Universidad de Valladolid

Escuela de Doctorado Universidad de Valladolid

PROGRAMA DE DOCTORADO EN INGENIERÍA QUÍMICA Y AMBIENTAL

TESIS DOCTORAL:

Study of the concentration process of municipal wastewater using forward osmosis membranes

Presentada por **Mónica Salamanca Verdugo**
para optar al grado de
Doctora por la Universidad de Valladolid

Dirigida por:
Dra. María del Mar Peña Miranda
Dra. Laura Palacio Martínez
Dr. Pedro L. Prádanos del Pico

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Resumen

Los desafíos globales de la escasez de agua y su contaminación, debido a las demandas industriales y el crecimiento demográfico, han generado una preocupación alarmante. El sexto objetivo de desarrollo sostenible de la agenda 2030 destaca la necesidad de disponibilidad y gestión sostenible del agua y el saneamiento. Para abordar estas preocupaciones críticas, es esencial una gestión eficiente de los recursos hídricos, y las plantas de tratamiento de aguas residuales (EDAR) desempeñan un papel fundamental. Las EDAR municipales están diseñadas no sólo para mitigar la contaminación sino también para salvaguardar la calidad ambiental, la salud humana y aprovechar recursos valiosos como el agua, los nutrientes y la energía. A medida que aumentan las poblaciones urbanas, las EDAR deben adaptarse a las cambiantes limitaciones ambientales y hacer la transición hacia sistemas de tratamiento más sostenibles y resilientes que prioricen el bajo impacto ambiental y la eficiencia energética. El tratamiento convencional de aguas residuales abarca diversos procesos físicos, químicos y biológicos para eliminar sólidos, materia orgánica y ocasionalmente nutrientes de las aguas residuales. Si bien es eficaz con los contaminantes convencionales, tiene dificultades para eliminar los contaminantes emergentes, como los productos farmacéuticos y las hormonas. En consecuencia, se han dirigido grandes esfuerzos al desarrollo de tecnologías avanzadas de tratamiento de aguas residuales, como filtración por membrana, adsorción y procesos avanzados de oxidación, para mejorar la eficiencia de eliminación de contaminantes y nutrientes. La tecnología de membranas, en particular, ha surgido como alternativa prometedora para depurar agua de diversas corrientes de aguas residuales, lo que resulta prometedor para la recuperación de recursos y la sostenibilidad ambiental.

En este contexto, esta tesis profundiza en la utilización de la tecnología de Ósmosis Directa (FO, de su término en inglés Foward Osmosis) para el tratamiento de aguas residuales municipales. Esta tecnología permite usar la presión osmótica de una disolución salina como fuerza impulsora, en vez de un gradiente de presión mecánica como se haría en un proceso de Ósmosis Inversa (RO, de su término en inglés Reverse Osmosis). Esto supone un considerable ahorro energético a favor de la FO. El estudio investiga el rendimiento de diferentes membranas de FO y se centra en eliminar los contaminantes emergentes de las aguas residuales, arrojando luz sobre el potencial y los desafíos de esta tecnología innovadora.

Con todo lo anterior, el Capítulo 1 se centra en una breve introducción al problema medioambiental de la escasez de agua en el mundo, el papel que juegan las depuradoras de aguas residuales urbanas, el desarrollo de la tecnología de membranas en el tratamiento de aguas y las diferentes características y particularidades del proceso de ósmosis directa. La justificación, los objetivos y el alcance de la tesis se resumen en el Capítulo 2 y los materiales utilizados y los procedimientos experimentales se describen en el Capítulo 3. En los Capítulos 4, 5 y 6 se presentan los resultados experimentales de la tesis que se corresponden a los artículos ya publicados.

Para este propósito, en el Capítulo 4, se estudia el rechazo de 24 contaminantes de preocupación emergente (CEC) utilizando un módulo biomimético de FO de acuaporina de fibra hueca. La membrana demuestra con éxito altas tasas de rechazo para la mayoría de los CEC, y se estudian los efectos del peso molecular, la carga y la hidrofobicidad de los contaminantes para comprender mejor su comportamiento.

El Capítulo 5 centra la atención en el tratamiento de aguas residuales urbanas reales utilizando la misma membrana que en el Capítulo 4. Este estudio explora la presencia de 51 CEC de las aguas residuales urbanas y encuentra 18 contaminantes en las aguas residuales urbanas objetivo, siendo el NaCl la solución de extracción óptima para este propósito. La membrana demuestra ser eficaz para reducir significativamente los contaminantes en las aguas residuales, produciendo agua ecotoxicológicamente segura con buenas tasas de recuperación, particularmente para compuestos de mayor peso molecular. Posteriormente, con el objetivo de estudiar el proceso de escalado del sistema de FO y del tipo de membrana, se utilizó un modulo multicanal de mayor superficie de área activa (2.3 m^2) en el Capítulo 6. El estudio evalúa el rendimiento de una membrana tubular cuando se trata con aguas residuales municipales y compara los modos de funcionamiento de FO y ósmosis inversa de baja presión (LPRO) como alternativas a los tradicionales procesos de membrana impulsados por presión. La investigación enfatiza la idoneidad del FO debido a sus menores niveles de contaminación y ofrece nuevos conocimientos sobre el tratamiento de aguas residuales de baja energía y la recuperación de energía, particularmente en lo que respecta al FO y LPRO para la concentración de aguas residuales. Además, el estudio investigó el potencial bioquímico para la producción de metano a partir de aguas residuales municipales concentradas mediante procesos FO y LPRO a 35 °C, comparando ambos métodos y evaluando el impacto de la sal en la producción de metano.

Los resultados obtenidos en la presente tesis mejoraron el rendimiento de tecnologías de membranas innovadoras como la Ósmosis Directa (FO) en procesos de tratamiento de aguas residuales y representaron un primer paso en el escalado de esta tecnología hacia la industrialización. La comercialización de esta tecnología contribuiría a abordar las preocupaciones ambientales y la escasez de recursos de una manera rentable y ambientalmente sostenible. En conjunto, estos capítulos subrayan el panorama cambiante del tratamiento de aguas residuales y resaltan el papel fundamental de las FO en este contexto.

Summary

The global challenges of water pollution and scarcity due to industrial demands and population growth, have generated alarming concern. The sixth sustainable development goal of the 2030 agenda highlights the need for availability and sustainable management of water and sanitation. To address these critical concerns, efficient water resource management is essential, and wastewater treatment plants (WWTPs) play a critical role. Municipal WWTPs are designed not only to mitigate pollution but also to protect environmental quality and human health and to take advantage of valuable resources such as water, nutrients and energy. As urban populations increase, WWTPs must adapt to changing environmental constraints and transition toward more sustainable and resilient treatment systems that prioritize low environmental impact and energy efficiency. Conventional wastewater treatment encompasses various physical, chemical and biological processes to remove solids, organic matter and occasionally nutrients from wastewater. While effective on conventional contaminants, it struggles removing emerging contaminants such as pharmaceuticals and hormones. Consequently, great efforts have been directed to the development of advanced wastewater treatment technologies, such as membrane filtration, adsorption and advanced oxidation processes, to improve the removal efficiency of contaminants and nutrients. Membrane technology, in particular, has emerged as a preferred manner of recovering water from various wastewater streams, which holds promise for resource recovery and environmental sustainability.

In this context, this thesis delves into the utilization of Forward Osmosis (FO) technology for the treatment of municipal wastewater. This technology makes possible to use the osmotic pressure of a salt solution as the driving force, instead of a mechanical pressure gradient as would be done in a Reverse Osmosis (RO) process. This results in considerable energy savings in favor of RO. Our study investigates the performance of different FO membranes and focuses on the remotion of emerging contaminants from wastewater, shedding light on the potential and challenges of this innovative technology.

With all the above, Chapter 1 focuses on a brief introduction to the environmental problem of water scarcity worldwide, the role played by urban wastewater treatment plants, the development of membrane technology in water treatment and the different characteristics and particularities of the forward osmosis process. The justification, objectives and scope of the thesis are summarized in Chapter 2 and the materials used and

the experimental procedures are described in Chapter 3. Chapters 4, 5 and 6 of the experimental results of the thesis are presented below, corresponding to the already published papers.

For this purpose, in Chapter 4, the focus is on the rejection of 24 Contaminants of Emerging Concern (CECs) using a biomimetic hollow fiber aquaporin FO module. The membrane successfully demonstrates high rejection rates for the majority of CECs. The influence of their molecular weights, charge, and hydrophobicity is studied to better understand their behavior.

Chapter 5 shifts the spotlight to urban real wastewater treatment using the same membrane as in the Chapter 4. This study explores the presence of 51 CECs from urban wastewater, finding 18 contaminants in the target urban wastewater with NaCl as the optimal draw solution for this purpose. The membrane proves effective in significantly reducing the pollutants in wastewater, producing ecotoxicologically safe water with good recovery rates, particularly for higher-molecular-weight compounds. In order to scale the FO system, a membrane with a larger surface area was used in Chapter 6. The study assesses a tubular membrane's performance when dealing with municipal wastewater and compares FO and Low-Pressure Reverse Osmosis (LPRO) operating modes as alternatives to traditional pressure-driven membrane processes. The research emphasizes the suitability of FO due to its lower fouling levels and offers new insights into low-energy wastewater treatment and energy recovery, particularly concerning FO and LPRO for wastewater concentration. In addition, the study investigated the biochemical potential for methane production from concentrated municipal wastewater through FO and LPRO processes at 35 °C, comparing both methods and evaluating the impact of salt on methane production.

The results obtained in the present thesis improved the knowledge of the performance of innovative membrane technologies like Forward Osmosis (FO) in wastewater treatment processes and represented a first step in the scale up of this technology towards industrialization. The commercialization of this technology would contribute to addressing environmental concerns and resource scarcity in a cost-effective and environmentally sustainable way. Collectively, these chapters underscore the evolving landscape of wastewater treatment and highlight the pivotal role of FO in this context.

List of publications included in this Thesis

Salamanca, M.; López-Serna, R.; Palacio, L.; Hernández, A.; Prádanos, P.; Peña, M. Study of the Rejection of Contaminants of Emerging Concern by a Biomimetic Aquaporin Hollow Fiber Forward Osmosis Membrane. J. Water Process Eng. 2021, 40, 101914. https://doi.org/10.1016/j.jwpe.2021.101914.

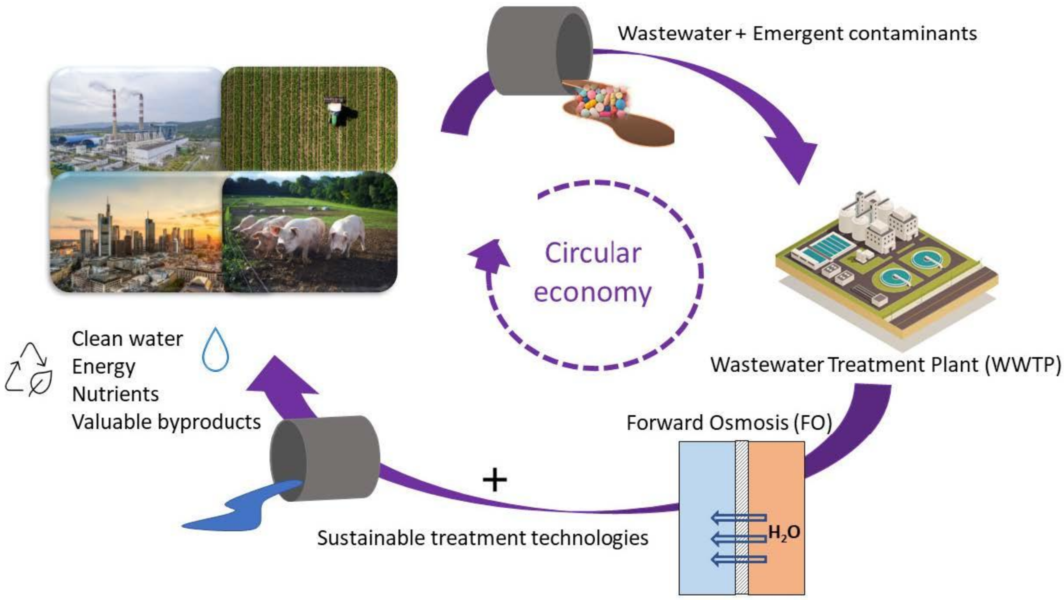
Salamanca, M.; López-Serna, R.; Palacio, L.; Hernández, A.; Prádanos, P.; Peña, M. Ecological Risk Evaluation and Removal of Emerging Pollutants in Urban Wastewater by a Hollow Fiber Forward Osmosis Membrane. Membranes 2022, 12(3), 293, https://doi.org/10.3390/membranes12030293.

Salamanca, M.; Palacio, L.; Hernández, A.; Peña, M.; Prádanos, P. Evaluation of Forward Osmosis and Low-Pressure Reverse Osmosis with a Tubular Membrane for the Concentration of Municipal Wastewater and the Production of Biogas. Membranes 2023, 13(3), 266, https://doi.org/10.3390/membranes13030266.

Salamanca, M.; Peña, M.; Hernandez, A.; Prádanos, P.; Palacio, L. Forward Osmosis Application for the Removal of Emerging Contaminants from Municipal Wastewater: A Review. Membranes2023,13(7), 655. https://doi.org/10.3390/membranes13070655

Chapter 1

Introduction



The introduction section is taken from the published review article:

Salamanca, M.; Peña, M.; Hernandez, A.; Prádanos, P.; Palacio, L. Forward Osmosis Application for the Removal of Emerging Contaminants from Municipal Wastewater: A Review. Membranes **2023**, 13(7), 655. https://doi.org/10.3390/membranes13070655

1.1. Wastewater treatment and current state of the art

Water scarcity and contamination are considered serious problems of worldwide concern, in relation to both industrial requirements and population growth [1,2]. In addition to current water scarcity, it is estimated that water shortage could increase up to 60% by 2025 [3,4]. The sixth sustainable development goal of the 2030 agenda focuses on the availability and sustainable management of water and sanitation for all.

Therefore, an efficient management of water resources is necessary. In the prosecution of this aim, wastewater treatment plants (WWTPs) play a fundamental role. It should be noted that municipal WWTPs are designed to reduce pollution and to protect environmental quality and human health, in addition to obtaining benefits such as water, nutrients, and energy [5,6].

WWTPs are facilities that treat the wastewaters (WW) generated by an area or city; therefore, an increase in urban population directly influences WW discharges that must be controlled and treated so that they do not pose a risk to humans and the environment.

Increasing environmental constraints worldwide are creating the need to adapt conventional wastewater plants to more sustainable and robust treatment systems, employing new treatment technologies and combining low environmental impact and energy efficiency [7,8]. The design of sustainable wastewater treatment systems must focus on environmental protection, while minimizing energy and resource consumption [9]. Conventional wastewater treatment typically consists in a combination of physical, chemical, and biological processes and operations in order to remove solids, organic matter, and sometimes, nutrients from wastewater [10]. The physical processes include screening, sedimentation, and filtration, while the chemical processes include coagulation, flocculation, and disinfection. The biological processes involve the use of microorganisms to break down organic matter and nutrients in wastewater [11]. The combination of these processes and operations can effectively treat wastewater and reduce its potential impact on the environment and human health. While this approach effectively treats wastewater and reduces its environmental and health implications, it is less efficient in eliminating emerging pollutants such as drugs, hormones, and pesticides. Consequently, significant efforts have been dedicated to develop effective wastewater treatment technologies aimed at removing pollutants and establishing eco-friendly processes [12].

Different advanced wastewater treatment technologies, such as membrane filtration, adsorption, and advanced oxidation processes are under investigation to enhance the removal efficiency of emerging pollutants and nutrients [13]. It is important to consider the advantages and disadvantages of different treatment technologies and their effectiveness in removing pollutants from wastewater when selecting a treatment process. Membrane technology has emerged as a favorite choice for reclaiming water from different wastewater streams for reuse [14]. The integration of resource recovery in wastewater treatment plants can also contribute to environmental sustainability by reducing waste and producing valuable resources [15].

WWTPs include different levels of treatment, beginning with a primary treatment, which removes a portion of the organic matter and suspended solids, followed by a secondary treatment to eliminate biodegradable organic matter and nutrients. In some instances, ending with a tertiary treatment or advanced wastewater treatment to remove suspended solids and disinfect water [16]. However, many developing countries lack complete WWTPs, often limited to primary and secondary treatment stages without tertiary treatment or advanced sludge processing [17]. Although inadequate WWTP design and operation can result in severe local and global environmental issues [18].

Currently, the conventional activated sludge (CAS) processes are the most common treatments in WWTPs [19]. These treatments consume a large amount of energy due to the high electrical demand for aeration; moreover, the cost increases due to the necessary treatment of the resulting sludge [20,21]. Moreover, in this aerobic treatment of activated sludge, the carbon content of the wastewater is not effectively utilized, resulting in its conversion into biomass and carbon dioxide without being fully exploited [22].

Anaerobic digestion is a promising approach for energy and nutrient recovery from wastewater [23]. This treatment yields less sludge and consumes less energy, aligning with the circular economy concept. It leverages the organic matter present in urban wastewater to generate biogas, a renewable energy source, while reducing CO_2 emissions compared to aerobic treatment [24].

However, despite the advantages mentioned above, there are some difficulties in the application of anaerobic digestion for direct wastewater treatment. One of the difficulties is the low organic load of wastewater, which causes a significant increase in digester heating per unit of biogas production and, therefore, directly influences the economic viability of the process [25,26,27,28]. Nevertheless, the limitations of anaerobic wastewater treatment can be overcome with processes that pre-concentrate the organic content and nutrients of the wastewater, thus turning cost-effective anaerobic treatment into biogas production and nutrient recovery [25,27,28,29,30,31].

This requires new developments and technologies to establish more energy efficient systems on water treatment and reuse, with membrane technology being a promising alternative [32,33].

1.2. Membrane technologies

The development of synthetic membranes in the 1950s and 1960s led to the commercialization of membrane devices for industrial applications. Membrane technology has emerged as a preferred choice for reclaiming water from different wastewater streams for reuse [14]. The exact date when membrane technology was first used in wastewater treatment is not clear. Depending on the type of membrane, the selective separation of certain individual substances or substance mixtures is possible. In the simplest case, filtration is achieved when the pores of the membrane are smaller than the diameter of the undesired substance, such as harmful microorganisms.

The energy cost of membrane technology in water treatment varies depending on the type of membrane, the size of the plant, and the specific application [34]. While membrane technology can be energy-efficient compared to other treatment processes, it involves non-negligible capital and maintenance costs, and it needs intense redesign, that can altogether slow its adoption rate. The application of membrane technology for wastewater treatment and biofuel production not only reduces pollution but also decreases production costs. The cost–benefit analysis and technical efficiency evaluation of membrane bioreactor (MBR) technology for wastewater treatment showed that, with respect to the cost/energy efficiencies, the process is favorable [35]. Although, there are also some drawbacks, for example membrane fouling is a common issue in membrane technology, which can increase energy consumption and reduce the efficiency of the process [14]. Of course, it is important to consider in detail the energy cost and other factors when selecting a membrane technology for water treatment.

Different types of membranes, mainly using pressure as the driving force, are applied in water treatment processes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and forward osmosis (FO) [14,36,37]. The main difference between these membranes is their pore size and the level of filtration accuracy they provide. Both FO and RO membranes are used for the separation of water from dissolved solutes, such as salts, and can be used in combination with other membrane processes, such as UF, NF or MF [38]. RO needs to be preceded by another of these processes, whereas FO can be used as a standalone process or as a step-in hybrid process as convenient. The selection of a membrane type depends on the specific application, the quality of the feedwater, and the desired level of filtration accuracy.

In FO processes, it is not necessary to apply external pressure since an osmotic pressure gradient is generated between the feed solution (FS) (for example, wastewater) and the draw solution (DS). This is an important advantage due to its lower energy consumption and due to the lower fouling of the membrane compared to pressure-driven processes [39,40,41]. In addition, the process has low fouling due to the nature of the driving force, and this slight fouling is mostly reversible [42]. However, taking into account the energy consumption required to recover the DS to get rid of the salts to obtain clean water, the costs could approach those of RO. Thus, FO can concentrate wastewater and, consequently, organic matter and nutrients to feed subsequent anaerobic treatment to facilitate resource recovery.

1.3. Forward Osmosis Development

1.3.1. Background of FO

FO, as an alternative membrane process in wastewater treatment, has attracted increasing interest in recent years. FO is the process in which water molecules pass through a semipermeable membrane, which separates two solutions, as shown in Figure 1. This transport and movement of molecules takes place due to the osmotic pressure difference ($\Delta\pi$) which is the driving force in this phenomenon, as opposed to pressure-driven membrane processes. Thus, water is permeated passing through the membrane from the lowest solution concentration, FS, to the highest solute concentration solution, DS, while other solutes molecules are rejected [19,43]. FO has been investigated in various applications, such as seawater desalination [43], power generation [44], food processing [45], and wastewater treatment [46,47].

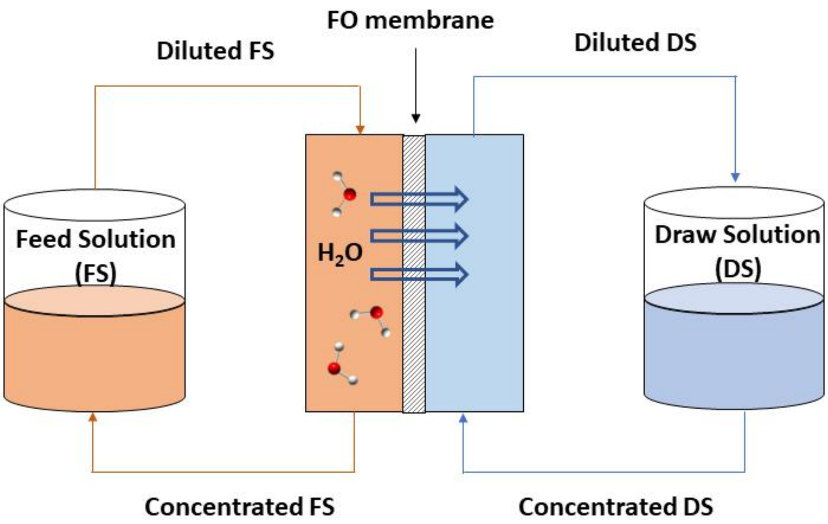


Figure 1. Scheme of the FO process. From Forward Osmosis Application for the Removal of Emerging Contaminants from Municipal Wastewater: A Review, by Salamanca, M.; Peña, M.; Hernandez, A.; Prádanos, P.; Palacio, L, 2023, *Membranes* 13(7), 655. Copyright 2023 by the authors.

The beginning of the interest in FO dates back to the 18th century [48,49], while interest in this field has increased due to the commercialization of membranes designed for this process [2]. Figure 2 shows the rising interest in membranes of FO in the last 20 years by analyzing the number of publications on the topic.

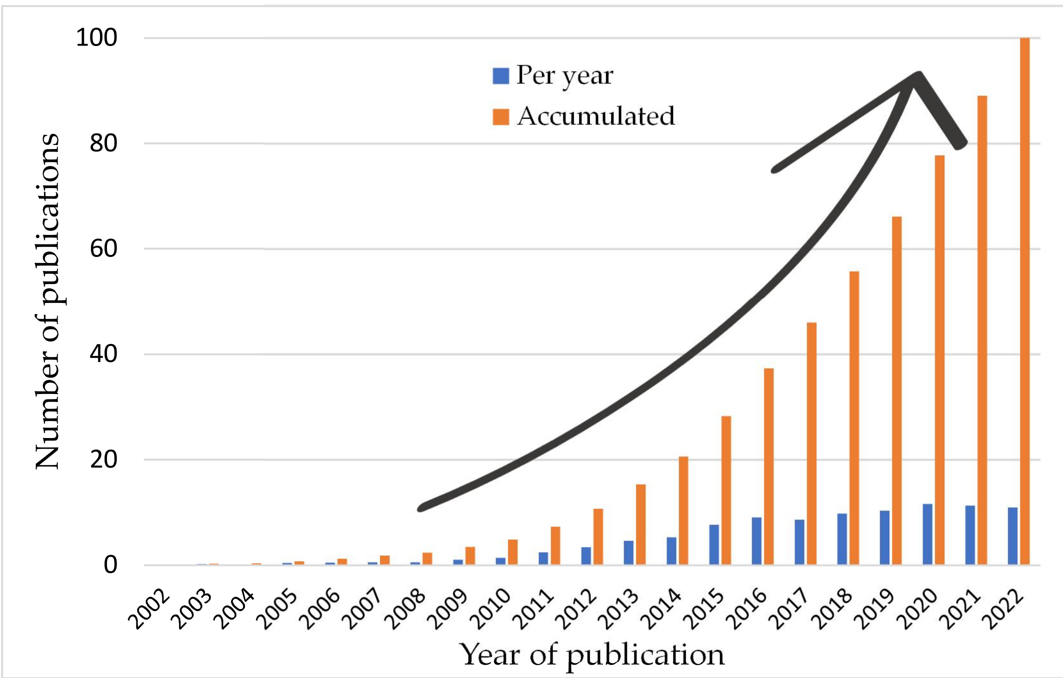


Figure 2. Yearly and accumulated numbers of publications on FO membranes (database: Scopus; search parameters: "forward osmosis membrane" in title, abstract, and keywords). From Forward Osmosis Application for the Removal of Emerging Contaminants from Municipal Wastewater: A Review, by Salamanca, M.; Peña, M.; Hernandez, A.; Prádanos, P.; Palacio, L, 2023, *Membranes* 13(7), 655. Copyright 2023 by the authors.

1.3.2. Types of FO Membranes

Forward osmosis membranes are of interest if they have elevated water permeability while keeping salt retention high. In addition, they must present low concentration polarization, which is a phenomenon that, in the forward osmosis process, causes the osmotic pressure to decrease, leading to a reduction in the flow of water through the membrane. Furthermore, good chemical and mechanical stability to withstand working conditions is required [50].

FO membrane modules can be classified into plate and frame, spiral wound, tubular, hollow fiber, and flat sheet, according to the various geometric structures. The most used FO membrane modules are flat sheets and especially hollow fibers because these configurations require little space and can separate large volumes, which are advantageous factors when compared with other membrane module configurations [51].

The most common FO commercial membranes, with respect to the material used, are cellulose acetate/triacetate (CA/CTA)-based membrane and thin-film composite (TFC) membranes of polyamide, polysulfone, or polyester layers [52,53,54,55,56,57]. A recent study proposed a classification of the emerging FO membranes into four categories according to their fabrication methods: cellulose acetate (CA), thin-film composites (TFCs), polybenzimidazole (PBI), and aquaporin (AQP), with TFCs the most competitive according to their properties [58].

The first commercialized FO membranes, i.e., CA/CTA membranes, have advantages such as good mechanical resistance, low tendency to fouling, good permeate fluxes, and high resistance to chlorine [59]. However, the operation pH range (3–8) is somewhat limited. To improve the characteristics of CA/CTA membranes, TFC membranes with a pH range of 2–11 and with higher permeate fluxes have been produced [2,51].

In addition to commercial membranes, numerous recent studies tried to modify the structure of the support layer using different methods or additives such as silica, graphene, zeolite, and TiO2 to improve the properties of commercial membranes [51,60,61,62,63].

1.3.3. Main Manufacturers of FO Modules

Various industrial companies offer FO membranes and commercial FO systems. Initially, the pioneering company for the supply of FO membranes was Hydration

Technology Innovations (HTI) founded in 1986 in Albany (NY, USA). Later, another company called Oasys Water Inc. began to commercialize FO modules in the year 2010 in Cambridge (MA, USA). Another firm that manufactures FO membranes is FTS H2O™, also working in Albany (USA), specializing in CTA membranes in flat sheets. Next, the company Aquaporin Inside™ introduced FO membranes with aquaporin proteins that are highly selective, facilitating the transport of water molecules. These thin-film composite membranes are available in both flat sheet and hollow fiber configurations. In addition, Aquaporin A/S, a developer of these biomimetic membranes based in Lyngby (Denmark), recently signed a development agreement with another leading tubular membrane manufacturing company called Berghof Membrane Technology based in Leeuwarden (the Netherlands) to launch new membranes. Other companies have manufactured or have collaborated in the manufacture of FO modules such as Toray, Toyobo, Koch membrane systems, and Porifera, as well as some intermediary companies for marketing this type of module such as Sterlitech [64]. It should be noted that the supply of this type of FO membranes has facilitated studies and research related to FO that otherwise would have been much less developed today.

1.3.4. Important Factors

The operating conditions significantly affect the performance of FO. Therefore, their optimization is necessary to make the FO process more efficient. For example, it is necessary to optimize the concentration of DS and FS, the flow rates of FS and DS, the pH, the temperature, and the orientation of the membrane, which can be the active layer facing FS (AL-FS) or active layer facing DS (AL-DS). Furthermore, it is important to control the characteristics and properties of the membrane such as material, mechanical and chemical stability, active area, porosity, and hydrophobicity [65].

In addition to the above, there are other relevant factors influencing the FO process that must be considered to solve possible drawbacks. Despite the wide variety of FO applications and the extensive FO-related research, there are some process issues and challenges that require still special attention for the process to maximize its commercial and industrial possibilities. These include the choice of the draw solution, the reduction in reverse salt flow, the regeneration of DS, and the reduction in concentration polarization and membrane fouling, as shown in Figure 3 [46].

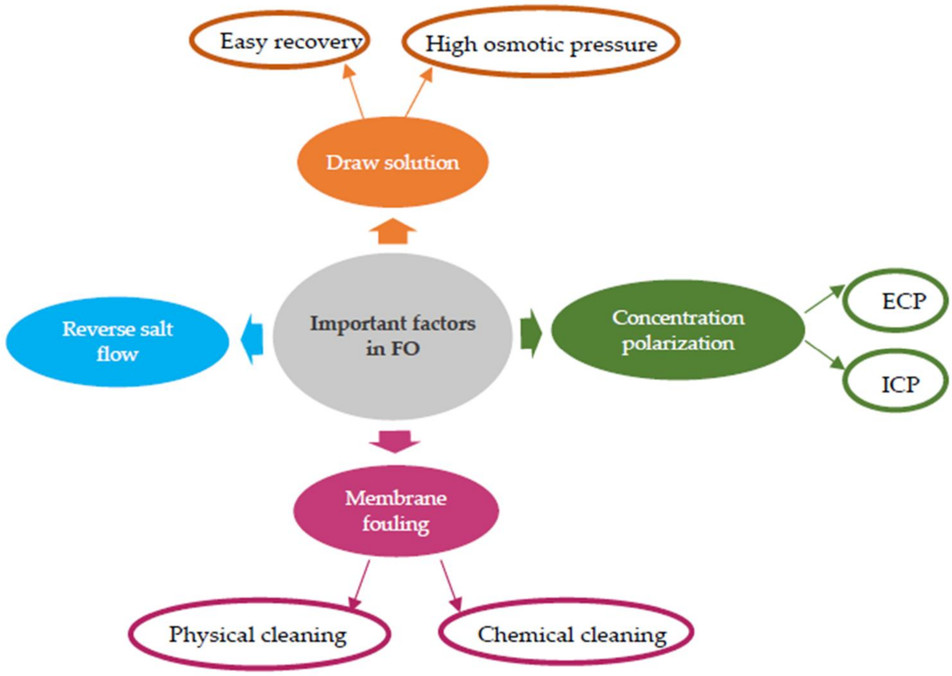


Figure 3. Important factors influencing the FO process. From Forward Osmosis Application for the Removal of Emerging Contaminants from Municipal Wastewater: A Review, by Salamanca, M.; Peña, M.; Hernandez, A.; Prádanos, P.; Palacio, L, 2023, *Membranes* 13(7), 655. Copyright 2023 by the authors.

1.3.4.1. Draw solution

To choose the possible draw solutions, it must be taken into account that they should meet a series of characteristics and requirements. Some important qualities are that it must generate high osmotic pressures [43,66], be economic, safe, and nontoxic, give minimal reverse draw solution flux, be stable, not react with the membrane material, and be easy to recover [67]. Commonly, solutes with a high solubility in water are selected to avoid their diffusion through the membrane. To improve the performance of the membrane by reducing concentration polarization on the surface of both sides, it is favorable to choose solutes with small molecular weight, giving low viscosity in the aqueous solution. Another important criterion, from an energetic point of view, is to have an easy and/or useful recovery or regeneration [67]. Extractive solutions with very varied solutes (inorganic salts, volatile compounds, organic solutes, etc.) have been suggested and studied. To date, most inorganic salt solutions as NaCl, $MgCl_2$, KNO_3, and $MgSO_4$ have been tested due to their low cost and high osmotic pressure, with sodium chloride (NaCl) frequently selected as a reference DS for several reasons. First, it is generally used for standard membrane tests allowing a comparison of the results obtained with data from the literature because NaCl is commonly used as a DS. Furthermore, seawater and reverse osmosis concentrate are widely used as DSs in several interesting applications [68]. However, there are other interesting potential inorganic DSs depending on their characteristics and applications. For example, $K_4P_2O_7$, KCl, and NH_4PO_3, which have the advantage of having fertilizing properties and providing high osmotic pressure, can be used as DSs if the end use of the water recovered is in irrigation. In this case, DS recovery would not be necessary [69,70], with subsequent economic savings. Organic-based solutes, compared to inorganic solutes, tend to have higher molecular weights, making their utilization somewhat more 19hallengingg. These solutes typically include sugars, diethyl ether, or organic salts. Studies have been conducted using common food additives such as monosodium glutamate (MSG), saccharin (SAS), and trisodium citrate (TSC), which generate slightly higher osmotic pressures but lower water flux than NaCl [71].

In addition, in some processes, gases such as CO_2, SO_2, and NH_3 have been used due to their good solubility in water. However, they have not been implemented in real processes due to their limited osmotic pressure and high energy consumption requirements. There are also other less developed proposals for using magnetic solutes and hydrogels, which currently make the processes more expensive and are not sufficiently understood [72,73].

At present, the choice of DS and its regeneration are key issues in the application of FO. Energy-consuming solute recovery is one of the major considerations in selecting the DS. Some regeneration methods may consist of their direct use without ulterior recovery [74]. In some cases, DS is regenerated by membrane separation, such as RO [75], NF [76], UF [77], MD [78], ED [79], chemical precipitation [80], or thermal separation [81]. Other options are magnetic recovery and electrolytic recovery. Although there are various methods for DS regeneration, each method has its advantages and limitations for the application of the FO process [51].

1.3.4.2. Reverse Salt Flow or Reverse Solute Diffusion

Another important requirement to be taken into account in the selection of the extraction solution is to minimize the diffusive transport of salt; that is to reduce as much as possible the flow of salt from the DS to the FS [83]. To experimentally calculate the reverse salt flowJ_S, the equation (1) is usually used [8].

$$J_S = \frac{C_{FS\,t_{i+1}} V_{FS\,t_{i+1}} - C_{FS\,t_i} V_{FS\,t_i}}{A(t_{i+1} - t_i)} \qquad (1)$$

Where $C_{FSt_{i+1}}$ is the salt concentration of the feed solution in time t_{i+1}, C_{FSt_i} the salt concentration of the feed in time t_i, $V_{FSt_{i+1}}$ and V_{FSt_i} are the feed volumes in times t_{i+1} and t_i respectively and the surface area of the active side of the membrane, A.

This flow is known as reverse solute diffusion (RSD), where the solute passing through the membrane from the DS to FS causes a decrease in the driving force for water flow and increases membrane fouling via a cake-like mechanism [83].

RSD is unavoidable in the FO process but should ideally be minimal [84]. This is affected by the DS physicochemical properties (for example, ion/molecule size, viscosity, ion charge, and diffusivity) [85], flow rate [86], membrane structure characteristics (e.g., thickness and porosity) [87], concentration polarization [88], etc. Eventually, RSD would alter the chemistry and composition of the FS [42]. For example, the flow of chlorides when NaCl is used as a DS with real urban wastewater as the FS hinders the correct determination of organic matter and interferes with or even inhibits subsequent anaerobic treatment [89,90].

Although it is impossible to eliminate RSD, it can be reduced and mitigated by choosing a less permeable extraction solute, developing specific advanced membranes, or optimizing the operation conditions [83]. However, many studies lack RSD data, making it difficult to explore and understand how to mitigate solute reverse flow.

1.3.4.3. Concentration Polarization

Concentration polarization is an inevitable and common phenomenon in both osmosis processes and pressure-driven membrane processes [46,91,92]. This phenomenon, in osmotic processes, takes place due to the difference in concentration between the feed solution and the extraction solution that separates an FO membrane.

Concentration polarization (CP) can occur in two ways in FO processes: external concentration polarization (ECP) and internal concentration polarization (ICP). Commonly, ECP occurs on the surface of the active layer of the membrane, and ICP occurs within the porous support layer of the membrane. Furthermore, there are two types, concentrative CP and dilutive CP, depending on the orientation of the membrane. For FO in AL-FS mode, concentrative ECP and dilutive ICP take place, whereas, in AL-DS, dilutive ECP and concentrative ICP take place. In pressure-driven membrane processes, the difference is that only concentrative ECP can take place [46,51]. However, regardless of membrane orientation, both ICP and ECP occur simultaneously. CP, in the FO process, influences water flow, salt reverse flow, and contaminant retention.

In FO, the water flux in AL-FS mode (when the FS is in contact with the active layer and the DS is in contact with the support stratum) can be calculated using Equation (2) [43,93].

$$J_w = A\left[\pi_{Draw,b} \exp(-J_w K) - \pi_{Feed,b} \exp\left(\frac{J_w}{k}\right)\right] \quad (2)$$

The water flux in AL-DS mode can be expressed as Equation (3).

$$J_w = A\left[\pi_{Draw,b} \exp\left(-\frac{J_w}{k}\right) - \pi_{Feed,b} \exp(J_w K)\right] \quad (3)$$

Where J_w is the water flux; A is the pure water permeability coefficient; $\pi_{Feed,b}$, $\pi_{Draw,b}$ are the osmotic pressure of FS and DS in the bulk solution; K is the solute resistivity for diffusion within the porous support layer and k is the mass transfer coefficient.

In the FO process, the appearance of ECP, which usually occurs on the surface of the active layer, can decrease the transmembrane osmotic pressure difference, resulting in decreased water flux. Optimizing the flow of water and improving parameters such as flow velocity or turbulence could reduce or mitigate ECP [46,94].

The ICP that takes place in the support layer is associated with porosity, hydrophobicity, membrane thickness, tortuosity, and other membrane characteristics [95]. Therefore, the characteristics of the membrane must be considered, since they can increase consumption and operating costs by requiring exhaustive cleaning due to fouling [2,51]. In fact, these possible drawbacks are comparatively of low impact because FO is characterized by low fouling and high energy efficiency.

1.3.4.4. Membrane fouling

Membrane fouling is unavoidable for most membrane processes [51,96], but it is key when membranes are used for the treatment and desalination of wastewater. Regarding membrane fouling, FO has emerged as one of the promising membrane processes and alternatives to reverse osmosis (RO). It should be noted that the formation of a cake layer on the membrane surface is common in FO and RO processes. However, in the case of RO, the cake layer must be compacted under pressure, making it more irreversible compared to FO. The non-compaction nature of FO allows tangential flow across the membrane surface to combat fouling more effectively [97].

Factors such as membrane orientation, hydrophobicity, charge, material, feed substrate, and operating conditions or flow direction can influence membrane fouling [98,99]. There are different types of membrane foulants in the feed solution, such as colloidal or particulate matter, inorganic or organic components, chemical reagents, microorganisms, and microbial species, with colloidal fouling being the predominant fouling mechanism in urban wastewater treatment [97].

Fouling is an important factor in FO, since it reduces the flow of water and the efficiency and useful life of the membrane. The fouling of the membrane, in addition to affecting the reduction of the water flow, also affects the retention of contaminants present in the feed solution, for example, when using municipal wastewater as a feed solution [8]. This is because it can improve the retention of contaminants that remain retained or adsorbed on the active surface of the membrane, due to chemical interactions that take place between the contaminant and the membrane [51,95,100].

In this sense, there has been a recent increase in publications related to the fabrication and modification of membranes to minimize fouling, to increase the flow of water without increasing the reverse flow of salt, i.e., to improve the properties of commercial membranes with antifouling or antibacterial characteristics. Some studies showed the incorporation of functionalized hydrophilic nanomaterials into the membrane [101] or surface coating [102] to be effective methods to improve the performances of membranes [64,97]. For example, many nanomaterials (such as zeolite [63], metal or metal oxide nanoparticles [103], or graphene oxide [104]) have been used to fabricate membranes, enhancing both the permeability and the antifouling capacity [105].

In addition, to remediate the consequences that fouling of the membrane could have on the water flow, membrane cleaning methods are necessary to recover the water flow [94]. Cleaning methods can be physical cleaning, chemical cleaning, or a combination of both [51]. Physical cleaning can consist of surface washing or/and osmotic backwashing. Fouling is generally reversible, and the initial flow can be recovered by physical cleaning at high flow rates after short-term experiments [106]. Physical cleaning has great advantages when the fouling is superficial; however, if the fouling is strongly adhered to the membrane, physical cleaning is ineffective, and chemical cleaning is necessary [42]. Chemical cleaning requires the use of commonly used chemical reagents such as NaOH, HNO_3, and NaOCl. However, the use of reagents may decrease membrane life due to modifications in the membrane material, as well as facilitate subsequent irreversible fouling, or it may not completely eliminate membrane fouling [51].

Although, to mitigate fouling, there are possibilities such as optimization of process parameters and cleaning methods, or membrane modifications to improve antifouling properties, as discussed above, there is another way to avoid fouling: feed solution pretreatment [8,107,108].

In summary, it can be concluded that the fouling and cleaning of the membrane are among the drawbacks of FO since it increases the cost and energy consumption of the operation [109]. Although additional studies and research are required to understand the fouling mechanism in forward osmosis during long periods of operation on an industrial scale [64], recent studies have shown that, with new materials, the fouling of FO membranes is a reversible process in many cases [110,111].

1.4. Wastewater contamination

Pollution is one of the most important environmental problems that affect our world, and it is the result of the introduction of substances into the environment in such a quantity as to cause adverse effects in humans, animals, plants, or materials exposed to doses that exceed acceptable levels in nature [34].

Traditionally the environment has been divided, for its study and interpretation, into three components: air, water, and soil. However, this division is merely theoretical since most pollutants interact with more than one element in the environment [112]. The sources of contamination can be natural sources or of anthropogenic origin such as industrial, commercial, agricultural, and domestic activities.

1.4.1. Contaminants of Emerging Concern or Micropollutants

The interest in contaminants of emerging concern (CECs) has grown in recent decades. They are organic pollutants that are present in the environment in increasing concentrations and can cause damage to the environment and human health [113,114].

Contaminants of emerging concern are not necessarily new chemicals and generally include contaminants that have been present in the environment, but whose presence, significance, and effects (toxicity) are only now being evaluated. Previously, some of these compounds were not included in environmental legislation because they were previously not easily detected due to the lack of sufficiently robust analytic methods. However, thanks to new methodologies and increasing knowledge on their effects, concentration limits are beginning to be considered and established; therefore, some of these pollutants have now been included in environmental legislation [115,116,117,118].

The main sources of emerging pollutants are anthropogenic in nature. They are derivatives of agriculture and livestock such as pesticides and veterinary drugs or compounds found in cattle food additives. There are also pharmaceutical and personal care products (PPCP) that the population uses daily. Discharges of effluents from hospitals, industrial plants, and urban WWTPs are highly relevant to the aquatic environment due to the presence of this type of contaminant in their effluents [119,120,121,122]. All these sources can cause occasional contamination, but pollution can also spread by seeping into surface and groundwater from rainfall, soil infiltration, and surface runoff.

Although WWTPs are designed to remove solid materials and to reduce levels of metals, bacteria, and other pathogens, most are not designed to specifically remove organic contaminants. Numerous studies around the world have detected the presence of different groups of pollutants in wastewater, and significant concentrations of pollutants are detected in both influents and effluents in concentrations from the ng/L to the mg/L range [114,123,124,125,126,127]. The concentration of each pollutant varies from one plant to another depending on the country, the size of the plant, the population, and many other factors.

The list of pollutants of emerging interest or micropollutants includes a wide variety of compounds with different structures and uses, as well as metabolites and transformation products. Table 1 shows the most representative contaminants of emerging interest that have been found in WWTPs [128].

Table 1. List of major emerging contaminant groups found in municipal wastewater. From Forward Osmosis Application for the Removal of Emerging Contaminants from Municipal Wastewater: A Review, by Salamanca, M.; Peña, M.; Hernandez, A.; Prádanos, P.; Palacio, L, 2023, *Membranes* 13(7), 655. Copyright 2023 by the authors.

Emerging contaminant group	Examples
Antibiotics	Ciprofloxacin, ofloxacin, sulfamethoxazole, sulfadiazine, metronidazole, erythromycin, clarithromycin, amoxicilin
Analgesics/ antiinflammatories	Diclofenac, naproxen, ibuprofen, salicylic acid, acetaminophen
Lipid regulators	Clofibric acid, gemfibrozil
Psychiatric drug/anticonvulsants	Carbamazepine
Antimicrobials	Triclosan
Hormones	17-α-Etinilestradiol (EE2),17-β-estradiol (E2), estrone (E1), progesterone
X-ray contrast	Iohexol, iopromide
Stimulants	Caffeine
Anti-itching	Crotamiton
Insect repellant	DEET (N, N-Diethyl-meta-toluamide)
Herbicides	Atrazine
Artificial sweeteners	Acesulsame, sucralose, aspartame
Preservatives	Methylparaben, ethylparaben
Cardiovascular drug	Propranolol
Plastics additives	Bisphenol A
Surfactants	4-tert-octylphenol, 4-nonylphenol
UV-filters	Benzophenone

1.4.1.1. Environmental Effects

It is known that the presence of CEC in the aquatic environment potentially affects aquatic organisms and can cause changes that threaten the sustainability of aquatic ecosystems [113,129]. The presence of pollutants in the environment can cause negative biological toxic effects on organisms such as mutagenicity, estrogenicity, and genotoxicity. Many of them are toxic or are classified as endocrine disruptors, which implies that exposure to them can lead to alterations in the growth, development, reproduction, and behavior of living organisms [130].

Some of these effects cause the inhibition of the growth rate of the organism or the masculinization of marine gastropods, producing a decrease in the population. For example, carbamazepine can alter metabolic activities, slow growth, reduce fecundity, and alter steroid levels in fish [131]. Exposure to diclofenac in fish may adversely affect cardiovascular development and cause oxidative stress or a reduction in steroid hormones. UV filter compounds cause endocrine-disrupting effects as they are capable of interfering with the thyroid axis and the development of reproductive organs, as well as the brain, in both aquatic and terrestrial organisms [132].

Figure 4 shows some of the possible effects that contaminants cause in humans because of the food chain.

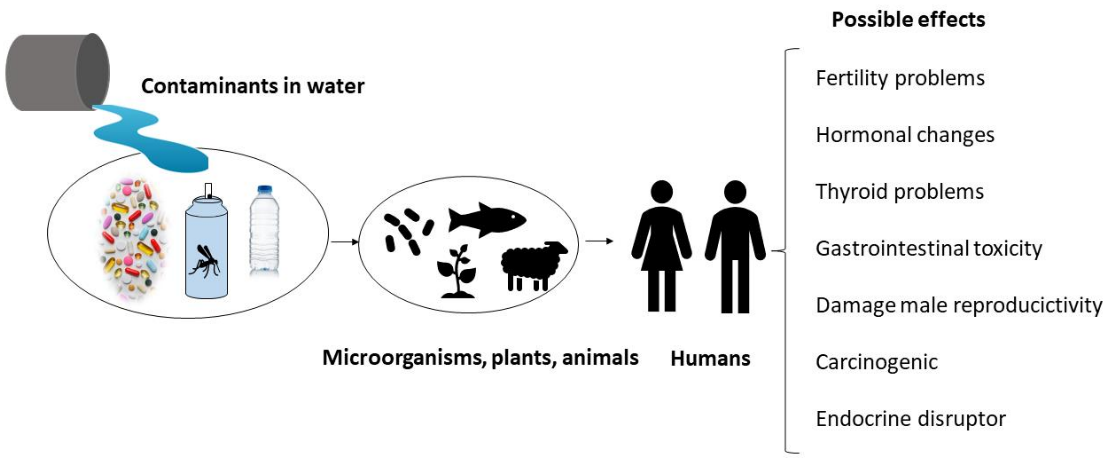


Figure 4. Some harmful effects on human health of emerging contaminants. From Forward Osmosis Application for the Removal of Emerging Contaminants from Municipal Wastewater: A Review, by Salamanca, M.; Peña, M.; Hernandez, A.; Prádanos, P.; Palacio, L, 2023, *Membranes* 13(7), 655. Copyright 2023 by the authors.

1.4.1.2. Ecotoxicological Risk Evaluation

In general, environmental risk depends on three factors [133]:

- Amount of the substance present in the environment (for example, soil, water, or air).
- Exposure time of the receptor with the contaminated environment.
- The inherent toxicity of the substance.

In the evaluation of environmental risk, data and observations are collected on the harmful effects that toxic substances can generate toward the environment and health, in order to be able to assess the risk they imply. The evaluation consists of obtaining data to determine the dose of exposure of an organism to a contaminant and the response that this will cause. Empirical dose–response data are compared with the exposure received by humans or other living organisms, to have a complete evaluation of the risk generated in a certain contaminated environment [134,135].

Environmental risk assessment can be as suggested by the EPA (Environmental Protection Agency) guide [134,135,136], which divides the process into four steps (Figure 5).

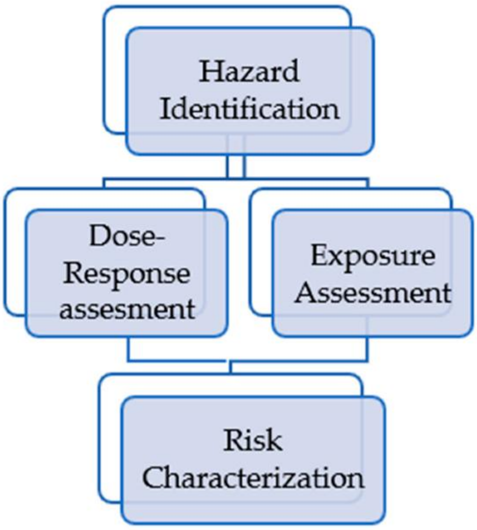


Figure 5. Stages of environmental risk assessment. From Forward Osmosis Application for the Removal of Emerging Contaminants from Municipal Wastewater: A Review, by Salamanca, M.; Peña, M.; Hernandez, A.; Prádanos, P.; Palacio, L, 2023, *Membranes* 13(7), 655. Copyright 2023 by the authors.

Environmental risk assement is assessed by considering the following parameters [134].

- Median Effective Concentration (EC50): Concentration obtained statistically or graphically estimated that causes a given effect in 50% of the group of organisms, under specified conditions.
- Median Lethal Concentration (LC50): Statistically derived or graphically estimated concentration (in air or water) that causes death, during exposure or within a defined period after exposure, of 50% of the group of organisms during a given period and other specific conditions. LC50 is generally expressed in mg/L.
- Median Lethal Dose (LD50): Individual dose of a substance that is statistically, or graphically estimated, lethal to 50% of the group of organisms under specified conditions. Generally, LD50 is expressed in mg/kg of body weight.
- No Observable Effect Level (NOEL): The highest concentration or amount of a substance found experimentally or by observation that does not cause alterations in the morphology, functional capacity, growth, development, or life span of organisms, distinguishable from those observed in organisms normal (control) samples of the same species and strain, under conditions identical to those of exposure.

Given the great complexity of aquatic ecosystems, it is not possible to assess the effect of pollutants on all the organisms that live in them. For this reason, in order to assess the individual effects of pollutants, test species representative of the ecosystems are used. The choice of the test species is made considering a series of criteria, such as ecological importance, sensitivity to contaminants or feasibility of growing in laboratory conditions. One of the most widely used organisms to perform toxicity bioassays is the genus Daphnia. This organism plays an important role in the trophic chain of freshwater systems, being the dominant consumer of primary producers and it is an important source of food for vertebrate and invertebrate predators [137].

Generally, three aquatic organisms are studied (fish, green algae, and Daphnia magna) as standard species is recommended by the EC (European Commission), OECD (Organization for Economic Cooperation and Development), and ISO (International Organization for Standardization) ecotoxicity tests. In addition, they are presented as bioindicators to assess environmental risk, since they belong to three different orders of the food chain, giving an idea on how the concentration of contaminants affects the different levels of the aquatic food chain [138].

For the ecological risk assessment, an estimated risk ratio (RQ) can be calculated for each CEC using Equation (4).

$$Risk\ Quotient\ (RQ) = \frac{C_{X\ (EFFLUENT)}}{PNEC} \quad (4)$$

The variable C_X (effluent) represents the concentrations in the final treated effluent (in $ng \cdot L^{-1}$), and PNEC represents the predicted no-effect concentrations (in $ng \cdot L^{-1}$), which until now were not always available in the literature. Thus, PNECs are calculated on the basis of toxicity data, such as LC_{50} or EC_{50}, and the safety factor (AF), which is typically 1000 for short-term toxicity data, as recommended by the Water Framework Directive [139,140]. If the RQ is <0.1, it indicates low risk; if the RQ is between 0.1 and 1.0, it corresponds to moderate risk; if the RQ is ≥1.0, it indicates high risk [141,142].

1.4.2. Options to Contaminants of Emerging Concern Removal in Wastewater

Conventional WWTPs have been designed to eliminate eutrophic contamination, avoiding excessive organic and mineral nutrients that could support an overabundant plant life, which in the process of decaying would deplete the oxygen supply. However, they are not designed to eliminate these new micropollutants; hence, additional treatments are required for their elimination before their introduction to surface waters

[131,143,144,145]. Thus, additional techniques to remove the emerging contaminants need to be implemented.

In addition, it must be kept in mind and be aware that CECs have a wide variety of chemical properties; therefore, removal success varies depending on their particular properties. Wastewater treatment is a more complicated process than water treatment due to the characteristics of wastewater that must be thoroughly considered so that it can be safely integrated into the environment [146].

There are different urban wastewater treatments for the removal of pollutants as shown in Figure 6.

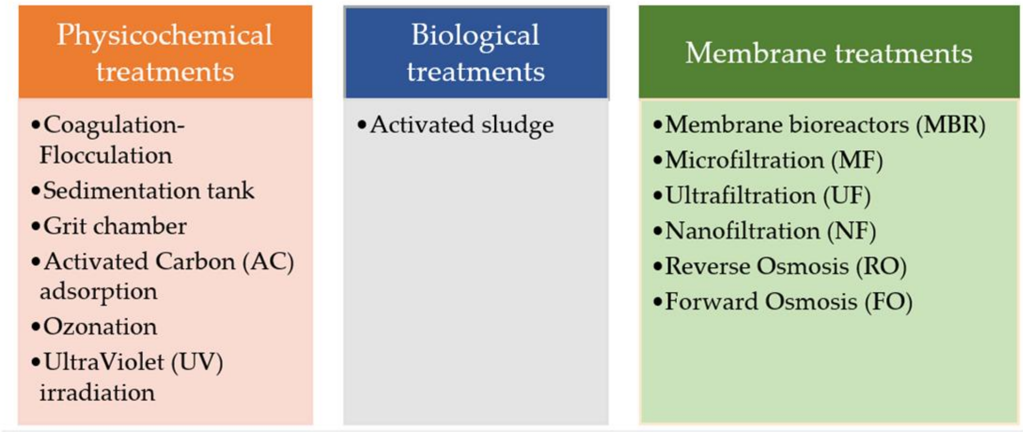


Figure 6. Treatments to remove contaminants from the wastewater. Treatments to remove contaminants from the wastewater. From Forward Osmosis Application for the Removal of Emerging Contaminants from Municipal Wastewater: A Review, by Salamanca, M.; Peña, M.; Hernandez, A.; Prádanos, P.; Palacio, L, 2023, *Membranes* 13(7), 655. Copyright 2023 by the authors.

- *Physicochemical treatments*: The conventional physicochemical techniques used to remove solid particles, ash, and organic matter, among other suspended solids, include grit chambers, sedimentation, or coagulation-flocculation. However, although coagulation-flocculation treatment yielded higher organic matter removal, it has been found to be unable to remove microcontaminants. [147]. This group of physiochemical treatments also includes processes such as activated carbon (AC) adsorption or ultraviolet (UV) irradiation. Another example in this field involves advanced oxidation technologies that can eliminate some of these microcontaminants from residual waters such as ozonation. Although oxidation is a promising process for removing pollutants from wastewater, especially using chlorine or ozone, the reaction of these chemicals produces byproducts, and the effects of these byproducts are unknown. Therefore, special care must be taken when using these chemicals for wastewater treatment [148].

- *Biological treatments*: Activated sludge can convert organic compounds into biomass, among other compounds. However, while this is a great achievement, not all compounds are completely broken down into biomass in this process. Biological treatment is a common method for wastewater treatment that uses microorganisms to remove pollutants. However, it is only capable of removing a part of a wide range of emerging pollutants [149].

- *Membrane treatments*: These include membrane bioreactors (MBR) and membrane filtration processes [150,151]. Pressure-driven membrane techniques such as microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), and nanofiltration (NF) have also been used to treat water contaminated with micropollutants [152]. Both NF and RO can remove contaminants such as suspended and dissolved solids, organic matter, viruses, and bacteria, but RO is additionally capable of eliminating smaller molecules such as ions. However, these processes, due to membrane concentration polarization and the high hydraulic pressures required, have high costs and are difficult to scale [92]. A possible alternative to overcome the disadvantages of pressure-driven membrane techniques could be the use of FO processes [153]. In the forward osmosis process, the driving force is the osmotic gradient rather than the pressure-driven force, which could be an important advantage with respect to membrane fouling, as already mentioned. In this process, the osmotic pressure gradient facilitates the passage of water across a semipermeable membrane between a concentrated extraction solution and a less concentrated feed solution, while retaining other solutes. This leads to dilution of the extraction solution, while the solutes in the feed stream become concentrated [43,154].

1.4.2.1. Forward Osmosis in the Removal of Contaminants of Emerging Concern from Wastewater

FO has shown promising potential in the removal of various contaminants from water sources. As previously commented, the absence of applied hydraulic pressure could reduce operational and energy costs and provide a better fouling control than high-pressure-driven membrane processes due to physically reversible fouling. There are several recent studies that corroborated the feasibility of this membrane process in the elimination of contaminants in water [8, 93, 100, 154 - 175]. In these studies, membranes of different configuration, different materials, and different contaminants were used, all of which had good contaminant removal in common. For example, a study by Cartinella et al. focused on the removal of two hormones (estrone and estradiol) using a CTA flat sheet FO membrane. The results demonstrated hormone rejection between 96% and 97% [157]. Another study by Salamanca et al. using TFC hollow fiber FO membranes with aquaporin inside focused the rejection of 24 contaminants [93]. The study demonstrated remarkable rejection rates, exceeding 93% for all the tested compounds.

In previous studies, most investigations regarding FO for contaminant removal have predominantly focused on clean or synthetic water samples. However, there are few examples in the literature that examined the application of FO using real urban wastewater as the feed solution. Nonetheless, a limited number of studies have explored this aspect. To provide an overview of these investigations, in Table 2 is summarized the relevant studies in which real wastewater was employed as the feed solution in FO processes, categorized according to the year of publication.

Table 2 displays recent studies conducted between 2011 and 2023, serves as a valuable resource in understanding the practical applications of and challenges focusing on FO applications in real wastewater. It can be found that NaCl or synthetic seawater are commonly used as DSs, while membrane materials such as CTA and TFC membranes are frequently employed. The location of the feed solution indicates the countries where the studies were conducted, including Australia, Chile, China, Japan, the Netherlands, Spain, Sweden, and the United Kingdom. It is worth mentioning that, among the investigations using real wastewater as a feed solution, only a limited number examined the contaminants present in the water and their removal efficiency [8,176,184,187], as shown by a √ sign in Table 2 in the column of contaminants.

Table 2. Publications per year when feed solution in FO process is from WWTP. From Forward Osmosis Application for the Removal of Emerging Contaminants from Municipal Wastewater: A Review, by Salamanca, M.; Peña, M.; Hernandez, A.; Prádanos, P.; Palacio, L, 2023, *Membranes* 13(7), 655.

Year	Membrane configuration	Membrane material	Supplier	FS location	DS	Contaminants	Reference
2011	Spiral wound	CTA with embedded polyester mesh	HTI	WWTP Amsterdam West (The Netherlands)	NaCl and $MgCl_2 \cdot 6H_2O$	-	[107]
2013	Flat sheet	CTA with embedded woven mesh	HTI	WWTP Wollongong (New South Wales, Australia)	NaCl	√	[178]
2014	Spiral wound	CTA with embedded polyester mesh	HTI	WWTP Queensland (Australia)	NaCl	-	[179]
2015	Three flat-sheet membranes (TFC, CTA-1, CTA-2)	TFC with polyamide on polysulfone with embedded support CTA-1 with embedded polyester mesh CTA-2 with embedded nonwoven support	HTI	WWTP (Japan)	Synthetic seawater	-	[180]
2016	Three flat sheet membranes	CTA with embedded polyester mesh CTA with embedded nonwoven mesh TFC with embedded polyester screen support	HTI	WWTP Temuco (Chile)	NaCl	-	[181]
2016	Spiral-wound	CTA	HTI	WWTP Shanghai (China)	NaCl	-	[182]
2016	Flat sheet	CTA with embedded polyester mesh	HTI	WWTP (Japan)	Synthetic seawater	-	[183]
2016	Flat sheet	CTA with embedded polyester mesh	HTI	WWTP (China)	Synthetic seawater	-	[184]
2018	Flat sheet	TFC with polysulfone with embedded support	Porifera	WWTP New South Wales (Australia)	NaCl and NaOAc	-	[25]
2018	Flat sheet (proprietary, PFO-100)	ABS (wetted), Carbon Fiber (structural) with aquaporins	Porifera	WWTP (Sweden)	NaCl	-	[185]

Table 2. Publications per year when feed solution in FO process is from WWTP (continue).

Year	Membrane configuration	Membrane material	Supplier	FS location	DS	Contaminants	Reference
2018	Flat sheet	CTA with embedded polyester mesh	HTI	WWTP, Beijing (China)	NaCl	√	[186]
2018	Flat sheet	CTA	HTI	WWTP (China)	Synthetic seawater	-	[187]
2019	Spiral wound	TFC	Toray	WWTP Valencia (Spain)	NaCl and $MgCl_3$	-	[188]
2019	Flat sheet	CTA with embedded polyester mesh	HTI	WWTP Beijing (China)	NaCl	-	[90]
2019	Flat sheet	TFC	Homemade	WWTP Jinan (China)	Synthetic seawater	-	[108]
2021	Spiral wound	TFC	Toray	WWTP Girona (Spain)	Sea salt	√	[189]
2022	Hollow fiber and flat sheet	TFC	Singapore Membrane Technology Centre	WWTP Southampton (UK)	NaCl	-	[190]
2022	Hollow fiber	TFC with aquaporins	Aquaporin A/S	WWTP Valladolid (Spain)	NaCl, $MgSO_4.7H_2O$, $C_6H_{12}O_6$, CH_3COONa, and $MgCl_2.6H_2O$	√	[8]
2022	Flat sheet	CTA with embedded polyester mesh	HTI	WWTP Temuco (Chile)	NaCl	-	[191]
2023	Tubular (TFO-D90)	PVC with aquaporins	Berghof Membrane Technology GmbH	WWTP Valladolid (Spain)	NaCl	-	[91]

Nutrient recovery and water reuse

When using FO for the treatment of urban wastewater, an opportunity arises to obtain a concentrated solution containing organic matter and contaminants. This concentrated solution can then be directed toward additional processing, such as anaerobic treatment. By doing so, valuable resources can be extracted from the organic matter, leading to the generation of biogas. Additionally, some contaminants present in the concentrated solution can be effectively removed and degraded, further enhancing the overall treatment efficiency and environmental benefits [190]. However, the appearance of emerging contaminants in sludge can eventually inhibit anaerobic digestion and can induce health problems when sludge is recycled to agriculture, requiring methods to remove contaminants either before or after anaerobic treatment. Some of the pollutant remediation methods include electrooxidation, ultrasonication, thermal hydrolysis, ozonation, and bioaugmentation [191]. Concurrently, a diluted DS would be obtained, which, depending on its composition and intended application, can be regenerated, subjected to desalination processes to yield clean or potable water, or even utilized directly as fertilizer for irrigation purposes. This holistic approach presents a pathway toward resource recovery and the sustainable management of wastewater as shown in Figure 7.

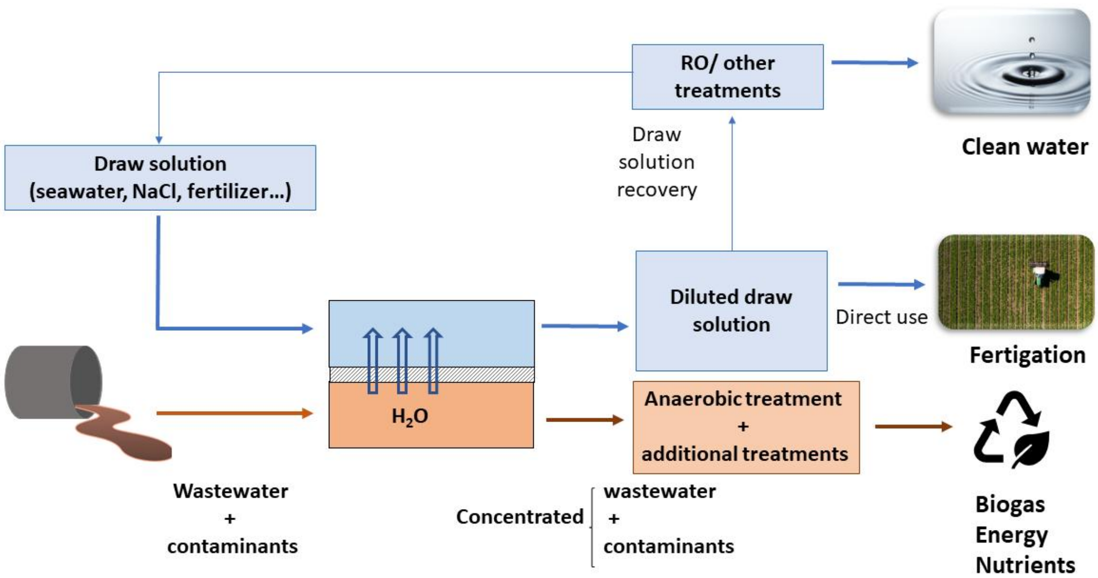


Figure 7. Diagram of the integration of FO as a process of concentration in the wastewater treatment to obtain resources and reuse of water. From Forward Osmosis Application for the Removal of Emerging Contaminants from Municipal Wastewater: A Review, by Salamanca, M.; Peña, M.; Hernandez, A.; Prádanos, P.; Palacio, L, 2023, *Membranes* 13(7), 655. Copyright 2023 by the authors.

Hence, it is crucial to promote the practical implementation of FO technology for water and wastewater treatment. This entails exploring a wider range of DS and conducting studies on contaminants present in real wastewater.

Thus, the present thesis addresses a topic of vital importance in today's world: the global water scarcity and the water contamination. This environmental problem demands innovative solutions, and this is where membrane technology, specifically the forward osmosis process, is implemented. Across the three papers corresponding chapters 4-6, this research aims to analyzes in detail the behavior of FO membranes, focusing on their ability to remove emerging contaminants from urban wastewater. The overall objectives of this study (described in chapter 2) include assessing membrane performance under different operational conditions, studying the adsorption of organic matter on membranes and its recovery, as well as evaluating the rejection of the FO membranes and the ecotoxicological risk of emerging contaminants. To achieve these objectives, a comprehensive methodology (included in chapter 3) is employed, using two different FO membranes, combining laboratory-scale experimental analyses with pilot-scale studies. In addition, plenty of contaminants that are commonly present in urban wastewater are investigated in this thesis. The obtained results are expected to provide a deeper understanding of the forward osmosis process and its applicability in urban wastewater treatment.

By expanding the scope of research in these areas, the potential industrial applications of FO can be further extended. Moreover, this is a critical step toward the promotion of commercial markets for the FO process, unlocking its full potential and addressing the diverse needs of water treatment in various sectors.

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Chapter 2

Aims and scope of the thesis

2.1. Justification of the thesis

The issues of global water scarcity and contamination, driven by industrial demands and population growth, underscore the critical need for effective water resource management. The inclusion of water and sanitation among the sustainable development goals in the 2030 agenda emphasizes the importance of addressing these challenges on a global scale.

Efficient water resource management is vital. For this, wastewater treatment plants (WWTPs), particularly municipal ones, play a crucial role. They not only reduce pollution but also protect the environment and human health while providing valuable resources like water, nutrients and energy.

As urban populations grow, WWTPs face increased wastewater volume, needing to adapt the conventional wastewater treatment plants in order to careful control and prevent harm to people and the environment. New technologies aim to strike a balance between low environmental impact and high energy efficiency while focusing on environmental protection and resource conservation. Traditional wastewater treatments combine physical, chemical, and biological processes to remove impurities. However, conventional WWTP cannot remove efficiently emerging contaminants as hormones, pesticides and drugs. Efforts to develop eco-friendly wastewater treatment technologies targeting the removal of emerging pollutants have intensified over recent decades.

Innovative technologies like membrane filtration, adsorption, and advanced oxidation processes are being explored to enhance pollutants and nutrients removal. The choice of the treatment method depends on its effectiveness, advantages, and disadvantages. Membrane technology is a good option to reuse water from various wastewater sources. Forward osmosis has advantages over pressure-driven membrane processes. When FO is used for urban wastewater treatment, the opportunity arises to obtain a concentrated solution containing both organic matter and contaminants. This concentrated solution can then be directed to further processing, such as anaerobic treatment. In this way, valuable resources can be extracted from organic matter, which leads to the generation of biogas. However, the occurrence of emerging contaminants in sludge may eventually inhibit anaerobic digestion and may induce health problems when sludge is recycled for agriculture, requiring methods to remove contaminants before or after anaerobic treatment. At the same time, a diluted DS would be obtained that, depending on its composition and intended application, can be regenerated, subjected to desalination processes to obtain clean or drinking water, or even used directly as fertilizer for irrigation.

Therefore, for the implementation of this technology on a large industrial scale, more research is needed to optimize the process and ensure the viability of this promising technology.

2.2. Main objectives

The general objective of this thesis was to evaluate and study the behavior of forward osmosis membranes in the treatment of urban wastewater. By concentrating these waters, the rejection of the membranes to the emerging contaminants in said waters was evaluated, as well as the possibility of obtaining biogas through the concentration of organic matter obtained from the concentration of urban wastewater. More specifically, to achieve this overall goal, the following individual objectives were pursued:

1. Optimization of permeate fluxes and reverse salt flux of a hollow fiber aquaporin FO membrane using different flow rates and concentrations of DS salts and different salts as DS.
2. Evaluation of the behavior of a hollow fiber aquaporin FO membrane to study the rejection of a total of 24 emerging contaminants that are commonly present in urban wastewaters.
3. Evaluation of the concentration FO process of real urban wastewater using a hollow fiber aquaporin membrane and the study of concentration and recovery of the contaminants present in the urban wastewater from Valladolid EDAR. Ecotoxicological risk assessment of these contaminants was also evaluated.
4. Evaluation and comparison of Forward Osmosis (FO) and Low-Pressure Reverse Osmosis (LPRO) with a tubular pilot-scale membrane for the concentration of municipal wastewater and the production of biogas.

2.3. Thesis overview

This thesis is divided in eight chapters. **Chapter 1** focuses on a brief introduction to the environmental problem of water scarcity worldwide, the role of urban wastewater treatment plants, the development of membrane technology in water treatment and different characteristics and peculiarity of the forward osmosis process. The justification of the thesis and the objectives and scope of the thesis are summarized in **Chapter 2**. The materials used and the experimental procedures are described in **Chapter 3**. The behavior of a hollow fiber aquaporin forward osmosis membrane and the membrane's rejection of 24 emerging contaminants was studied in **Chapter 4**. Also, changes in membrane flow, different Draw Solution (DS) concentrations, and different doping concentrations of some of the contaminants were investigated to better understand the membrane behavior. The behavior of a forward osmosis hollow fiber membrane in treating urban wastewater subjected to different pretreatments (centrifuged and filtered, only centrifuged, and without pretreatment) was studied in **Chapter 5**. In addition, changes in the membrane flux, different types of salt in the DS, and different DS concentrations were investigated to determine the permeate flow and the reverse saline flow under each one of these conditions. The adsorption of organic matter on the membrane and/or in the system and its recovery after performing several osmotic washes was studied. The presence of emerging pollutants in urban wastewater at the outlet of the primary settler of the Valladolid WWTP was studied, as well as the concentration and recovery of these emergent contaminants when passing them through a forward osmosis hollow fiber membrane. Ecotoxicological risk assessment of these contaminants was also evaluated. In **Chapter 6**, the efforts of a tubular membrane with an effective area of 2.3 m^2 were studied in two processes: Forward Osmosis (FO) and Low-Pressure Reverse Osmosis (LPRO). In addition, we established a pilot-scale membrane system to concentrate real municipal wastewater from the Valladolid municipal WWTP into both FO and LPRO. Changes in membrane flux, reverse saline flux, fouling, as well as the concentration capacity of organic matter in each of the processes were also studied. In addition, the biochemical potential for methane production from concentrated municipal wastewater through both FO and LPRO processes at 35 °C was investigated. Moreover, both processes were compared and the influence of salt on methane production was evaluated. Finally, **Chapter 7** summarizes the main conclusions and future work recommendations derived from this thesis and **Chapter 8** collects the major information about the author.

Chapter 3

Material and methods

3.1 Materials

3.1.1. FO membranes

Two different FO membranes were used in this thesis. One is a hollow fiber module that contains 0.6 m^2 of a membrane with an active layer of a thin film composite (TFC) polyamide with integrated aquaporin proteins manufacturer by Aquaporin Inside™ (Aquaporin A/S, Kongens-Lyngby, Denmark) (see Figure 1A). The other FO membrane was a tubular module (TFO-D90) that contains 2.3 m^2 of active surface area (see Figure 1B). It was recently manufactured by Berghof Membrane Technology GmbH (Berghof Membrane Technology Leeuwarden, Friesland, The Netherlands), a company that specializes in tubular membranes for the filtration and separation of industrial process streams and wastewater.

A) Hollow fiber aquaporin module

B) Tubular membrane

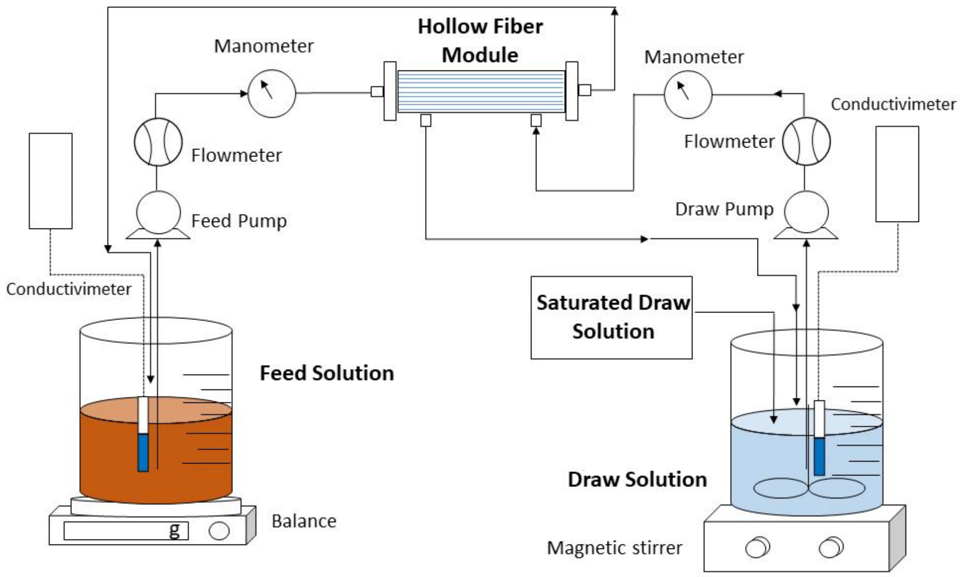
Figure 1. Forward Osmosis Modules. 1A: Hollow fiber aquaporin module and 1B: Tubular membrane.

3.1.2. Experimental setup

The FO concentration is a process in which water molecules pass through a semipermeable membrane, which separates two solutions: the feed solution (FS) and a draw solution (DS) compartments. This transport and movement of molecules happens due to the appearing osmotic pressure difference ($\Delta\pi$) which is the driving force in this phenomenon, as opposed to pressure-driven membrane processes. Figure 2 shows an image and diagram of the system used for hollow fiber membrane, while for tubular membranes they are shown in Figure 3. Thus, water is permeated passing through the membrane from the lowest solution concentration, FS, to the highest solute concentration solution, DS, while other solute molecules are rejected. Counter-current (hollow fiber membrane) or co-current recirculation (tubular membrane) closed circuits of the feed and draw solutions were applied on each side of the FO membrane via two pumps. In all experiments, the FS was passed through the lumen side (active side), while the DS was passed along the outer or shell side.

The feed solution is prepared with milliQ water spiked with contaminants, or municipal wastewater. This feed solution becomes more concentrated as the process proceeds. The extraction solution is a salt solution, in most of the cases NaCl or other type of salt solution with different concentrations. All changes in volume of DS were measured by weighing using digital electronic scales or graduated tanks to calculate the water flux. Moreover, a conductivity meter was immersed in both solutions to measure concentration and to evaluate the saline flux. To know the FS and DS flow rates through the corresponding loops and the inlet and outlet pressures, two flowmeters and two manometers were placed.

A



B

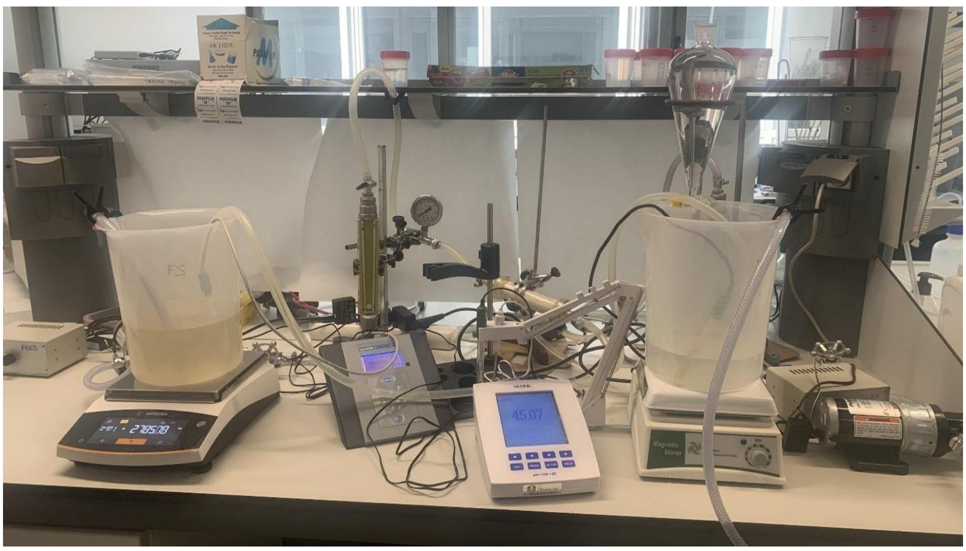


Figure 2. Experimental setup using hollow fiber aquaporin forward osmosis membrane. A: diagram of the FO system. B: picture of the FO system.

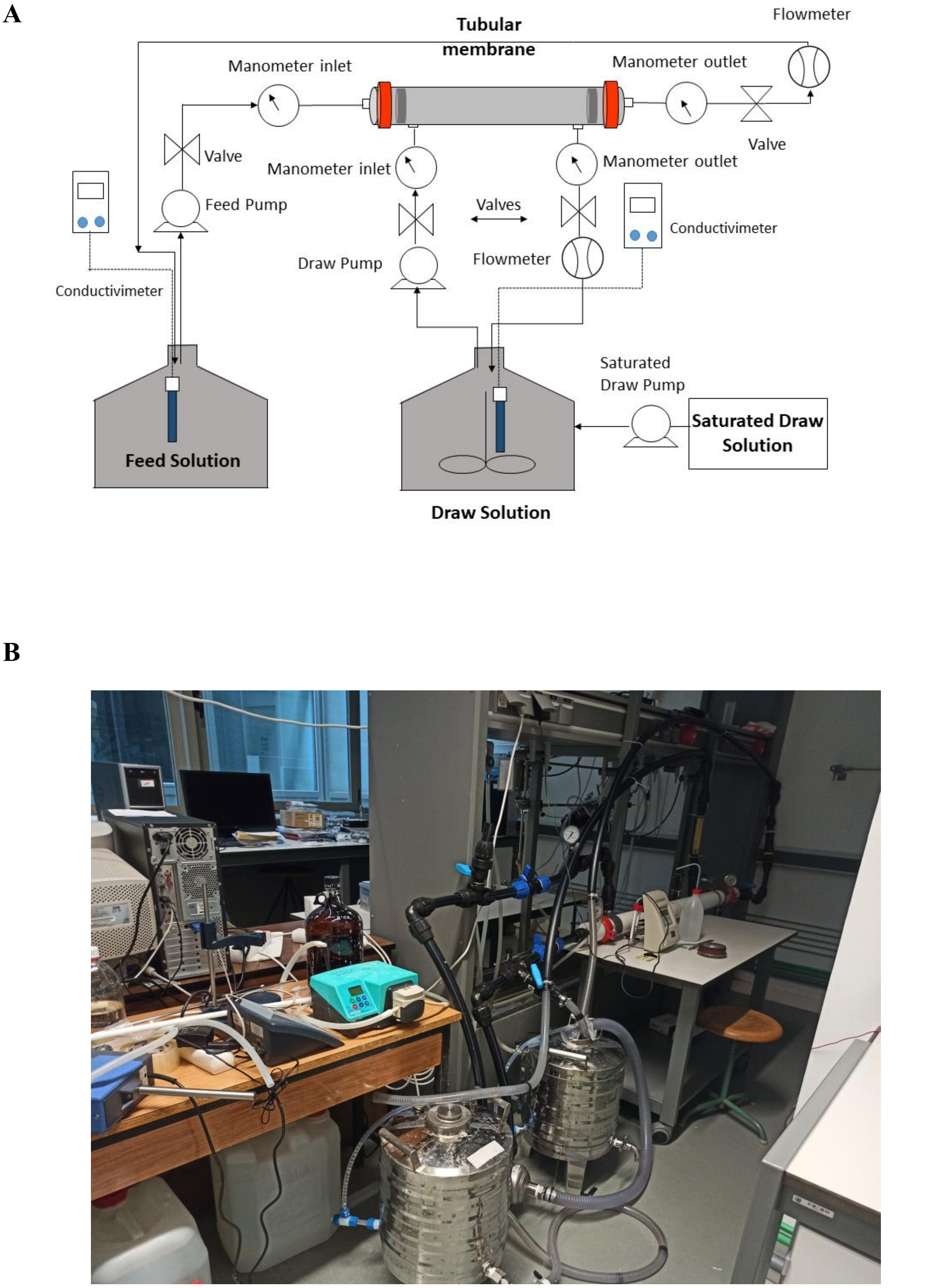


Figure 3. Experimental setup using tubular forward osmosis membrane. A: diagram of the FO system. B: picture of the FO system.

3.1.3. Membrane characterization

In order to calculate the reverse salt flux, J_s and the water flux J_w, volume or weight and conductivity data were collected in both vessels.

Equation (1) is used to calculate J_w:

$$J_w = \frac{V_{FS\,t_{i+1}} - V_{FS\,t_i}}{A(t_{i+1} - t_i)} \quad (1)$$

Where $V_{FS\,t_{i+1}}$and $V_{FS\,t_i}$ are the volumes permeated from the feed in timest_{i+1} and t_i respectively and A is the surface area of the active side of the membrane.

To determineJ_s, Equation 2 was used:

$$J_s = \frac{C_{FS\,t_{i+1}} V_{FS\,t_{i+1}} - C_{FS\,t_i} V_{FS\,t_i}}{A(t_{i+1} - t_i)} \quad (2)$$

Here $C_{FS\,t_{i+1}}$is the salt concentration of the feed solution in time t_{i+1}, $C_{FS\,t_i}$ the salt concentration of the feed in time t_i.

3.1.4. Emerging contaminants

In the spiking experiments involving emerging contaminants, all targeted contaminants of emerging concern (CEC) were sourced from Sigma Aldrich (Merck KGaA, Saint Louis, MO, USA), Fisher (Fisher Sci., Waltham, MA, USA), and Scharlab (Scharlab, Barcelona, Spain). These contaminants were individually prepared in stock solutions at a concentration of 1000 mg/L in methanol (MeOH), except for amoxicillin, which was prepared in MeOH/H_2O (1:1), and ciprofloxacin and ofloxacin, which were prepared in 0.2% HCl MeOH/H_2O (1:1). These solutions were stored in a freezer at −80 °C. Subsequently, each stock solution was diluted to 20 mg/L with MeOH and stored in a freezer at -20 °C until used in the experiments.

The chosen doping concentrations were based on the average concentrations typically found for each analyte in the influent wastewater of European urban wastewater treatment plants (WWTPs), particularly in Spain, as reported in scientific literature [1,2]. It's worth noting that the concentration range at the WWTP's inlet and outlet is similar because WWTPs are not designed to eliminate such contaminants. These concentrations typically ranged from 2 to 20 µg/L.

Furthermore, the presence of fifty-one contaminants from the WWTP in the city of Valladolidin was assessed, and their concentrations were quantified. Additionally, the concentration of these contaminants was measured after passing through the FO membrane, and the membrane's rejection capacity for each contaminant was evaluated.

Rejection

Rejections of contaminants were calculated by using the following Equation (3) [1],

$$R = \left(1 - \frac{V_{DS\,end}\,C_{DS\,end}}{V_{total}(C_{FS0} + C_{FS\,end})/2}\right) \quad (3)$$

Here $V_{DS\,end}$ is the end volume of the draw, $C_{DS\,end}$ the end draw concentration, C_{FS0} the initial feed concentration, $C_{FS\,end}$ the end feed concentration and V_{total} the total transported water volume.

Ecological risk assessment

The ecological risk assessment (RQ) of pollutants aims to analyze whether concentrations found in urban wastewater pose a threat to three key reference groups: daphnia, fish, and green algae. Given that natural waters are the primary recipients of wastewater treatment plant effluents, aquatic organisms were logically chosen for risk assessment. The three aquatic organisms studied (fish, green algae, and Daphnia magna) are standard species in ecotoxicity tests (recommended by organizations such as EC (European Commission), OECD (Organization for Economic Cooperation and Development), and ISO (International Organization for Standardization)) and are presented as bioindicators to assess environmental risk. Additionally, as they belong to different trophic chain orders, these organisms offer insights into how pollutant concentrations impact various levels of the aquatic trophic chain.

For the ecological risk assessment of each contaminant, an estimated risk ratio (RQ) was calculated for each CEC using the following Equation (4),

$$Risk\ Quotient\ (RQ) = \frac{C_{X\,(EFFLUENT)}}{PNEC} \quad (4)$$

Here C_x (effluent) represents the concentrations in the final treated effluent (in ng L^{-1}) and PNEC denotes the predicted no-effect concentrations (in ng L^{-1}), which may not always be readily available in existing literature. Consequently, PNECs are typically derived from EC50 values (the concentration equired to achieve a 50% of the maximal effect), adjusted by a safety factor of 1,000, as recommended by the Water Framework Directive [2]. RQ values below 0.1 signify a low risk, RQ values between 0.1 and 1.0

indicate a moderate risk, and an RQ equal to or greater than 1.0 means a high risk [3,4]. This risk parameter was used in three aquatic organisms examined (fish, green algae, and Daphnia magna) are commonly used species in ecotoxicity tests, recommended by organizations like the EC (European Commission), OECD (Organization for Economic Cooperation and Development), and ISO (International Organization for Standardization). They are established as bioindicators for evaluating environmental risk.

3.1.5. Wastewater

In this research, municipal wastewater from the wastewater treatment plant (WWTP) of the city of Valladolid (Spain) was used. Wastewater was collected from the outlet of the primary settler, and it was used to be concentrated in the membrane processes. The general characteristics of the collected urban wastewater as measured were an average of (300.5 - 345.6) mgO_2/L in Chemical Oxygen Demand (COD), 63.5 mg TOC/L (Total Organic Carbon), (0.94-0.96) g/Kg in Total Solids (TS) and (0.41-0.45) g /Kg in Volatile Solids (VS).

It is important to highlight that the organic matter properties of the wastewater can vary considerably based on the day of collection, given that the samples were not uniform over time and are influenced by factors like rainfall.

3.1.6. Biochemical Methane Potential (BMP) tests

The BMP tests were carried out in 160 mL serum bottles with a working volume of 60 mL, containing approximately 25 g of inoculum and 35 g of substrate samples. After sealing the bottles with rubber septum and aluminum crimp caps, they were purged with helium gas and placed in a New Brunswick Scientific G10 Gyratory Shaker in a hot chamber at 35 °C. All experiments were conducted in triplicate, and the average results were recorded. To determine specific methane production (SMP), the biogas produced in control samples (containing only inoculum and milli-Q water instead of concentrated wastewater) was subtracted from that generated in other tests with concentrated wastewater.

The specific methane production (SMP) was expressed as milliliters of methane produced per gram of total organic carbon added as substrate (mL CH4/gTOCsubs) under standard conditions (p = 1 atm and T = 0 °C).

3.2 Analytical Methods

COD, TOC, TS and VS of municipal wastewater from WWTP were measured according to standard methods [5]. A ShimCEadzu (Nakagyo-ku, Kyoto, Japan) analyzer (TOC-L) was used to determine the concentration of TOC in the samples where COD could not be made, due to the interference of salts. However, salts also affect in the TOC analyzer and, for this reason, in some samples, dilutions for TOC measurement were necessary to decrease salt effects and to ensure that the measurement was correct. pH was measured using a pH meter pH Basic-20 Crison, (Hach, Loveland, CO, USA).

Anions (Cl^-, SO_4^{2-}, PO_4^{3-}, NO_2^-, NO_3^-) were determined by High-performance liquid chromatography HPLC Waters (Milford, MA, USA) with conductivity detector 432, flow rate 2 mL/min, injection volume 20 μL, and oven temperature 25 °C.

The samples with the emerging contaminants were analyzed by Ultra-High-Performance Liquid Chromatography (UHPLC) – tandem Mass Spectrometry (MS/MS) in Selected Reaction Monitoring (SRM) mode. More specifically, the chromatographic separation was carried out by a Sciex Exion UHPLC (Danaher, Washington, DC, USA) and a Phenomenex (Danaher, Washington, DC, USA) reversed-phase column Kinetex EVO C18 (2.1 mm × 50 mm, particle size 1.7 μm), making use of H_2O and MeOH-based mobile phases containing 0.1 % formic acid as modifier. The column was heated up to 40 °C. Injection flow rates varied from 15 to 500 μL, depending on the analyte and its initial FS concentration, in order to get optimum analytical conditions. Gradient flow rate was set at 0.5 ml/min ($8.3\cdot10^{-9}$ m^3/s) and total chromatographic run time was 10 min. Mass detection was performed by a Sciex 6500+ QqQ, both positive and negative electrospray ionization (ESI) modes in the same run.

The biogas (CH_4) production in the BMP test was measured using a gas chromatograph Varian CP-3800 GC (Varian, Palo Alto, CA, USA) coupled to a thermal conductivity detector and equipped with a CP-Molsieve 5 A column (15 m × 0.53 mm × 15 μm) and another CP-Pora BOND Q column (25 m × 0.53 mm × 15 μm). A pressure sensor IFM PI 1696 (IFM Electronic, Essen, Germany) was used to monitor the pressure of the bottles.

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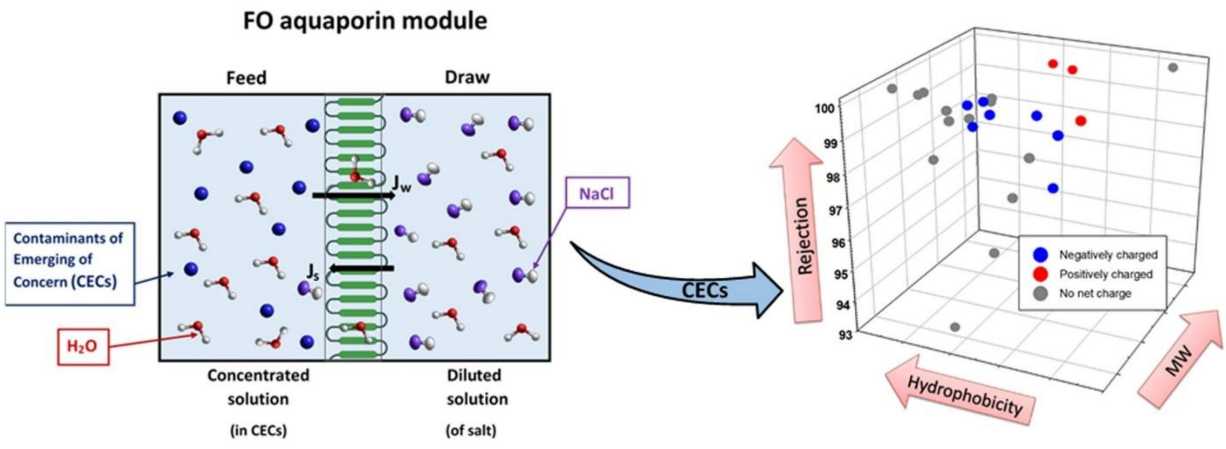
Chapter 4

Study of the rejection of contaminants of emerging concern by a biomimetic aquaporin hollow fiber forward osmosis membrane



Salamanca, M.; López-Serna, R.; Palacio, L.; Hernández, A.; Prádanos, P.; Peña, M. Study of the Rejection of Contaminants of Emerging Concern by a Biomimetic Aquaporin Hollow Fiber Forward Osmosis Membrane. J. Water Process Eng. **2021**, 40, 101914. https://doi.org/10.1016/j.jwpe.2021.101914.

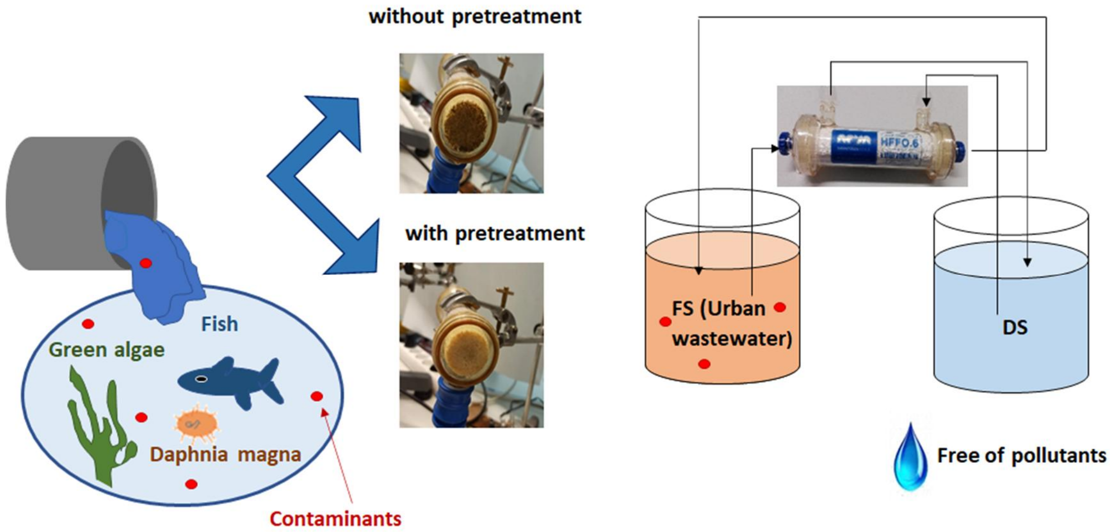
ABSTRACT

Forward osmosis (FO) plays an increasingly important role in membrane processes because of its advantages compared to traditional pressure-driven membrane processes. There are different types of water-selective FO membranes. In this study, a biomimetic hollow fiber module comprising an active layer of polyamide thin film composite (TFC) with integrated aquaporin proteins and an effective area of 0.6 m^2 is used to study the rejection of 24 Contaminants of Emerging Concern (CECs). The rejections obtained for all the contaminants studied were higher than 93 % and for 19 of them rejections of up to 99 % were reached. It was observed that although all the tested compounds showed rejections very close to 100 %, they were not completely recovered in the feed solution which makes the retention within the membrane an important factor to be considered. Hence, two membrane rinses were necessary after each membrane operation to completely recover each contaminant. The results were analyzed considering the physicochemical properties (molecular weight, charge and hydrophobicity) of the contaminants.

Keywords: Forward Osmosis (FO); Aquaporin membrane; Contaminants of Emerging Concern (CECs); Hollow fiber module

Chapter 5

Ecological Risk Evaluation and Removal of Emerging Pollutants in Urban Wastewater by a Hollow Fiber Forward Osmosis Membrane



Salamanca, M.; López-Serna, R.; Palacio, L.; Hernández, A.; Prádanos, P.; Peña, M. Ecological Risk Evaluation and Removal ofEmerging Pollutants in Urban Wastewater by a Hollow Fiber Forward Osmosis Membrane. Membranes **2022**, 12(3), 293,https://doi.org/10.3390/membranes12030293.

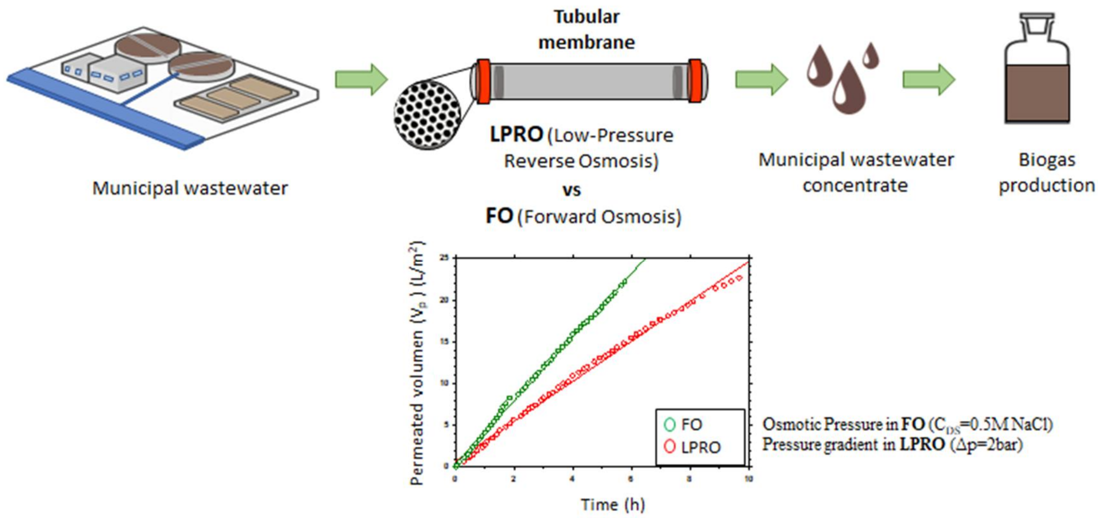
ABSTRACT

Forward Osmosis (FO) is a promising technology for the treatment of urban wastewater. FO can produce high quality effluents and pre-concentrate urban wastewater for subsequent anaerobic treatment. This membrane technology makes it possible to eliminate the pollutants present in urban wastewater, which can cause adverse effects in the ecosystem even at low concentrations. In this study, a 0.6 m^2 hollow fiber aquaporin forward osmosis membrane is used for the treatment of urban wastewater from Valladolid Wastewater Treatment Plant (WWTP). A total of 51 Contaminants of Emerging Concern (CECs) have been investigated, of which 18 were found in the target urban wastewater. They have been quantified and their ecotoxicological risk impact evaluated. Different salts with different concentrations have been tested as draw solution to evaluate the membrane performances when working with pretreated urban wastewater. NaCl was found as the most appropriate salt since it leads to higher permeate fluxes and lower reverse saline fluxes. The membrane can eliminate or significantly reduce the pollutants present in the studied urban wastewater, producing water without ecotoxicological risk or essentially free of pollutants. In all cases a good recovery was achieved which increases with molecular weight, although chemical and electrostatic interactions also play a role.

Keywords: Urban wastewater; Forward Osmosis (FO); Organic matter concentration; Contaminants of Emerging Concern (CECs), Ecological risk quotient

Chapter 6

Evaluation of Forward Osmosis and Low-Pressure Reverse Osmosis with a Tubular Membrane for the Concentration of Municipal Wastewater and the Production of Biogas



Salamanca, M.; Palacio, L.; Hernández, A.; Peña, M.; Prádanos, P. Evaluation of Forward Osmosis and Low-Pressure Reverse Osmosis with a Tubular Membrane for the Concentration of Municipal Wastewater and the Production of Biogas. Membranes **2023**, 13(3), 266,https://doi.org/10.3390/membranes13030266.

ABSTRACT

Currently, freshwater scarcity is one of the main issues that the world population has to face. To address this issue, new wastewater treatment technologies have been developed such as membrane processes. Among them, due to the energy disadvantages of pressure-driven membrane processes, Forward Osmosis (FO) and Low-Pressure Reverse Osmosis (LPRO) have been introduced as promising alternatives. In this study, the behavior of a 2.3 m^2 tubular membrane TFO-D90 when working with municipal wastewater has been studied. Its performances have been evaluated and compared in two operating modes such as FO and LPRO. Parameters such as fouling, flow rates, water flux, draw solution concentration, organic matter concentration, as well as its recovery have been studied. In addition, the biogas production capacity has been evaluated with the concentrated municipal wastewater obtained from each process. The results of this study indicate that the membrane can work in both processes (FO and LPRO) but, from the energy and productivity point of view, FO is considered more appropriate mainly due to its lower fouling level. This research may offer a new point of view on low-energy and energy recovery wastewater treatment and the applicability of FO and LPRO for wastewater concentration.

Keywords: Municipal wastewater; Forward Osmosis (FO); Low-Pressure Reverse Osmosis (LPRO); Tubular membrane, Biogas production

Chapter 7

Conclusions and future work

Conclusiones y trabajo futuro

In this thesis, the concentration process of municipal wastewater with forward osmosis membranes was carried out on a laboratory and pilot scale while successfully rejecting emerging contaminants commonly present in these types of waters.

The behavior of a hollow fiber forward osmosis membrane in rejection of 24 emerging contaminants was evaluated in **Chapter 4**. It was possible to report that the membrane can reject more than 93% of the 24 emerging contaminants analyzed. Membrane rejection was probably influenced by the physicochemical properties of the contaminants and the interaction with the active layer of the membrane. It could say that the aquaporin hollow fiber membrane is very good in contaminant rejection; however, a global mass balance reveals that some of the CECs are retained through adsorption within the porous matrix of the membrane. As a result, it was necessary to perform up to two complete rinses in order to fully recover each contaminant. A clear relationship between adsorption (low recovery) and low molecular weight was found because small molecules could reach the porous structure of the active layer of the membrane and adsorb on a larger surfaces.

Since rejection was successfully in pure water, rejection of contaminants in real urban wastewater and the ecotoxicological risks of the contaminants found in urban wastewater from the Valladolid WWTP was evaluated in **Chapter 5** Out of the 51 pollutants investigated, 18, which are commonly used in daily life, were detected in varying concentrations in Valladolid's urban wastewater. These pollutants encompass antibiotics (sulfamethoxazole, trimethoprim, sulfapyridine, ofloxacin, clarithromycin, levofloxacin, and ciprofloxacin), analgesics (naproxen, diclofenac, and ibuprofen), antihypertensives (atenolol), stimulants (caffeine), insect repellent (DEET), antiparasitics (fenbendazole), preservatives (methylparaben), and various medications for different ailments (gemfibrozil, atorvastatin, and carbamazepine). In all cases, good recovery was achieved, which increased with molecular weight, although chemical and electrostatic interactions also played an important role. A clear trend of recovery corresponding to molecular weight emerged, indicating lower recoveries for low-molecular-weight compounds. The study underscored the membrane's capacity to eliminate or substantially mitigate the ecotoxicological risk of contaminants in aquatic ecosystems by concentrating them. Additionally, it is crucial to emphasize the necessity of implementing osmotic washing in this type of system to reclaim any remnants that could have become adsorbed on the membrane. Futhermore, research underscores the importance of addressing membrane fouling in urban wastewater treatment and emphasizes the need for pretreatment. NaCl, with its high permeate flux and low reverse salt flux, was identified as the optimal salt solution, offering potential cost savings in coastal regions where seawater with similar concentrations could be used.

Trying to scale-up the FO process system, in **Chapter 6** a tubular FO membrane with 2.3 m^2 of active area was used in to concentrate municipal wastewater in two different modes: (Forward Osmosis) FO and (Low-Pressure Reverse Osmosis) LPRO. The membrane characterization study allows us to choose the optimal operational parameters for enhancing FO performance. Our selections for feed flow rate, Q_{FS} (20 L/min), draw flow rate, Q_{DS} (2.5 L/min), and NaCl concentration (0.5 M) as the draw solution are made with a focus on both productivity and cost-effectiveness. In terms of methane production capacity, the wastewater from both concentration processes (WWFO and WWLPRO) exhibits similar performance. While FO may marginally elevate chloride levels, it's worth noting that the initial urban wastewater typically contains a substantial salt concentration. Consequently, the inhibitory effects on methane production are a critical consideration in designing such applications. Therefore, the inclusion of supplementary pretreatment stages for salt removal becomes essential to enhance the long-term methane production.

In the future, further research and development in the field of FO to optimize the systems and overcome existing challenges would help to improve the technology and expand its practical applications. This thesis has identified several important areas for future investigation and enhancement, including:

- Enhancing FO systems through the development of advanced membrane materials, the exploration of innovative fouling prevention methods, the investigation of novel draw solution recovery techniques, and conducting experiments with actual wastewater under real-world conditions.
- Investigating process integration and hybrid systems that involve combining FO with other water treatment methods like reverse osmosis or electrochemical processes to enhance overall treatment effectiveness. Such hybrid systems may present distinct benefits for specific applications.
- Scaling up and commercializing FO technology, transitioning from laboratory-scale experiments to large-scale implementation, necessitating the resolution of engineering challenges and the optimization of system designs.

A deeper understanding of the technology and its advantages will facilitate the exploration of new applications and new avenues. The technology's advantage in removing emerging contaminants can be extrapolated, for example, to address heavy metals found or nano or microplastics in industrial waters, demonstrating FO's potential for advances in water treatment technologies to address various environmental challenges. Collaborative efforts between academia and industry will be essential to drive progress in FO research and promote its implementation on a larger scale. With further research and innovation, FO can be applied practically in desalination, industrial wastewater treatment, resource recovery and water reuse.

En esta tesis se llevó a cabo a escala de laboratorio y piloto el proceso de concentración de aguas residuales municipales con membranas de ósmosis directa rechazando con éxito los contaminantes emergentes comúnmente presentes en este tipo de aguas.

En el **Capítulo 4** se evaluó el comportamiento de una membrana de ósmosis directa de fibra hueca en el rechazo de 24 contaminantes emergentes. Se pudo concluir que la membrana puede rechazar más del 93% de los 24 contaminantes emergentes analizados. El rechazo de la membrana probablemente estuvo influenciado por las propiedades fisicoquímicas de los contaminantes y la interacción con la capa activa de la membrana. Podríamos decir que la membrana de fibra hueca de acuaporina es muy buena en el rechazo de contaminantes; sin embargo, un balance de masa global revela que algunas de las CEC se retienen mediante adsorción dentro de la matriz porosa de la membrana. Como resultado, fue necesario realizar hasta dos enjuagues completos para recuperar completamente cada contaminante. Se encontró una clara relación entre adsorción (baja recuperación) y bajo peso molecular porque moléculas pequeñas podían alcanzar la estructura porosa de la capa activa de la membrana y obtener una mayor superficie de adsorción.

Dado que el rechazo fue exitoso en agua pura, en el **Capítulo 5** se evaluó el rechazo de contaminantes en aguas residuales urbanas reales y los riesgos ecotoxicológicos de los contaminantes encontrados en las aguas residuales urbanas de la EDAR de Valladolid. De los 51 contaminantes investigados, 18, que son de uso habitual en el día a día, se detectaron en concentraciones variables en las aguas residuales urbanas de Valladolid. Estos contaminantes incluyen antibióticos (sulfametoxazol, trimetoprima, sulfapiridina, ofloxacina, claritromicina, levofloxacina y ciprofloxacina), analgésicos (naproxeno, diclofenaco e ibuprofeno), antihipertensivos (atenolol), estimulantes (cafeína), repelentes de insectos (DEET), antiparasitarios (fenbendazol) conservantes (metilparabeno) y diversos medicamentos para diferentes dolencias (gemfibrozilo, atorvastatina y carbamazepina). En todos los casos se logró una buena recuperación, que aumentó con el peso molecular, aunque también jugaron un papel importante las interacciones químicas y electrostáticas. Surgió una clara tendencia de recuperación correspondiente al peso molecular, lo que indica menores recuperaciones para compuestos de bajo peso molecular. El estudio destacó la capacidad de la membrana para eliminar o mitigar sustancialmente el riesgo ecotoxicológico de los contaminantes en los ecosistemas acuáticos al concentrarlos. Además, es fundamental enfatizar la necesidad de implementar un lavado osmótico en este tipo de sistemas para recuperar los restos que hayan podido quedar adsorbidos en la membrana. Además, la investigación subraya la importancia de abordar la contaminación de las membranas en el tratamiento de aguas residuales urbanas y enfatiza la necesidad de un tratamiento previo. El NaCl, con su alto flujo de permeado y bajo flujo inverso de sal, fue identificado como la solución salina óptima, ofreciendo ahorros potenciales de costos en regiones costeras donde se podría usar agua de mar con concentraciones similares.

Intentando ampliar el sistema de proceso de FO, en el **Capítulo 6** se utilizó una membrana tubular de FO con 2,3 m^2 de área activa para concentrar aguas residuales municipales en dos modos diferentes: (ósmosis directa) FO y (ósmosis inversa de baja presión) LPRO. El estudio de caracterización de membranas nos permite elegir los parámetros operativos óptimos para mejorar el rendimiento de FO. Nuestras selecciones de caudal de alimentación, QFS (20 L/min), caudal de extracción, QDS (2,5 L/min) y concentración de NaCl (0,5 M) como solución de extracción se realizan centrándose tanto en la productividad como en la rentabilidad. En términos de capacidad de producción de metano, las aguas residuales de ambos procesos de concentración (WWFO y WWLPRO) presentan un comportamiento similar. Si bien la FO puede elevar marginalmente los niveles de cloruro, vale la pena señalar que las aguas residuales urbanas iniciales suelen contener una concentración sustancial de sal. En consecuencia, los efectos inhibidores sobre la producción de metano son una consideración crítica en el diseño de tales aplicaciones. Por lo tanto, la inclusión de etapas de pretratamiento suplementarias para la eliminación de sales se vuelve esencial para mejorar la producción de metano a largo plazo.

En el futuro, una mayor investigación y desarrollo en el campo de la FO para optimizar los sistemas y superar los desafíos existentes ayudaría a mejorar la tecnología y ampliar sus aplicaciones prácticas. Esta tesis ha identificado varias áreas importantes para futuras investigaciones y mejoras, que incluyen:

- Mejorar los sistemas de FO mediante el desarrollo de materiales de membrana avanzados, la exploración de métodos innovadores de prevención de incrustaciones, la investigación de técnicas novedosas de recuperación de soluciones de extracción y la realización de experimentos con aguas residuales reales en condiciones reales.
- Investigar la integración de procesos y sistemas híbridos que implican combinar FO

con otros métodos de tratamiento de agua como ósmosis inversa o procesos electroquímicos para mejorar la efectividad general del tratamiento. Estos sistemas híbridos pueden presentar distintos beneficios para aplicaciones específicas.

- Ampliar y comercializar la tecnología de FO, pasando de experimentos a escala de laboratorio a una implementación a gran escala, lo que requiere la resolución de desafíos de ingeniería y la optimización de los diseños de sistemas.

Una comprensión más profunda de la tecnología y sus ventajas facilitará la exploración de nuevas aplicaciones y vías. La ventaja de la tecnología para eliminar contaminantes emergentes se puede extrapolar, por ejemplo, para abordar los metales pesados o nano o microplástios que se encuentran en aguas industriales, lo que demuestra el potencial de FO para que los avances en las tecnologías de tratamiento de agua aborden diversos desafíos ambientales. Los esfuerzos de colaboración entre la academia y la industria serán esenciales para impulsar el progreso en la investigación de FO y promover su implementación a mayor escala. Con más investigación e innovación, la FO se puede aplicar prácticamente en la desalinización, el tratamiento de aguas residuales industriales, la recuperación de recursos y la reutilización del agua.

Chapter 8

About the author

Biography

Mónica Salamanca Verdugo (Segovia,1996) started a Chemical degree in 2014 at the University of Valladolid.

In September 2018, she began the *Master of Advanced Techniques in Chemistry, Quality control and chemical analysis* at the University of Valladolid and obtained the extraordinary Master's award. In addition, she obtained a 6-month scholarship from the General Foundation of the University of León (FGULEM) for internships at the pharmaceutical company Amri.Inc (now called Curia) in the department of Quality Assurance (QA).

In October 2019, Mónica Salamanca began a contract as a researcher at the Institute of Sustainable Processes – University of Valladolid, where she then began her doctoral research within two groups of that institute, Surfaces and Porous Materials (SMAP) group and the Environmental Technology Group. Her doctoral studies focused on the study of urban wastewater concentration using forward osmosis membranes for the use and improvement of water resources.

During her doctoral studies, she carried out a research stay (Sept 2022-Dec 2022) at the Technical University of Denmark (DTU) in the department of DTU Sustain under the supervision of Dr. Weijing (Angela) Zhang. Also, she has combined her PhD with the Master in Teacher of Secondary Education, specializing in physics and chemistry, which she completed in July 2023.

Publications in international journals

1. Salamanca, M.; López-Serna, R.; Palacio, L.; Hernández, A.; Prádanos, P.; Peña, M. Study of the Rejection of Contaminants of Emerging Concern by a Biomimetic Aquaporin Hollow Fiber Forward Osmosis Membrane. J. Water Process Eng. 2021, 40, 101914. https://doi.org/10.1016/j.jwpe.2021.101914.
2. Salamanca, M.; López-Serna, R.; Palacio, L.; Hernández, A.; Prádanos, P.; Peña, M. Ecological Risk Evaluation and Removal of Emerging Pollutants in Urban Wastewater by a Hollow Fiber Forward Osmosis Membrane. Membranes 2022, 12(3), 293, https://doi.org/10.3390/membranes12030293.
3. Salamanca, M.; Palacio, L.; Hernández, A.; Peña, M.; Prádanos, P. Evaluation of Forward Osmosis and Low-Pressure Reverse Osmosis with a Tubular Membrane for the Concentration of Municipal Wastewater and the Production of Biogas. Membranes 2023, 13(3), 266, https://doi.org/10.3390/membranes13030266.
4. Salamanca, M.; Peña, M.; Hernandez, A.; Prádanos, P.; Palacio, L. Forward Osmosis Application for the Removal of Emerging Contaminants from Municipal Wastewater: A Review. Membranes 2023, 13(7), 655, https://doi.org/10.3390/membranes13070655.

Contribution to conferences

1. Salamanca, M.; López-Serna, R.; Palacio, L.; Hernández, A.; Prádanos, P.; Peña, M. Estudio del rechazo de contaminantes emergentes mediante una membrana de ósmosis directade fibra hueca con acuaporinas. VII Conference of Women Researchers of Castilla y León 2021, April 15 and 16, 2021, Valladolid, Spain. (**Oral presentation**)
2. Salamanca, M.; López-Serna, R.; Palacio, L.; Hernández, A.; Prádanos, P.; Peña, M. Evaluación del riesgo ecológico y eliminación de contaminantes emergentes en aguas residuales urbanas mediante membrana de ósmosis directa. VIII Conference of Women Researchers of Castilla y León 2022, April 21 and 22, 2022, Burgos, Spain. (**Poster**).

3. Salamanca, M.;, Rebeca López-Serna, L. Palacio, A. Hernández, P. Prádanos, Mar Peña. Study of the rejection of contaminants of emerging concern by a biomimetic aquaporin hollow fiberforward osmosis membrane.12th Micropol and Ecohazard Conference (International).6-10 June, 2022, Santiago de Compostela (USC), Spain. (**Poster with pitch**).
4. Salamanca, M.; Palacio, L.; Hernández, A.; Peña, M.; Prádanos, P. Evaluación de una membrana tubular para la concentración de aguas residuales municipales: comparación entre ósmosis directa (FO) y ósmosis inversa de baja presión (LPRO). Participation in IX Conference of Women Researchers of Castilla y León 2023, February 9 and 10, 2023, Salamanca, Spain. (**Poster**).

Research stays

- Stay from Sept 22-Dec 22 at the Technical University of Denmark (DTU) in DTU Sustain, Denmark. Supervisor: Weijing (Angela) Zhang.

Participation in Research Projects

1. Strategic research program of the institute of sustainable processes according to order EDU/956/2018, of september 11 (REFERENCE CLU-2017-09), executed by research structures of excellence within the framework of the strategy regional research and innovation for intelligent specialization (RIS3) of Castilla and León 2014-2020. P.I: Pedro García Encina.
2. Project in reutilización de aguas depuradas-regeneradas de la urbanización "El Soto" y la urbanización "Los Aljibes" para el riego de zonas verdes públicas. Diputación de Valladolid. P.I: Rubén Irusta
3. Project in Procesos de membrana en biogás y separación deolefinas/parafinas. Reference: PID2019-109403RB-C21. P.I: Laura Palacio Martínez.

Fellowships

1. UVa-Predoctoral researcher Fellowship (2022).
2. Short term for research stay in DTU (Denmark Technique University), Denmark (2022). ERASMUS +programme (KA131).

Teaching and students mentoring

1. Tutor of a Master Thesis in the Master´s in Environmental Engineering at University of Valladolid. Student: Mulenga Mwamba. Thesis title: *The use of forward osmosis to concentrate organic matter in urban wastewater* (July 2021).
2. TÉCNICAS EXPERIMENTALES EN FÍSICA II (Thermodynamics laboratory) Assistant Professor, 1.53 ECTS. Physics Degree. 2nd course, academic year 2023/2024, University of Valladolid (Spain).

Attended short-courses and seminars

1. Denomination: Tratamiento de datos personales en la investigación.

   Organisms/University: Doctoral School of the University of Valladolid

   Duration/Number of credits: 4 h.

   Date: 22 of January 24
2. Denomination: Jornadas DAAR (Digestión Anaerobia para el Aprovechamiento de Residuos.

   Organisms/University: Instituto de Procesos Sostenibles- Universidad de Valladolid

   Date: 5-6 Oct 23
3. Denomination: SGrop BIP in Doctoral Education

   Organisms/University: Doctoral School of the University of Valladolid

   Duration/Number of credits: 3 ECTS.

   Date: sep- oct 23.
4. Denomination: Máster en Profesor de Educación Secundaria Obligatoria y Bachillerato, Formación Profesional y Enseñanza de Idiomas

   Organisms/University: University of Valladolid

   Duration/Number of credits: 60 ECTS.

   Date: oct-2021-july-23.
5. Denomination: Realización de figuras de calidad para artículos científicos.

   Organisms/University: Programa de Doctorado en Tecnologías de la Información y las Telecomunicaciones de la Universidad de Valladolid

   Duration/Number of credits: 8 h.

Date: 25 may -29 june 23.

6. Denomination: III Jornadas didácticas de innovación “Experiencias de elaboración de materiales audio/visuales y su incorporación a la docencia/aprendizaje

   Organisms/University: Centro de Enseñanza Online, Formación e Innovación Docente (VirtUVa)

   Duration/Number of credits: 10 h.

   Date: 11-12 May 23.

7. Denomination: Pon en valor tu investigación en Ciencias Experimentales.

   Organisms/University: Doctoral School of the University of Valladolid

   Duration/Number of credits: 6 h.

   Date: 25-26 april 23.

8. Denomination: Taller de divulgación científica para personal investigador.

   Organisms/University: Doctoral School of the University of Valladolid

   Duration/Number of credits: 15 h.

   Date: 21-23 march 23.

9. Denomination: Procesos Térmicos de Valorización de residuos

   Organisms/University: Escuela de Ingenierías Industriales de la Universidad de Valladolid

   Duration/Number of credits: 4 h.

   Date: 31 January 23.

10. Denomination: El arte de ser profesional.

    Organisms/University: Escuela de Ingenierías Industriales de la Universidad de Valladolid

    Duration/Number of credits: 8 h.

    Date: 26 -30 January 23.

11. Denomination: Seminario ¿cómo realizar una evaluación económica en proyectos de ingeniería?.

    Organisms/University: Doctoral School of the University of Valladolid

    Duration/Number of credits: 4h.

Date: 24 of June 2022.

12. Denomination: Cómo orientar tu carrera académica.

    Organisms/University: Doctoral School of the University of Valladolid

    Duration/Number of credits: 8h.

    Date: 26-27 of May 2022.

13. Denomination: "A happy PhD": productividad, bienestar y progreso del doctorando.

    Organisms/University: Doctoral School of the University of Valladolid

    Duration/Number of credits: 10h.

    Date: 10 -31 of March 2022.

14. Denomination: Introducción a Teams.

    Organisms/University: Centro de Enseñanza Online, Formación e Innovación Docente de la Universidad de Valladolid (VirtUVa)

    Duration/Number of credits: 3h.

    Date: 4-11 of February 2022

15. Denomination: Introdución a la Ciencia Abierta, una pincelada a los datos de investigación

    Organisms/University: Doctoral School of the University of Valladolid

    Duration/Number of credits: 4 h.

    Date: 4 of February 22.

16. Denomination: Ética y buenas prácticas en la investigación.

    Organisms/University: Doctoral School of the University of ValladolidDuration/Number of credits: 4h.

    Date: 29 of November 2021

17. Denomination: workshop: Anaerobic digestion ¿quo vadis?

    Organisms/University: Instituto de procesos sostenibles (Universidad de Valladolid) y CRETUS (Universad de Santiago de Compostela).

    Duration/Number of credits: 4.5h.

    Date: 21 de octubre de 2021.

18. Denomination: Análisis de ciclo de vida: Fundamentos y casos prácticos.

Organisms/University: Doctoral School of the University of Valladolid

Duration/Number of credits: 5h.

Date: 21 of October 2021

19. Denomination: Writing in English B2.

    Organisms/University: Doctoral School of the University of ValladolidDuration/Number of credits: 50h- 2 ECTS.

    Date: 03 March-02 June 2021

20. Denomination: “Professional Development”.

    Organisms/University: IMFAHE FOUNDATION.

    Duration/Number of credits: 30h.

    Date: 23 octubre-29 diciembre 2020.

21. Denomination: Formación en Comunicación y Soft Skills.

    Organisms/University: Doctoral School of the University of ValladolidDuration/Number of credits: 8h.

    Date: Nov 2020.

22. Denomination: Course “Valorización de resultados de investigación. Grados científico-técnicos”.

    Organisms/University: Parque Científico Universidad de Valladolid.

    Duration/Number of credits: 6h.

    Date: 14-15 of July 2020.

23. Denomination: Abstracts y articles in English.

    Organismos/Universidad: Doctoral School of the University of ValladolidDuration/Number of credits: 16h.

    Date: 08-22 of June 2020.

24. Denomination: 3 courses of SCOPUS. Perfil de autor e instituciones, trabajando con los resultados, sources y comparación de revistas.

    Organisms/University: SCOPUS.

    Duration/Number of credits: 3h.

    Date: 15-26 of June 2020.

25. Denomination: 2 cursos de buscar y analizar la producción científica de una institución y hacer búsquedas avanzadas en la WOS.

    Organisms/University: Web Of Science (WOS).

    Duration/Numberof credits: 2h.

    Date: 11-28 of May 2020.

26. Denomination: Course of Listening & Speaking.

    Organisms/University: Fundación General de la Universidad de Valladolid (FUNGE UVA).

    Duration/Number of credits: 50h / 4.5 ECTS.

    Date: Oct 2019-April 2020.

27. Denomination: Iniciación a la escritura y publicación de artículos científicos.

    Organisms/University: Doctoral School of the University of Valladolid.

    Duration/Number of credits: 4h.

    Date: 17 of December 2019.

28. Denomination: Taller Práctico sobre Técnicas Analíticas Fisicoquímicas e Instrumentales.

    Organisms/University: Doctoral School of the University of Valladolid.

    Duration/Number of credits:8h.

    Date: Nov-Dec 2019.

29. Denomination: Course of formación de primeros auxilios en laboratorios.

    Organisms/University: Servicio de prevención de riesgos laborales de la Universidad de Valladolid.

    Duration/Number of credits: 2h.

    Date: Nov 2019.

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