate quality obtained using the r-UF membrane was slightly better than that obtained with the c-MF membrane. With regard to the membrane retention capacity, intrinsic properties of UF membrane (especially the lower molecular weight cut-off (MWCO)) seemed to make a difference in the retention efficiency of, e.g., dissolved solids (mainly organic macromolecules) [144]. For the r-UF membrane, the MWCO was estimated in previous studies and is considered to be around 20 kDa [134].

Table 7. Permeate quality and removal efficiency average values of the four different operating stages (Ia, Ib, IIa, and IIb). The *p*-values marked as * indicate the ANOVA results between permeate quality of the two membranes for every stage that were statistically significant with a confidence level over 95%.

	Permeate Quality		**Removal (%)**		**p-Value**
	(Ia) c-MF	**(II a) r-UF**	**(Ia) c-MF**	**(II a) r-UF**	**r-UF-c-MF**
Turbidity (NTU)	0.14 ± 0.01	0.04 ± 0.02	-	-	0.000246 *
TOC (mg/L)	3.00 ± 0.26	1.82 ± 0.12	98.2 ± 0.2	98.9 ± 0.1	0.0006 *
Total N (mg/L)	26.01 ± 1.79	24.23 ± 2.59	17.2 ± 5.7	22.85 ± 9.5	0.40
Total P (mg/L)	3.68 ± 0.29	3.26 ± 0.65	29.9 ± 5.4	37.9 ± 14.2	0.50
COD (mg/L)	5.05 ± 0.64	5.93 ± 0.88	99.1 ± 0.2	98.8 ± 0.3	0.216
BOD_5 (mg/L)	1.25 ± 0.35	<1	99.5 ± 0.1	99.7 ± 0.1	0.293

	Permeate Quality		**Removal (%)**		**p-Value**
	(Ib) c-MF	**(II b) r-UF**	**(Ib) c-MF**	**(II b) r-UF**	**r-UF-c-MF**
Turbidity (NTU)	0.29 ± 0.32	0.01 ± 0.05	-	-	0.0919
TOC (mg/L)	2.28 ± 0.38	1.57 ± 0.20	98.6 ± 0.2	99.0 ± 0.1	0.01 *
Total N (mg/L)	22.21 ± 3.56	17.40 ± 6.34	29.3 ± 11.3	51.2 ± 14.3	0.02 *
Total P (mg/L)	3.58 ± 0.75	3.43 ± 0.31	31.8 ± 14.3	38.6 ± 6.6	0.39
COD (mg/L)	7.97 ± 1.73	4.52 ± 1.34	98.3 ± 0.4	98.9 ± 0.3	0.05
BOD_5 (mg/L)	<1	<1	99.7 ± 0.1	99.6 ± 0.0	1

3.2.2.2. *Membrane permeability stability and preliminary fouling assessment*

Figure 22 shows the transmembrane pressure evolution of both membranes (r-UF and c - MF) performing at 12 and 14 L·m^{-2}·h^{-1}. It was observed that c-MF membrane barely exhibited a TMP increase when operated at 12 L·m^{-2}·h^{-1} (stage Ia). Even when the flux increased to 14 L·m^{-2}·h^{-1}, a constant yet mild TMP increase was observed. Concerning r-UF membrane, it was observed that its behavior changed depending on flux value. At 12 L·m^{-2}·h^{-1}, the r-UF membrane presented a small TMP increase that lasted up to seven days, followed by a rather stable TMP profile for the next three days. On the other hand, the r-UF working at 14 L·m^{-2}·h^{-1} showed a sharp TMP increase between days 5 and 6, that could not be attributed to a specific reason. However, after this sharp increase the TMP seemed to stabilize.

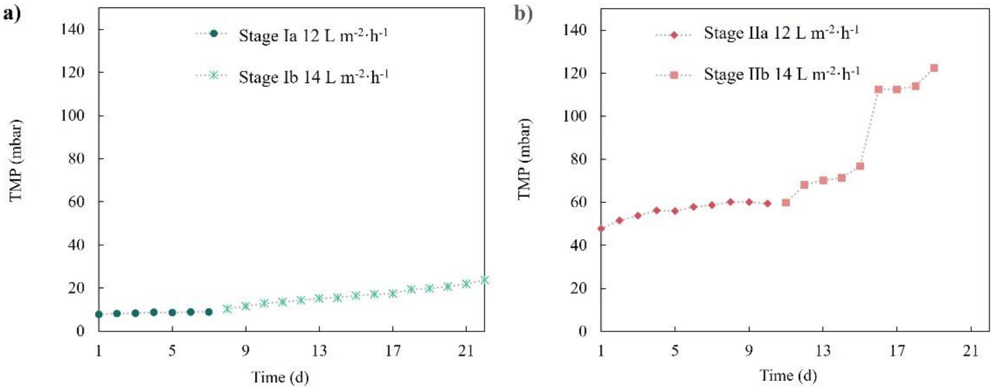


Figure 22. TMP temporal profile for (a) the c-MF membrane in stages Ia and Ib and (b) the r-UF membrane in stages IIa and IIb.

To further asses the membrane filtration performances, the evolution of the membranes′ permeability was calculated. Figure 23 presents the permeability temporal profile for both membranes, together with the calculated linear permeability decline rate. The c-MF membrane presented an evident permeability decline during both experimental periods, when performing at 12 and 14 L·m^{-2}·h^{-1} (stages Ia and Ib). At the same time, the r- UF membrane clearly presented a milder permeability decline, especially when performing at 12 L·m^{-2}·h^{-1} (stage Ia).

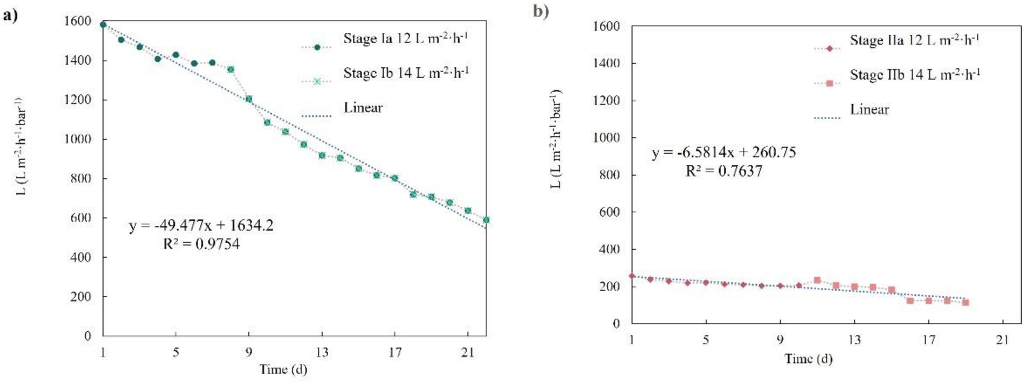


Figure 23. (a) Permeability evolution for the c-MF membrane in stages Ia and Ib and (b) the r-UF membrane in stages IIa and IIb.

The permeability decline rates were also calculated for the different operating stages and are summarized in Table 8. Summary of permeability decline values for the different operating stages and statistics. The permeability decline values of the r-UF membrane were quite low when operating at both 12 and 14 L·m^{-2}·h^{-1}. The permeability decline range obtained with r-UF membranes was similar to the commercial membrane range reported in Adham et al. for membranes with similar mean permeability (140- 200 L·m^{-2}·h^{-1}·bar^{-1}), operating at a MLSS concentration of 8 - 12 g·L^{-1} [145]. Therefore, upon a first look it seems that the performance feature of the r-UF was comparable to commercial membranes although long-term tests should be performed in future studies to confirm these results. The permeability decline rate was also slightly better than the permeability decline of the c-MF membrane under rather similar operating conditions.

Table 8. Summary of permeability decline values for the different operating stages and statistics.

Membrane	Flux ($L \cdot m^{-2} \cdot h^{-1}$)	Data series	Permeability decline rate ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1} \cdot d^{-1}$)	R^2	P-value
c-MF	12	Days 1-7	43.9±7.9	0.864	0.0025
c-MF	14	Days 8-22	51.6±4.3	0.941	7.70×10^{-07}
r-UF	12	Days 1-10	5.3±0.7	0.835	0.00022
r-UF	14	Days 11-19	15.8±1.9	0.911	6.35×10^{-05}

A major factor affecting permeability is the fouling phenomenon, comprising the adsorption and deposition of solutes. Among other factors and membrane properties, the membrane MWCO has an important effect on the fouling phenomena. Moreover, Li et al. reported that flux decline would be more pronounced in membranes with a larger MWCO due to membranes with larger pores being more prone to pore blocking [146]. In the present work, the r-UF membrane showed a rather steady permeability decline, which, after the sixth day, appeared to be reduced or even stabilized. Due to the complex and highly variable nature of the biological sludge, the filtration performance would also depend on the particular characteristics of the sludge. This makes it necessary to take into consideration other membrane characteristics to explain the whole phenomenon. Besides the MWCO, another important factor that affects membrane behavior is surface roughness [147]. The r-UF membrane's roughness was published by Rodríguez-Sáez et al. [133]. The r-UF membrane exhibited a roughness value (R_a = 4.7 ± 0.6 nm, R_q = 6.3 ± 1.2 nm) two orders of magnitude lower than the roughness value of the c-MF membrane. Furthermore, the obtained roughness values for the r-UF membrane were similar to the values obtained measuring commercial polysulfone UF membranes [148]. Long-term flux decline was additionally associated with the cake layer formation, where membranes with greater roughness are more prone to fouling [149]. Furthermore, it is assumed that membranes with higher hydrophilicity are less susceptible to present fouling issues [147]. The wettability of the membrane would be determined by the material that membranes are made of. According to Molina et al., the measured contact angle (CA) for r-UF membranes is over 66–68° [134]. The more hydrophilic character of the r-UF membrane, together with its lower MWCO and the lower surface roughness, probably contributed to the lower permeability decline rate compared with the c-MF membrane.

3.2.2.3. *Evaluation of fouling mechanisms*

Results obtained regarding membrane fouling mechanisms are presented in Figure 24 using the resistance in series (RIS) analysis after the end of the operating period of each membrane. The presented R_c values include both reversible and irreversible cake layer resistance, whereas R_{ir} values comprise the resistances of the irreversible cake layer and the pore- blocking mechanism.

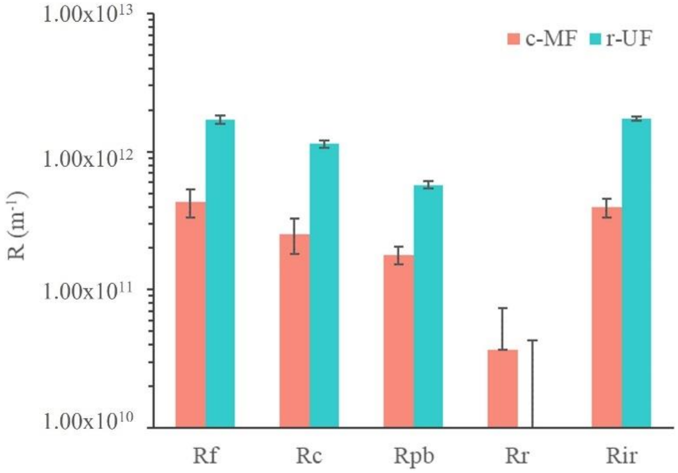


Figure 24. Estimated filtration resistances for the c-MF and r-UF membranes after stages Ib and IIb

It is important to note that R_m of the r-UF membrane was, as expected, higher than that of the c-MF membrane; the R_m for the r-UF membrane was $1.57 \pm 0.01 \times 10^{12}$ m^{-1}, and for the c-MF membrane, it was $0.27 \pm 0.01 \times 10^{12}$ m^{-1}. This was due to the smaller pore size of the r-UF membrane that led to a higher resistance to water permeation. Moreover, R_m values for the r-UF membrane were in accordance with the R_m obtained for commercial polysulfone UF membranes with a similar MWCO to the r-UF one [150]. This resistance is characteristic of the intrinsic properties of the membranes.

The overall resistance to fouling was higher in the case of the r-UF membrane compared with the c-MF membrane (i.e., $1.71 \pm 0.11\times10^{12}$ m^{-1} compared with $0.43 \pm 0.10\times10^{12}\,m^{-1}$). The main difference was due to the resistance of the cake layer that developed on the r-UF membrane ($1.13 \pm 0.08\times10^{12}$ m^{-1}), compared with the c-MF membrane ($0.25 \pm 0.07\times10^{12}\,m^{-1}$). This could be explained by the fact that the smaller pores of the r-UF membrane led to higher rejection rates, thus probably increasing the deposition of cake material. Moreover, the intrinsic higher membrane resistance resulted in higher TMP operation (even for clean membranes), thus promoting compaction of the forming cake layer. It was proposed that the cake layer in MBR is highly compressible [151], and that compaction of the (cake) fouling layer further increases the fouling resistance and renders the cake layer removal through backwashing or relaxation less effective [152].

Resistance values for R_{pb} were estimated as being rather similar for both the c-MF and r-UF membranes (i.e., $0.57 \pm 0.03\times10^{12}$ m^{-1} compared with $0.18 \pm 0.03\times10^{12}$ m^{-1}, respectively), although the R_{pb} of the r-UF was still higher. Considering the pore sizes of the membranes used in the present study (0.4 μm for the c-MF membrane and 12 nm for the r-UF membrane), it was expected that the r-UF membrane would have presented a lower R_{pb}. One possible explanation could be that the cake layer deposition that occurred quite quickly may provide a barrier (physical membrane/filter) for colloids and macromolecules that were supposed to participate in the pore-blocking process in both membranes. Nonetheless, smaller colloids and molecules could pass more easily through the cake layer and then participate in the blockage of smaller pores than the ones existing on UF membranes, as mentioned by Le-Clech et al., who observed that this tendency changes for long-term experiments [45]. Concerning, the reversibility of the membrane fouling layer, both membranes exhibited irreversible fouling mechanisms that accounted almost exclusively for the overall observed membrane fouling. Table 9 summarizes the contribution of the different fouling mechanisms to the observed fouling resistance. It was obvious that the irreversible fouling mechanisms were mainly responsible for the observed fouling phenomenon, thus making maintenance cleaning (mechanical and/or chemical) of both membranes necessary to restore their initial filtration performance.

Table 9. Relative contribution (%) of different membrane fouling mechanisms for the c-MF and r-UF membranes after stages Ib and IIb.

Membrane	**Membrane fouling mechanisms**			
Type	**Cake Layer**	**Pore blocking**	**Reversible**	**Irreversible**
c-MF	58.6 ± 16.6%	41.4 ± 6.1%	8.5 ± 8.5%	91.5 ± 14.1%
r-UF	66.4 ± 4.4%	33.6 ± 1.9%	0.0 ± 2.5%	100.0 ± 3.8%

Overall, it was observed that the relative contribution of each fouling mechanism was quite similar for c-MF and r-UF membranes. The resistance due to the irreversible fraction R_{ir} was the main resistance affecting R_f in both cases. Furthermore, the r-UF membrane showed a lower relative R_{pb} contribution but higher relative R_c. However, in both membranes, the cake layer remained the main fouling mechanism, accounting for approx. 60% of the overall fouling resistance.

3.2.3. *Critical factors affecting economic sustainability*

The sustainability of emerging technologies must be analyzed in the very early stages of their development. Ex-ante studies are more frequent and allow for the identification of trends and critical aspects to be resolved during the posterior research stages [153]. This section presents an analysis of the potential economic feasibility of the r-UF membranes. The analysis was performed in terms of two main units: (i) the cost of the production of 1 m^2 of the r-UF membrane and (ii) the recycling cost of one module. Table 10 describes the results of the adaptation of the r-UF spiral wound module (originally a Toray TM-720 EoL-RO module) into five different commercial MBR flat sheet frames [37].

Table 10. Cost of the production of the r-UF for use in an aMBR depending on the targeted membrane frame size.

Commercial membrane modules/frames	Sheet dimensions (mm)	Number of sheets cut	Area recovered (m^2)	Area recovered per module (%)	Cost (€·m^2)
Recycled Toray TM 720	960x845	1	37	-	-
Kubota-510 SINAP-80	490 x 1000	1	22.2	60	6.89
Kubota-203	226 x 316	8	25.9	70	5.91
SINAP-25	340 x 470	2	14.4	39	10.56
SINAP-10	220 x 320	8	25.5	69	5.99

The different MBR frames were analyzed to allow for a membrane area recovery between 39% and 70%. The smaller frames allowed for a higher surface recovery due to the adaptation of the shape to the membrane sheet dimensions. However, the largest frames that are more common in the MBR membrane industry (with dimensions of 490 mm × 1000 mm) have a membrane area recovery above 60%. In all the cases, the cost is between 5.91– 10.56 EUR·m^{-2}, thus lower compared with commercial MBR prices (12.38–20.63 EUR·m^{-2}) [56]. This lower cost could open the technological niche where the membrane replacement frequency is high or relatively higher, i.e., the treatment of harsh wastewaters or very intense processes where membranes are frequently damaged and replaced, such as for landfill leachate treatment. In this process, the membranes have a shorter expected lifespan (3–5 years), thus a high replacement ratio, representing 17% of the overall cost [154,155]. Data obtained in the present work showed that the permeability decline of the r-UF membrane would be slightly better under similar operating conditions (Table 8). Moreover, fouling analysis (Figure **24**) showed that the r-UF membrane presented similar characteristics to the c-MF membrane. Therefore, the use of r-UF membranes could reduce the replacement cost. In the contrast, the r-UF is expected to have a higher energy cost due to the lower permeability. Membrane stability and low replacement cost could lead to an overall cost reduction of the process. Nonetheless, long-term tests should be performed to verify this hypothesis.

Table 11. Cost contribution analysis

Cost type	**Process**	**Cost per module (€·module^{-1})**	**Cost contribution**	**Source**
CAPEX+OPEX	Module transformation, characterization and logistics	80	51.96%	[142]
OPEX-Labor	Disassembling and sheets cutting	51.17	33.24%	Own data
OPEX-Labor	Re-assembling in new frames	11.37	7.39%	Own data
OPEX-Energy	Electricity use during the processing	0.03	0.02%	[123]
Total cost	Recycling of one module	153.95	100%	

Besides the overall cost, the contribution analysis could identify crucial process steps (Table 11). The most expensive step in the process is the transformation of the whole module into the r-UF membrane and the logistics processes. These processes include, as shown in Figure 20, the transport processes (collection and distribution) and the chemical attack (with NaOCl) that transforms surface properties into an ultrafiltration membrane, as well as other downstream processes (washing and wastewater treatment). These costs were analyzed in detail in Senán-Salinas et al. [156]. However, within the new process steps, the main contributor was the manual disassembling, compromising 34% of the total cost of the treatment of one module (EUR 154 per module). This process needs to be done manually and its automatization through mechatronics engineering is challenging, although indispensable to reduce the cost of recycling. The same is true for the assembling and gluing of the sheets into new frames, which contributed approx. 7.4% to the overall cost. However, the sensitivity analysis, summarized in Table 12, identified the influence of changes in the main parameters on the overall cost. The sensitivity analysis pointed out the influence of the area recovered. Therefore, the development of a new frame with different sizes for the optimization of the area recovery could be useful for the scaling up.

Table 12. Sensitivity analysis results of the principal parameters affecting the r-UF membrane production cost.

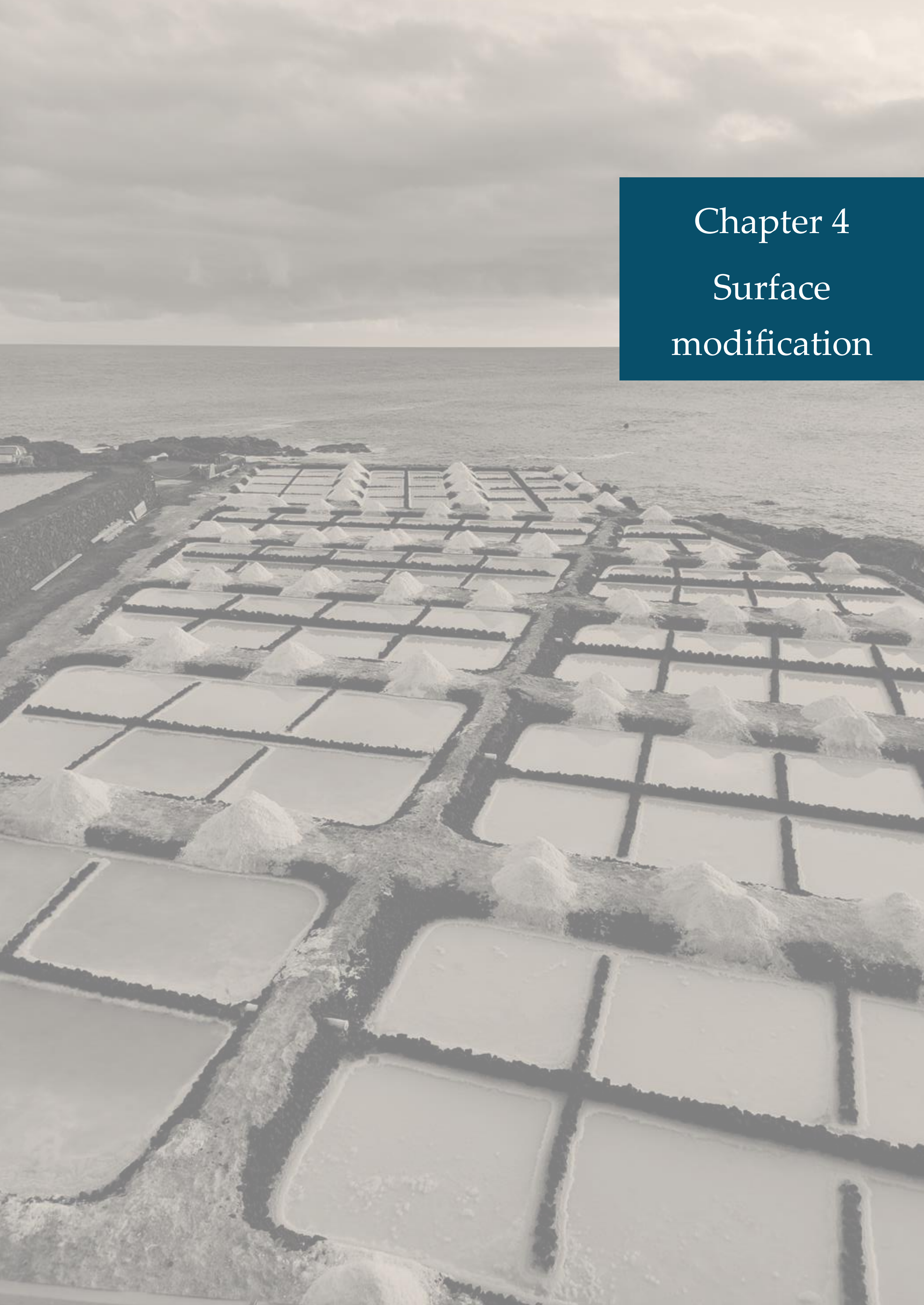
Parameter	Effect (Δ %)	Ratio (of Δ% effect / Δ% parameter)
Reduction 25% of area recovered	33	1.32
Change 25% of transformation cost	13	0.52
Change 25% of labor cost	12	0.48

One more factor that should be discussed concerning the potential implementation of r-UF membranes in MBR applications is the specific energy consumption (SEC) during the operation. SEC has been widely discussed and, for commercial MBRs, varies from 0.3 to 2.3 kWh·m^{-3} [157,158]. The most important factors affecting the SEC are the plant scale, the required permeate quality, and the blowers, as well as the operating conditions, including the net flow. As mentioned before, the permeability range is similar to other aMBR membranes with larger pore sizes (Figure 21) [93]. Therefore, the expected SEC can be similar. Furthermore, according to the literature, the contribution of permeate pumping is normally low compared with the overall aMBR processes (below 15%). Another critical factor is the permeability decline rate, ultimately leading to membrane chemical cleaning. As discussed in Section 3.2.2.2, the r-UF membrane presented a lower permeability decline rate over the whole experimentation period, during both 12 and 14 $L \cdot m^{-2} \cdot h^{-1}$ operation. It was reported in other studies that smaller membrane pore sizes are usually related to a slower TMP increase rate, thus resulting in longer membrane operation before chemical cleaning compared with larger pore membranes [159]. Even though the reported results in this study are preliminary and long-term test data are required to evaluate other main issues, such as the optimization of cleaning cycles and fouling dynamics, it seems that the r-UF membrane can perform comparably with the c-MF.

3.3. Conclusions

In the present work, a first reported proof-of-concept study to evaluate the feasibility of the use of recycled r-UF membranes as aMBR submerged membranes is provided. Overall, this study showed that the use of r-UF membranes in a flat sheet configuration in an aMBR system led to promising results. The TMP temporal evolution revealed that r-UF membranes exhibited a lower permeability decline rate, which may be beneficial for long-term working periods, whereas the fouling resistance analysis showed that the r-UF exhibited comparable characteristics to the widely employed c-MF membrane. However, the r-UF membrane permeability was much lower than MF membranes, which may negatively affect the cake layer fouling resistance due to the compaction of the cake. In terms of permeate quality, using the r-UF membrane, the laboratory-scale aMBR system exhibited excellent results regarding all studied parameters.

These encouraging results point to a very interesting alternative use of recycled EoL RO membranes in MBR systems and other UF processes where membrane replacement costs represent one of the main OPEX of the plant due to the elevated membrane replacement rate and/or important fouling issues. Although promising results were obtained, long-term experiments should be planned, including multiple experimental runs (replicates), especially to assess membrane fouling behavior in prolonged conditions. Moreover, planning new experimentation procedures at a larger scale should be considered. The collected data would be used for the performance of a detailed environmental sustainability assessment through life cycle analysis.



Chapter 4

Surface modification

Surfaces and Interfaces 23 (2021) 100978

Contents lists available at ScienceDirect

Surfaces and Interfaces

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Study of surface modification of recycled ultrafiltration membranes using statistical design of experiments

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ARTICLE INFO

Keywords:
End-of-life membrane
Statistical design of experiments
Surface modification
Surface characterization
Recycling
Ultrafiltration

ABSTRACT

Membrane surface modification on recycled ultrafiltration membrane was conducted using statistical design of experiments by two levels full factorial design. Dip-coting using catechol (CA) and polyethyleneimine (PEI) was chosen as the membrane surface modification method because its simplicity, energy saving characteristics and bio-based character. The factors studied were: CA and PEI concentration (1g/l and 4 g/l), temperature (30°C and 50°C) and reaction time (2 and 7 hours). The studied responses were the relative permeability (Pr) and the flux recovery ratio (FRR). A model with good validity was obtained for both responses. Membranes were deeply characterized using several techniques: Scanning electron microscopy (SEM); Attenuated total reflectance–Fourier transform infrared (ATR–FTIR) spectroscopy; X-ray photoelectron spectroscopy (XPS) and Atomic force microscopy (AFM). Statistical design of experiments resulted on a useful tool to understand how the factors affect the surface modification. Surface modification conducted at mild conditions (2 hours; 30 °C and 1g/l) improved membrane permeability and flux recovery ratio. Moreover, interaction between factors turned out to be significant in the modification process which was an unexplored field in previous works. Modification of recycled membranes is an innovative process that follows a Circular Economy approach.

1. Introduction

Membrane technology is widely used for wastewater treatment and many other technological and environmental processes for many years now. This technology has been also deeply improved over the years [1, 2]. Specifically, reverse osmosis (RO) technology is broadly implemented [3]. The most used membranes for this purpose are aromatic polyamide (PA) based membranes. The main drawbacks related to membrane performance have been identified to be the energy consumption, membrane fouling and the membrane replacement rate [4,5]. Most of the countries manage the disposal of RO membranes according to their own legislation which means that, normally, most of them end up on landfills following the traditional model of linear economy [6]. Nonetheless, this current practice goes against the European Union principles associated to Circular Economy [7,8].

Related to EoL RO membranes, several alternative scenarios to landfill disposal have been considered [9,10]. Framed on Life Cycle Assessment (LCA), Lawler et al. [11] studied the EoL RO membranes disposal alternatives in order to compute the environmental impact of each one. Conclusion resulting of that research showed that landfill disposal was the least environmentally friendly option. On the contrary, direct reuse turned out to be the most environmentally favorable alternative, which consists on using the membrane module without altering the structure of the module itself. Nonetheless, the condition of EoL RO membranes modules does not always allow the direct reuse. Considering this issue, RO membrane recycling is also possible by varying or eliminating their membrane active layer using an oxidant chemical such as sodium hypochlorite (NaClO). By mean of this procedure, it is possible to achieve ultrafiltration (UF) membranes by totally removing the active polyamide layer [6,12,13].

Several studies have already presented the use of recycled UF membranes for wastewater treatment processes [14–16]. Still, performance parameter, such as permeability of recycled UF membranes should be further studied along with fouling behavior, operational costs saving, energy consumption reduction, resource recovery, etc. [17–19].

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https://doi.org/10.1016/j.surfin.2021.100978
Received 21 September 2020; Received in revised form 22 January 2021; Accepted 25 January 2021

4. Membrane surface modification

The aim of the work presented in this chapter (Scientific paper 2) is to gain, by means of statistical design of experiments, a deep understanding of the main factors affecting the surface modification of recycled UF membranes. In this way, surface modification was conducted to improve membrane hydrophilic character and fouling resistance. Also, as a novelty, the interaction between factors will be studied to understand if they have any impact in the modification reaction and, therefore, in the membrane performance. Moreover, membrane surface characterization will be conducted to contrast obtained results.

4.1. Experimental part

4.1.1. Materials

Coupons (216 cm^2 area) from recycled EoL RO membrane model TM720-400 (Toray) were used. The chemicals consumed along this study were sodium hypochlorite (NaClO 10 % w/v), ethanol (96% EPR Ph.Eur. LABKEM (Spain)), polyethylenimine, branched (average Mw 800 by LS, average MN 600 by GPG. ALDRICH), 1,2-dihydroxybenzene (ReagentPlus®, ≥99% by Sigma Aldrich), Trizma hydrochloride (reagent grade ≥ 99.0%, SIGMA (Spain)), Trizma base (reagent grade ≥ 99.9% primary standard and buffer were purchased from SIGMA (Spain)), Bovine Serum Albumin (MW: 67 kDa) (lyophilized powder, ≥96% by SIGMA), E. coli (CECT434 (batch 23/03/2017)). Samples and solutions were prepared using Milli-Q water.

4.1.2. Membrane recycling and modification

Recycled UF membranes were obtained by removing the polyamide layer of the EoL RO membranes. For this purpose the process developed was the one described at Pacheco et al. [113]. The recycling process was performed with a passive transformation pilot applied to the whole module, maintaining its integrity [131]. After that, a membrane autopsy was conducted. Module was opened to obtain membrane samples to characterize and to use for filtration and fouling experiments. The modification step was conducted by one step co-deposition using catechol (CA) and polyethyleneimine (PEI) (Figure 25). pH adjustment was made by means of tris-buffer solution.

As Figure 25 shows, membranes were attached to the modification system to remain vertically during the dip coating process. After surface modification, membranes were rinsed with Milli-Q water in order to remove any CA/PEI co-deposition particles left.

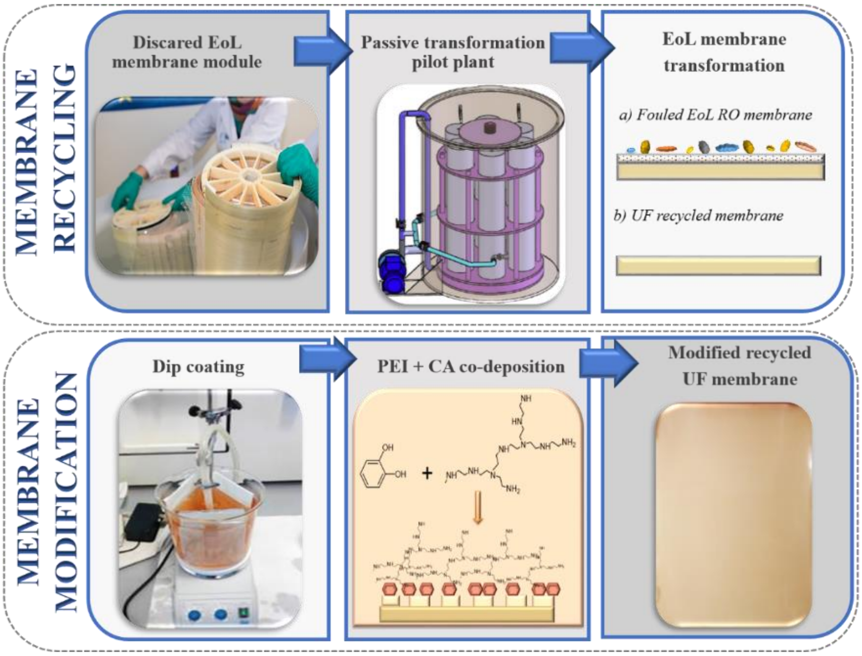


Figure 25. Membrane preparation flow chart

4.1.3. Statistical Design of Experiments: permeability and flux recovery ratio

MODDE Go software (Umetrics) was used for the design of experiments and data analysis. Specifically, a two-level full factorial design was employed. The factors studied were i) concentrations of catechol (CCA), ii) concentration of PEI (CPEI), iii) exposure time (t) and iv) temperature (T). Three center points were added to the experimental set. The process performance of the membranes was defined in terms of two main responses i) relative permeability (L_r) and ii) flux recovery ratio (FRR). Preliminary results show that permeability values on recycled membranes varied from

0% to 35%. Due to the experimental variability of the permeability of the recycled membrane coupons, the permeability values were normalized by calculating the relative permeability L_r.

The responses were obtained by conducting the filtration experiments as follows:

4.1.3.1. Filtration experiments

Filtration experiments were conducted in a stirred cell (Merk Stirred Cell XFUF04701) with an effective membrane area of 4.7 x10^{-2} m^2 at room temperature. The flat sheet membranes used were i) recycled UF and ii) modified recycled UF membranes. The FRR of the membranes was estimated using a solution of Bovine Serum Albumin (BSA) at 1 g/L solution concentration as fouling agent.

Each experiment was divided in the subsequent steps: i) Milli-Q water was forced to pass through the membrane at the stipulated pressure to obtain an initial permeability value, ii) BSA (1 g/L) solution pass at the specified pressure, iii) the membrane was extracted to receive a manual cleaning with Milli-Q water, iv) Milli-Q water was enforced to go through the membrane and v) lastly, a last permeability test with clean Milli-Q water was done.

Permeability (L; $L \cdot m^{-2} \cdot h^{-1} bar^{-1}$), was calculated as follows (equation (1)):

$$L = {}^{J}/_{TMP} \tag{1}$$

Where TMP (bar) is the transmembrane pressure and J ($L \cdot m^{-2} \cdot h^{-1}$) is the permeate flux of the studied membranes (equation (2)):

$$J = \frac{Q}{S \times h} \tag{2}$$

Where Q ($L.h^{-1}$) is the membranes permeate flow, S (m^2) represents the membrane surface and h shows time in hours.

Permeate flow (Q), at laboratory, was calculated by measuring permeate weight (W, g) according to time (t, h). Solution density (ϱ, g/L) considered was 1,000 g/l (equation (3)):

$$Q = \frac{W}{\rho \times t} \tag{3}$$

Relative permeability (L_r) was obtained dividing the individual permeability (L_i) obtained for each coupon over the average permeability ($L_{average}$) of all coupons studied (equation (4)).

$$L_{r=L_i/L_{average}} \tag{4}$$

The value of FRR was calculated as (equation (5))

$$FRR = {}^{J_2}/_{J_1} \tag{5}$$

Where J_1 ($L·m^{-2}·h^{-1}$) is the Milli-Q water permeability before BSA experiment and J_2 ($L·m^{-2}·h^{-1}$) is the Milli-Q water permeability after BSA experiment.

4.1.3.2. Model validity

The validity of the empirical models fitted with multiple linear regressions (MLR) was tested with analysis of variance (ANOVA). The confidence level used was 95%. The model was also evaluated in terms of the coefficient of determination (R^2), adjusted coefficient of determination (R^2_{adj}) and the response variation percentage predicted by the model according to cross validation (Q^2= 1–PRESS/SS); PRESS is the prediction residual sum of squares and SS is the total sum of squares of Y corrected for the mean).

Table 13 shows all the experiment conducted for fitting the model. As Table 13 shows, three center points were included to analyze the reproducibility of the experiments.

Table 13.Conducted experiments

Factorial Design				
Membrane	CCA(g/l)	CPEI(g/l)	T(ºC)	t (hours)
1	1	1	30	2
2	4	1	30	2
3	1	4	30	2
4	4	4	30	2
5	1	1	50	2
6	4	1	50	2
7	1	4	50	2
8	4	4	50	2
9	1	1	30	7
10	4	1	30	7
11	1	4	30	7
12	4	4	30	7
13	1	1	50	7
14	4	1	50	7
15	1	4	50	7
16	4	4	50	7
17	2.5	2.5	40	4.5
18	2.5	2.5	40	4.5
19	2.5	2.5	40	4.5

Given the results of the fitted model, four membranes were selected for surface characterization. To obtain a fine representation of parameters' level, the selected membranes were nº 1, nº 5, nº 9 and nº 13. Moreover, a blank membrane (recycled membrane with no modification conducted) was also characterized.

4.1.4. Membrane surface characterization

To assess if the modification was successful and to determinate its intensity, membrane surface characterization was conducted. Scanning electron microscopy (SEM) employing S-8000 Model (Hitachi) image device was employed to examine the surface of the membranes. Furthermore, to determine the average pore diameter of modified membranes, Digital Image

Analysis (DIA) was performed by using ImageJ software (Java-based image processing program) for porous size analysis [160]. Attenuated total reflectance–Fourier transform infrared (ATR–FTIR) spectroscopy using a Perkin-Elmer RX1 spectrometer was used to analyze the functional group on the membrane surface. To investigate the surface chemical composition of the membranes, X-ray photoelectron spectroscopy (XPS) was conducted with a SPECS system (Berlin, Germany) equipped with Phoibos 150 1D-DLD analyzer and monochromatic radiation source Al Kα (1486.7 eV) (wide scan: step energy 1 eV, dwell time 0.1 s, pass energy 80 eV). Specific analysis of the detected elements was performed (detail scan: step energy 0.08 eV, dwell time 0.1 s, pass energy 30 eV) with an exit angle of the electrons of 90º. The roughness of the membrane surfaces was examined by atomic force microscopy (AFM) using a Multimode topographical AFM (Vecco Instruments, Santa Barbara, California) equipped with a Nanoscope Iva control system (software version 6.14r1). Silicon tapping probes (RTESP, Veeco) were used with a resonance frequency of ~300 kHz and a scan rate of 0.5 Hz, 5 × 5, 3 × 3, 2 × 2 y 1 × 1 µm2 AFM images were taken for each sample.

4.2. Results

4.2.1. Model validity

When evaluating the validity of the fitted model for the relative permeability with ANOVA results (Table 14), it shows that F_{value} (10.893) > $F_{tabulated}$ (3.135) and $p < 0.05$. Therefore, the regression model is statistically significant with the 95% confidence level. In addition, the lack of fit is not significant with the 95% confidence level ($p > 0.05$). The coefficient of determination, R^2 (0.884), and the response variation percentage predicted by the model, Q^2 (0.674), also show a good validity of the model developed.

When evaluating the validity of the fitted model for the FRR with ANOVA results (Table 15), it shows that F_{value} (7.053) > $F_{\text{tabulated}}$ (4.0600) and $p < 0.05$. Therefore, the regression model is statistically significant with the 95% confidence level. In addition, the lack of fit is not significant with the 95% confidence level ($p > 0.05$). The coefficient of determination, R^2 (0.746), and the response variation percentage predicted by the model, Q^2 (0.529) also show an acceptable validity of the model developed.

Table 14. ANOVA table for relative permeability model.

L_r	DF	SS	MS	F_{value}	$F_{tabulated}$ (α=0,05)	Probability (p)	SD
Total	18	15.5592	0.8644				
Constant	1	15.272	15.272				
Total corrected	17	0.287178	0.0168928				0.129972
Regression	7	0.253883	0.036269	10.8932	3.315	0.001	0.190444
Residual	10	0.033295	0.0033295				0.0577018
Lack of Fit	8	0.0328284	0.00410354	17.5867	19.371	0.055	0.0640589
Pure error	2	0.00046667	0.00023333				0.0152752

Table 15. ANOVA table for FRR model.

FRR	DF	SS	MS	F_{value}	$F_{tabulated}$ (α=0,05)	Probability (p)	SD
Total	18	19.6349	1.09083				
Constant	1	17.9401	17.9401				
Total corrected	17	1.69485	0.099697				0.315748
Regression	5	1.26443	0.252886	7.05036	4.060	0.003	0.502877
Residual	12	0.430421	0.0358685				0.18939
Lack of Fit	10	0.396555	0.0396555	2.34186	19.40	0.336	0.199137
Pure error	2	0.0338667	0.0169333				0.130128

4.2.2. Effects of factors and its interactions on permeability

Based on the satisfactory model obtained, the effect of factors and interaction between factors on the permeability could be evaluated (Figure **26**). CCA has not been taken into consideration for the analysis since, according to the model, it has no significant effect. This might be due to the range of CCA used in the present study. As Figure 26 illustrates, the principal factor affecting permeability values is CPEI, having a negative effect on it. This means that when CPEI increases, permeability decreases. This might be because, at higher PEI concentration, more PEI molecules are attached to the membrane surface, obtaining a thicker modification layer that adds a higher resistance to the water flow, reducing the permeability [81,161,162].

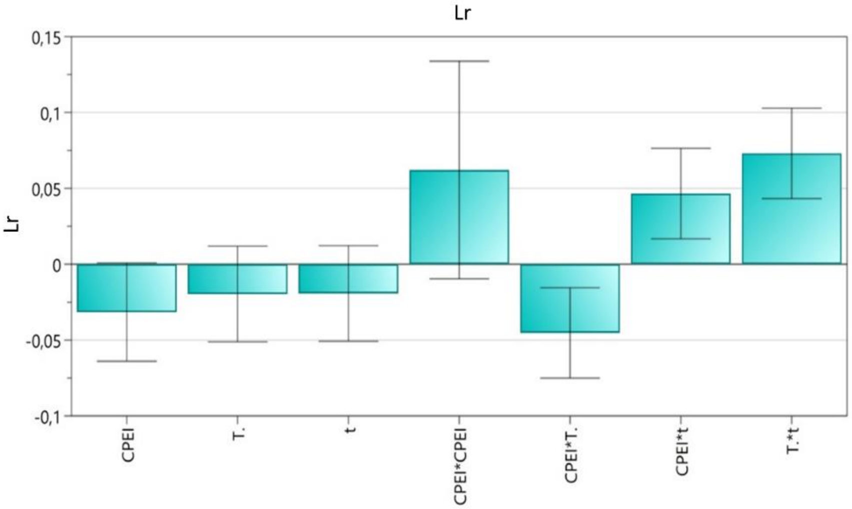


Figure 26. Effects on relative permeability (MODDE_12 Software). 95% confident level is shown as error bar.

It is important to note that also three main interactions seem to be statistically significant (Figure **27**Figure **26**). When an interaction between two factors is significant, the effect of one of the factors depends on the level of the other factor, i.e. the factors are not independent from each other. There is evidence that previous studies did not take into consideration the importance of the interaction between factors and this could mean obtaining incomplete conclusions. For instance, Xu et al. conducted the experiments with same reaction time (6 hours), temperature (30ºC) and chemical compounds ratio (1:1; 3 g/L) modifying, only PEI Mw. Xu et al. concluded that low Mw of PEI provided a thinner coating layer along with an excellent separation characteristic, especially with PEI Mw 600. However, the levels of the remaining factors present on the experiments had not been evaluated and, consequently, it is difficult to evaluate if at high temperature levels or lower reaction times the results would be similar [162]. Xue et al. carried out the experiments with variations of CA/PEI mass ratio (1.2 g/L of CA) and co-deposition time but same temperature (25 ºC) preparing the membrane for an additional modification. Xue et al. concluded that the most suitable reaction conditions were CA concentration 1.2 g/l, mass ratio CA: PEI 4:1 and 8 hours reaction time, respectively. Once more, it is not possible to infer what the results would have been with temperature variation [163]. Zhang et al. developed a surface modification using PEI and PDA and they took into consideration the variation of some of the parameters involved in the reaction (PEI concentration, temperature or reaction time). Even though Zhang et al, did not study the effect of interactions between factors, they discussed the possible effects that PEI concentration, temperature and time could have into the chemical reaction. The study of Zhang et al. concluded that mild modified membranes showed quite good performance and that controlling modification parameters, different modification layers and membrane performance can be achieved [81].

As Figure 27 shows, in this study three main interactions seem to be statistically significant: i) CPEI-temperature; ii) CPEI-time and iii) temperature-time.

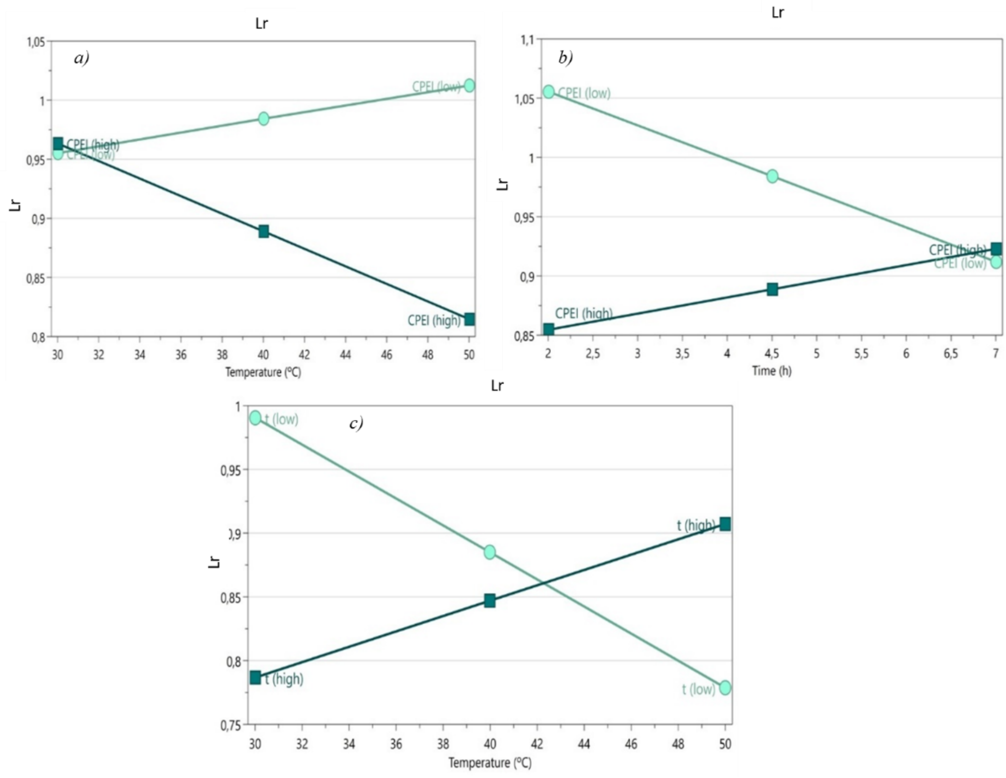


Figure 27. Interactions affecting relative permeability: a) CPEI - Temperature; b) CPEI – Time.

4.2.2.1. *CPEI - Temperature*

The effect of CPEI has not a significant effect when temperature is low (Figure 27 a). Nevertheless, when membrane modification was made at higher temperature the high values of CPEI have a clear negative effect on permeability. As Zhang et al. had already observed, this may be due to Schiff base reaction or/and Michael addition, which are both endothermic reactions. This could mean that the temperature allows more molecules to attach to the membrane surface. Then, the thickness could be higher along with temperature affecting, consequently, to the permeability [81].

4.2.2.2. CPEI – time

The effect of CPEI clearly changes depending on the reaction extent (Figure 27 b). At low reaction time, high CPEI lead to lower permeability levels. On the contrary, low CPEI and time combination results on higher permeability values. As it can be observed, when the reaction time is higher, there is barely a difference on the permeability values depending on the CPEI. As Zhang et al. observed, at low reaction times all positions on the membrane surface are suitable of being occupied and PEI molecules could get to the membrane surface with no apparent effort. Nonetheless, at longer reaction times, PEI molecules would be influenced by electrostatic repulsion and steric hindrance and making its way to the surface more difficult [81].

Consequently, independently of having higher concentrations of PEI in the solution the thickness of the modification layer will not be increased at long reactions times obtaining similar permeability values.

4.2.2.3. Temperature – time

As it can be noticed in Figure 27 c, the effect of the temperature varies along the reaction time. At minor time, there exists a considerable difference of the effect between high and low temperature effect. The smaller the temperature and the reaction time are, the higher the permeability is. Nonetheless, at long reaction times, the difference of the effect due to the temperature decreases. This situation may occur due to the fact that when time or temperature levels are extensive enough, they permit that an enough amount of PEI molecules would be attached to the membranes. This would become in a thicker modification layer than the one obtained with mild conditions. [81,161,162].

For better understanding and corroboration of the presented hypotheses, membrane surface characterization was conducted. Initially, to determine if the modification could have affected the superficial pore size of the membranes, membrane surface SEM micrographs were acquired (Figure **28**).

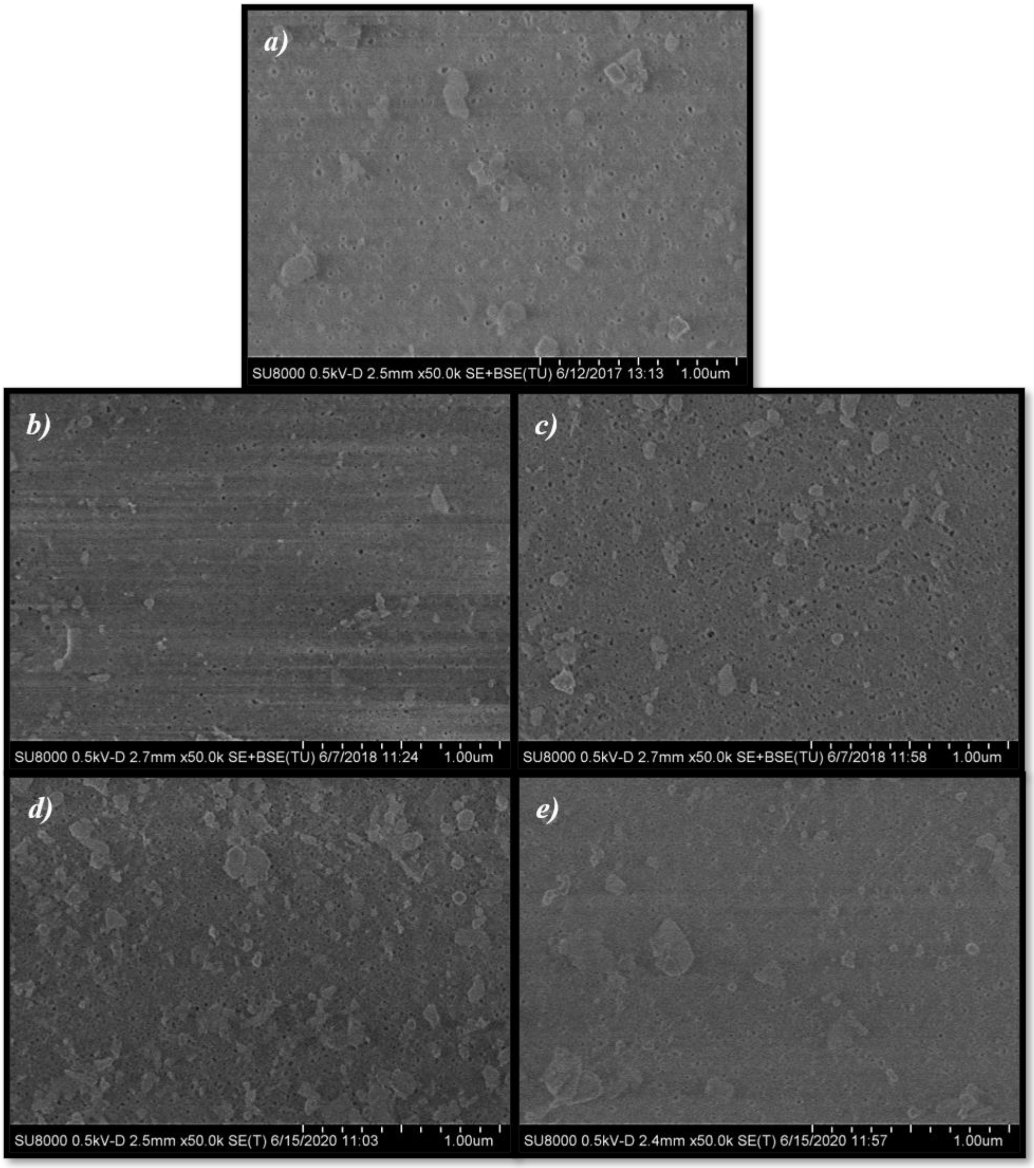


Figure 28. Surface SEM images of a) blank membrane (recycled; no modified), b) Membrane 1 (2h; 30ºC; 1 g/l), c) Membrane 5 (2h; 50ºC; 1 g/l), d) Membrane 9 (7h; 30ºC; 1 g/l) and e) Membrane 13 (7h; 50ºC; 1 g/l)

SEM images on Figure 28, showed a very similar surface morphology. Pores can be still perceived in all of them. The estimation of the average pore size, was conducted by DIA following the analytical procedure described in Molina et al. [164]. The average pore size, Feret Diameter (d_F), of each membrane was calculated and shown in Table 16.

Table 16. Pore diameter values for analyzed membranes

	Feret Diameter, d_F, (nm)
Blank	11.9±6.5
Nº 1	11.3±5.8
Nº 5	11.0±5.3
Nº 9	10.4±5.7
Nº 13	9.8±5.9

As it can be seen in Table 16, pore size presented a minor variation for the different modifications studied. This might be due to the mild conditions used during the modification process. However, it needs to be considered that other studies have shown that when the levels of the modification change (i.e. higher PEI concentration) pore size of the membranes would be affected. [81]. Moreover, membrane surface was examined by the ATR-FTIR spectroscopy. Figure 29 shows ATR-FTIR spectra for the blank and for the selected modified membranes.

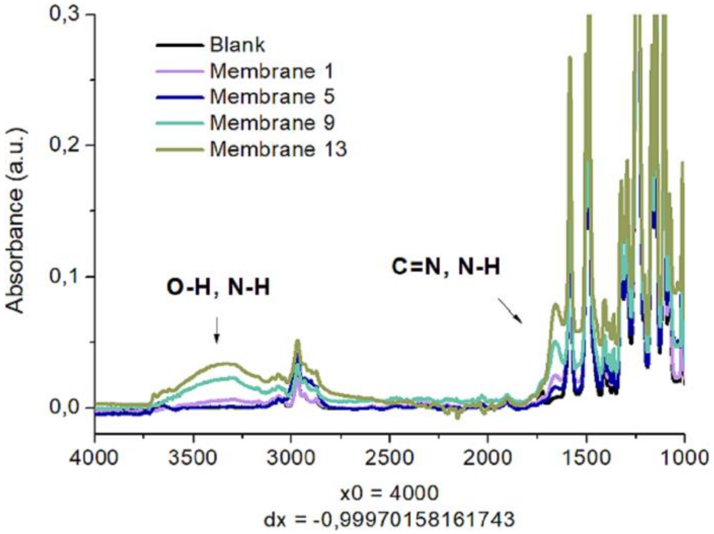


Figure 29. TR-FTIR spectra

All the spectra were normalized to band at 1,240 cm^{-1}, of phenylene ether stretching vibration of the PSF support layer. Spectra from the modified membranes show peaks at 3,400 and 1,542 cm^{-1} both compatible with amine and alcohol groups, which indicates the co-deposition of the CA and PEI. All studied membranes provided a higher signal than the blank membrane. However, all the obtained signals were considerably weak. This may be due to the mild modification conditions of the selected membranes, which were intentionally chosen to improve membrane characteristics without compromising membrane performance in terms of permeability. The intensity of these signals is especially weak in membranes 1 and 5 (2 hours modification). Even though the parameters on the modification process were varied (30ºC and 50ºC respectively), both membranes showed very similar spectra. Conversely, in the case of membranes 9 and 13 (7 hours modification; 30ºC and 50ºC respectively), although spectra of both membranes still presented a weak signal, the difference between these membranes is more accentuated. This could be explained having into consideration the effect of the interaction between factors. Temperature may lead to a more disorganized reaction which, in combination with low reaction times, could lead to a lower attachment of PEI molecules to the membrane surface. Still, that did not happen at long reaction times resulting on a thicker modification layer for the membrane modified at the highest temperature.

Once more, the intensity of these bands was weak because of the mild conditions set for the surface modification. Consequently, it might happen that the thickness of the deposited layer might be thinner than the penetration depth of ATR beam. For this reason, deeper analysis by mean of XPS was conducted. Table 17 shows the surface element composition of several membranes.

Table 17. Surface element composition obtained by XPS

	Blank	**Membrane 1**	**Membrane 5**	**Membrane 9**
Carbon %	70.85	64.01	73.59	69.04
Oxygen %	23.73	29.72	19.94	23.63
Nitrogen %	2.65	4.47	3.41	5.40
Sulphur %	2.77	1.79	3.05	1.93
RATIO NITROGEN / SULPHUR				
	0.96	2.49	1.12	2.80

It was detected that the modified membranes have higher atomic percentage of nitrogen than the blank membrane, which could be attributed to the nitrogen element of PEI. Moreover, the N/S ratio of the modified membranes is also superior to the blank. Results of membrane 5 (1:1; 50ºC; 2h), which N/S ratio was lower than membrane 1(1:1; 30ºC; 2h) should be highlighted. These results were in concordance with the ones obtained with FTIR-ATR analysis. As Zhang et al. previously reported, due to the endothermic character of the reaction, an increase of the temperature would lead to a higher degree reaction. This would permit more PEI molecules to attach to the membrane surface shortly. [81]. However, it could be possible that this fast PEI attachment also entails an increase of electrostatic repulsion making more difficult for new molecules to reach the surface (Figure 30).

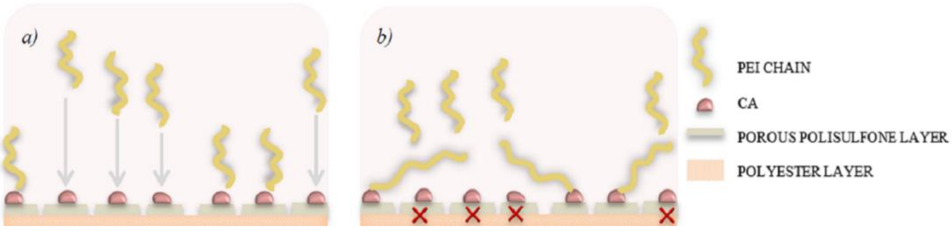


Figure 30. CA-PEI co-deposition reaction scheme: a) Ordered co-deposition reaction; b) Disordered co-deposition reaction.

According to the obtained model, at low reaction time and for low CPEI values, temperature has a negative effect on the attachment of PEI molecules. Moreover, membrane 1 and 9, both modified at 30º C, presented a very similar N/S ratio even though reaction time is different (2 hours and 7 hours respectively). The reason was that, at the beginning of the reaction, as PEI molecules reach the surface of the membrane very easily. Still, as long as the reaction goes by, PEI molecules have to deal with steric hindrance and a progressive lack of reactive sites for PEI causing a more difficult approaching more and making the reaction grade slower[81].

4.2.3. Effects of factors and interaction on FRR

Earliest results obtained by running the model showed that FRR values varied from 0% to 50%. Main factors and interactions affecting the FRR values are shown in Figure 31. It can be observed that main factors affecting the response are temperature and time both of them negatively.

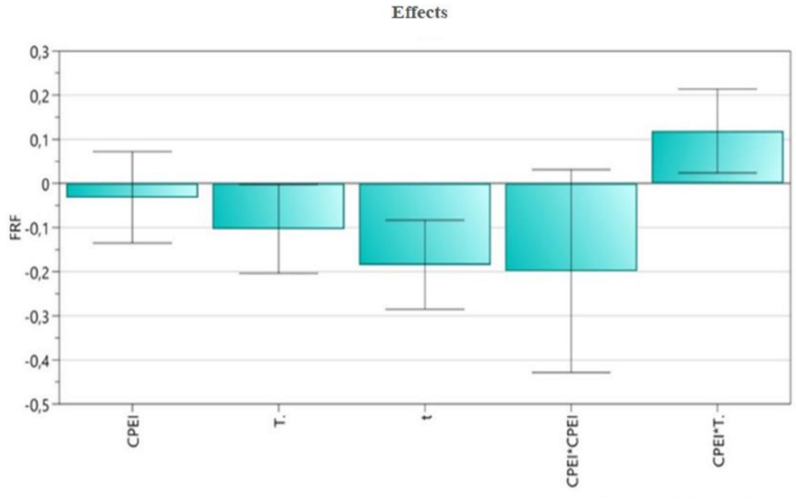


Figure 31. Factors and interaction affecting FRR response. 95% confident level is shown as error bar.

One interaction was statistically significant: CPEI – Temperature (Figure 31).

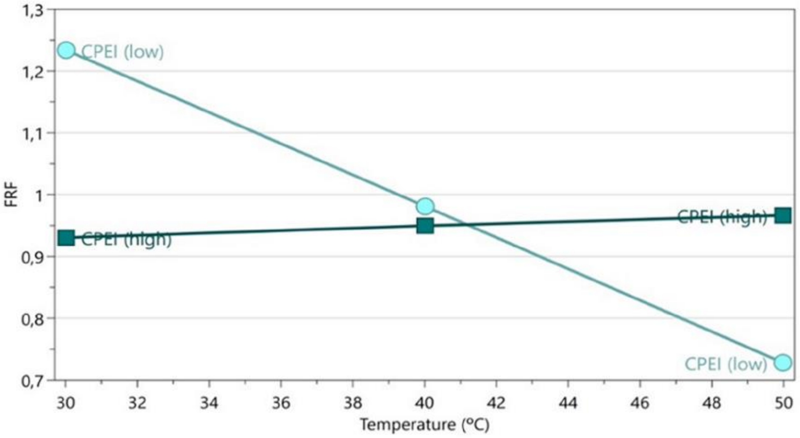


Figure 32. CPEI – Temperature interaction on FRR

The negative effect of time and temperature reaction might be explained because membrane surface roughness was increased. As it can be observed in Figure 32, at high CPEI values, FRR values were rather similar and did not change when increasing the temperature. On the other hand, at low CPEI levels, the FRR values changed significantly with the temperature. At low CPEI and low temperature the reaction was conducted at mild conditions where PEI molecules could reach the reactive sites on membrane surface in a homogeneous way. However, when temperature is high and due to the endothermic character of the reaction, reaction grade will be higher making more PEI molecules reach the surface faster. Due to the deposition, there would be more electrostatic repulsion and steric hindrance, being more difficult for the following PEI molecules to reach the surface homogeneously. Therefore, roughness will be higher. As it was reported in previous works [149,165], membranes with higher roughness tend to have more fouling issues. That is why, membranes with lower roughness would have better FRR.

The effect of main affecting factors and interaction has been analyzed and corroborated together with AFM. Membranes chosen to be evaluated by this technique were those with concentrations of modification solution of 1 g/l modified at different times and temperatures.

Figure 33 shows the AFM images and Table 18 shows the average roughness (R_a, the average deviation of the peaks and valleys regarding the average height) and root mean square roughness (R_q, standard deviation of both valleys and peaks).

Table 18. Surface roughness of membranes studied by AFM

Membrane	**R_a (nm)**	**R_q(nm)**
Blank	4.7±0.6	6.3±1.2
Membrane 1	5.2±0.9	7.5±1.3
Membrane 5	5.7±0.8	7.9±1.3
Membrane 9	8.8±3.0	11.5±4.1
Membrane 13	10.2±2.8	13.5±3.6

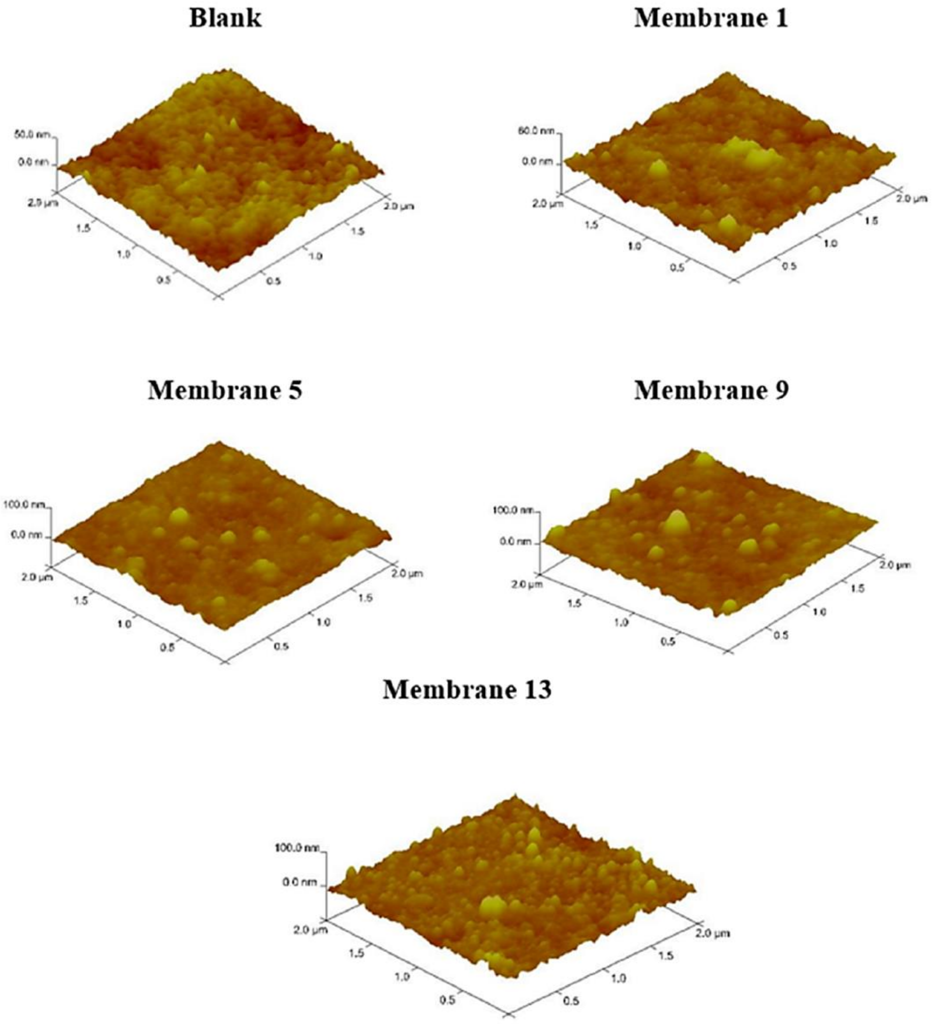


Figure 33. AFM images of the recycled and modified membranes

As it can be seen, R_a and R_q values of all modified studied membranes are higher than the blank one. It can be observed that at longer reactions time, roughness is higher. Membranes 1 and 5 presented a rather higher roughness values than the blank, although they are not so accentuated. On the other hand, membranes 9 and 13 had a clear intensification on roughness values, compared with membranes 1 and 5. However, in both cases, membranes modified at the highest temperature (50ºC; membranes 5 and 13) presented a slightly higher roughness value in comparison with the membranes which had been modified at same reaction times but lower temperature (30ºC; membranes 1 and 9). This fact might be explained by taking into consideration the characteristics of the chemical reaction as it was explained in section 4.2.2. PEI molecules reach the membrane via Michael and/or Schiff endothermic reactions. Faster reaction might cause that all PEI brushes would not reach the surface in an identical or homogeneous position boosting the steric hindrance of the reaction (Figure 34) [81].

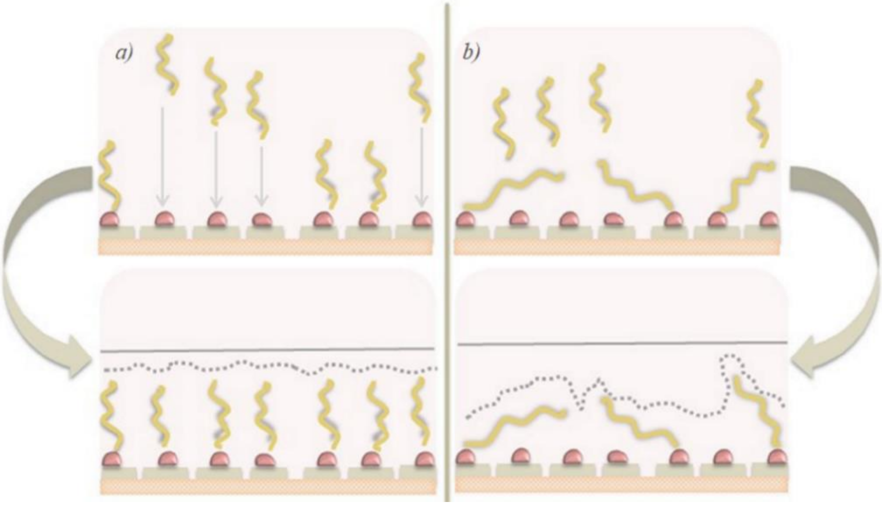


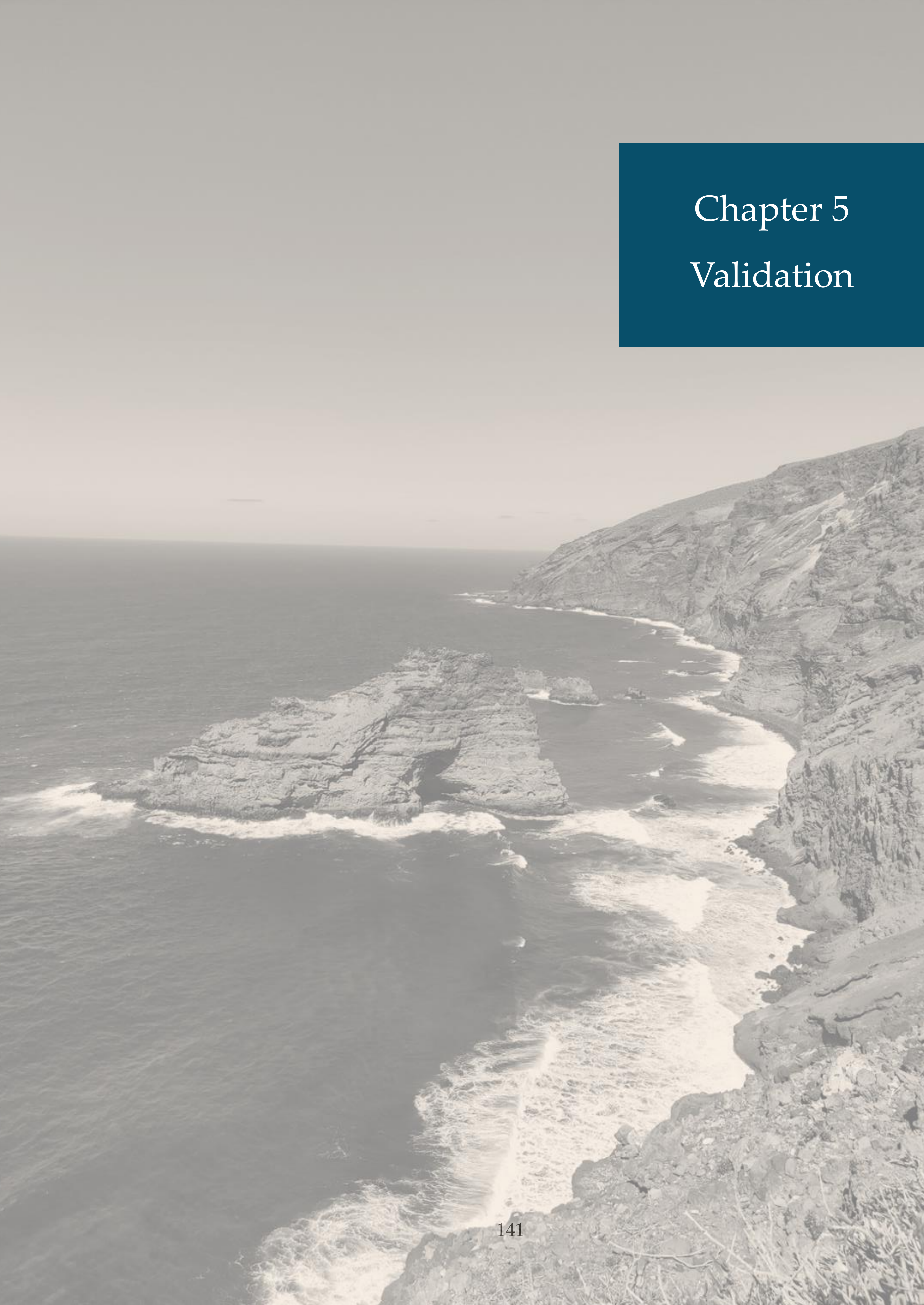
Figure 34. Surface roughness: a) Roughness resultant in an ordered co-deposition reaction; b) Roughness resultant in a disordered co-deposition reaction

It is important to note that although membranes 1 and 9 were modified with the same temperature (30ºC), membrane 9 showed superior roughness than membrane 1. During the time the co-deposition reaction is happening more molecules of PEI would be able to reach a position on membrane surface. Still, the more the PEI molecules are, the more the electrostatic repulsion forces are and the less the free spaces to attached are. This situation would lead to more PEI molecules trying to reach the surface in a more disorganized form. Consequently, the surface roughness would be increased with both, time and temperature.

4.3. Conclusions and future work

In this study surface modification by dip-coating of recycled membrane with environmentally friendly compounds (CA and PEI) was successfully conducted, obtaining improvements on the membrane performance. Statistical design of experiments demonstrated to be a very valuable tool to develop the study of membrane surface modification using CA and PEI and its performance. Membranes with higher roughness presented a worst flux recovery after fouling experiments. In addition, long reaction times used in the dip coating process resulted in thicker modification layer.

Given the results obtained when the model was fitted, it was demonstrated that the interactions between factors were as much significant as the main factors. Considering the improvement of L_r and FRR, having surface modification at mild conditions (1 g/l CA: 1 g/l PEI 600 Mw; 30 ºC; 2 hours) seem to obtain best membrane process performance for our study ($L_r = 1.12$; FRR = 1.38). In addition, conducting surface modification in mild conditions follows the path of working at low energy and chemicals consumption. This combined with the use of recycled membranes could be a very interesting alternative for those processes that have a high membrane replacement rate and/or important fouling issues such as membrane bioreactors (MBR). Following this approach, further studies will be conducted where recycled and modified UF membranes will be used in MBRs for urban wastewater treatment. In addition, further optimization experiments using statistical design of experiments should be conducted in order to optimize the surface modification process. Finally, this study shows that the combination of recycled membranes modified with bio inspired low-cost surface modification along with the obtained results is very promising in terms of sustainability in membrane technology.



Chapter 5

Validation

membranes

MDPI

Article

Application of Recycled Ultrafiltration Membranes in an Aerobic Membrane Bioreactor (aMBR): A Validation Study

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Abstract: A validation study using recycled ultrafiltration membranes (r-UF) on an aerobic membrane bioreactor (aMBR) was conducted for the first time. Four different polyethersulfone (PES) membranes were tested using synthetic urban wastewater (COD 0.4–0.5 g/L) during two experimental periods: (i) recycled ultrafiltration membrane (r-UF) and commercial UF membrane (molecular weight cut-off (MWCO) 150 kDa) (c-150 kDa); (ii) r-UF membrane modified by dip-coating using catechol (CA) and polyethyleneimine (PEI) (mr-UF) and c-20 kDa membrane. Permeability, fouling behavior, and permeate quality were evaluated. Extensive membrane characterization was conducted using scanning electron microscopy (SEM), atomic force microscopy (AFM), energy-dispersive X-ray (EDX), and confocal laser scanning microscopy (CLSM). Permeate quality for r-UF and mr-UF membranes was excellent and comparable to that obtained using commercial membranes under similar conditions. Additionally, r-UF and mr-UF membranes presented a steadier performance time. Additionally, r-UF membrane demonstrated less tendency to be fouled (R_f, m^{-1}) r-UF 7.92 ± 0.57 × 10^{12}; mr-UF 9.90 ± 0.14 × 10^{12}, c-150 kDa 1.56 ± 0.07 × 10^{13} and c-20 kDa 1.25 ± 0.50 × 10^{13}. The r-UF membrane showed an excellent antibiofouling character. Therefore, r-UF membranes can be successfully implemented for wastewater treatment in aMBR, being a sustainable and cost-effective alternative to commercial membranes that can contribute to overcome membrane fouling and membrane replacement issues.

Keywords: membrane bioreactor (MBR); end-of-life membrane; surface modification; antibiofouling; recycled ultrafiltration membrane; recycling

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Citation: Rodríguez-Sáez, L.; Landaburu-Aguirre, J.; García-Calvo, E.; Molina, S. Application of Recycled Ultrafiltration Membranes in an Aerobic Membrane Bioreactor (aMBR): A Validation Study. *Membranes* **2024**, *14*, 149. https://doi.org/10.3390/membranes14070149

Academic Editor: Juan L. Acero

Received: 4 June 2024
Revised: 27 June 2024
Accepted: 2 July 2024
Published: 5 July 2024

1. Introduction

Membrane technology has been successfully used and improved for wastewater treatment and many other technological, industrial, and environmental processes for many years now. Particularly, membrane bioreactors (MBRs) for wastewater treatment have acquired great importance due to their great removal/recovery efficiency and lower space requirements compared to conventional activated sludge (CAS) systems resulting from the use of membranes. The installed MBR capacity in 2019 was estimated at over 20 gigalitres per day [1]. Economically speaking, the global market of MBRs is expected to reach EUR 4.9 billion by 2026 [2]. However, MBR processes also present some drawbacks, such as membrane fouling that leads to large chemical consumption; therefore, there is a need for replacement membranes, which substantially increase MBRs' operational costs [3,4]. The rate of membrane replacement in membrane bioreactor facilities is generally estimated to be between 5 to 10 years [5]. This is why, in recent years, several studies have focused on producing cost-effective membrane alternatives and membranes with antifouling properties. Among them, there is a promising trend of studies based on recycled ultrafiltration membranes (r-UF) that come from end-of-life reverse osmosis membranes (EoL-RO), developed as a viable alternative [6,7]. According to Salinas et al., around 30,000 tons of EoL-RO membranes will be generated and placed into landfills worldwide by 2025, a

5. Validation

The present work entails a validation study (Scientific paper 3) aiming to assess the viability of r-UF and modified r- UF obtained from EoL RO membranes, as submerged flat-sheet membranes in aMBR system. The performance of the r-UF a mr-UF membranes is compared to the performance of two different UF commercial membranes commonly used on MBR systems that present very similar characteristics of the r-UF membranes. Four membranes were tested simultaneously in pairs maintaining similar working conditions. The process performance has been evaluated in terms of i) membrane permeability, ii) resulting permeate quality and iii) membrane fouling behavior.

5.1. Materials and Methods

5.1.1. Experimental set-up

A laboratory scale aMBR (tank capacity of 20 L) was used. Two flat sheet membrane cartridges (with an effective membrane area of 0.11 m^2 per membrane) were placed simultaneously in a submerged configuration (Figure 35).

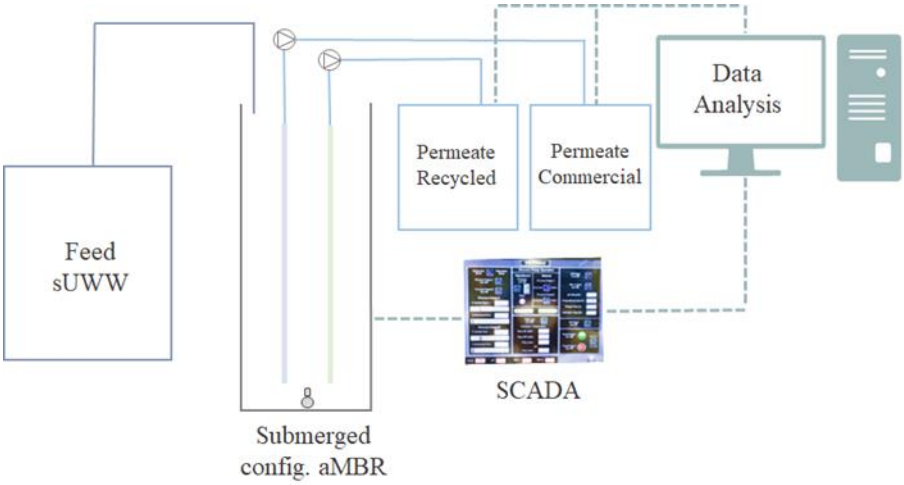


Figure 35. MBR system outlines

Four different membranes (see section 5.1.5) were tested in two different periods: Period I and Period II. Membranes were tested using synthetic wastewater simulating urban wastewater (uSWW) (Table 19).

Table 19. Synthetic urban wastewater characteristics

	Average	Standard deviation
EC (mS/cm)	2.9	0.4
COD (mg/L)	421.4	23.1
BOD_5 (mg/L)	226.3	17.4
TOC (mg/L)	132.5	9.6
TN (mg/L)	31.4	2.0
TP (mg/L)	5.0	0.9

The primary sludge inoculum was obtained from the Municipal Wastewater Treatment Plant of Guadalajara. To rate the MBR performance, Trans-Membrane-Pressure (TMP), pH, and temperature data were monitored constantly. MBR feed and permeate from both membranes in use in every period were sampled and analyzed twice a week. Characterization of the mixed liquor was also performed. Mixed liquor suspended solids (MLSS) were determined using UNE-EN 872 [166], BOD_5 was determined using UNE-EN ISO 9408 [167], COD was determined based on UNE 77004 [168], and TN and TP were determined photometrically (SpectroQuant Pharo 100, Merk) based on UNE-EN ISO 6878 for TP and UNE-EN 25663 for TN [169,170]. DIN 38405 D9 ($N\text{-}NO_3$), and the UNE EN ISO 6878 ($P\text{-}PO_4$) methods were used , after sample digestion [169,171]. TOC was determined using the TOC-V CSH ASI-V model (Shimadzu) based on Standard Methods for the examination of water & wastewater alkalinity 2320 B. E. coli and total coliform were detected and enumerated following membrane filtration technique based on UNE-EN ISO 9308-1 using chromogenic culture medium CHROMagar™ CCA (Scharlau) [172].

Constant flux (J; 16 L m^{-2} h^{-1}) operation and variable TMP were selected to assess the membrane performance. Membranes operated on cycles of 8 min of suction followed by 2 min of relaxation. After a start-up period in which the biomass was acclimatized to the operating conditions, the laboratory-scale aMBR plant operated in two different experimental periods. During Period I, the membranes used were as follows: (Ia) c-150 kDa (96 days; 16 L m−2 h^{-1}) and (Ib) r-UF (96 days; 16 L m^{-2} h^{-1}). During Period II, the membranes used were as follows: (IIa) c-20 kDa (64 days; 16 L m^{-2} h^{-1}) and (IIb) mr-UF (64 days; 16 L m^{-2} h^{-1}). Due to experimental planning on the aMBR system, Period II needed to be limited to 64 days. The laboratory-scale aMBR unit operated at a hydraulic retention time (HRT) of 15 h. For Period I, apart from the samples necessary for analyses and monitoring, 1,000 mL/d of mixed liquor (sludge retention time (SRT) ~20 days) was wasted. The MLSS during Period I was approx. 10.64 g/L ± 1.12 g/L; the MLSS during Period II was approx. 7.24 g/L ±1.69 g/L. Regarding Period II, except for the samples necessary for analyses and monitoring, no biomass was wasted from the reactor (resulting in a SRT of ~∞). Throughout both periods, membrane mechanical cleaning was conducted whenever a sudden pressure spike was observed and/or some problem occurred during the experimental period; otherwise, it was carried out approximately every 20– 28 days. Additionally, one chemical cleaning was conducted after the first sudden pressure spike in every experiment (with approx. 1% NaOCl solution for 30 min). Membrane fouling was analyzed at the end of each membrane's operating period using a resistance-in-series model proposed by Di Bella et al. to assess the relative importance of pore blocking and cake layer formation on the studied membranes [141,173]. Additionally, additional membrane coupons of every studied membrane were placed into the tank for the experimental period to study the biofouling attached to the membrane at different experimental times i) one week; ii) two weeks; iii) one month and iv) two months.

5.1.2. *Membrane fouling analysis.*

Membrane fouling analysis was conducted at the end of both periods applying the resistance-in-series model (RIS) suggested by Di Bella et al in order to measure the importance of the different fouling mechanisms affecting membranes [141,173]. The analysis was conducted following the exact procedure shown in the previous proof-of-concept study [174].

5.1.3. Chemicals

The chemicals consumed along this study were sodium hypochlorite (NaClO 10% w/v); ethanol (96% EPR Ph.Eur. LABKEM, Barcelona, Spain); polyethylenimine, branched (average Mw 800 by LS, average MN 600 by GPG; 1,2-dihydroxybenzene (ReagentPlus®, ≥99%. Merck Life Science, Darmstadt, Germany, S.L.U); Trizma hydrochloride (reagent grade ≥ 99.0%; Trizma base (reagent grade ≥ 99.9%; primary standard and buffer; glucose ($C_6H_{12}O_6$) D(+) glucose anhydrous, extra-pure, Ph Eur, BP, USP); meat peptone; urea (reagent-grade urea ACS); sodium chloride (reagent-grade NaCl, ACS, ISO, Reag. Ph Eur); sodium bicarbonate ($NaHCO_3$, extra-pure, Pharmpure®, Ph Eur, BP, USP); di-potassium hydrogen phosphate, anhydrous (K_2HPO_4 for analysis, ExpertQ®, ACS, Reag. Ph Eur); calcium chloride dihydrate ($CaCl_2.2H_2O$ powder, for analysis via ExpertQ®, ACS); magnesium sulfate heptahydrate ($MgSO_4$.7H2O for analysis via ExpertQ®, ACS, Reag. Ph Eur); iron (III) chloride hexahydrate ($FeCl_3.6H_2O$ ACS reagent, 97%); pyridine (C_5H_5N ExpertQ®, ACS, Reag. Ph Eur were purchased from Merck Life Science, Darmstadt, Germany, S.L.U. Sodium hydroxide (reagent-grade NaOH, ACS, Iso, Reag. PhEUr) were purchased from Scharlab S.L., Barcelona, Spain. The ultrapure water (Milli-Q) used in the experiments was obtained from Millipore, Molsheim, France, equipment (conductivity less than 0.055 $\mu S\ cm^{-1}$).

5.1.4. Membrane characterization

Extensive membrane surface characterization was also conducted. Scanning electron microscopy (SEM) combined with energy-dispersive X-ray (EDX) spectroscopy using an S-8000 Model (Hitachi) image device was employed to inspect the surface of the membranes and their elemental composition. Membrane surface roughness was examined by atomic force microscopy (AFM) using a Multimode topographical AFM (Vecco Instruments, Santa Barbara, CA, USA) equipped with a Nanoscope Iva control system (software version 6.14r1). Silicon tapping probes (RTESP, Veeco) were used with a resonance frequency of ~300 kHz and a scan rate of 0.5 Hz; $2 \times 2\ \mu m^2$ AFM images were taken for each sample. The confocal biofilm images were obtained under a confocal laser scanning microscope (CLSM Leica SP5, Leica Microsystems). Surface wettability was analyzed using a sessile drop static water contact angle (WCA) using an optical contact angle measurement system (KSV Cam 200 Instrument, Finland). A live/dead backlight bacterial viability kit (Molecular Probes™) was used to observe bacterial accumulation over the membrane surface. To assess if the membranes had been in contact with halogenated compounds, a Fujiwara test was conducted.

5.1.5. Membranes

For the present study, two recycled and two commercial UF membranes (c-20 kDa and c-150 kDa) were evaluated in terms of i) membrane permeability, ii) permeate quality, and iii) membrane fouling behavior. All the studied membranes' properties are presented in Table 20. A previous membrane characterization was conducted to assess the properties of the membranes.

Table 20. Membranes technical data

		c-150 kDa	**r-UF**	**c- 20 kDa**	**mr-UF**
Material		Polyethersulfone (PES)	Polyethersulfone (PES)	Polyethersulfone (PES)	Polyethersulfone (PES)
Backing material		Polypropylene (PP)	Polyethylene terephthalate (PET)	Polypropylene (PP)	Polyethylene terephthalate (PET)
Permeability (L·m^{-2}·h^{-1} bar^{-1})		566.17±9.39	39.03±1.74	56.97±1.55	192.68±1.57
M.W.C.O (kDa)		87.64±0.65	33.76±4.16	24.63±3.82	85.04±6.87
Contact angle		58.00±0.99	59.01±1.25	57.05±1.25	59.21±1.76
Roughness	*R_a (nm)*	8.4±2.6	4.7±0.6	11.7±3.7	5.2±0.9
	R_q (nm)	6.6±2.2	6.3±1.2	8.9±2.7	7.5±1.3

Coupons (0.06 m^2 area) from four different membranes were used: i) r-UF membrane model TM720-400 (Toray, Japan); ii) mr-UF membrane model TM720-400 (Toray, Japan) modified using CA and PEI; iii) c-20 kDa membrane (Microdyn, Wiesbaden, Germany) model Nadir UP020 20 kDa; and iv) c-150 kDa membrane (Microdyn, Wiesbaden, Germany) model Nadir UP150 150 kDa. The r-UF membranes were obtained by removing the polyamide layer of EoL-RO membranes by means of exposure to a NaClO dose of 800,000 ppm·h [133]. Adapting the work of Rodríguez-Sáez et al., a scaled-up mr-UF membrane was prepared using a dip-coating process applying the optimized modification conditions established in the previous research (1h; 30ºC; CA:PEI ratio 1:1) [133]. Additionally, two commercial membranes were selected as a control to set the performance standards.

5.2. Results and discussion

5.2.1. Membrane performance.

Membrane performance was studied by monitoring TMP and permeate quality over the course of the whole experiment. Regarding permeates, overall results showed that the quality obtained using the r-UF and mr-UF membranes was high, and such permeates were also similar to the permeate obtained with the studied commercial membranes. Figure 36 shows the removal efficiency (%) for every membrane during each experimental period.

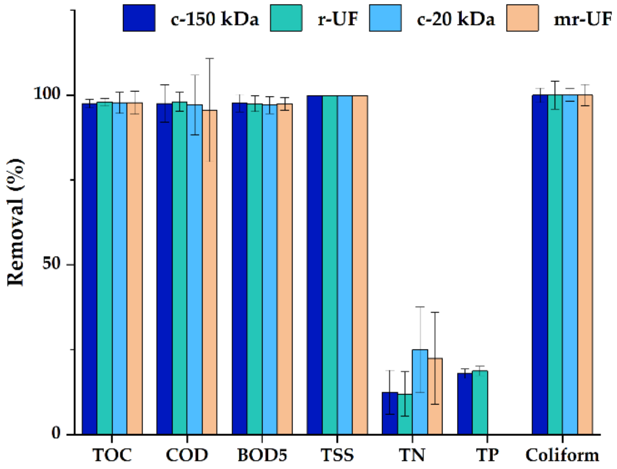


Figure 36. Membrane removal efficiency (R%) for every analyzed parameter of each membrane´s permeate

Reduction percentages for all studied membranes were above 99.9% in terms of suspended solids and Coliform bacteria. Additionally, every membrane achieved a reduction of above 97.0% for BOD_5. For COD, all membranes exceeded 95.0% reduction, with r-UF and c-150 kDa obtaining the best results. Further, TOC reduction remained above 95.0% for all the membranes, but the r-UF membrane obtained the best results (98.3%). shows the membrane behavior in terms of TMP over time for experimental Period I and Period II.

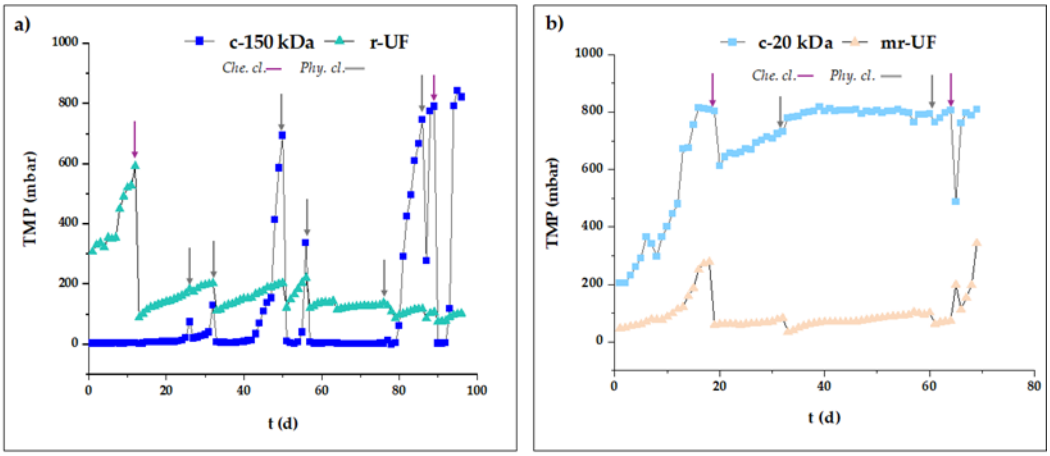


Figure 37. TMP (mbar) for every membrane: a) Period I; b) Period II.

The r-UF membrane presented an increase in TMP and therefore a decline in permeability, but after day 11, performances remained quite steady. Moreover, considering the entire experimental period, the general tendency for both r-UF and mr-UF membranes was rather similar, presenting an increase in permeability that was maintained until the end of the experiment. Regarding the c-20 kDa membrane, after the first significant TMP increase, it showed a steady TMP until the end of the experiment. It is possible that this membrane suffered from some grade of irreversible fouling in pore blocking form given its lower MWCO. On the other hand, the c-150 kDa membrane presented a quite low and stable TMP until day 48 when it exhibited a first sharp TMP increase. For the rest of the experiment, the c-150 kDa membrane presented very unstable performance. This is in concordance with the behavior observed by He et al. for PES membranes between 20 – 70 kDa, membranes with a lower MWCO that showed a faster decline in permeability in the early stages of the experimentation period. However, this tendency changes with time in experiments; significant flux variations have been observed throughout the later stages of membrane filtration with higher MWCO [175].

Nonetheless, a number of factors might be considered for deeper understanding of membrane fouling mechanisms that affect membrane permeability, such as hydrophilicity and surface roughness [175,176]. In the present study, membrane wettability was rather similar for all studied membranes. This was unexpected, especially considering the mr-UF membrane, where lower contact angle values were expected due to the modification process conducted on the membrane surface. However, in order to not compromise other membrane properties (e.g., permeability and roughness) a light modification was selected [133] achieving a null improvement in the hydrophilic character of the modified membrane.

Figure 38 shows AFM images and roughness values for every membrane. The r-UF membrane showed the lowest roughness value (R_a= 4.7±0.6 nm; R_q= 6.3±1.2 nm) [133] followed by the mr-UF membrane (R_a= 5.2±0.9 nm; R_q= 7.5±1.3 nm) [133]. On the other hand, the c-20 kDa membrane presented the highest roughness values (R_a= 11.7±3.7 nm; R_q= 8.9±2.7 nm).

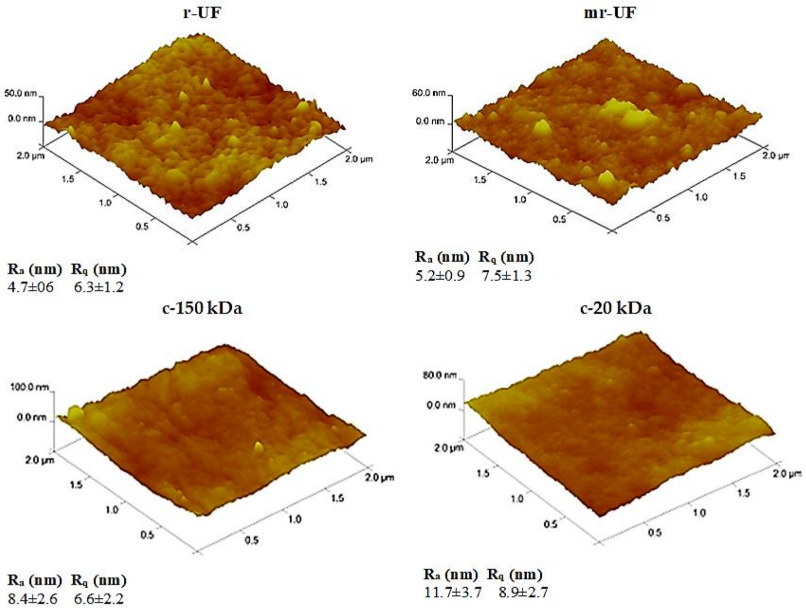


Figure 38. AFM images (2 × 2 µm2) for pristine membranes.

Membranes with higher surface roughness tend to be more prone to developing fouling issues that enhance their decline in permeability [177]. Moreover, membranes that have higher roughness values tend to respond worse to both physical and chemical maintenance cleanings. This leads to worse performance compared to membranes with lower surface roughness in long-term experiments [175]. The same behavior was observed in this study, where for both experimental periods (I and II), the commercial membranes had the highest surface roughness and greater long-term decline in permeability compared to the r-UF and mr-UF membranes.

5.2.2. *Membrane resistance in series (RIS) analysis*

According to fouling resistance analysis, the r-UF and mr-UF membranes presented lower fouling resistance due to fouling (R_f) (7.92 ± 0.57 x 10^{12} m^{-1} and 9.90 ± 0.1 x 10^{12} m^{-1}, respectively), compared with the c-150 kDa and c-20 kDa membranes (1.56 ± 0.07 x 10^{13} m^{-1} and 1.25 ± 0.50 x 10^{13} m^{-1}, respectively). This is most probably due to the higher surface roughness values of commercial membranes compared to recycled ones. As mentioned before, membrane fouling formation is a multifactorial process affected by several factors including membrane roughness [149,165]. Additionally, Figure 39 shows the different influential fouling mechanisms. Cake layer resistance includes reversible and irreversible cake layer resistance, while irreversible resistance values consist of both irreversible cake layer and pore blocking mechanisms.

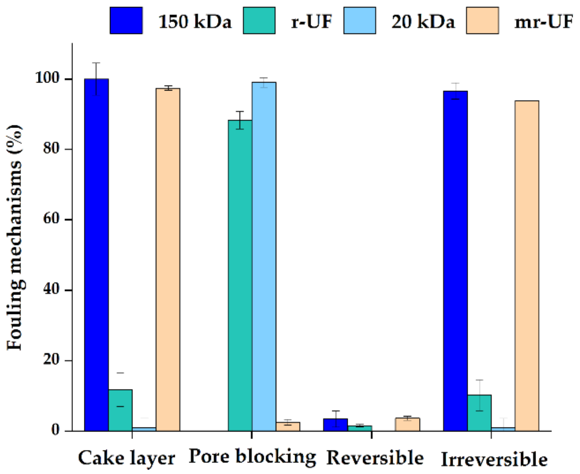


Figure 39. Membrane fouling resistance mechanisms.

For both membranes that presented lower MWCO (r-UF and c- 20 kDa) the main mechanism affecting fouling was pore blocking. On the other hand, for membranes with higher MWCO (c-150 kDa and mr- UF membrane) the main mechanism was cake layer deposition. Even though it could be expected that pore blocking would be larger on membranes with higher MWCO, it could be that cake layer deposition itself happened faster than pore blocking, provoking the formation of a physical barrier on the membrane surface. Then, larger molecules that would have been participating in pore blocking would be retained by this barrier, with only the smaller molecules reaching pores (and even blocking the smaller ones) (Figure 40) [45]

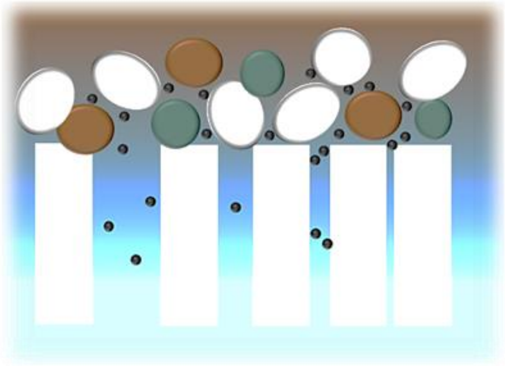


Figure 40. Cake layer deposition acting as a previous filter.

Adapted from [45]

It is interesting to note that both the c-150 kDa and mr-UF membranes presented greater irreversible fouling. According to Le-Clech et al., irreversible fouling deposition over the membrane's surface and interior pores more seriously affected membranes with larger-sized pores in the long term [45]. Additionally, it is important to know which type of fouling affected the membranes most. Even though membranes for water and wastewater treatment suffer from various types of fouling, biofouling is the main type of fouling affecting these membranes [60,64]. To check if membranes were affected by biofouling deposition during the experimental period, CLSM images were taken (Figure 41).

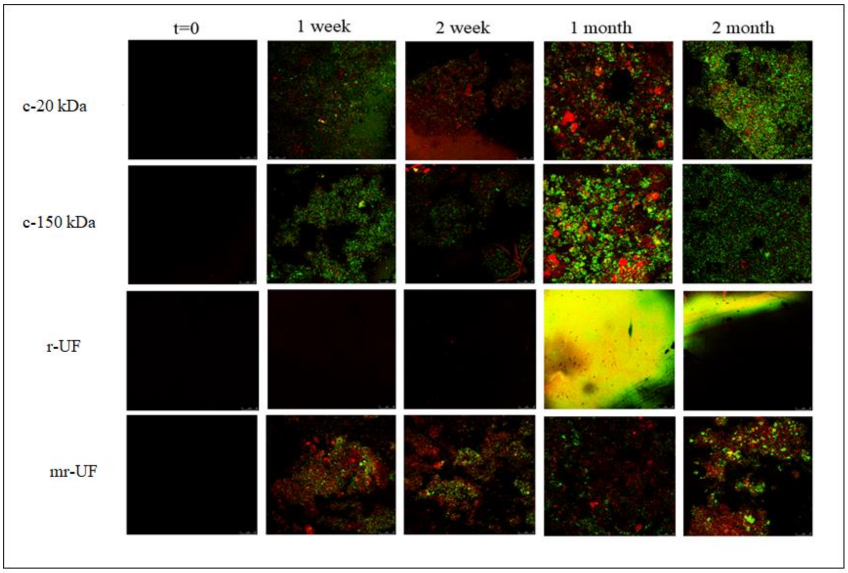


Figure 41. Confocal laser scan microscope (CLSM) images.

Confocal images show that both commercial membranes (c-150 kDa and c-20 kDa) present more attached biofouling, particularly at the late stages of the experimental period. On the other hand, the r-UF membrane, according to CLSM images, does not have any attached biofouling. This result is very promising because it clearly shows the antibiofouling character of the r-UF membrane. Moreover, the mr-UF membrane showed some degree of attached biofouling on the membrane surface that did not vary significantly during the experimental time, although, in general, it also presented less biofouling than the commercial membranes. Additionally, other works have already emphasized that r-UF membranes could be less prone to fouling due to contact with NaOCl during the recycling process [133,174]. Firstly, to confirm that the r-UF membrane was affected by halogenated compounds, a Fujiwara test was performed. The results are presented in Figure 42. As expected, both recycled membranes (r-UF and mr- UF) produced positive results.

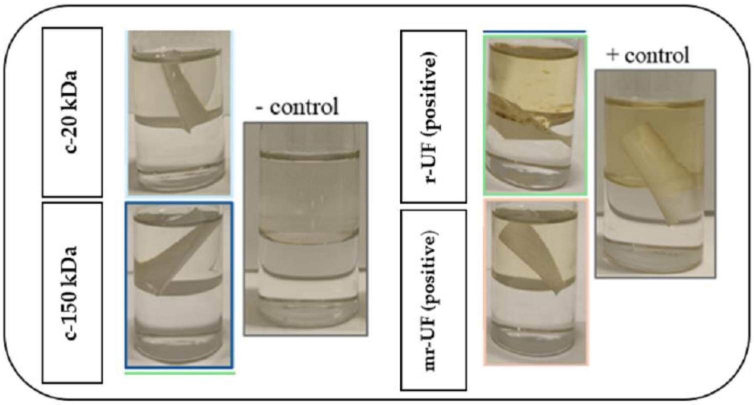


Figure 42. Fujiwara test results

Finally, an EDX analysis was conducted to study the chemical composition of the membranes' surface and to ensure that chlorine is, in fact, present on the membrane surface (Table 21). The obtained results revealed that, as expected, chorine was present in higher amounts on recycled membranes. Specifically, the amount of chlorine in r-UF and mr-UF was around four times higher than in the commercial membranes (c-20 kDa and c-150 kDa). The presence of chlorine on the membrane surface is probably a consequence of the recycling process. The chlorinated compounds used in the recycling process may have changed the properties of the membrane's surface, providing the recycled membrane with an antibiofouling character. The chlorine on the membrane surface might prevent the attachment of the bacteria found in the MBR system, ultimately reducing the biofouling phenomena on the membrane. This behavior on membranes that have chlorinated compounds on their surface has previously been observed [178]

On the other hand, the percentage of nitrogen in mr-UF is three times higher than in r-UF, which could be attributed to the nitrogen element of PEI used in the modification process, as observed in previous work [133]. Even though CA-PEI modification is intended to supply an antibiofouling character to membranes, the antibiofouling properties of the r-UF membrane itself have been shown to be even more effective. However, CA-PEI surface modification may have overlayed the chlorine compounds, reducing the antibiofouling properties of the mr-UF membrane compared to the r-UF membrane.

Table 21. Chemical composition analysis by EDX.

	c-150 kDa		**r-UF [17]**		**c-20 kDa**		**mr-UF [17]**	
	% weight	% atomic	% weight	% atomic	% weight	% atomic	% weight	% atomic
C	59.12	68.69	69.75	77.51	59.74	69.25	64.25	71.94
N	2.91	2.90	1.32	1.26	2.84	2.82	3.57	3.34
O	27.18	23.70	21.94	18.30	26.79	23.31	26.47	22.25
S	10.48	4.56	5.97	2.49	10.52	4.57	5.23	2.19
Cl	0.13	0.05	0.42	0.16	0.11	0.04	0.49	0.18

5.3. Conclusions

For the first time, an innovative long-term study to validate the use of r-UF membranes as aMBR submerged membranes has been conducted. The r-UF membrane and the mr-UF show excellent permeate quality that is comparable to different commercial UF membranes commonly used in MBR systems. Additionally, both the r-UF and mr-UF membranes showed a steadier pressure and less decline in permeability as the experimental period proceeded. The r-UF and mr-UF membranes also presented lower fouling resistance compared to commercial membranes. However, the more noteworthy result is that r-UF did not develop any biofouling during the experimental period (96 days) and presented the lowest fouling resistance value among all studied membranes. The present work also confirms that r-UF membrane surface contains chlorine that comes from the recycling process, granting the r-UF membrane its outstanding antibiofouling character. Therefore, this study shows that r-UF itself could be used on aMBR systems without the need for additional surface modification.

The results obtained regarding r-UF membranes are encouraging. Membranes' acquisition and replacement costs, along with maintenance costs, represent a high percentage of expenses involved in membrane processes. Consequently, the results obtained in this study regarding r-UF membranes are encouraging, consolidating the r-UF membrane as a very promising alternative for use in aMBR systems. Moreover, the indirect recycling of end-of-life RO membranes could also be a valuable tool in confronting the challenges involved in waste management, helping to save raw materials, energy consumption, and pollutant emission within environmental applications or industry processes in which membranes are used and, therefore, aligning with the principles of the Circular Economy.

Chapter 6

Conclusions

6. General conclusions

MBR systems have been proved to be an incredible tool to treat urban and industrial wastewater but presenting the same drawbacks related to membrane life span than other membrane treatment systems which increase significantly the operation costs. Moreover, desalination using RO membranes is expected to continue growing and, consequently, also producing EoL membranes. Therefore, membrane replacement will keep generating an increasing amount of discarded EoL RO modules. This is a scenario where membrane recycling must be contemplated as a needed and valuable tool to overcome the situation. The compendium of the scientific papers addressed in the present doctoral thesis set the fundaments for the indirect recycling of EoL RO membranes as UF membranes for their use in aMBR systems. The r-UF membranes have been extensively characterized to achieve a deep insight of their properties, with the objective to reveal the effect of their characteristics on membrane performance. Also, the quality of the treated water obtained with the recycled membranes was evaluated and compared to the water quality obtained by implementing the commercial membranes. The main conclusions from this doctoral thesis can be summarized as follows:

The proof of concept developed (*Chapter 3*) showed that r-UF membranes were suitable for their use in aMBR systems. The studied r-UF membrane presented an excellent performance in terms of permeability, permeate quality and permeability decline. Additionally, under the studied conditions, the r-UF membranes showed, in general, similar resistance behavior due to fouling than the commercial membrane (c-MF). Moreover, the overall performance was comparable to the performance of commercial membranes widely used in aMBR systems. Nevertheless, membrane resistance for r-UF membrane was higher than the resistance of the other c- MF membrane and, therefore, transmembrane pressure of the r-UF membrane was also higher. Additionally, preliminary economic assessment showed that, even though several factors must be considered e.g. membrane permeability, membrane frame type or percentage or recovered membrane, the cost of recycling the EoL membranes appears to be competitive. However, some steps of the processes such as the module disassembling must be further studied and automatized to achieve more competitive scenario.

With the aim to enhance the hydrophilicity of the r-UF membrane and consequently improve the resistance to fouling, a membrane surface modification was conducted (*Chapter 4*). For the first time, a surface modification using CA and PEI by dip-coating process was successfully conducted in a r-UF membrane. Moreover, statistical design of experiment resulted in an excellent tool to study not only the level factors in the modification process but also the interactions between those factors. It was confirmed that the interactions between factors were as statistically significant as the main factors themselves. Apart from that, it was confirmed that r-UF membranes modified at mild conditions resulted on improved permeability and enhanced fouling recovery. This way, mild conditions using less chemicals and less energy resulted suitable for its use on r-UF membranes continuing the path of Circular Economy.

Finally, a validation of developed r-UF membranes was conducted (*Chapter 5).* Along with r-UF and mr-UF membranes, two commercial UF membranes were tested. Both r-UF and mr-UF membranes showed an excellent performance related to permeate quality. Moreover, both membranes presented less resistance due to fouling which is extremely important for membranes, especially for those working on environments such the one that an MBR provides. Among the extensive membrane characterization conducted, EDX analysis showed that r-UF membrane presented on its surface more amount of chlorine than the rest of the membranes. Moreover, confocal images analysis showed that no bacteria was attached to the r-UF membrane surface during the experiment. Regarding mr-UF membrane, confocal images showed some extent of bacteria attachment even though it was less than the exhibited on the commercial membranes. This was probably due to the coverage of the chlorine in the surface by the co-deposition of CA and PEI.

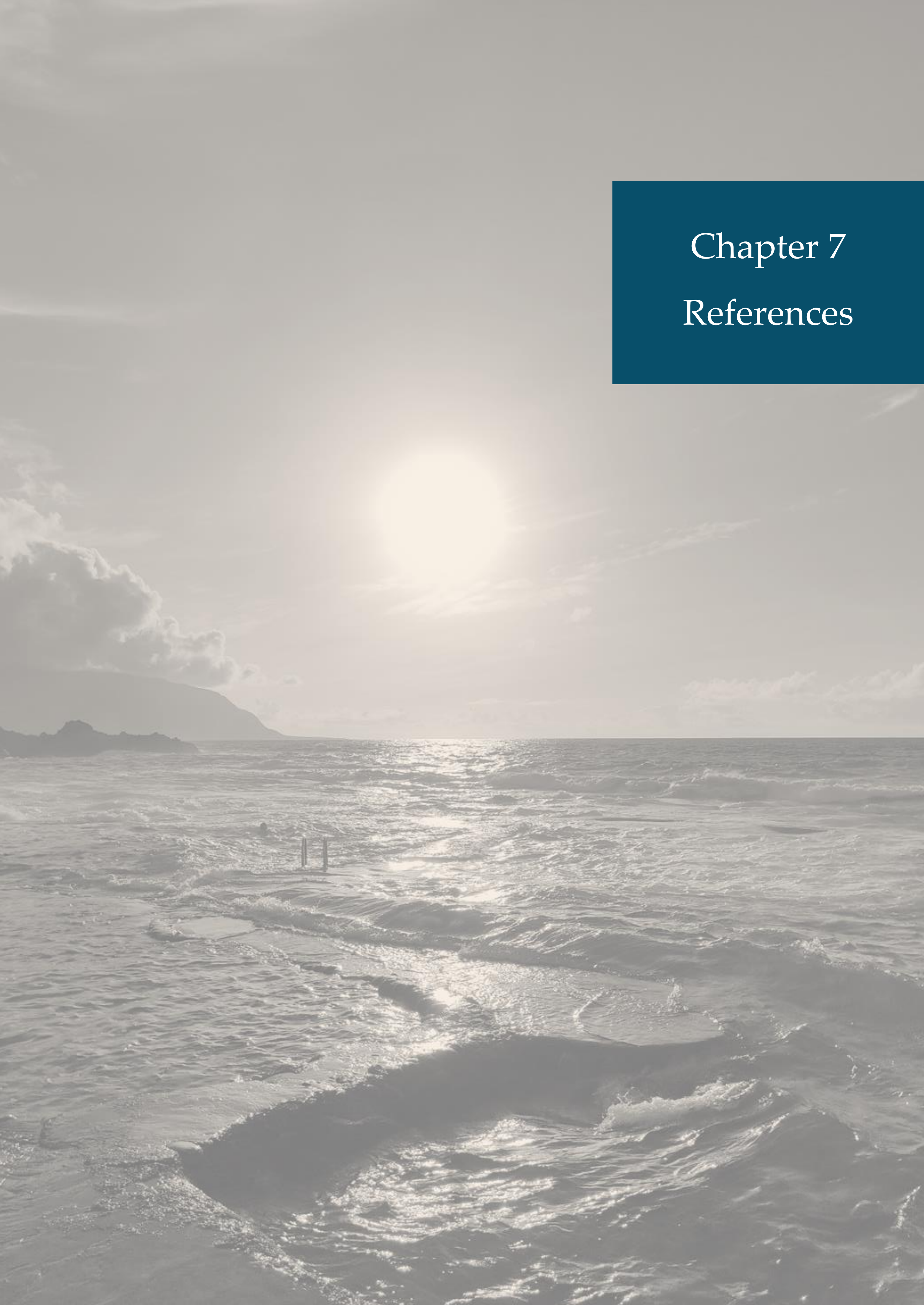
Overall, the present thesis has provided new experimental knowledge on the indirect recycling of EoL RO membranes for its use as r- UF membranes in aMBR. Thereby, this membrane recycling approach gathers the objectives of the Circular Economy promoted by the European Union. It follows the path of a sustainable economic growth, by extending the lifespan of existing products, and therefore, reducing raw materials and energy consumption along with a waste generation reduction. Consequently, the present thesis is directly compromised with the European strategic policies, as a part of the 2008/98/CE directive on waste, the European Green Deal and the Circular Economy Action Plan.

Nonetheless, certain questions remain unsolved and further research would be needed for tackling them in the future.

Future research should evaluate the performance of recycled membranes when treating real urban wastewater. Real wastewater exhibits seasonal fluctuations and intermittent compositional changes, which would provide valuable insights into membrane behavior under dynamic conditions. Scaling up the membrane assembly process is also essential to assess the feasibility of implementing r-UF membranes in full-scale MBR systems. This should be complemented with a more extensive LCA and cost analysis to detect and evaluate the key steps on the membrane recycling process, ensuring the attractiveness of the process for the industry.

Additionally, the behavior of r-UF membranes in MBR systems treating emerging contaminants such as pharmaceutical, biological compounds, microplastics among others, warrants investigation. Membrane performance under these conditions should be evaluated, along with the impact of these substances on membrane fouling and membrane integrity.

Furthermore, the integration of r-UF membranes in different systems such as anaerobic MBR is a promising avenue for exploration. This combination could expand treatment capabilities, enhance treated water quality, and potentially increasing the overall sustainability of the process. Additionally, other recycled membranes like NF-like recycled membranes may be tested in MBR systems allowing to obtain higher water qualities.



Chapter 7

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