

Títol del treball:

**FORWARD OSMOSIS MEMBRANES FABRICATION AND
CHARACTERIZATION**

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RESUM

L'osmosi directa (OD) ha emergit com una nova i prometedora tecnologia de membrana per al tractament d'aigües i altres aplicacions industrials gràcies a les seves característiques, els seus baixos requisits energètics i la seva possibilitat d'operar a baixos valors de temperatura i pressió. A diferència d'una de les tecnologies de membrana més utilitzades, l'osmosi inversa, que depèn de la pressió hidràulica, l'osmosi directa utilitza la pressió osmòtica com a força impulsora, fent-la així una opció més energèticament eficient.

Aquest estudi se centra en la fabricació i posterior caracterització de membranes polimèriques d'osmosis directa amb l'objectiu de millorar la seva eficiència i selectivitat. Aconseguint així la fabricació de membranes amb gran potencial de rebuig de sal i evitant el màxim possible efectes com la "incrustació" i concentració polarització, típics d'aquest tipus de membranes.

Aquestes membranes orgàniques han estat fabricades usant diversos polímers a partir de mètodes com la inversió de fase i la polimerització interfacial amb la capa de suport de polisulfona i la capa selectiva de poliamida respectivament. Resultant en membranes asimètriques de dues capes, amb una capa selectiva més fina i una de suport més gruixuda. El gruix de la capa de suport de polisulfona ha estat variada per tal d'observar els seus efectes en les propietats de la membrana.

Aquestes van ser posteriorment caracteritzades mesurant el seu flux d'aigua, permeabilitat, capacitat de repulsió de sals i morfologia, emprant diferents tècniques, incloent-hi microscòpia electrònica de rastreig (MER) i monitoratge del flux d'aigua i conductivitat.

Els resultats de l'estudi mostren una bona estructura de la capa de suport, morfologia uniforme amb porus semblants a dits, així com una bona resistència mecànica. Tot i això, es van trobar problemes en l'adhesió de la capa de poliamida, el seu flux d'aigua i permeabilitat, factors crítics a l'hora de la utilització de la membrana per al seu propòsit. Els resultats indiquen que la capa de poliamida no és homogènia, així ho demostren l'alta permeabilitat i el gran pas de sals. A més, durant la prova de flux, es va observar un flux significativament baix en OD, indicant la possibilitat de que es dugués a terme un efecte de concentració de polarització a la capa de suport.

En resum, s'han aconseguit bons resultats en la fabricació de la membrana de suport, indicant una estructura favorable, però es necessiten millores en la fabricació de la capa selectiva de poliamida per tal d'optimitzar-la i aconseguir fer-la una opció més viable per les seves diverses aplicacions en l'osmosi directa.

RESUMEN

La ósmosis directa (OD) ha emergido como una nueva i prometedor tecnología de membrana para el tratamiento de aguas y otras aplicaciones industriales gracias a sus características, sus bajos requisitos energéticos y su posibilidad de operar a bajos valores de temperatura y presión. A diferencia de una de las tecnologías de membrana más utilizadas, la ósmosis inversa, que depende de la presión hidráulica, la ósmosis directa utiliza la presión osmótica como fuerza impulsora, haciéndola así una opción más energéticamente eficiente.

Este estudio se centra en la fabricación y posterior caracterización de membranas poliméricas de ósmosis directa con el objetivo de mejorar su eficiencia y selectividad. Consiguiendo así la fabricación de membranas con gran potencial de repulsión de sal y evitando lo máximo posible efectos como la "incrustación" y concentración polarización, típicos de este tipo de membranas.

Estas membranas orgánicas han sido fabricadas usando varios polímeros a partir de métodos como la inversión de fase y la polimerización interfacial con la capa de soporte de polisulfona y la capa selectiva de poliamida respectivamente, resultando en membranas asimétricas de dos capas con una capa selectiva más fina y una de soporte más gruesa. El grosor de la capa de soporte de polisulfona ha sido variado para observar sus efectos en las propiedades de la membrana.

Éstas fueron posteriormente caracterizadas midiendo su flujo de agua, permeabilidad, capacidad de repulsión de sales y morfología, empleando diferentes técnicas, incluyendo microscopía electrónica de barrido (MEB) y monitorización del flujo de agua y conductividad.

Los resultados del estudio muestran una buena estructura de la capa de soporte, con una morfología uniforme con poros similares a dedos, así como una buena resistencia mecánica. Sin embargo, se encontraron problemas en la adhesión de la capa de poliamida, su flujo de agua y permeabilidad, factores críticos al momento de la utilización de la membrana para su propósito. Los resultados indican que la capa de poliamida no es homogénea, así lo demuestran la alta permeabilidad y el gran paso de sales. Además, durante la prueba de flujo, se observó un flujo significativamente bajo en OD, indicando la posibilidad de que se produjese un efecto de concentración de polarización en la capa de soporte.

En resumen, se han logrado buenos resultados en la fabricación de la membrana de soporte, indicando una estructura favorable, pero se necesitan mejoras en la fabricación de la capa selectiva de poliamida para optimizarla y conseguir hacerla una opción más viable por sus diversas aplicaciones en la ósmosis directa.

ABSTRACT

Forward osmosis (FO) has emerged as a promising membrane technology for water treatments and other industry applications due to their characteristic, it's low energy requirements and ability to operate without high temperature or pressure values. Unlike the more commonly used membrane technology, reverse osmosis, which relies on hydraulic pressure, forward osmosis uses the osmotic pressure as its main driving force, making it a more energy-efficient option.

This study focuses on the fabrication and rear characterization of polymeric forward osmosis membranes with the aim of improving their efficiency and selectivity. Achieving the fabrication of a membrane with great salt rejection and avoiding as much possible fouling and concentration polarization effects, typical of this type of membranes.

The organic membranes were fabricated using various polymers through phase inversion and interfacial polymerization methods with a polysulfone (Psf) support layer and a polyamide selective layer respectively. Resulting in two-layers asymmetric membranes, with a thin selective layer over a thicker support layer. The thickness of the support Psf layer was varied to investigate its effect on membrane properties.

These were then characterized by measuring their water flux and permeability, salt rejection and morphology, using various techniques, including scanning electron microscopy (SEM), water flux and conductivity measurements.

The results of the study revealed a well-structured support layer, with a uniform and finger-like porous morphology and good mechanical resistance. However, there were encountered issues with polyamide layer adhesion, water flux and permeability, which are critical factors in membrane purpose. The experimental results indicate that the polyamide layer is not homogeneous, as evidenced by the high permeability to water and passage of salts. Moreover, during the flux test, a significantly low flux was observed in FO, indicating the possibility of polarization concentration effect in the support layer.

In summary, the study achieved good fabrication results for the support layer, indicating a favourable structure, but further improvement is needed for the polyamide selective layer to optimize the membrane's fabrication methods and make it a more viable option for FO applications.

AGRAÏMENTS

M'agradaria agrair principalment al meu tutor Gaetan per tota l'ajuda oferida d'ençà que vaig començar aquest TFG i per tot el que he pogut aprendre d'ell, per aquesta introducció al món de les membranes d'osmosis directa i les diverses metodologies per a la seva fabricació. També al grup de recerca LEQUIA per la gran acollida als seus laboratoris i al servei STR de l'UdG per la seva gran forma de treballar. En últim lloc, agrair a la meva família pel suport constant, així com als amics que m'han donat aquests quatre cursos del grau de ciències ambientals a la Universitat de Girona.

REFLEXIONS

REFLEXIÓ D'ÈTICA I SOSTENIBILITAT

Aquest treball té com a finalitat aprofundir i contribuir en la recerca de noves tecnologies per al tractament aigües, en concret la tecnologia de membrana d'osmosi directa. Aquesta recerca és molt important principalment per dos factors correlacionats. En primer lloc, el context climàtic actual afecta negativament els recursos hídrics, provocant l'esgotament dels recursos potables, afavorint a la reducció del seu volum i contaminació. Per garantir l'abastament d'aigua a tota la població és necessari recórrer a la recerca exhaustiva de nous mètodes efectius per al tractament d'aquestes aigües, inclús per a la potabilització de l'aigua marina, que representa aproximadament el 97% de l'aigua total del planeta. En segon lloc, existeix la necessitat de que aquestes tecnologies de tractament d'aigua siguin el més sostenibles possible, perquè si s'utilitzen mètodes que contribueixen al canvi climàtic, es crearia un cicle en el qual s'estaria afavorint indirectament al problema que s'aspira resoldre. Així, aquest treball pretén contribuir a la recerca en noves tecnologies per al tractament d'aigua, garantint la sostenibilitat i la salut del planeta.

PERSPECTIVA DE GÈNERE AL MÓN CIENTÍFIC I DOCENT

Les conseqüències del rol femení en un món establert des de la perspectiva masculina han estat representades històricament per la desigualtat. La jerarquització de poders és percebuda com un indicador alarmant en les relacions socials i professionals durant els anys actius de les dones, per això no és sorprenent veure com la representació de dones al món científic ha estat sempre per sota de la representació masculina. L'antic pensament de classificar a les dones per certes feines i no validar-les per altres ha repercutit en què durant anys, dones no consideressin el seu perfil adequat per a enfocar-se en la ciència i la recerca. Actualment, cada vegada hi ha més dones que es dediquen a aquests camps i han fet contribucions significatives, però alhora hi ha manca de representació en posicions de lideratge.

La participació de la dona a la recerca científica és necessària per a la resolució dels molts reptes globals que enfronta la humanitat. Considerant això, penso que s'ha d'actuar per millorar aquesta situació, concretament crec fermament amb l'ús de la perspectiva de gènere en l'ensenyament. Una educació basada des de la igualtat entre els dos gèneres, les classes socials, l'ètnia o la sexualitat, pot tenir un impacte beneficiós en les relacions i comunicació social entre les persones. La discriminació és avui en dia un dels problemes més encoberts per la cultura de la societat, per la qual cosa, la desconstrucció de certs comportaments que afavoreixen a aquesta situació s'haurien de canviar mitjançant una eina molt potent que és la docència.

INDEX

1.	Introduction.....	1
1.1-	Forward osmosis processes.....	1
1.2-	Applications.....	2
1.3-	Forward osmosis membrane.....	2
1.3.1-	Membrane types.....	2
1.3.2-	FO membrane structure.....	3
1.3.3-	Limiting factors.....	4
2.	Objectives.....	5
3.	Materials and methods.....	6
3.1-	Support layer (polysulfone) membrane fabrication.....	6
3.1.1-	Chemicals.....	6
3.1.2-	Instruments.....	6
3.1.3-	Step-by-step preparation.....	6
3.2-	Selective layer (polyamide) fabrication.....	7
3.2.1-	Chemicals.....	7
3.2.2-	Instruments.....	7
3.2.3-	Step-by-step preparation.....	8
3.3-	Characterization.....	8
3.3.1-	Permeability test.....	8
3.3.1.1-	Hydraulic pressure driven system.....	9
3.3.2-	Flux and salt rejection test.....	10
3.3.2.1-	Forward osmosis system.....	10
3.3.3-	SEM analyses.....	12
3.3.3.1-	Morphological characterization.....	12
3.3.3.2-	Thickness measure.....	12
4.	Results and discussion.....	13
4.1-	Permeability test.....	13
4.1.1-	Hydraulic pressure driven System – Support membrane.....	13
4.1.2-	Hydraulic pressure driven System – Selective membrane.....	14
4.2-	Flux and salt rejection test.....	15
4.2.1-	Forward osmosis system – Selective membrane.....	15
4.3-	SEM analyses.....	16
4.3.1-	Morphological characterization.....	16
4.3.1.1-	Support Psf membrane.....	16
4.3.1.1.1-	Top layer.....	16
4.3.1.1.2-	Cross-section.....	17
4.3.1.1.3-	Bottom layer.....	17
4.3.1.2-	Selective Pa + Psf support membrane.....	18
4.3.1.2.1-	Top layer.....	18
4.3.1.2.2-	Cross-section.....	19
4.3.1.2.3-	Bottom layer.....	20
4.3.2-	Thickness measure.....	21
5.	Conclusions.....	22
6.	Bibliography.....	23

1. INTRODUCTION

The current environmental scenarios have been characterized by rising temperatures and declining precipitation in most parts of the world, resulting in direct and indirect impacts on water resources and contributing to their scarcity. This requires society to increasingly innovate in new methods and technologies to mitigate this situation and to find alternative sources of water like by desalinating water from the sea or reusing wastewater. Membrane technologies play a crucial role since they can separate contaminants (including salts) from water for its purification. Therefore, emerging technologies such as osmotically driven membrane processes (ODMP) have gained significant traction in recent years (C. Klaysom et al., 2013). Although reverse osmosis membranes have been the most commonly used and studied, interest in forward osmosis membranes has recently increased due to their unique characteristics that can offer advantages over reverse osmosis in specific cases (A.A. Shah et al., 2017) .

1.1- Forward osmosis processes

The forward osmosis (FO) process is a type of membrane separation process that involves the selective diffusion of water across a semi-permeable membrane. The membrane allows certain compounds to pass through while rejecting others, resulting in a transfer of water from a more diluted solution to a more concentrated solution. This transfer is driven by the osmotic pressure gradient that exists between two solutions due to their different concentrations.

During the forward osmosis process, the flow of water continues until the two solutions reach equilibrium, which occurs when the concentrations of the two solutions are equal. As a result, the concentration of the draw solution is gradually reduced until it reaches the same level as the feed solution.

Compared to other membrane separation processes, such as reverse osmosis (RO) or nanofiltration, the main difference with the forward osmosis process lies in the driving force. In forward osmosis, the driving force is purely chemical and no external factor is required beyond the difference in osmotic pressures of the solutions. In contrast, reverse osmosis relies on an external hydraulic pressure to overcome the difference in osmotic pressure between the two solutions. Nanofiltration, on the other hand, separates molecules based on size and charge, rather than relying on osmotic pressure differences.

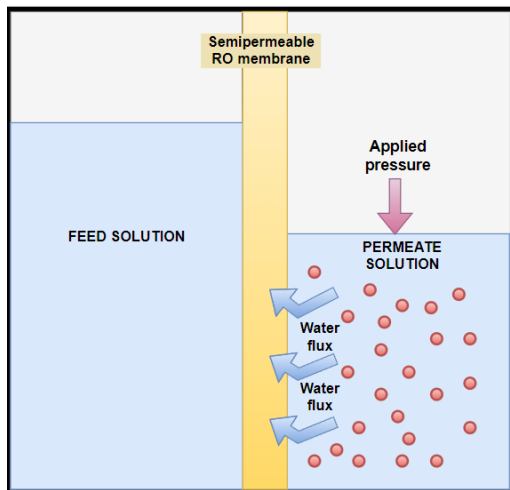


Fig. 1. Schematic representation of RO process

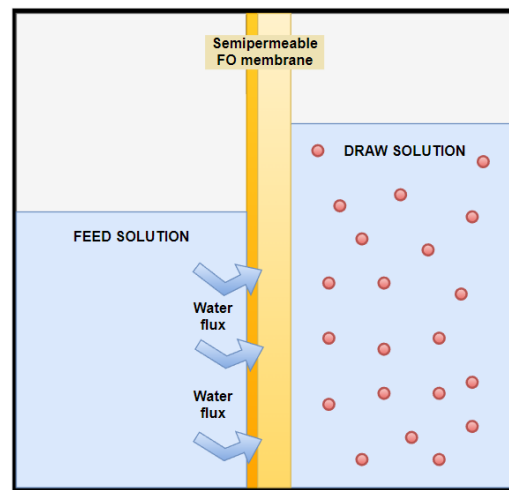


Fig. 2. Schematic representation of FO process

1.2- Applications

Forward osmosis is a versatile process that finds various applications due to its ability to concentrate liquid streams without the need for hydraulic pressure or high temperatures (Font et al., 2014). One of the primary uses of forward osmosis is in the treatment of wastewater and the production of drinking water. It is also commonly used in desalination processes, where it can be combined with reverse osmosis to achieve optimal results (S. Lee et al., 2019). Another important application is the concentration of liquid foods, which helps to preserve their quality without compromising their nutritional or sensory properties (Sant'Anna et al., 2012; Zhao et al., 2012). Apart from these, FO membranes have potential applications in the fields of pharmaceuticals, fertilizers, and energy generation, among others (Font et al., 2014). Overall, forward osmosis offers a low-cost, energy-efficient, and environmentally friendly alternative to traditional separation processes, making it an attractive option for a wide range of industries.

1.3- Forward osmosis membrane

1.3.1- Membrane types

Forward osmosis processes rely on semi-permeable membranes to carry out the main function of filtration. To improve the efficiency of these processes, researchers have developed various types of membranes, which are mainly differentiated based on the materials used for their manufacture and their porosity.

Two families are distinguished based on the materials used for the membrane fabrication, ceramics and polymeric. Inorganic membranes, such as ceramics, offer superior thermal and chemical resistance compared to polymeric membranes (A. K. Fard et al., 2018). However, they tend to be more expensive and fragile to handle. These, including metallic or carbon membranes,

represent a small percentage of the actual market compared to polymeric membranes and are not suitable for direct osmosis processes (A. K. Fard et al., 2018)..

Polymeric membranes, which are made of organic materials, are a commonly used type in osmotic processes. Various polymers can be used to construct them, the selectivity potential and resistance to external factors may vary depending on the specific polymer used. While there is no specific recipe for making polymeric membranes, the literature suggests that certain polymers, such as Polysulfone and Polyamide, are optimal for manufacturing effective forward osmosis membranes (J. Wei et al., 2011).

Membranes can also be differentiated based on their porosity. Porous membranes are typically used in microfiltration and ultrafiltration processes, and they have larger, more visible pores that allow water and other molecules up to 1 μm and 100 nm respectively to pass through (X. Tan et al., 2019). On the other hand, dense membranes are typical in reverse and forward osmosis processes, and they have smaller pores that do not exceed 1 nm in diameter (X. Tan et al., 2019). In this way, water passes through and small molecules like salts are rejected. Water molecules pass through dense membranes via diffusion inside the membrane.

In this study, the goal is to manufacture effective forward osmosis membranes. Therefore, polymeric and dense layers will be utilized with specific polymers selected for their properties. A thin film composite membrane consists of several layers of polymers for FOs and ROs. Therefore, there will be two layers. The porous support layer will be made from polysulfone, while the dense selective layer will be made from polyamide. These polymers will be constructed through phase inversion and interfacial polymerization, methods that have been shown to be effective for producing high-quality FO membranes according to literature (J. Wei et al.,2011).

1.3.2- FO membrane structure

The forward osmosis membrane is structurally and compositionally asymmetric, often consisting of two layers: a thicker (75-150 μm) porous polysulfone support layer and a thinner (<1 μm) and denser polyamide layer on top, which is the selective layer (K. Grzebyk et al, 2022). The polysulfone layer serves as a support, as the polyamide layer is too thin and fragile to be handled or used in the filtration process on its own.

Polysulfone (PSf) is commonly used as a support material, and other additive polymers such as polyvinylpyrrolidone (PVP) may be used to improve the hydrophilicity and porosity of this layer (B. Chakrabarty et al.,2008).

As for the selective layer, it is mainly formed through interfacial polymerization, which involves depositing the selective layer onto the porous support layer. The polymerization reaction takes place at the interface between two immiscible solvents containing highly reactive monomers. The

most commonly studied monomers are aliphatic or aromatic diamines and acid chlorides, with MPD and TMC being the most commonly used, respectively (C. Klaysom et al., 2013).

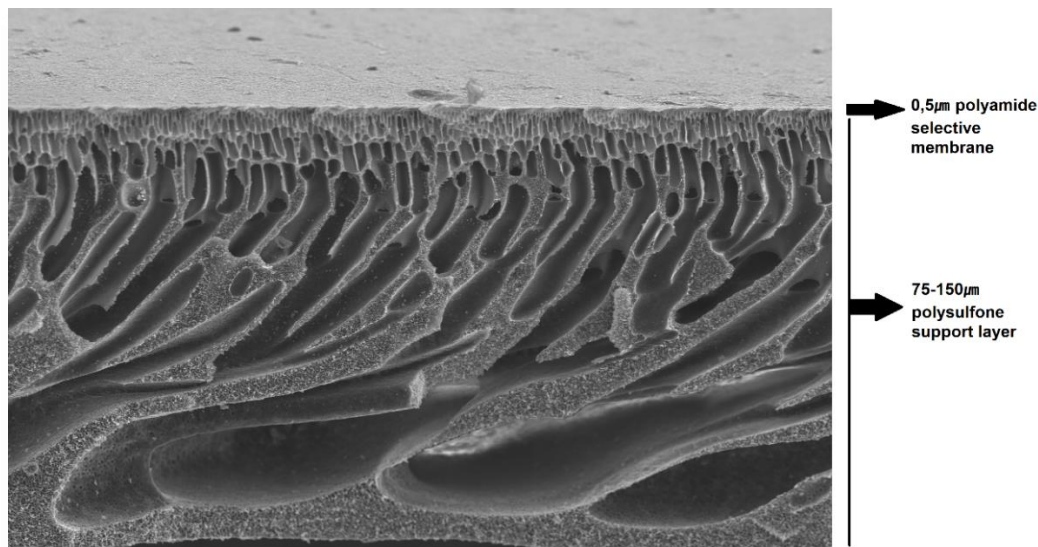


Fig. 3. FO membrane layers in a cross-sectional SEM image

1.3.3- Limiting factors

Reverse osmosis and forward osmosis membranes are very selective in allowing only water to pass through. However, limiting factors such as concentration polarization and fouling can cause problems when using these membranes.

Fouling, is an effect that directly affects filtration capacity since it occurs when pollutants/impurities are deposited on the selective layer, which adds additional resistance to filtration, until another layer forms which finally makes it impossible for the water to be passed. It can be caused by various factors such as biological, mineral, and organic matter, and it is difficult to completely prevent it (Y. Chun et al, 2017). However, regular cleaning and limiting the use of the membrane depending on the application can help to reduce this factor.

Concentration polarization, on the other hand, decreases effective osmotic pressure by reducing the driving factor (Sablani et al., 2001). In these processes, polarization can be seen as an external and an internal phenomenon (Font et al., 2014). Among the different kinds of this limiting factor, external concentration polarization is the easiest to solve, since it results from the accumulation of ions rejected by the membrane in the liquid solution in contact with the porous layer. It is solved by increasing the level of turbulences in that area. On the other hand, internal concentration polarization consists of this same concentration of ions but within this porous layer of the membrane. In order to reduce this value of polarization, the structure of the membrane needs to be changed, making it thinner and more porous (C. H. Tan et al., 2008). This effect explains why

the concentration inside the membrane is not completely linear and is more concentrated in the support layer. Once inside the porous layer, the diluted polarization concentration level increases and is reduced once inside the selective layer as it appears on the Figure 4 diagrams.

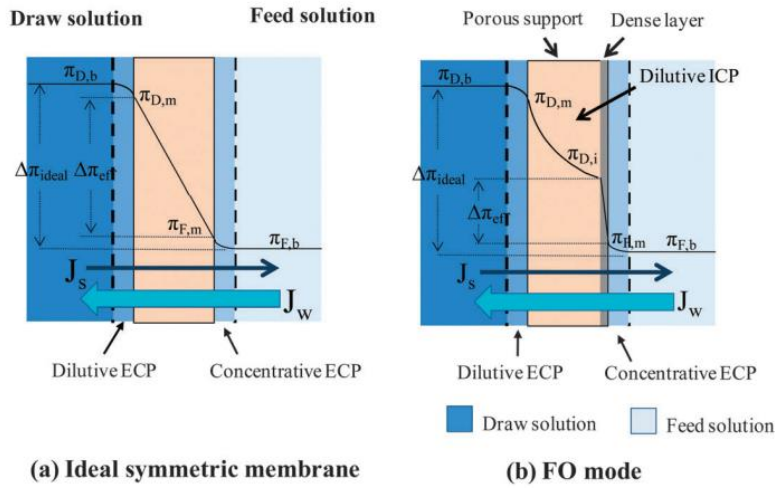


Fig 4. Schematic diagrams of external and internal concentration polarization developed (a) in a symmetric membrane, (b) in an asymmetric membrane in FO operating mode. (Chem. Soc. Rev., 2013, 42, 6959—6989)

2. OBJECTIVES

The main objective in this TFG is to fabricate forward osmosis membranes with improved efficiency and selectivity compared to existing membranes and quantify their characteristics. This goal has been broken down into four sub-objectives:

1. Develop a support layer as thin as possible with good mechanical strength and structure.
2. Investigate the effects of varying thickness of the support layers on membrane properties.
3. To synthesised polyamide layer on the top of the polysulfone layer.
4. To characterize the fabricated membranes by measuring their water flux and permeability, salt rejection, and morphology, using various techniques such as scanning electron microscopy, water flux and conductivity measurements.

3. MATERIALS AND METHODS

3.1- Support layer (polysulfone) membrane fabrication

The manufacturing of forward osmosis membranes begins with the support layer, which provides mechanical resistance to the membrane. The materials used were:

3.1.1- Chemicals

The chemicals used in this process were two polymers, Polysulfone (Psf, Acros Organics) and Polyvinylpyrrolidone (PVP, Acros Organics), as well as an organic solvent, 1-Methyl-2-pyrrolidone (NMP, 99.8% Scharlau) and pure water by Millipore.

3.1.2- Instruments

A Stuart magnetic stirrer with a temperature regulator of up to 300 degrees Celsius, a glass plate of approximately 40 x 25 cm, and an Elcometer 4340 membrane casting machine are the most relevant instruments for manufacturing the first layer of the membrane. This machine is a Motorized Film Applicator that consists of a clamp to hold the glass plate on which the membrane will be automatically spread. There is also a knife included that connected to the casting machine allows to spread the solution and control its thickness.

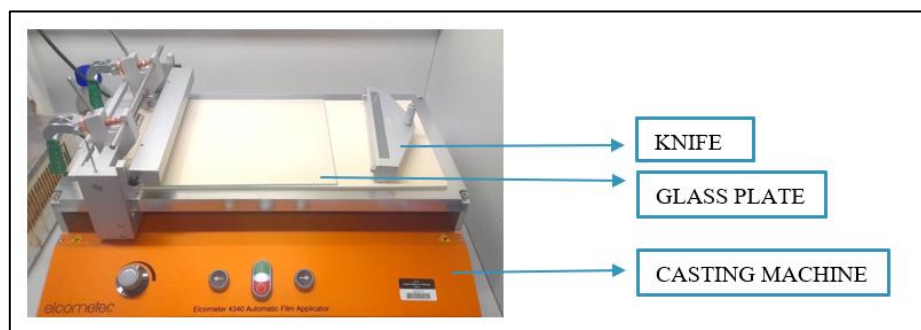


Fig.4. Membrane casting machine and its equipment photo

3.1.3- Step-by-step preparation

Support membranes were fabricated in the laboratory using approximate reference values for commercial polyamide membranes. It is imperative that all processes be performed in a fume hood, with gloves and goggles on, in order to ensure effective safety precautions.

Step 1: For the casting solution place 0.05g of PVP, 1.75g of PSf and 7.95mL of NMP in a glass container.

Step 2: The mixture in the stirrer should be left covered with parafilm in a fume hood for at least 24 hours at 70°C and medium speed. It will become transparent and homogeneous.

Step 3: After this time, the casting solution is poured as quickly as possible onto the glass plate in the casting machine with the thickness of the knife already determined based on the thickness we want to make the membrane. In this study, thicknesses of 75, 100, 150 and 200 μm have been tested.

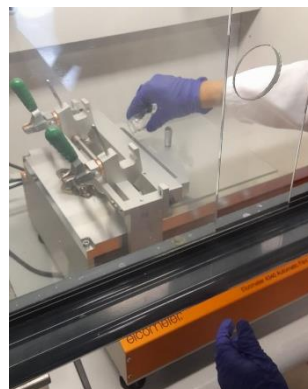


Fig.5. Step 3 elaboration photo

Step 4: After the solution has been spread with the knife, the glass plate will be submerged in the container with pure water at room temperature to ensure the membrane's polymerization (phase inversion). Polymerizing the membrane homogeneously is most effective when it is placed horizontally and gently dropped in water.



Fig.6. Step 4 elaboration photo

Step 5: For further impurity removal, immerse the membrane again in pure water.

3.2- Selective layer (polyamide) fabrication

Then came the second layer, the selective one, which rejects salts and allows only water to pass through. This is done over the support layer and its procedure is more complex than the previous one.

3.2.1- Chemicals

Two organic solvents were used in this process, m-Phenylenediamine (MPD, 99% Aldrich) and Hexane (98%, Scharlau). In addition, 1,3,5-benzenetricarboxylic acid chloride (TMC, 98% Aldrich) and Millipore pure water were used.

3.2.2- Instruments

The instruments mainly used were an air tube, a glass plate smaller than the previous one, around 20x10 cm, and high-power insulating tape with solvent-resistant glue.

3.2.3- Step-by-step preparation

Step 1: Place the support membrane previously manufactured on the smaller glass plate (cutting the membrane to the specific dimensions if necessary) and cover the edges with strong insulating tape so that the solution does not leak under the membrane when it is flooded.

Step 2: For one minute, immerse the glass plate horizontally with the membrane in a half-liter solution of 2% m-Phenylenediamine (MPD) in pure water.

Step 3: Using an air tube, extract the excess MPD solution by turning the plate vertically.

Step 4: Flood the plate again horizontally in a 0.15% solution of 1,3,5-Benzenetricarboxylic acid chloride (TMC) in hexane for one minute.

Step 5: Finally, submerge the plate vertically in boiling pure water for 2 minutes and remove it.

3.3- Characterization

To characterize the membranes and to be able to assess that they have been made correctly, two parameters have been calculated. Hydraulic permeability and membrane structure are key factors.

3.3.1- Permeability test

The two types of permeability tests require the use of a cell to encapsulate the membrane and simulate the different processes. This cell will consist of two inlet and outlet openings for the upper and lower cells. On the inside there will also be two plastic grids, as spacers to create a kind of protection over water flows.

Since the membrane is not homogeneous and the top layer is not the same as the bottom, it is critical to take that into account when placing it within the cell. At naked eye, it is possible to distinguish between the top and bottom layers by the brightness of the top and the matteness of the bottom layer.

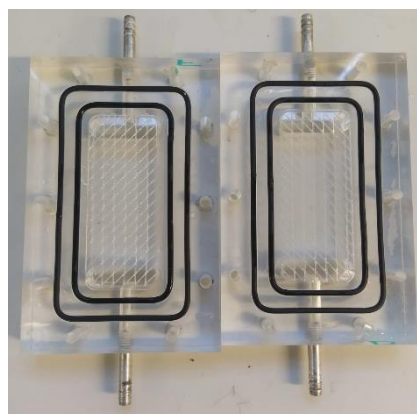


Fig. 7. Membrane cell photo

3.3.1.1- Hydraulic pressure driven system

It was first determined the hydraulic permeability of the membranes using an external pressure system, as if a reverse osmosis process were taking place. In this setup the pressure exerted and the amount of solution weighed by the membrane were taken into account to determine its permeability. In this case, there was no draw solution since osmotic pressure was not intended, there was just pure water and the solution that permeated across the membrane. The system works as follows: Water is pumped into the cell where the encapsulated membrane is, through a path leading to the upper part of the membrane, by a pump (Watson Marlow) at 100 rpm. A pressure transducer will be placed in a tube where the water will exit the opposite way and give information about the pressure it is working at. After that, it meets a pressure valve that will regulate this pressure, it will work at 0.5 bar, although there may be slight variations due to the pump moving. During the recirculation of the feed solution, water will pass from the upper to lower cell of the membrane until it reaches the permeate solution container. The weight of the solution will be continuously monitored using an analytical balance. Readings will be taken every 10 seconds and transmitted to our device along with pressure readings from the pressure transducer. The system must be in operation for approximately 1.5 hours.



Fig. 8. Hydraulic pressure driven set photo

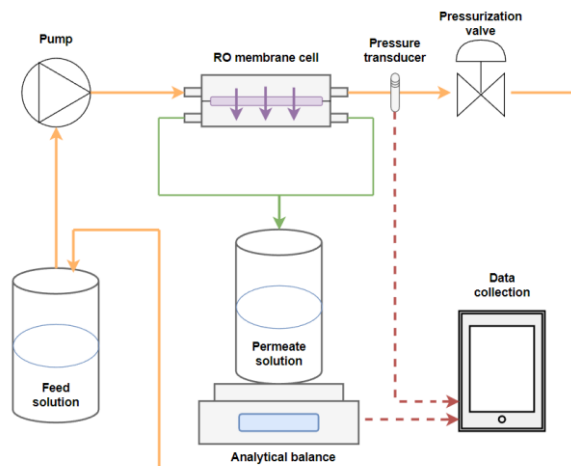


Fig. 9. Schematic representation of the hydraulic pressure driven set

To calculate the permeability of the membrane with this system (Eq.1), the three main variables collected in our device must be taken into account, the pressure (mbar), and the weight of the draw solution (g) in every 10 seconds of the analysis. Besides the membrane surface parameter, which was 27.88 cm in the RO membrane cell, should also be considered.

$$Permeability = \frac{(\Delta m \text{ draw})/1000}{\Delta t (s)} \cdot \frac{3600}{P (bar)} \cdot \frac{1000}{Am}$$

Eq.1. Permeability for hydraulic pressure system formula

Additionally, the water flow was also analysed using the Equation 2 to provide a better graphic representation of the results.

$$Water \text{ flow} = \frac{(\Delta m \text{ draw } (g))/1000}{\Delta t (s)} \cdot \frac{3600}{Am (m^2)}$$

Eq.2. Water flow for hydraulic pressure system formula

Where:

Am = membrane surface (square metres)

t = time (s)

M draw = draw solution's weight (g)

P = pressure (mbar)

3.3.2- Flux and salt rejection test

3.3.2.1- Forward osmosis system

In forward osmosis, the pressure does not come from external sources; it is generated by the osmotic difference itself, so the testing setup for permeability will differ from the other system. For this phenomenon to occur, there is a draw solution that contains salt ions. The solution is obtained by adding 35 grams of sea salt to 1L of water and agitating this solution for approximately 10 minutes to achieve complete dilution of the salt. Pure water will continue to be used as the feed solution. There is no element to regulate the pressure in this system. However, recirculation of the draw solution through the FO membrane cell is achieved by adding a second pump to the draw solution outlet tube. The two pumps must operate at a speed of 50 RPM. The water will flow from the feed solution to the draw solution through the membrane, increasing its

volume. Our device will only monitor the mass of the draw solution every minute, as the slower water flow due to the absence of pressure makes measuring it every second unnecessary. To determine the salt rejection capacity of the polyamide membrane, both the draw solution and the feed must be measured with a conductivity meter at the beginning and at the end of the test.



Fig. 10. FO pressure driven set photo

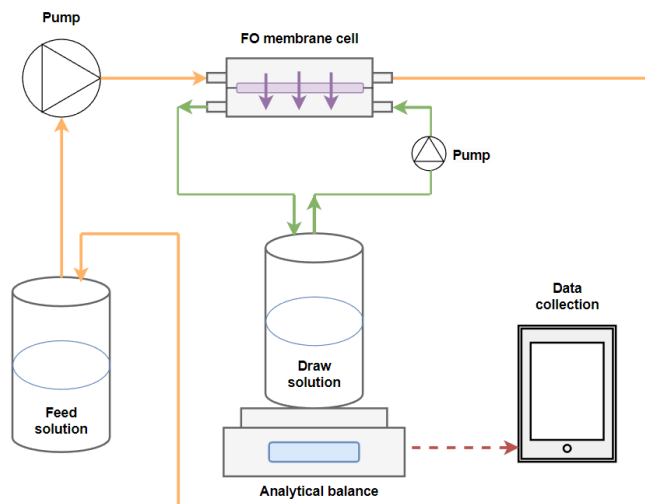


Fig. 11. Schematic representation of the FO pressure driven set

Based on the following equation (Eq.3), the membrane flux was calculated every 10 minutes using the following variables: membrane surface, time, and difference in draw solution weight.

$$J_w = \frac{(\Delta m \text{ draw})/1000}{(A_m \cdot 60)/\Delta t}$$

Eq.3. Water flux formula for FO system

Where:

J_w = water flux (L.m⁻².h⁻¹)

A_m = membrane surface (metres)

T = time (s)

M draw = draw solution's weight (g)

3.3.3- SEM analyses

3.3.3.1- Morphological caracterizacion

A scanning electron microscopy (FE-SEM Hitachi, Japan, model S-4100) examination of the various samples has been conducted in order to determine whether the membrane structure is correct (with the support of STR service of the UdG). The membrane has been evaluated in three parts: the top part, the bottom part, and the cross-section. For the cross section, a special sample had to be prepared, in which it was ruptured by immersion in liquid nitrogen prior to the viewing, so that the side of the membrane would appear as homogeneous as possible. All samples were dried beforehand at room temperature, then stuck on a sample holder and coated with carbon by the evaporation method (with an Emitech device, Germany, model K950 turbo evaporator). Quarz PCI was used to digitally record and process all images at a voltage of 7kV at different magnification.

3.3.3.2- Thickness measure

As a result of the images taken with SEM analysis, it was possible to measure the thickness of the membranes. It was to ascertain if they were made correctly or if any changes had been made during the process. For determining the final average thickness, 20 measurements of the membrane thickness were taken in an image of a cross-section using an image processing program called ImageJ.

4. RESULTS AND DISCUSSION

4.1- Permeability test

4.1.1- Hydraulic pressure driven System – Support membrane

Various factors, including the manufacturer, membrane composition, and operating conditions, can affect polysulfone ultrafiltration membrane permeability (Y. Jia et al, 2020). Due to this, the same composition and pressure values have been used for the permeability test, only the thickness was changed. Each membrane of different thickness has been tested, followed by the repetition of four membranes with the same thickness in order to analyze its variability.

The results were obtained by using hydraulic pressure permeability testing in the same way we would with reverse osmosis membranes. For membranes of different thicknesses, there is a significant heterogeneity on the results. With a permeability of 37 LMH/bar, the 200 μm membrane shows the least permeation, significantly lower than the rest of the thin membranes.

Otherwise, the repetition of four membranes with a thickness of 150 μm resulted in permeabilities ranging from 283 to 145 LMH/bar, more often exceeding 200 LMH/bar.

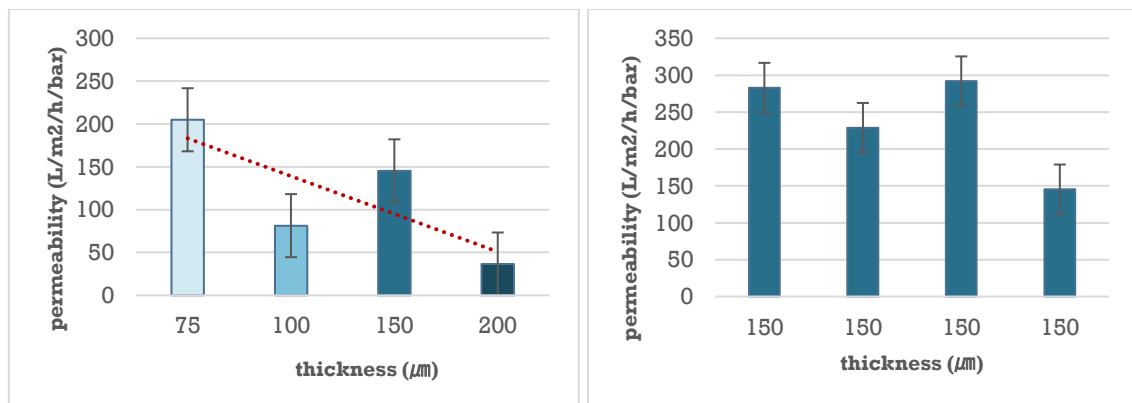


Fig. 12. Permeability results representation for each different thickness

Fig.13. Permeability results representation of 150 μm -thick membranes

The results demonstrate the importance of membrane thickness on the permeability of polysulfone ultrafiltration layer. The study found that the permeability of the membranes appear to be inversely proportional to the thickness of the membrane. In other words, thinner ones show signs of have a higher permeability compared to thicker ones. The permeability of the 200 μm membrane was significantly lower than that of the rest of the thinner ones, indicating that the layer thickness can have a substantial impact on membrane performance, since thicker are less likely to pass water through (Y. Jia et al, 2020).

Furthermore, the results also reveals the variability in permeability among the four membranes with the same thickness of 150 μm . This demonstrates that there can be some differences in membrane performance even when they have the same thickness and composition. Despite this, it has been possible to create membranes that are quite similar with permeabilities between 150 and 300 L/m²/h/bar. Therefore, it is essential to evaluate the performance of each one individually to ensure the quality and reliability of the membrane for a particular application.

However, the permeability values obtained in membranes of 150 μm and other thicknesses do not differ much from those obtained in other studies using this type of support layer (A.A. Shah et al, 2017), therefore it indicates that the methodology used is correct.

4.1.2- Hydraulic pressure driven System – selective membrane

As a dense layer is created over the porous polysulfone, the permeability is expected to decrease once the polyamide layer is applied over the support layer. Considering that the thickness for all these membranes is 150 μm , a wide heterogeneity of results can be observed. Polyamide membranes are tested at permeabilities ranging from 0.5 LMH/bar to 175 LMH/bar.

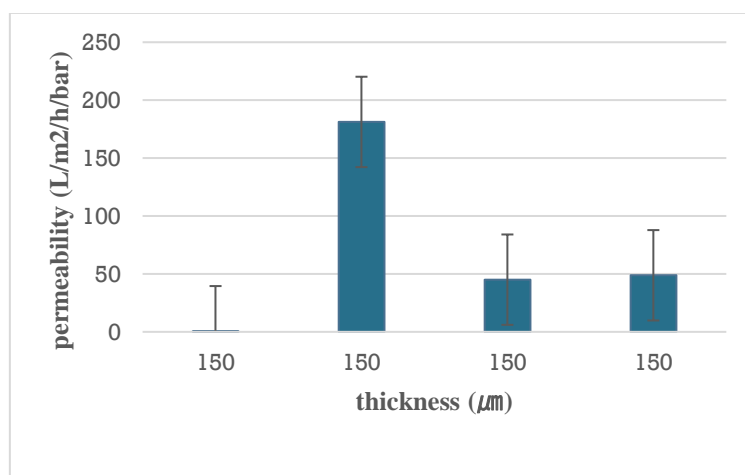


Fig. 14. Permeability results of PA membranes graphic representation

Based on the literature (J. Wei et al., 2011), it appears that only one of the membranes tested possesses a permeability value that is typical for this type of polymers, which is 0.513 LMH/bar. The other three ones have significantly higher permeabilities, from 50 to nearly 200 LMH/bar less than those with just a support layer. However, even these higher permeabilities are still too high for forward osmosis membranes, it exhibits more typical ultrafiltration membrane permeability values.

It is possible that the high permeabilities observed in this tests are due to issues with the technique used to create the polyamide layer, such as damage during handling or lack of uniform application

throughout the membrane. The presence of holes may also contribute to the higher permeability, allowing water to seep through.

Another factor to consider is the effect of reverse osmosis testing on the polyamide-coated membranes. It has been observed on Figure 15 that over time, the permeability increase to extremely high levels, up to 1000 LMH/bar. This suggests that the membrane may not have been able to withstand the pressure for such an extended period of time, leading to the creation of additional holes that allow water to pass through.

Overall, these results highlight the importance of careful manufacturing and testing procedures to ensure optimal membrane performance and durability.

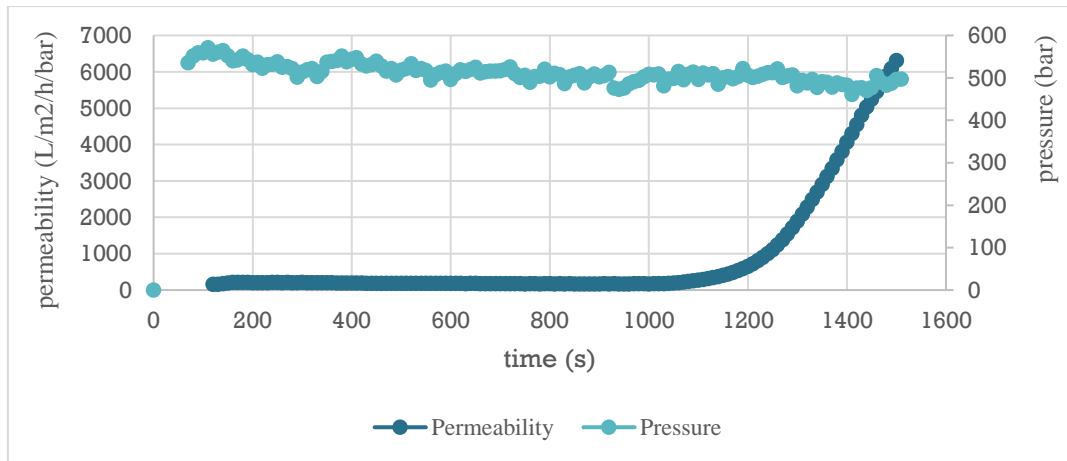


Fig. 15. Permeability and pressure results every second graphic representation

4.2- Flux and salt rejection test

4.2.1- Forward osmosis system – selective membrane

In order to evaluate how the membranes behaved in a forward osmosis system, which is what they were originally planning to use, two membranes were tested with the same thickness, composition, feed and draw solutions during different periods of time. Periods of operation were about 2 and 20 hours respectively.

Membrane ID	Operation time (h)	Flux (LMH)	Conductivity (mS/cm)
PA 1	20	0.563	3.37
PA 2	2	0.257	0.56

Table. 1. Operation time, water flux and final feed solution conductivity values for each membrane

The results of the performance tests collected on Table 1, show that the final feed solution conductivity values depend on the operating time and the membrane's intended use. The membrane operated for 2 hours demonstrated a lower conductivity than the one operated for a longer time, indicating the importance of considering the operating time when evaluating its performance. However, it is expected that the final feed solution conductivity of membrane PA2 will decrease with an increase in operating time, potentially reaching levels similar to the PA1 membrane's conductivity after 20 hours.

Since these values are so high, it implies that the PA layers are not rejecting salts as well, and that salt ions are moving from a draw solution into a feed solution, which is not helpful for the membranes' purpose. It is worth noting that the ideal salt rejection rate varies depending on the specific application. For instance, in drinking water production, a higher salt rejection rate is crucial, while in solution concentration applications, a lower rate may be acceptable.

Regarding water flux, both membranes showed low values (typically around 10-15 LMH (J. Wei et al., 2011)), likely due to the concentration polarization effect of the support layer. This effect can lead to a loss in osmotic pressure and a decrease in water flow. These results suggest that further optimization of the membrane structure and operating conditions may be necessary to improve both salt rejection and flow rate for practical applications.

4.3- SEM analysis

4.3.1- Morphological characterization

4.3.1.1- Support Psf membrane

4.3.1.1.1- Top layer

The top surface appeared smooth and opaque (Fig.16. a), but upon closer inspection, small wrinkles were observed (Fig.16. b). This is a typical characteristic of this type of membrane. Microorganisms were also present on this top layer (Fig.16. c), which is likely due to external contamination during storage in pure water.

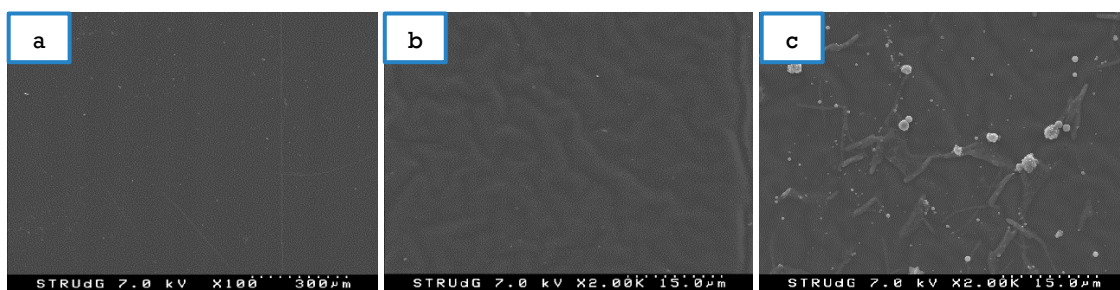


Fig. 16. Top layer Psf membrane SEM images at different magnitudes. a)x100, b)x2.000, c)x2000

4.3.1.1.2- Cross-section

The interior of the membrane displayed one of the most recognizable features of phase inversion polymer membranes, the finger-like pores (Fig.18. b). These are small pores located on the top surface that resemble holes created by fingers. In some membranes, small spheres can be seen within the finger-like pores

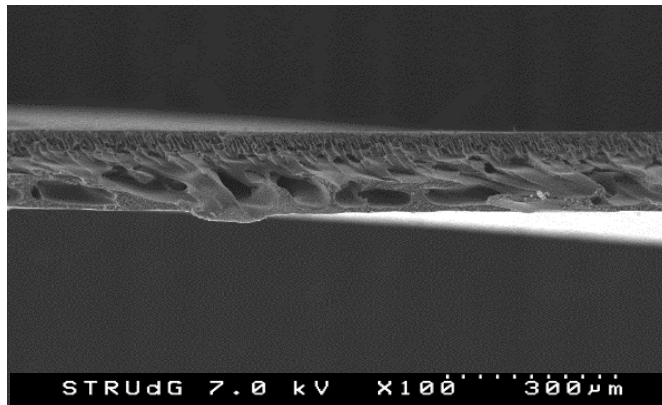


Fig.17. Cross-sectional Psf membrane SEM image at x100

(Fig.18. c). These may be remnants of polymer that did not fully polymerize or did not do so correctly during the phase inversion process. To resolve this issue, a few additional immersions in containers of pure water after manufacture may be necessary. At the bottom of the cross-section, pores become and the fully porous material of which the membrane is made are visible, indicating a structurally sound support layer (Fig.18. d).

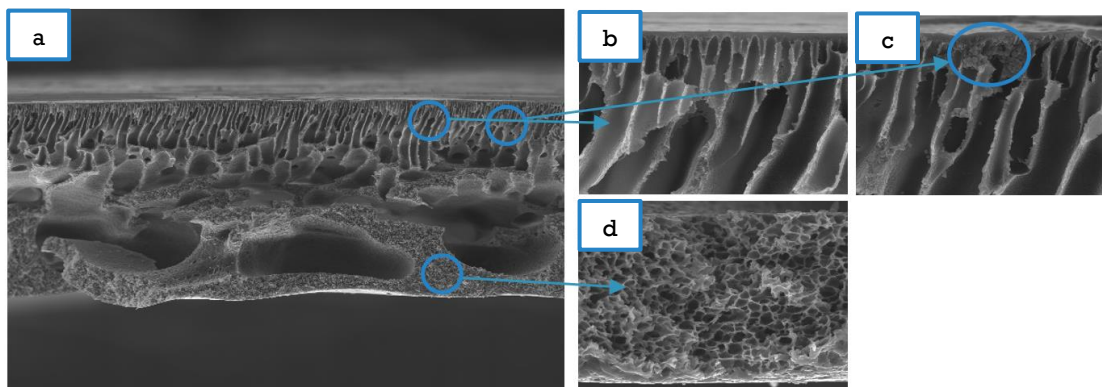


Fig. 18. a) cross-sectional SEM image at x300, b) magnification at x5.000 of the finger-like pores structure, c) magnification at x5.000 remnants of polymer spheres within the finger-like structure, magnification at x5.000 of the lower porous structure

4.3.1.1.2- Bottom layer

On the bottom surface of the membrane, the pores are clearly visible, unlike the top layer. With a maximum size of 2 μm they are spread evenly across the membrane. Besides, there are areas where they are more densely clustered or larger, appearing as white spots on the surface. Additionally, small spheres of unpolymersed polymer were observed between the pores.

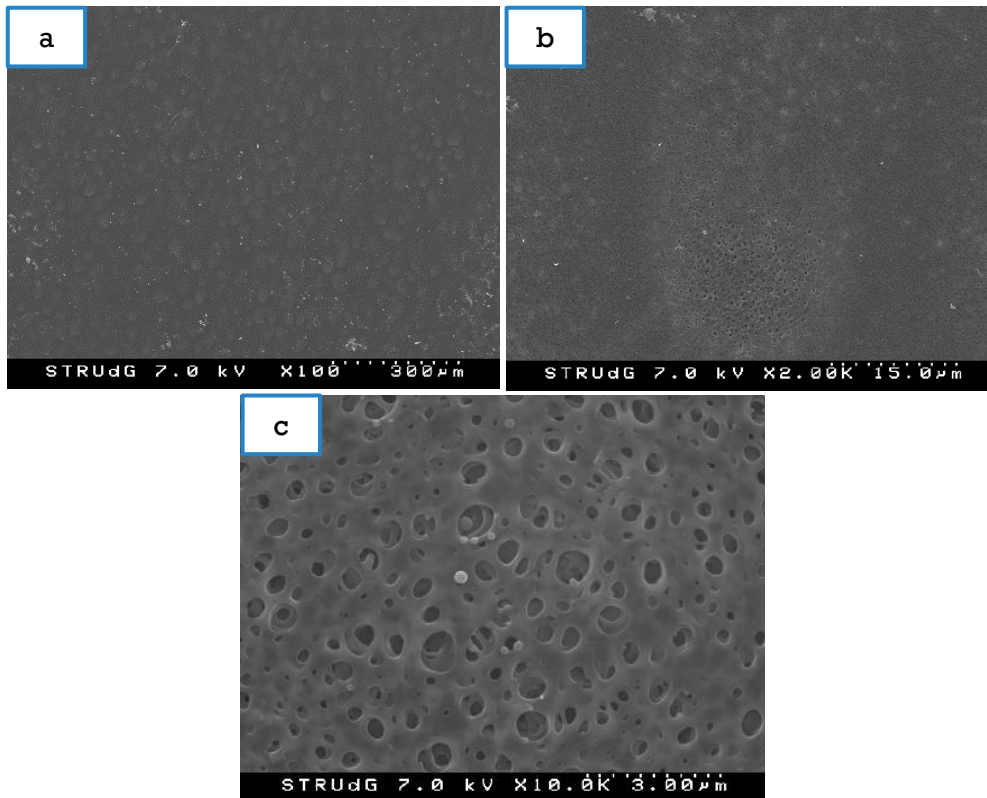


Fig. 19. Bottom layer Psf membrane SEM images at different magnitudes. a)x100, b)x2.000, c)x10.000.

4.3.1.2- Selective PA+Psf support membrane

4.3.1.2.1- Top layer

After the application of the polyamide rejection layer over the polysulfone layer, the top surface appears more irregular, with a ridge-valley structure that is typical of polyamide membranes formed by TMC and MPD monomers (M. Di Vincenzo et al., 2017; J. Wei et al., 2011). Some of the membranes show uneven spreading of the polyamide layer, with holes where the top of the polysulfone layer is visible (Fig.20. a & b). SEM images reveal poor adhesion of the typical polyamide structure in some areas.

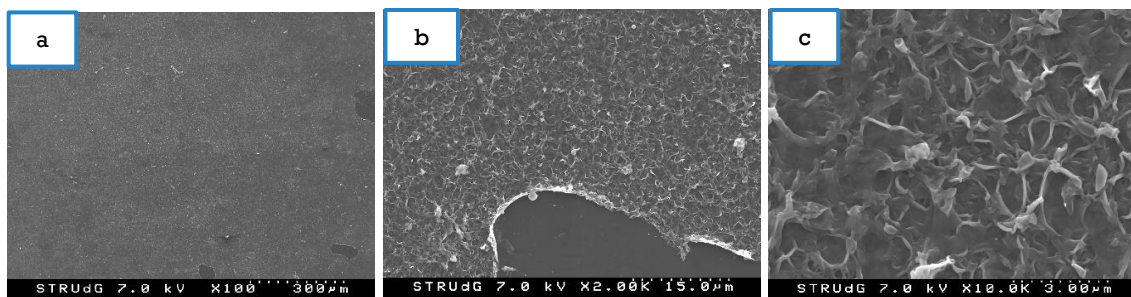


Fig. 20. Top layer Psf+Pa membrane SEM images at different magnitudes. a)x100, b)x2.000, c)x10.000.

4.3.1.2.2- Cross-section

The cross-sectional analysis of the membranes with the dual-layer composition reveals the presence of a polysulfone layer with its characteristic finger-like pore structure, overlaid by a thin and irregular layer of polyamide. The thickness of the polyamide layer varies between 0.3-0.7 μm on membrane surface, indicating its thin and highly selective nature.

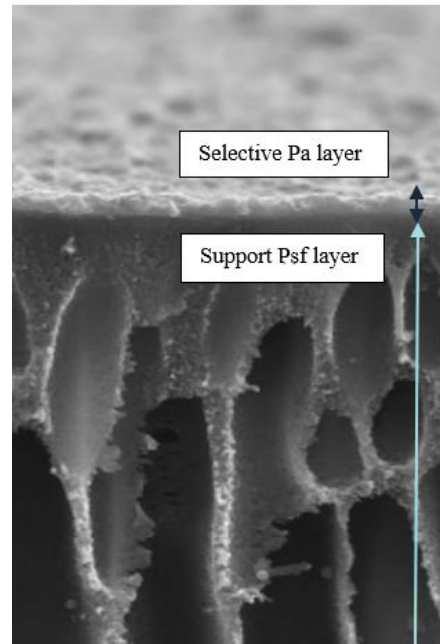


Fig.21. Cross-sectional image with the two layers of the membrane differentiated at x5,000.

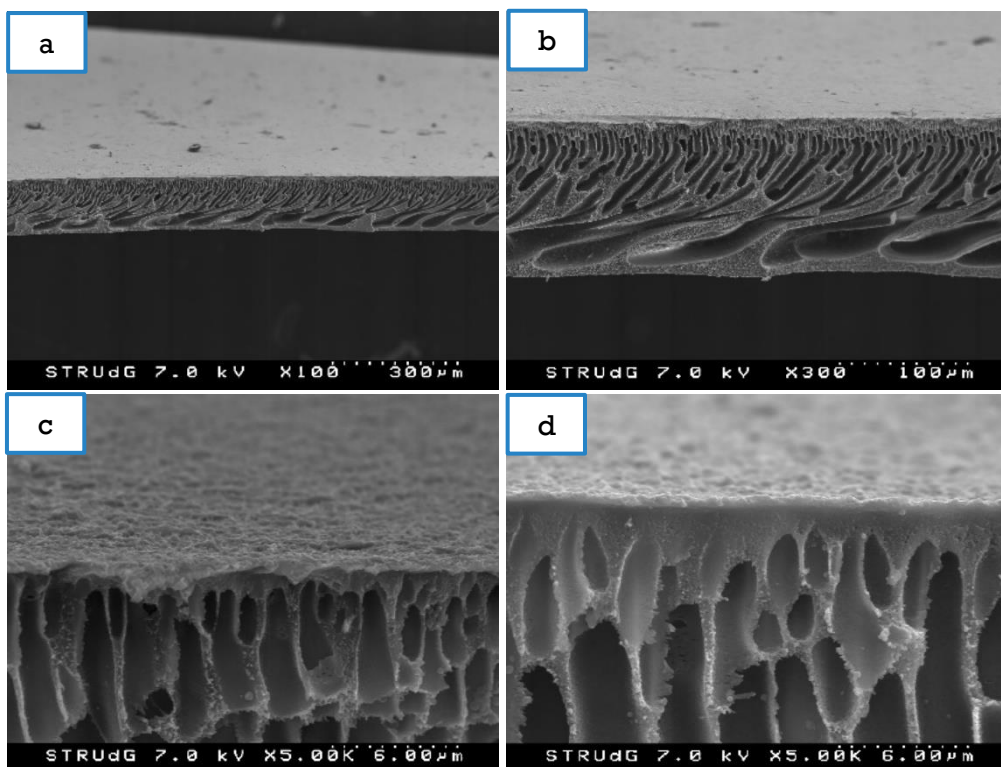


Fig. 22. Cross-sectional Psf+Pa membrane SEM images at different magnitudes. a)x100, b)x300, c)x5,000, d)x5,000.

4.3.1.2.3- Bottom layer

Regarding the bottom layer, the SEM images show the bottom surface of the polysulfone layer with its pores, as expected (Fig 23. a & b). However, in someones, it was also possible to observe the typical structures of the polyamide layer in the bottom layer (Fig 23. c & d). This could suggest that part of the polyamide solution might have infiltrated through the pores and reached the bottom layer where it just polymerized, resulting in the formation of the polyamide structures. The presence of these structures in the bottom layer could indicate a potential lack of control during the manufacturing process, resulting in an uneven distribution of the polyamide layer.

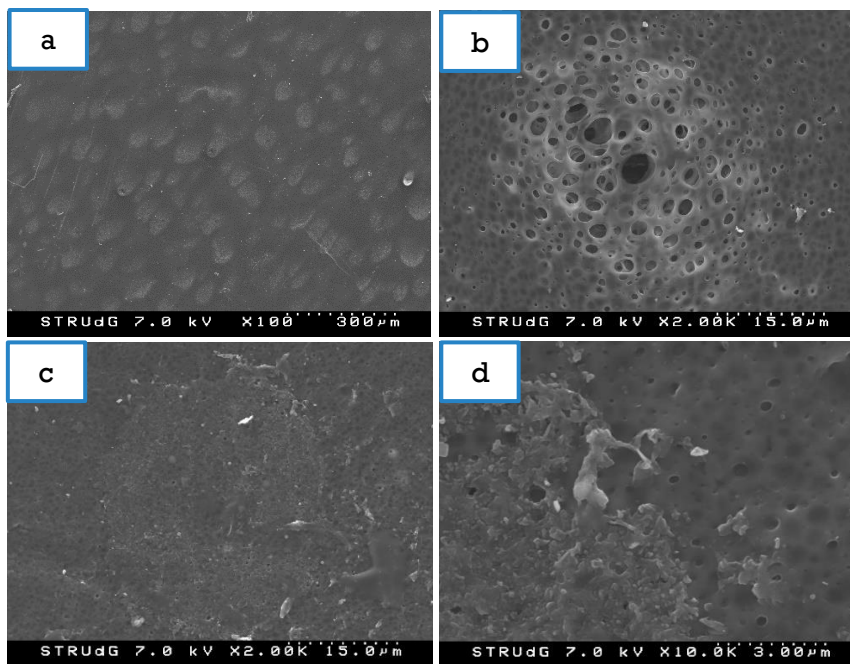


Fig. 23. Bottom layer Psf+Pa membrane SEM images at different magnitudes. a)x100, b)x2.000, c)x2.000, d)x10.000.

4.3.2-Thickness measure

There are no manufactured membranes with a real thickness equal to the theoretical one, indicating that the measured real thickness value is approximately 25-70 μm lower than that initially determined with the knife during the casting of the support membrane.

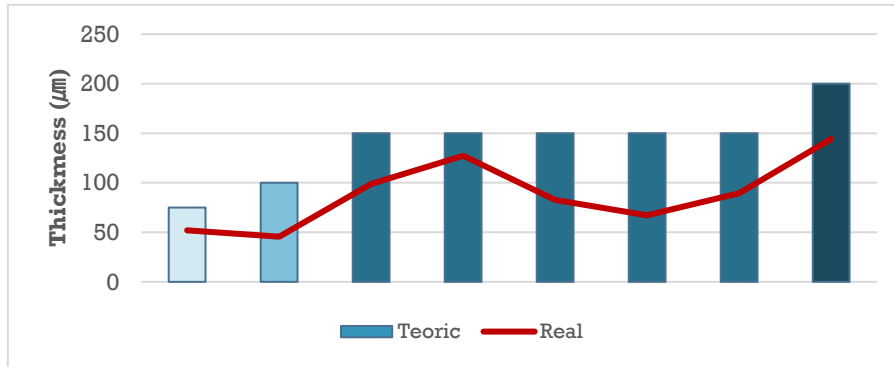


Fig. 24. Representation of teoric versus real support layer thickness values

It is important to note that the same factor affects the membrane's thickness equally, regardless of their thickness. Based on the information presented, it is possible that the membranes' thickness may have been affected by a variety of factors, which may have occurred during the manufacturing process or after the membrane was produced. It is possible that errors have occurred when the membrane was being manufactured, such as mistakes during the spreading process or in programming the thickness. Perhaps the membrane shrank once it has dried prior to SEM analysis or being pressed during the permeability test, which could lead to a reduction in thickness.

5. CONCLUSION

While the main objective of fabricating a total forward osmosis membrane with improved efficiency and selectivity was not entirely achieved in this study, valuable insights were made in several areas. The main issue has to do with the polyamide selective layer, and it is possible that the methods used for its manufacture were not optimal. This resulted in a large amount of salts passing through the membrane, adhesion problems between the polyamide and polysulfone layers, and indications of polarization concentration, among other issues.

However, the study yielded many positive results concerning the manufacture of the porous polysulfone support layer through phase inversion. The layer showed a well-structured and mechanically resistant structure, along with affordable permeability values. Moreover, investigating the effects of varying the thicknesses of the support layer provided valuable insights into how membrane behave.

The characterization of the fabricated membranes using various techniques, such as scanning electron microscopy and water flux and conductivity measurements, provided a deeper understanding of the membranes characteristics.

In summary, this work represents a contribution to the optimization of forward osmosis membranes, providing a foundation for further research in this area.

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