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Fouling behaviour in forward osmosis and preliminary comparison with reverse osmosis

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Abstract

The aim of this thesis project is to investigate the mechanism governing fouling in the emerging forward osmosis (FO) membrane technology. Fouling is inevitable in membrane filtration system and it is caused by the attachment of contaminants onto the membrane. It is fundamental to understand the mechanism affecting the fouling behaviour, since it represents a severe hurdle in membrane filtration, hindering the membrane performances over time. Even though fouling in FO has been extensively examined, there is a lack of research related to study the influence of operating conditions to fouling in FO. Within this topic, this thesis is presenting an in-depth analysis of the fouling behaviour in forward osmosis, analysing different operating parameters and performing a preliminary comparison with fouling behaviour in reverse osmosis (RO). A set of experimental tests were run with two lab scale set up filtration plants, using the same operating conditions in RO and in FO. Mixtures of organic foulants were used to induce fouling during filtration experiments. Different draw solutes were employed to understand the influence of ionic species on flux decline. Two distinct composition of the feed water was adopted in order to analyse weather the presence of specific ions (such as Calcium) would affect the fouling behaviour. Results suggest that the composition of the feed solution and the initial draw solution osmotic pressure represent two important parameters in FO fouling. Besides, the nature of the draw solution is important; divalent ions such as magnesium and calcium would strongly affect the forward osmosis performance while less sever flux decline (i.e. less fouling) was observed with DS with a low reverse solute diffusion. Fouling in Reverse Osmosis is instead strongly affected by the external hydraulic pressure applied. Moreover, with similar operating conditions, fouling in FO is less severe than in RO. Overall, the results suggest the possible application of forward osmosis for the treatment of complex water sources. However, further improvements of forward osmosis are needed to reach a full-scale implementation of this technology before real installations.

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1 INTRODUCTION

Membrane-based systems represent nowadays a widespread and high-tech technology to tackle water scarcity and increase water supply.

Reverse Osmosis has been employed heavily to produce high quality water from saline sources of water. This process exploits hydraulic pressure as driving force to perform separation between water and the unwanted compounds. However, since significant pressure is required, the purification of water involves an extensive consumption of energy. [45]

One of the main obstacles to the efficient application of membrane technology is fouling, because it is inevitable and severely affects the lifespan of the membrane, increasing the whole cost of operations. [16] Efforts have been focused on the evaluation of membrane fouling in pressure driven membrane processes and development of fouling controls strategies. [4, 14, 53]

At the same time, attention has been addressed to innovative membrane-based processes, such as Forward Osmosis. [5, 8]

Forward Osmosis has been gaining popularity as a promising alternative to pressure driven membrane processes for certain applications. [55] Its outstanding advantage stems from the fact that osmosis acts spontaneously without the application of an external force. FO exploits the osmotic pressure of concentrated draw solution, which drives water from the feed solution, across a semi-permeable membrane.

Studies have explored possible uses of FO as either alternative or complementary process, to treat complex water sources. [8, 27, 39] It has been evaluated as a potential application for seawater desalination, industrial and wastewater reclamation.

In the past decades, efforts have been made from various disciplines to a better understanding of the process and its further advances. [17, 27] A considerable amount of research has been addressed to membrane development [47, 52] and the selection of a suitable draw solute. [1, 39, 52]

Hence, to obtain high quality of water from a contaminated stream, FO requires a downstream separation process, to recycle the solute as well. Draw solute regeneration represents one of the main drawbacks of FO systems. It involves a further treatment step, that can be energy consuming and technically challenging, according to the type of draw solute. Thus, it leads to an increase in the combined costs of the system.

For this reason, investigations have been carried out on the overall system functioning and the effective regeneration of the draw solutions, to achieve an effective implementation of the whole system.

Apart from a first commercial desalination facility, [34], the development of this technology is still at pilot scale. There are a handful of examples of design of full- scale systems, coupled to the regeneration step, that can be another membrane process, such as Nanofiltration [12, 13]

One notable research area is certainly membrane fouling, addressed to FO fouling. Owing to its low energy requirements and potential low fouling propensity, more studies are emerging, inferring whether FO fouling would be less severe than pressure-driven membrane processes. [9, 29, 35]

For instance, the fouling behaviour of FO and RO has been compared for wastewater treatment, and a slower flux decline rate in FO has been observed. More studies have attributed FO lower fouling tendency to a different structure of the fouling layer. [2, 24, 31, 39] On the other hand, other studies have claimed that no differences can be observed in flux decline, or even that fouling in FO would be more severe than RO, despite the observed lower flux decline. [23, 42]

The reasons for the different findings can be attributed to different experimental methods used, not comparably controlled, or different types of membrane, whose different properties might affect the result. [42]

Even though membrane fouling in RO has been extensively understood, very few publications have been addressed to a systematic study of both FO and RO in a comparable manner, to fully evaluate the different behaviour of the two processes.

The growing interest in FO technology calls for more fundamental research on fouling in FO, that would lead to technology advances and development of measures for fouling mitigation.

The purpose of this thesis project is to understand the key physical and chemical interactions in forward osmosis and their role in fouling mechanisms.

A lab scale set up has been used to perform FO runs. Model foulants have been employed to simulate the rate of fouling as in a real wastewater. At first, the extent of fouling has been evaluated for increasing concentrations of draw solutes. Then, different draw solutes were assessed to identify the features of each one. Finally, different composition of the feed water was investigated, and this has provided further insights on the causes that mostly influence fouling in FO.

In the end, the results were compared to the ones obtained with a lab scale RO setup, performed in the same conditions as FO.

2 MEMBRANE FILTRATION

The aim of separation using membranes is to promote the passage through permeation of selected compounds, while holding back other unwanted compounds. [6, 46]

A membrane is a thin film layer that allows surface separation in a mixture of two or more compounds. It is a permselective barrier, so it allows the passage of water, while hindering other unwanted solutes. [8] The separation process occurs because of a driving force, exploited to create a chemical potential difference between the two sides of the membrane. [33]

Membrane processes can be classified according to membrane type, driving force and transport mechanism. [6, 33]

The differences between them arise primarily from the size of the solute and the membrane pores, therefore, on the range of contaminants that can get separated and the amount of driving force that must be exerted. Since the membrane can retain species that are larger than pores and let all the other compounds go through, there will be a suitable membrane and process according to the composition of the feed stream and the permeate requirements. [6]

Figure 2.1 shows membranes classification according to what they can separate.

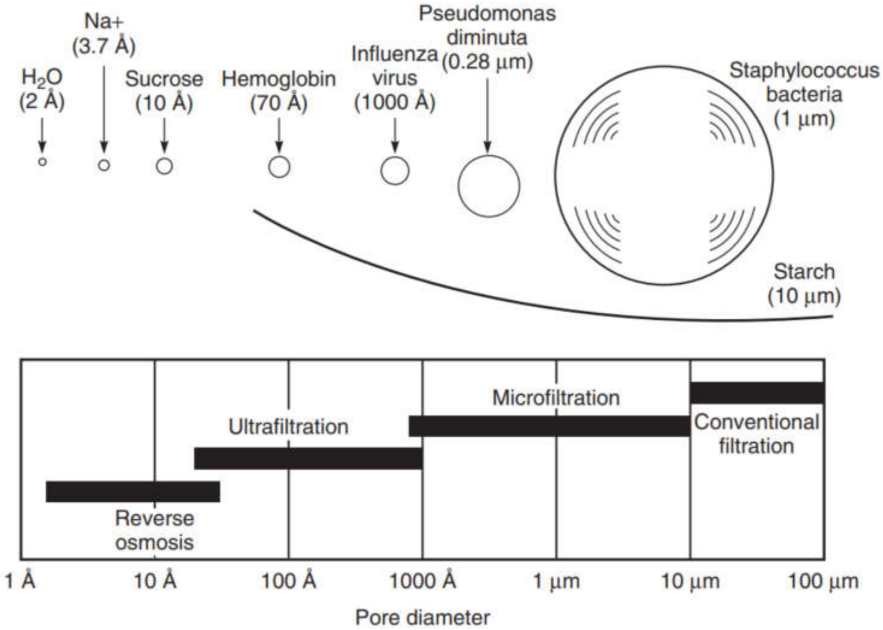

Figure 2.1 Relative size of the main compounds that can be removed by each class of membranes. Membranes can retain particles that are larger than its pores. With conventional filtration it is possible to separate particles like starch and bacteria up to 10 µm. Microfiltration has pores in the range of 0,1 and 10 µm, while Ultrafiltration can retain even smaller particles. Reverse Osmosis can hinder the transport to particles of the same size of the pores of the membrane, being able to separate solutes and water itself. [6]

We can distinguish between 4 main membrane-based processes, exploiting hydraulic pressure as driving force.

- Microfiltration membranes have micro-sized pores, between 0,1 and 10 micrometres. It can remove large particles such as starch, pathogens, eukaryotes.
- Ultrafiltration membranes have pores ranging from 1 nanometre to 300 nanometres and can reject macromolecules like bacteria (1 micron), viruses (50-500 nanometres), proteins, haemoglobin (in dialysis).
- Nanofiltration membranes, with pores between 0,5 nanometres to 5 nanometres, can retain molecules up to the ion size with high rejection of divalent salts and heavy metals.
- Reverse Osmosis membranes can retain all dissolved species present in the water, including monovalent ions, such as sodium and chloride.

The main strength of this technology is that it is possible to achieve high quality of water with a process which is mainly physical, that does not require heat or chemical substances to be added.

The drawbacks are investment costs, due to the exploitation of high-tech systems and cost of pumping in pressure- driven processes.

The pressure to be exerted is indeed higher, going from micro to nano and reverse osmosis; as pores get smaller, higher pressure is needed, as it can be seen in figure 2.2. [22, 33]

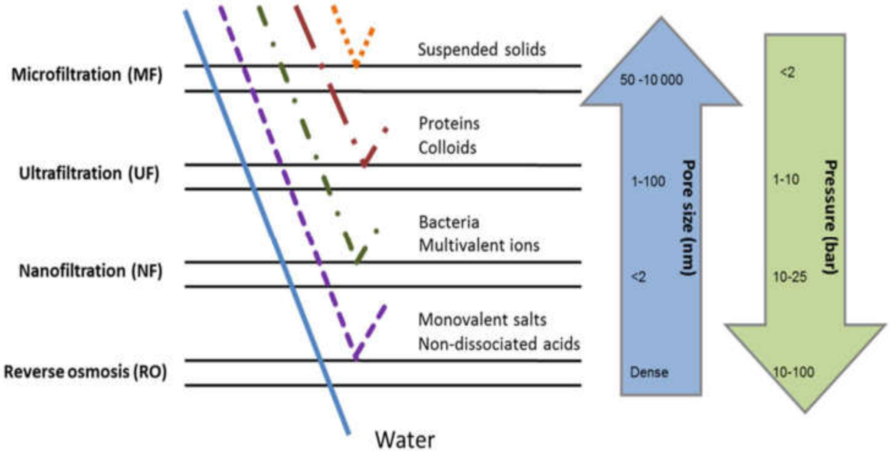

Figure 2.2: application of each membrane processes depends on pore size, but also on the pressure to be applied. Pressure is inversely related to pore size. [33]

Membrane process is nowadays a well-established technology, having large commercial application in the market, mostly in the field of water treatment.

Thanks to this technology, it is possible to perform separation on waters that could not be treated otherwise, such as seawater or brine, obtaining high quality water, thus representing a promising opportunity to reduce water shortage and increase water supply.

For example, membranes can be efficiently used in water treatment plants for potable water, to reduce the number of steps required to treat surface water and get rid of particles and dissolved contaminants. As Fig. 2.3 shows, a conventional treatment would require for instance a coagulation-flocculation, followed by sedimentation of aggregated particles, then filtration (sand or activated carbon filtration). All these steps can be substituted with a single membrane process, such as ultrafiltration.

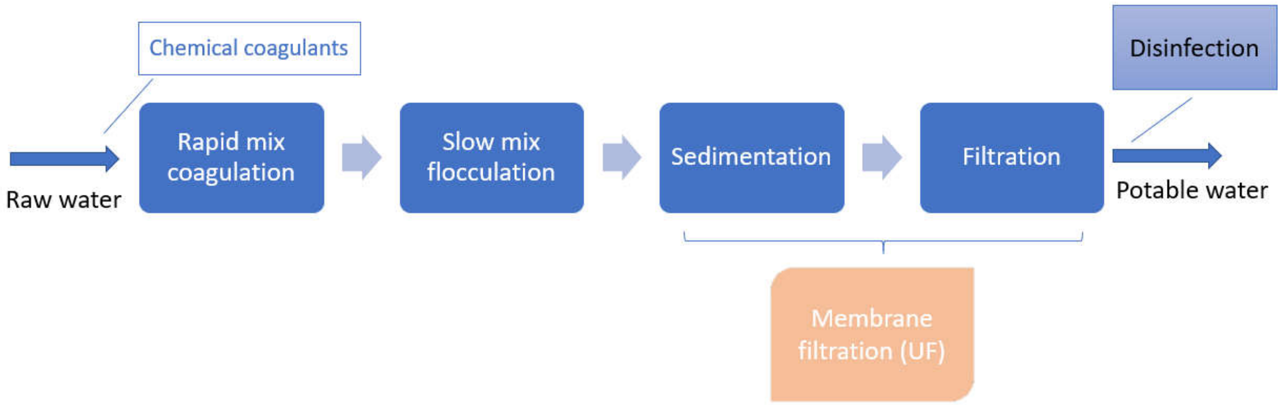

Figure 2.3: scheme of a conventional water treatment plant, compared to a membrane- based plant. The steps of sedimentation and filtration can be substituted by membrane, for example UF, and no chemicals are needed.

Moreover, with membrane processes it is possible not only to efficiently treat water for human consumption, but also purifying wastewater, that has very strict requirements for discharge in the environment and give it a higher quality. By adding a further membrane treatment step, the waste that would be discharged can be converted and become suitable for high- end uses, such as irrigation, potable water and cooling for industrial plants.

2.1 OSMOTICALLY AND PRESSURE-DRIVEN MEMBRANE PROCESSES

Osmosis is a natural phenomenon that occurs when a membrane separates two solutions at different osmotic pressures. The solution could be natural resources, waste streams, or high purity solution. [17] It is due to a chemical potential difference across the two sides, which constitutes the driving force of the process. [8]

Osmosis is a process that happens naturally, at low pressure and ambient temperature. Across a selective barrier, water tends to move from regions of higher chemical potential, to equal osmotic pressure on both sides of the membrane. Osmotic pressure, π, is related on the concentration of dissolved solids in the solution. [15, 22]

To reverse this tendency, a hydraulic pressure higher than the osmotic pressure difference between the two sides of the membrane must be applied. This applied pressure constitutes the driving force in Reverse Osmosis, that is characterised by going against the concentration gradient. Water is therefore forced to pass through the membrane in the opposite direction to that of osmosis. [22] At the same time, salt is concentrating on the influent surface of the membrane. [36]

Forward Osmosis, instead, is an emerging membrane technology, exploiting the same principle of osmosis. The driving force is the osmotic pressure itself, as water spontaneously flows to the less concentrated side of the membrane, without any applied pressure. [8]

As it can be seen in fig. 2.4, a membrane separates two solutions at different concentration. In FO, water will naturally go where concentration of solute is higher. This results in a dilution of the more concentrated solution (called draw solution), while the feed stream is being concentrated. [33]

Conversely, in RO, thanks to the external applied pressure, water flows from the more concentrated region to the less concentrated one (The external applied pressure must overcome the intrinsic osmotic pressure of the feed solution). Hence, the feed is concentrated and a less concentrated product, called permeate, is obtained.

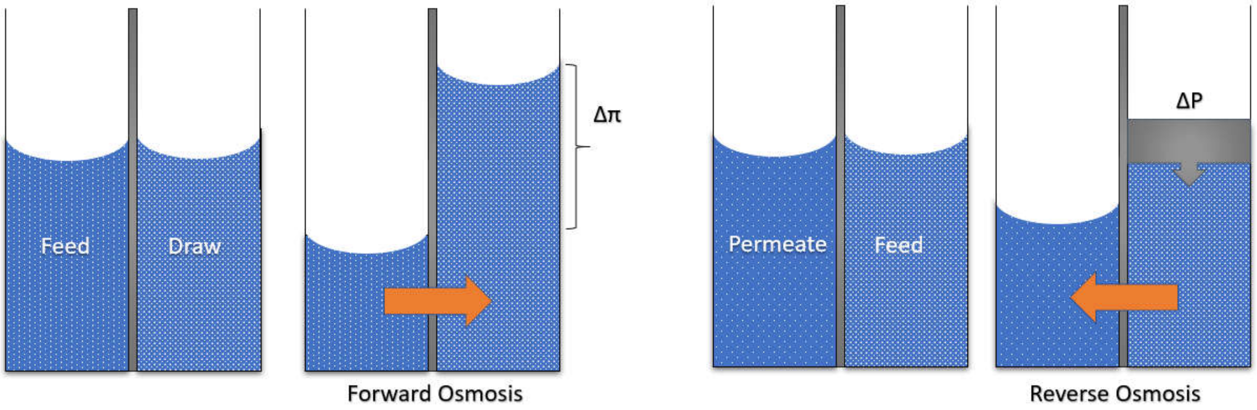

Figure 2.4: Water flux in FO and RO. At equilibrium, no movement occurs. In FO, due to a driving force, such as a difference in osmotic pressure, water is forced to pass to the more saline side of the membrane. (ΔP=0). For RO, water passes to the less saline side of the membrane, due to hydraulic pressure (ΔP>0)

2.2 MASS TRANSPORT: SOLUTION DIFFUSION MODEL

There are two models used to describe the mechanism of permeation in membrane processes. The difference depends on pore size, because different phenomena can predominate. [6]

We can distinguish between a pore-flow model, in which transport is described by Darcy's law, and a solution- diffusion model, in which the transport is described by the Fick's low. The latter is the one that best describes transport in forward and reverse osmosis, because the pores are so small that the compounds dissolve into the membrane, then diffuse through it. [6, 15]

The overall driving force of the process can be exerted in a number of ways, such as difference in pressure, temperature, concentration, electrical potential. These can all be expressed as a chemical potential gradient, related to the flux by a proportionality factor. [49]

Hence, the flux can be described in a general form as: [49]

$$J_i = -Y_i \frac{d\mu_i}{dx}$$

Where:

- J_i is the flux across the membrane;
- $\frac{d\mu_i}{dx}$ is the chemical potential gradient of species i;
- Y_i is a proportionality coefficient.

As regards diffusion, each molecule is in constant random molecular motion, with no preferred direction. Because of a concentration gradient, transport of matter will result from the more concentrated side to the less concentrated one. This can be expressed by the Fick law: [6]

$$J_i = -D_i \frac{dc_i}{dx}$$

Where:

- J_i is the flux across the membrane;
- $\frac{dc_i}{dx}$is the difference in concentration;
- D_i is the diffusion coefficient;

In this equation, the minus sign indicates that the direction of diffusion is down the concentration gradient.

Since diffusion is a slow process, it is possible to achieve a significant flux by creating considerable concentration gradients and by reducing the thickness of the membrane. [6]

Flux in both RO and FO can be generally described by the following equation: [41]

$$J_w = A(\Delta P - \Delta \pi eff)$$

Where A is the water permeability coefficient of the membrane, Δπeff is effective osmotic pressure difference across the membrane; ΔP is the net applied hydraulic pressure. The positive sign of J_w indicates the passage of water from the more concentrated side to the less concentrated side.

For RO, ΔP is higher than the osmotic pressure difference. That being so, to have the movement of water, the pressure that has to be applied must overcome the osmotic pressure difference. [8] Water goes from the area where the concentration of solute is high, to the one having low concentration of solute.

For FO, no hydraulic pressure is applied. Then ΔP=0 and water passes from lower concentration of solute, to higher concentration of solute. [41] the water flux is directly related to the difference in osmotic pressure. [8]

While water permeates across the membrane, salt diffuses in the opposite direction of water flux, because of the intrinsic characteristics of the FO membrane, which is not 100 % selective to ionic compounds . [9]

Reverse Solute Diffusion (RsD) is a relevant issue mostly in FO, because it causes not only loss of draw solute and increase of concentration polarization, but also a change in feedwater chemistry that may affect the fouling behaviour. [41] The reverse solute flux J_s can be described as: [6]

$$J_s = B\Delta C$$

Where B is the intrinsic solute permeability coefficient of the membrane, ΔC is the effective solute concentration difference across the membrane. [6]

A and B are two intrinsic parameters that are used for mathematical models. [27]

- A, which includes inside itself different parameters; it is always the proportionality constant between the water flux and the driving force,
- B, which gives the transport and leakage of solute, indeed it depends on the solute diffusion coefficient.

In FO, membranes with high performance in terms of both selectivity and permeability must have high A and low B. [20]

The performances of overall membrane system can be expressed in different ways. For instance, the Salt Rejection defines the capacity of the membrane to separate salts from the feed water.

$$R(\%) = 1 - \frac{c_p}{c_f} \cdot 100$$

Where:

- c_p is the concentration of solute in the permeate;
- c_f is the concentration of the solute in the feed.

Another factor to take into account is Recovery, which is defined as:

$$REC = \frac{Q_p}{Q_F}$$

Where

Q_p is the permeate flowrate and Q_F is the influent flowrate. [15, 22]

Another relevant parameter for a FO membrane is S, the structure parameter, which depends on mass transport across the membrane, since it is related to membrane thickness, tortuosity and porosity. [27]

Large S values lead to diminished performance, because a thicker and denser membrane hinders diffusion and increases boundary layer thickness. [27]

An ultimate FO membrane is required to have minimum structural parameter, to increase water flux, and the largest reverse solute flux selectivity, to avoid draw solute drop. [39]

2.2.1 Concentration polarization

Concentration polarization represents a significant obstacle in membrane processes, because it causes lower water flux than expected. This phenomenon can occur on both sides of the membrane, with different consequences according to the process we are considering. [22]

In pressure- driven membrane processes, only external concentration polarization (ECP) takes place, because solute mass transfer on the permeate side of the membrane can be neglected. [6, 38]

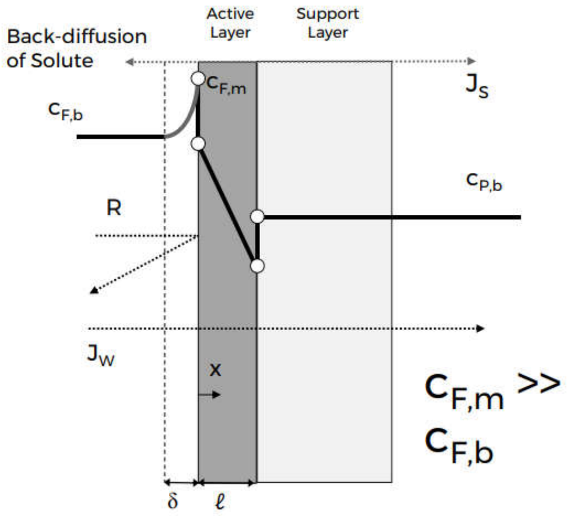

Figure 2.5: Concentration polarization stems from the solute back-up at the membrane surface, due to a difference in concentration of solute in the bulk and at the membrane. [6]

In RO, water and a little salt flow through the membrane, but most of the salt is rejected.

Concentration polarization is in this case caused by a solute build- up at the membrane – solution interface. [22]

For separation to occur, the concentration of salt at the membrane surface must be always higher than the one in the bulk. Consequently, the solute accumulates in a relatively stable boundary layer, between the membrane surface and the bulk solution. [6, 43]

The increase in the boundary layer concentration determines an increase in osmotic pressure, that lowers the effective driving force. Thus, it causes a decline in the water flux. It is then necessary to increase the ΔP to compensate this loss, resulting in higher power costs. [22]

To attenuate the effect of CP, it is possible to enhance the turbulent mixing at the membrane surface, reducing the thickness of the laminar boundary layer. This can be done by increasing the fluid flow velocity past the membrane surface, or by adding membrane spacers. However, there is always a technical limit to the turbulence, due to the energy consumption of the pumps and the pressure drops. [43]

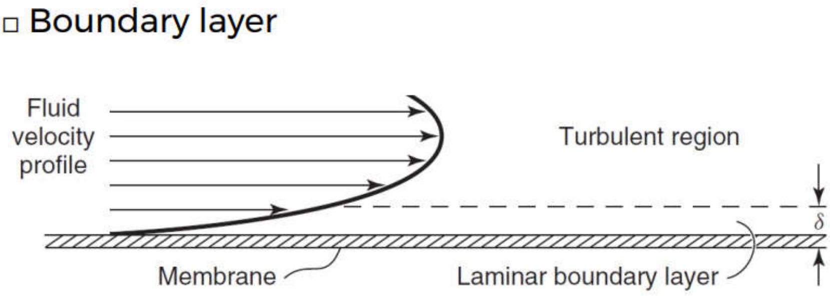

Figure 2.6: Fluid velocity profile at the membrane surface. Between the turbulent region and the membrane, there is a thin laminar layer, where the solute builds-up and causes concentration polarization. [6]

A consequence of CP is that the membrane retains salt at a higher rate than what can be observed. Real rejection of the membrane is larger than the observed one, because the salt concentration is higher. [6]

Conversely, in osmotic- driven membrane processes, two types of CP can occur, because solute mass transfer can be consistent on both sides of the membrane. External concentration polarization occurs on both the feed and the permeate sides of the membrane, because any process prevails on the others. Both phenomena lead to a decrease in the effective osmotic driving force. [55]

When the feed solution faces the active layer of the FO membrane, the extent of CP is like CP in pressure driven membrane processes. We refer to this as Concentrative External CP. [55]

As in RO, CP can be reduced by increasing the turbulent mixing or reducing the water flux. Nevertheless, water flux is already low in FO processes, compared to RO, so it cannot be further reduced.

Despite that, the effect of CP on water flux is much lower than in RO, due to the lower hydraulic pressure applied in FO. [8]

In FO asymmetric membranes, dilutive internal CP can occur on the permeate side of the membrane (fig. 2.7). Draw solution is diluted within the porous support of the membrane. It follows that the concentration of the draw solution on the inside of the active layer will be lower than the one in the bulk. [28]

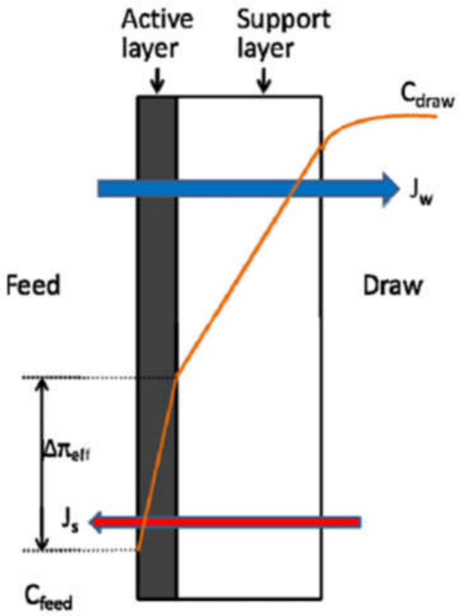

Figure 2.7: Dilutive Internal Concentration Polarization and External in Forward Osmosis. The active layer faces the feed stream. Since the Draw Solution is being diluted, its concentration inside the membrane is lower than the concentration in the draw side. [55]

Studies have showed that internal concentration polarization is one of the main obstacles in the overall performances and economic viability of osmotic driven membrane processes, because it depletes the water flux and enlarges solute transport. [27, 28]

2.3 REVERSE OSMOSIS

Nowadays Reverse Osmosis is a wide- spread technology in the field of membrane processes, used to separate dissolved solids, such as monovalent ions, from water. [6, 15, 22] With a salt rejection greater than 99%, RO membranes represent the finest filtration currently available. [7, 15, 22]

As it can be seen in Figure 2.8, one feed stream yields two effluent streams, the permeate, which is the product fresh water and the concentrate or retentate. [22]

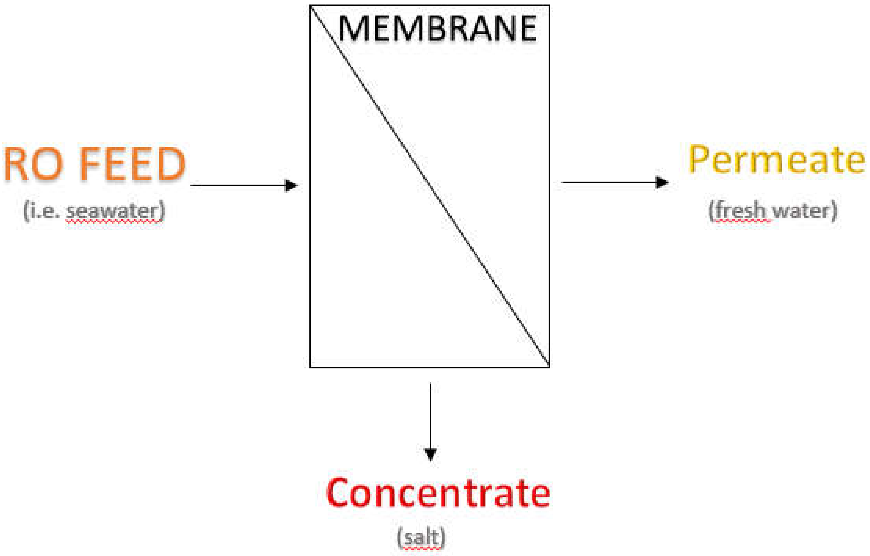

Figure 2.8 example of seawater RO plant. The feed stream, containing a certain amount of dissolved solids, is separated in a permeate stream, with less solids, and a concentrate stream, where the concentration of solutes is higher.

This technology has experienced a rapid growth in the past decades. Thanks to previous research interest, it has become more and more economical and efficient compared to other competitive technologies. [15]

Between the advantages of RO, there is the reduction of the number of units needed, limited use of chemicals, limited production of residuals. [25]

The plants also have small footprint, because it is possible to treat high quantities of water with a relatively small membrane area. Moreover, the membrane systems are packed and combined in modules, connected in series and/or parallel. They have thus large modularity and composability, together with facility of operation. On the other side, since RO is a high tech technology, its implementation requires knowledge and specialised workforce. [25]

Nevertheless, RO still presents some drawbacks that harms its effectiveness.

At first, as this process is opposed to osmosis, an external pressure is required to operate the separation. Because of the membrane resistance, the actual pressure to be applied is slightly higher than osmotic pressure.

This determines a limit in the capacity of RO membranes to treat highly saline seawater, because the pressure required would be higher than the maximum pressure permitted. [15]

As it can be seen in in fig. 2.9, the flux of water in RO depends on applied pressure, while the salt flux does not. There is no flux below the osmotic pressure. Then flux increases as applied pressure increases. The proportionality is represented by a linear line.

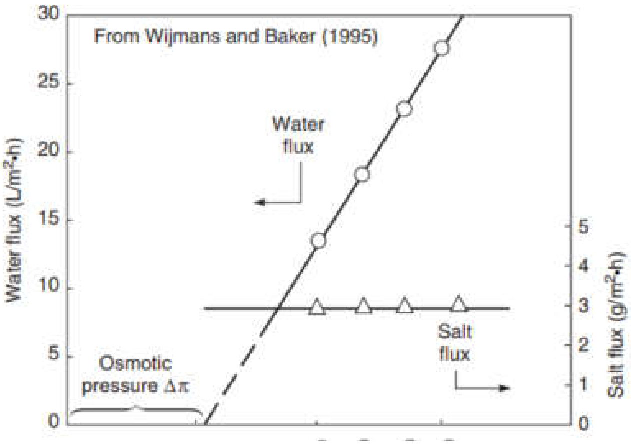

Figure 2.9: Water flux and salt flux over applied pressure. Below the osmotic pressure there is no flux. Water flux increases with applied pressure in a linear way. The salt flux has the same behaviour with increase in pressure. [49]

Regarding salt, by increasing the applied pressure, the salt flux does not change. Salt rejection is a function of applied pressure. It follows a logarithmic trend.

At some point the gain in rejection will be low, so it is not worthwhile going higher with applied pressure, because that means electric energy to apply the pressure itself. (fig.2.10)

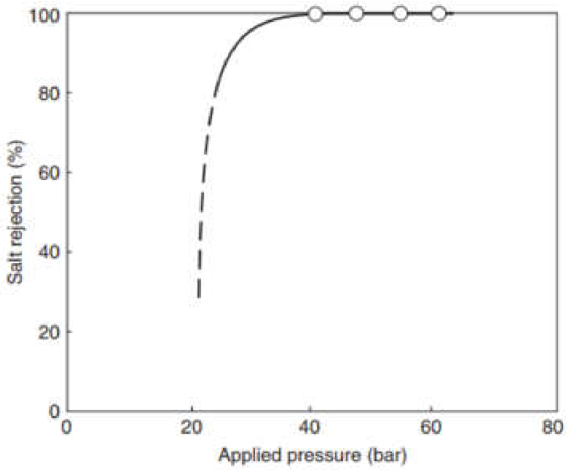

Figure 2.10:Salt rejection over applied pressure. This function is logarithmic and reaches a point in which by further increasing pressure, rejection slightly increases. [49]

Subsequently, there is a trade-off between membrane selectivity and permeability, that affects RO utilisation. As such, RO membranes treating brackish waters are characterised by higher product water flux, but lower salt rejection, thus operate at lower operating pressures, whereas seawater RO membranes, with a higher rejection of salt, require higher pressures to account for lower permeate fluxes. [15]

Even so, RO systems can reach recoveries up to 90%, depending on feed water composition, feed water salinity, pre-treatment, concentrate disposal options, energy design configuration. [15, 25]. However, Recovery is never 100% due to tangential transport, that cannot be avoided. [15] This parameter strongly affects the overall cost of the system. [50]

RO desalination plants have few negative environmental impacts, involving large water intakes of seawater or aquifer water, thus discharge of a high saline brine into the environment. Generally, the discharge is done into open ocean, or the concentrate is mixed with wastewater effluent. [15] A prior concern when discharging is that the concentrated stream has different temperature and salinity than the surrounding natural waters. it is then fundamental to ensure mixing and dispersion, in order to avoid damages to the environment. [17]

A relevant limit in RO, and in membrane processes, is the fact that the membrane performance over time is depleted due to the mechanism of fouling, namely the accumulation of compounds onto its surface. To decrease this effect, RO feed water is generally pre- treated with a membrane process of larger pore size (MF, UF, NF). This allows to reduce the membrane ageing, membrane replacement and the frequency of cleaning. The choice of the pre-treatment depends on the characteristics of the feed water. [15]

RO pre-treatment can efficiently limit this effect and is particularly convenient when water contains organic colloidal and suspended solids, such as in seawater open intakes and brackish surface waters. [15] Pre-treatment increases the overall quality of produced water. However, the cost of membrane pre-treatment is still higher than conventional pre-treatment. [37]

2.3.1.1 Applications of RO

Reverse Osmosis applications include brackish and seawater desalination to obtain potable water, municipal and industrial wastewater reuse, recycling and reclamation, generation of ultrapure water [22]

In 2003, RO desalination accounted for 75% of new production capacity, and has growth exponentially in the past decade, as it can be seen in fig. 2.11, compared to other desalination technologies. [15, 48]

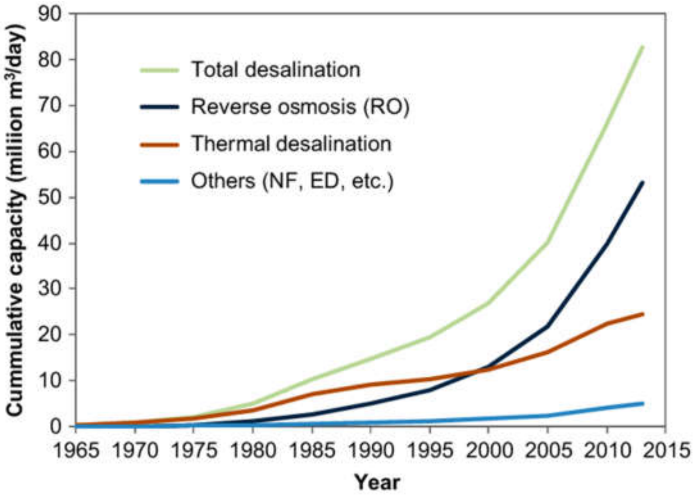

Figure 2.11: Increase in desalination capacity over the past years. The capacity of desalination has strongly increased, together with the implementation of Reverse Osmosis, compared to other desalination systems, such as Thermal. [48]

The plant size, the source of water and the energy source are determining factors in the cost of desalinated water. [15] Energy costs account for 75% of the operative costs of RO desalination plants. [17]

Over the past 30 years, RO desalination plants have experienced a decrease in capital and operation costs, thanks to improvements in membrane material and technology, and this process is expected to further improve. [15] The unit cost of water went from \$5.00/m^3 in the late 1970s to less than \$1.00/m^3 in 2004. [56]

2.4 FORWARD OSMOSIS

Forward Osmosis is an emerging technology in the field of membrane processes. The development of the process is still at pilot scale, although there are little examples of operative FO desalination plant. The first commercial FO desalination plant was built in Oman and has a design capacity of 200 m^3/day. [27, 34]

In fig. 2.12 there is an example of a conceptual FO system

Because of the difference in osmotic pressure, water permeates across the membrane, passing from the feed side of the membrane, where osmotic pressure is low, to a highly concentrated stream, named draw solution (DS). This leads to a more concentrated feed stream and dilution of the draw solution. [8]

The draw solution is an engineered solution, made of pure water and a solute, specifically selected for the purpose of the process. By re-concentrating the DS, it is possible to separate the product fresh water from the diluted solute. However, this requires a proper downstream recovery process, and a further treatment, which still represents one of the main drawbacks of FO and an obstacle to its implementation. [18, 41] [55]

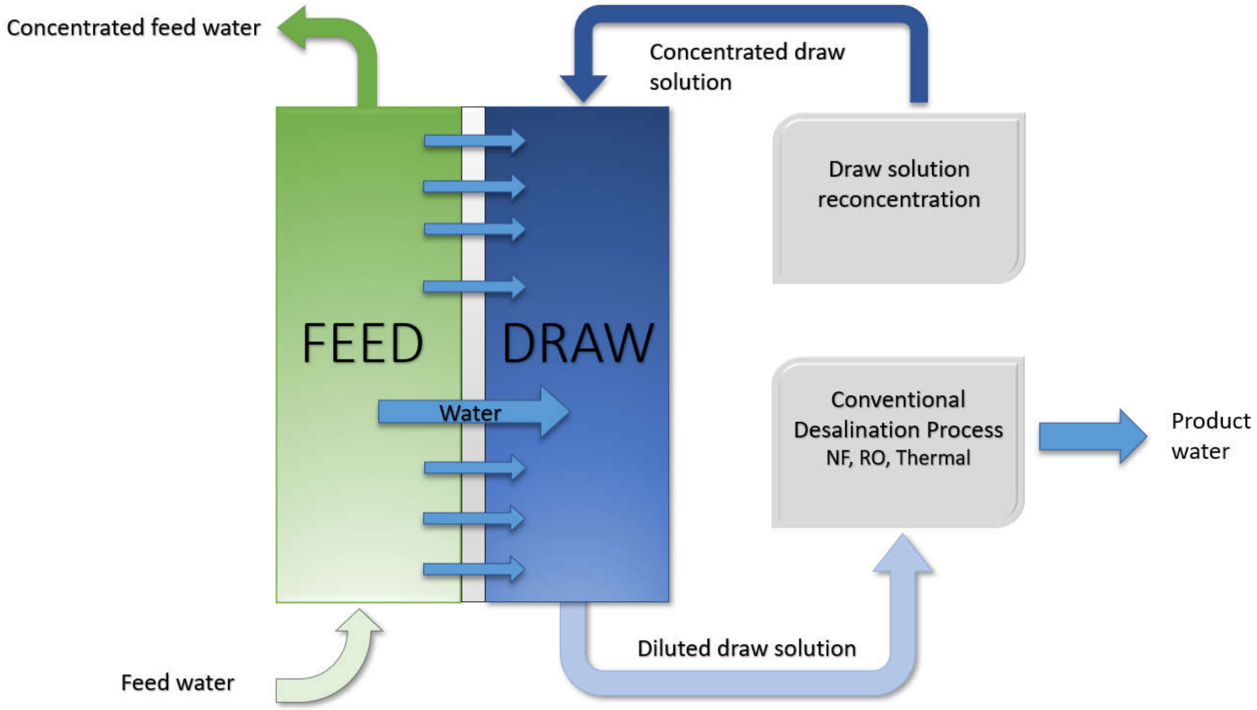

Figure 2.12: Scheme of a desalination process using FO as a pre-treatment. FO is able to dilute the feed water before it comes to the following treatment step, that could be RO, NF or a Thermal process, reducing the presence of foulants that would decrease the efficiency of the desalination process. The Concentrate can be sent back to FO, to be used as draw solution. [39]

Another hurdle in FO development is the matter that fluxes in FO are lower than RO, meaning larger membrane area is required. It has been seen that FO fluxes are 2-4 times lower than those for RO for the same application, thus FO plants would have higher footprint. [5]

Anyhow, FO arouse interest thanks to its main advantages and potential opportunities, when compared to the more conventional pressure-driven membrane processes.

Beyond its high rejection of a vast selection of contaminants, the dominant advantage of FO stems from the factor that it operates at almost no hydraulic pressure. As a result, the FO process would require lower energy consumption than RO and the plant would not need resistant materials, hence reducing the costs of fabrication. It can be applied also with particularly difficult stream waters.

The low hydraulic pressure may be affecting also the mechanisms of fouling, leading to more reversible fouling in FO than RO. Moreover, this would reduce the membranes life costs and the number of replacements. [34]

2.4.1 Draw solution and its reconcentration

The choice of DS is crucial because it controls the whole process performance, exerting influence on mass transport. [27]

Since the driving force is the difference in osmotic pressure, it is fundamental for the draw solution to have higher osmotic pressure than the feed solution. [8] The higher this difference is, the higher will be the flux. [55]

An appropriate draw solute should be inexpensive, stable, non- toxic, highly soluble and its regeneration has to be technically feasible and simple. [27, 39]

Moreover, high molecular size is required to limit reverse draw solute flux, which is the leaking of DS into the feed side of the membrane, causing a decrease in the osmotic pressure difference, thus a decrease of the driving force, impacting operation costs and the DS cost and may enhance membrane fouling,. [27]

NaCl is often preferred as draw solute, thanks to its high solubility, so high osmotic pressure, low cost and simplicity to be concentrated afterwards, avoiding scaling. [1, 8, 9]

Multivalent ions solution can be more appropriate when high rejection is desired. [8] In contrast, monovalent ions result in higher flux, thanks to higher diffusivity, but they cause more solute leakage. [10, 27]

Several other draw solutes have been studied, together with approaches for draw solute selection. [55]

For instance, sugars (i.e. glucose, fructose) have been used in the early developments of FO, because they do not need separation afterwards, or separation can be achieved under low pressures in RO. [21]

For its ready supply, seawater has also been used as DS, but it contains few components and particle that can enhance fouling. [11]

A critical issue is the reconcentration or regeneration of the draw solution after its dilution in the FO process, that has to be technologically and economically feasible. [55] This passage determines a strong increase in the energy demand for the overall process, making FO a less convenient technology, compared to other pressure-driven membrane processes. In NF or RO, the permeate obtained during the process has high quality and is already suitable to be applied, without further treatments. [51]

On that account, bypassing this stage can significantly shrink energy costs in FO technology operation. [17]

There are applications considering the direct use of the diluted draw solution. For instance, in commercially available personal hydration packs, the diluted draw solutes not only can be used as it is, but they add value to the extracted water, thanks to sugar and nutrient dissolved in it. [17]

2.4.2 FO Applications

Forward osmosis features various potential applications in several fields, such as water treatment, brackish and seawater desalination, wastewater reclamation. [55]

It presents large perspectives of increasing energy efficiency of existing technologies, reducing water shortages, reducing damages to the environment and exploiting wastewater as a resource. [8, 17]

For instance, FO can be used to concentrate industrial wastewater and for the treatment of landfill leachate. [8, 55] Leachate contains a wide distribution of pollutants, such as organic compounds, dissolved heavy metals, organic and inorganic nitrogen, and total dissolved solids (TDS). For this reason, it is particularly challenging to obtain high effluent quality with a conventional treatment, but FO is able to efficiently remove TDS from wastewater. [54]

FO basically constitutes a high-level pre-treatment step and not a final stage. It can be effectively and safely used as a pre-treatment for RO desalination plants, minimizing fouling in RO [8] and decreasing the energy requirements. [5, 51] With a combined plant FO/RO for sea water desalination, it is possible to achieve up to 50% of savings in energy as compared to conventional single pass RO. [5, 51]

This is due to the fact that RO would require less energy to treat a less saline seawater, because dilution decreases the osmotic pressure that must be overcome with applied hydraulic pressure. [11, 17]

Moreover, FO can employ sources of water, for example wastewater effluent, that do not have alternative use and cannot be mixed with seawater, because they would compromise the efficacy of RO and enhance fouling. Furthermore, this offers a multibarrier protection of drinking water, as FO membranes, as well as RO, completely reject pathogens. [11]

Along with RO desalination, FO can be used to downstream dilute the concentrate, minimizing the negative effect of discharge of RO desalination plants. [17]

Additionally, FO represents a promising tool to expand the water supply for irrigation, by exploiting brackish groundwater. In regions where groundwater is too saline, and freshwater is scarce, FO can make freshwater with the locally available brackish water. This also allows the use of a concentrated fertilizer as draw solution, that can be directly applied to crops. [17]

3 FOULING

Fouling constitutes the bottleneck in membrane's performances over time, as it reduces the membrane's lifespan, resulting in larger operating costs for membrane desalination. [15, 32]

It is generally due to the presence in the feed stream of dissolved organic or inorganic substances, colloids, bacteria or suspended solids. These materials interact between each other and with the membrane surface, accumulating, attaching or adsorbing within the pores of the membrane. [46]

Fouling is unavoidable and causes a reduction in the flux of permeate, leading to a decline in the efficiency of removal of contaminants. [39] Hence, it harms the quantity of permeate flux and quality, in terms of solute concentration, of the flux water. [14, 27]

Fouling can be affected by membrane properties, such as surface morphology, hydrophobicity, charge. Parameters that influence fouling are also temperature, composition of feed water, water chemistry, such as pH, ionic strength, divalent cation concentration, hydrodynamic characteristics. In consequence, the overall membrane separation efficiency strongly depends on variations of hydrodynamic conditions and chemical composition of the feed stream. [14]

Fouling can be reversible or irreversible. Reversible fouling can easily be removed with a physical process, by changing the parameters of the system or rinsing with water, whereas irreversible fouling is harder to eliminate or even impossible. To restore the initial flux, chemical cleaning, for example with caustic soda, or replacement of the membrane are compelled.

3.1 FOULANTS

Feedwater composition is one of the parameters that mostly affects fouling. Membrane fouling is caused by the different types of foulants that are present in waters, such as dissolved organic compounds, colloids, less soluble salts and biological growth. Different foulants can lead to different fouling mechanisms, namely: [6]

- Scaling: It is due to soluble salts, such as calcium sulphate, iron, manganese, silica. They are present in dissolved form but, due to changes in pH or to oxidation, may precipitate onto the membrane surface. Fouling by scale can be more severe and difficult to remove.
- Silt: due to suspended particles that can physically block the membrane pores, hindering transport and creating a cake layer.
- Biofouling: algae and microorganisms can create a biofilm, adhering to the membrane surface.
- Organic: dissolved compounds and colloids. Example of organic foulants are humic and fulvic acids, that adsorb on the membrane surface.

Major foulants components in wastewater are particulates, colloids and organic macromolecules, for instance polysaccharides, humic substances and proteins.

The membrane is generally fouled by a mixture of different foulants, so fouling will be affected by the combinations between them. Especially for organic foulants, it has been seen that foulant- foulant interactions significantly impact the extent of fouling [29, 41]

Between organic compounds, Natural Organic Matter (NOM) constitutes a severe fouling agent in membrane processes. [24] Model foulants, such as Sodium Alginate, Bovine Serum Albumin (BSA), Aldrich Humic Acid (AHA) have been used to simulate their behaviour, to further understand the complex fouling caused by NOM. [4, 26, 29, 44]

Hydrodynamic conditions strongly affect fouling, because more severe fouling occurs at higher water flux. [41] This is since there is a larger volume of water permeating through the membrane, hence more foulants in contact with the membrane. Moreover, concentration polarization is higher at higher flux, as well as the hydrodynamic drag force towards the membrane surface. [41]

Means to avoid and reduce fouling are the pre-treatment of the feed water, utilisation of spacers and change in design of the system and operating parameters (critical flux, temperature). This leads to additional costs and enlarges energy consumption. [9]

Periodic cleaning is also a proper solution to reduce the accumulation of foulants on the membrane. Even though it harms the membrane lifetime over time, it may be a measure to avoid successive chemical cleaning. [27]

Since the reduction of fouling is a relevant issue in membrane processes, the assessment of the extent of fouling in FO is crucial to understand whether this mechanism leads to lower and more reversible fouling.

Previous studies have observed that fouling in FO is lower than in pressure-driven membrane processes, because of the different structure of the foulant layer in FO. [19, 24, 29, 39] The absence of hydraulic pressure would lead to a less compact foulant layer in FO. [27, 41] The cake layer formed during RO appears densely compacted, while the one in FO thicker but much less compact. [24, 39]

It has been stated that the flux recovery in FO ranges from 80-100% of the initial flux through periodic rinses to clean the membrane surface. Hence, fouling in FO would be mostly reversible. On the other hand, RO fouling cannot be removed without chemical cleaning. [24, 39]

Under these circumstances, a systematic investigation of fouling is necessary, to further understand the potentiality of FO, compared to RO. Since RO and FO work at different operative flux, it is fundamental to study the fouling behaviour with the same hydrodynamic conditions.

3.2 CLEANING

A suitable cleaning protocol is compulsory to restore membrane performance and enlarge its longevity. The specific cleaning procedure depends on the chemical characteristics of the feed water, on the type of membrane and the fouling severity. [6, 27]

Physical cleaning can be done via hydrodynamic modifications or backwashing. [24]

Chemical cleaning may be required for more intense fouling. Chemical detergents generally used are acids, bases, oxidising agents, surfactants or chelating agents [6, 27]

The drawback is that the cleaning cycles gradually degrade the membrane and its selectivity. At the end of their lifetime, water flux reduction is at least 20% of the initial one, and the capacity of removal of salt declines. [6] Moreover, chemical cleaning involves further energy requirements. [27]

It has been reported that more than 96% of water flux recovery can be achieved in FO with a simple water rinse. [9, 30]

4 MATERIALS AND METHODS

The aim of this thesis project is to investigate fouling behaviour and mechanisms in forward osmosis, with a further comparison to reverse osmosis.

Laboratory experiments were performed to measure the reduction of flux occurred over time. To do so, two different lab scale setups were employed, one FO setup and one RO setup. To allow comparison between the two systems, identical flux and operation conditions were adopted. Hence, hydrodynamic operative conditions, as well as the chemical composition of the feed water, were the same in both FO and RO tests, and an equivalent plate and frame cell was employed.

Two different feed waters were investigated, with the same chemical composition but differing only in the presence of Calcium ions. This is because previous studies revealed that the presence of Calcium can potentially enhance fouling, forming complexes with the natural organic matter. [3, 29, 30]

4.1 MEMBRANE

The same type of membrane was used for FO and RO runs. Also, the same membrane orientation was employed, with the active layer facing the feed solution.

Polyamide- based TFC membranes, were purchased from Porifera Inc. (Hayward, CA, USA). The membrane had previously been characterised, determining transport and structural parameters, which are summarised in the following table:

A $Lm^{-2}h^{-1}bar^{-1}$	**S** μm
2.74±0.50	427±19

Figure 4.1: Values of A and S from previous membrane characterisation

A is the active layer water permeance, B the NaCl permeability coefficient and S is the support layer structural parameter. The membrane has a total area of 21,2 cm^2.

4.2 FEED WATER

Each fouling test was repeated twice, with a different composition of the feed water.

The feed water of the first set of tests was tap water, with the addition of a mixture of organic foulants, each one at the concentration of 75 mg/L. Alginate, Humic Acid, BSA (Bovine Serum Albumine) and Octanoic acid were chosen to simulate a typical composition of a wastewater effluent. They have been seen as the most common macromolecules that provide fouling, namely polysaccharides, natural organic matter, proteins and fatty acids. [24]

These compounds have a powder form and were dissolved in tap water, creating stock solutions. Alginate and Humic Acid were also filtered with a filter of 0.45μ.

A second set of tests was conducted with the same composition of the feed water, but without Calcium ions.

Sample of tap water were analysed and, based on the results obtained, a second set of stock solutions was prepared by addition of chemicals to deionized water.

The same organic foulants were added to the feed water, at the same concentration of 75 mg/L.

The composition of the two feed waters is reported in the following table. They have the same ionic strength but differ in ions and their concentrations.

Table 4.1: characterisation of feed 1 and 2, where feed 1 contains calcium ions and feed 2 was prepared with the same ionic strength, but without calcium ions

	Feed 1	**Feed 2**
Ions	**Conc (mg/L)**	**Conc (mg/L)**
Cl	19.0	98.0
NO_3	33.3	33.3
SO_4	52.0	52.0
HCO_3	256.7	257.0
CO_3	0.9	0.8
Ca	**88.7**	**0.0**
Mg	13.7	13.7
Na	18.7	171.5
K	1.3	1.3
NH_4	0.1	0.1
pH	7.5	7.5
IS	9.7	9.7

4.3 FO FOULING TESTS

4.3.1 Forward osmosis lab filtration setup

The FO setup, acquired from Sterlitech Corporation (Kent, WA, USA) has been schematized in fig. 4.2. It entails two reservoirs, one for the feed and one for the draw solution, two variable speed gear pumps (Cole-Parmer, Vernon Hills, IL), that allows to regulate the pressure at which the two streams are entering the system and a cell in which the membrane is located. Feed and draw solutions were recirculated to the respective reservoirs, as in batch mode. [13]

The system permits the measure of temperature and conductivity of both solutions through a programmable controller.

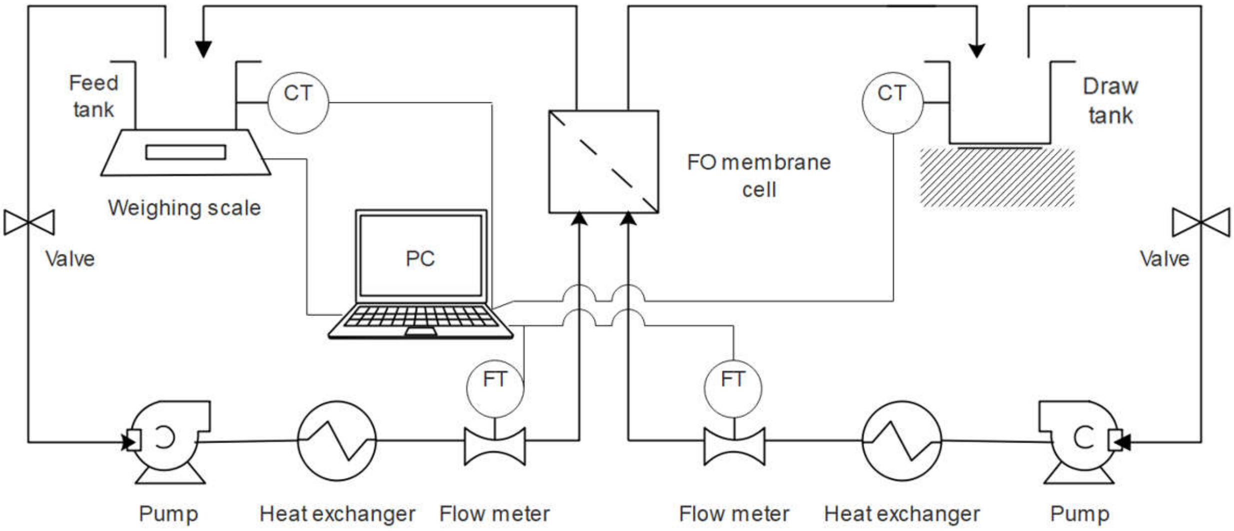

Figure 4.2: scheme of the FO lab scale set up

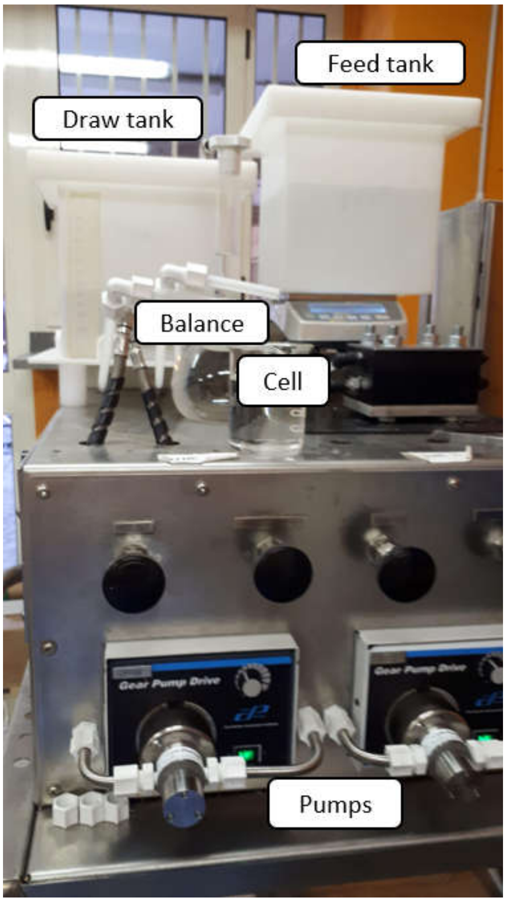

Figure 4.3: laboratory FO filtration plant

Figure 4.4: FO plant

The plant is connected to a data acquisition system with a computer – interfaced balance. (fig. 4.3 and 4.4) The balance measures the variation over time of the volume in the feed solution. This quantity can be directly related to the water flux across the membrane.

The experiments were performed in concurrent mode, meaning feed and draw solution entering and exiting from the same sides. Initial volume of feed and draw solutions was 6 L. During the runs, the crossflow rate was kept constant at 1.25 L/min.

4.3.2 Draw Solutes

Four inorganic salts were evaluated as draw solutes: NaCl, $MgCl_2$, Na_2SO_4 and $CaCl_2$, each one used individually. These salts were chosen because they are widely available and inexpensive, and can efficiently be regenerated, for example with nanofiltration. [1, 13]

The values of the salt permeability coefficient, B, for each draw solute are reported in table 4.2

Table 4.2: B of the draw solutes

Draw solute	B (LMH)
NaCl	0.94
CaCl2	0.16
Na2SO4	0.06
MgCl2	0.07

4.3.3 FO Filtration test

Different sets of fouling tests were performed: by changing the concentration and the flux, with different draw solutions, and with the two types of feed water described above.

At first, NaCl was employed as draw solute, at different concentrations, namely: 0.12M, 0.2 M, 0.31 M, 0.5 M, 0.95M, 2.2M.

Afterwards, a second set of tests was performed with different salts as draw solutes and tap water, with the addition of the organic foulants, as feed solution. The second set of tests was run with a water flux of 15 and 30 LMH, selected as target fluxes. These values were chosen as representative operative fluxes for FO. Lower fluxes would not be advantageous, because a larger membrane area would be required, while higher fluxes would need too high osmotic pressure, therefore high concentration of the draw solution.

The draw solutes were employed at a concentration suitable to obtain the target water flux, as it is showed in table 4.3, based on a model. According to the flux, it was possible to calculate the corresponding osmotic pressure and predict the concentration of each draw solute.

Table 4.3: concentration and osmotic pressure for each draw solute

Draw Solute	Conc (M)	π (bar)	Conc (M)	π (bar)
	15 LMH		30 LMH	
NaCl	0.31	14.04	1.15	54.3
CaCl2	0.27	17.79	1.91	202.9
Na2SO4	0.39	18.91	x	x
MgCl2	0.32	22.91	1.05	98.97

Indeed, osmotic pressure and concentration are related, and the trend differs for each solute, as it can be seen in fig. 4.5.

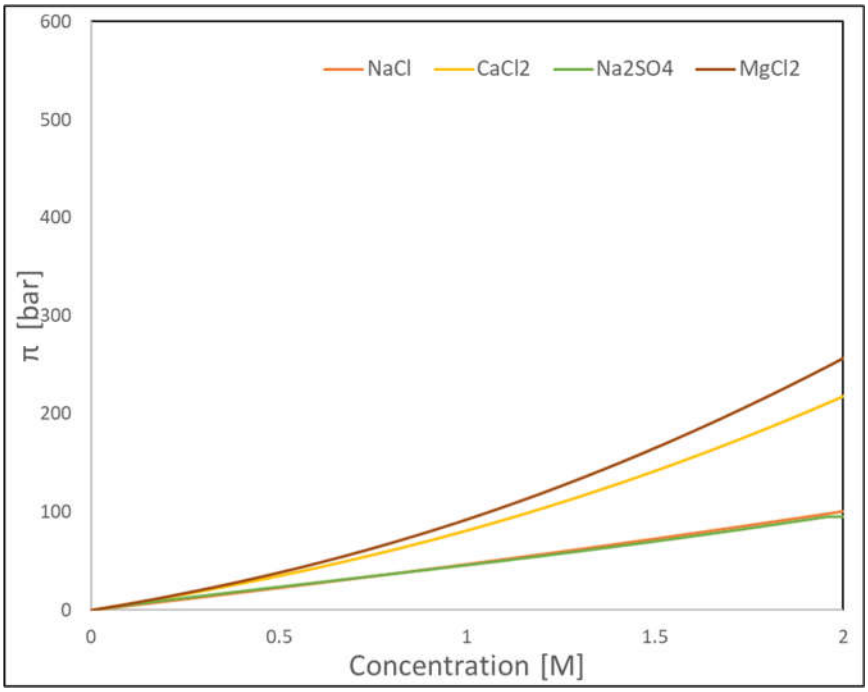

Figure 4.5: Concentration over osmotic pressure π for every draw solute considered. For MgCl2 and CaCl2, an increase in concentration corresponds to an increase in osmotic pressure. For solutes such as Na2SO4, this is true only until a certain point, after which to an increase in concentration does not correspond an increase in osmotic pressure

For each salt, osmotic pressure increases as concentration of salt increasing. While for $MgCl_2$ and $CaCl_2$, the gain in osmotic pressure due to increase in concentration follows an exponential trend, this is not true for other solutes. For Na_2SO_4, after a certain point the increase in concentration implies a slighter increase in osmotic pressure. For this reason, it was not possible to perform the run at 30 LMH, because the osmotic pressure required could not be reached.

Each test was then repeated with a different feed solution, that did not contain Ca ions.

4.4 RO FOULING TESTS

Fouling tests were then performed in Reverse Osmosis. RO fouling tests were conducted keeping the same hydrodynamic of the system, the same chemical characteristics of the feed water and with an identical cell as FO. What changed in this set of experimental tests was that it involved a different lab scale filtration setup, specifically designed for RO, since RO requires an external applied hydraulic pressure, that does not exist in FO.

The membrane was first compacted with water at the pressure of 10 bar for 3h30.

Fouling tests in RO were performed at the flux of 15 and 30 LMH, corresponding to a nominal pressure of 4 and 7.5 bar, respectively. The tests lasted for 18h.

4.4.1 Reverse Osmosis setup

The RO tests were performed in a lab scale filtration plant, like in fig. 4.6, that includes: a cell, in which the membrane is allocated (fig. 4.7-4.8), 3 collectors for feed, concentrate and permeate, a hydra-cell pump G03, through which it is possible to apply a maximum pressure of 1000 psi (70 bar), a manometer that measures between 0-10 bar, two valves to regulate pressure and a flowmeter to measure the flowrate and a chiller (-10 °C a 40 °C), that allows to keep constant the temperature of the feed water. (fig. 4.9-4.10)

The membrane was allocated inside the cell, with the active layer facing the feed stream. The cell is the same as in FO mode, but it presents two exits, one for the permeate and one for the concentrate. The concentrate is recirculated back in the feed reservoir, while the permeate is collected.

The variation in volume of permeate over time is measured through a computer-interfaced balance. This quantity can be directly related to the water flux across the membrane.

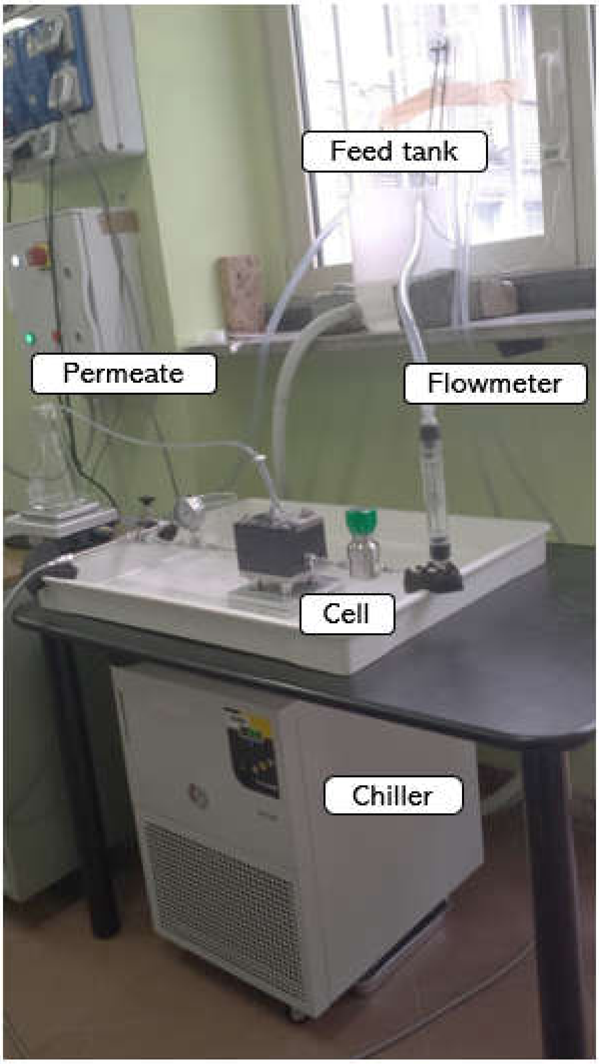

Figure 4.6: Laboratory Filtration plant

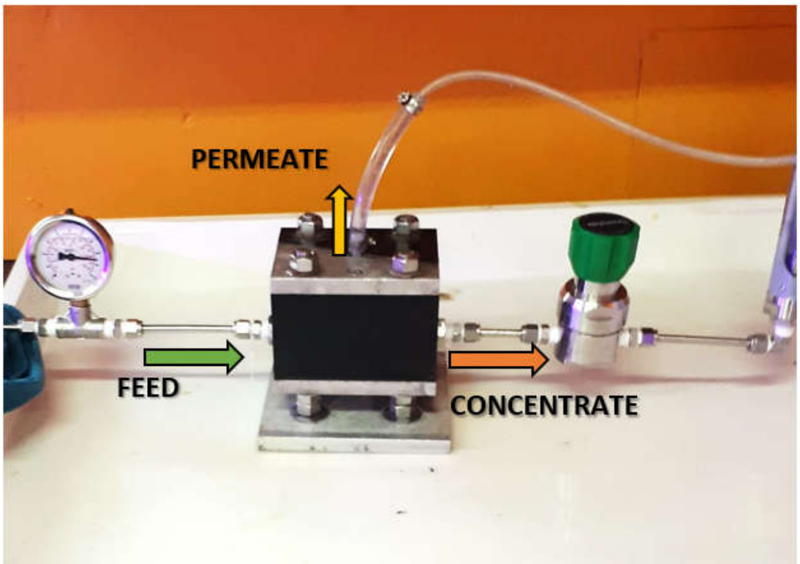

Figure 4.7: Cell used to allocate the membrane in RO mode

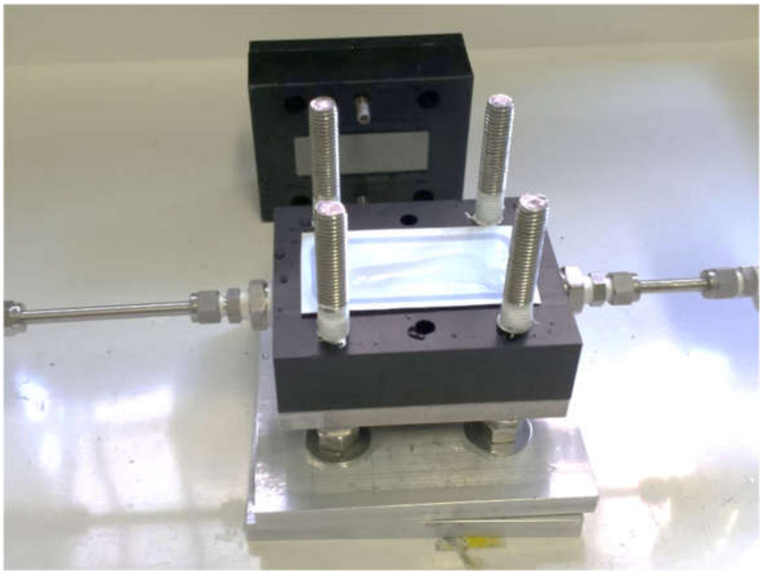

Figure 4.8: Membrane sample located inside the cell

Figure 4.9: hydra-cell pump G03, through which it is possible to apply a maximum pressure of 1000 psi (70 bar)

Figure 4.10: chiller a chiller to keep the temperature of the feed water constant

5 RESULTS AND DISCUSSION

A systematic study was performed to better understand the fouling mechanisms in Forward Osmosis and Reverse Osmosis, because fouling has strong influence on membrane performance and membrane plants costs.

Fouling can be depicted as the drop of water flux over time. The flux decline profiles obtained during FO and RO experiments are shown in the following graphs. The contribution to flux loss can be extrapolated from the differences between the profiles.

Fig. 5.1 and 5.2 correspond to FO runs with NaCl as draw solution, obtained by varying the concentration of the solute. Water flux increases as the concentration of the draw solution, thus the driving force, increases. Moreover, the extent of fouling increases with larger initial flux (figure 5.2). [35] This can be attributed to a larger hydrodynamic drag force, promoting foulants accumulation onto the membrane. [40]

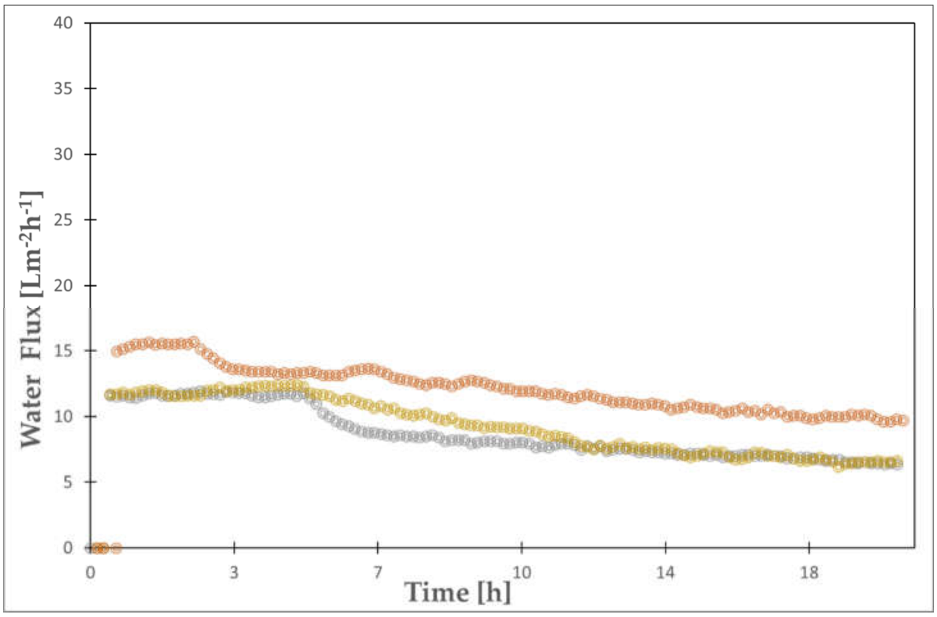

Figure 5.1 Results of the fouling tests performed with NaCl as draw solution, at different concentration, yielding different water fluxes, in the range between 0-15 LM.

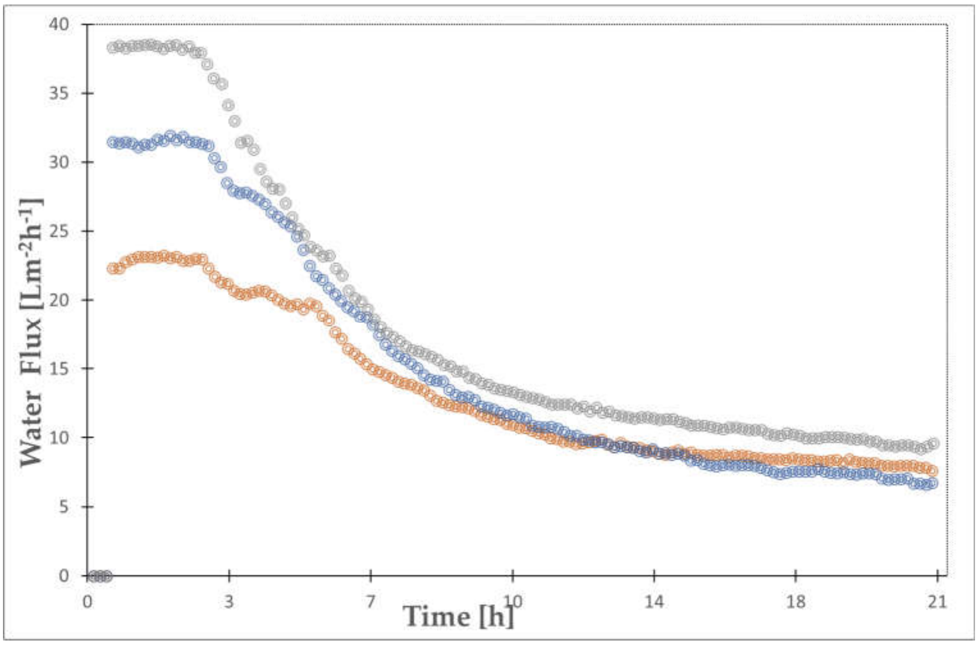

Figure 5.2: Results of the fouling tests performed with NaCl as draw solution at different concentration, yielding different water fluxes, in the range 15-40 LMH

With lower initial fluxes, there is a clear difference in behaviour between the profiles. Conversely, when going to higher initial fluxes, this difference becomes less evident, and all the curves collapse to a similar trend. The dissimilarity between the two ranges of flux suggests that for higher fluxes, the effect of the Reverse Salt flux is less significant, as the flux has more influence on fouling than chemical features.

Since the membrane is not completely selective to ionic compounds, there can be leakage of draw solute into feed solution that can alter the composition of the feed water and the fouling behaviour. Salt diffusion has few negative effects. It increases the osmotic pressure on the feed side of the membrane, and aggravate fouling because the salt can interact with the foulants present in the water, increasing its attaching on the membrane. [23] Furthermore, the consequent loss of driving force determines difficulties in the recovery of the DS, which is a critical step in FO plants.

The incidence of the effect of RsD can be clearly displayed for low fluxes, but at higher flues the hydrodynamic force hides the different trends.

This behaviour is then confirmed by the tests with different draw solutions, which were conducted to understand the influence of ionic species on fouling.

Fig 5.3 and 5.5 show the flux decline, by changing the draw solutions, with a feed water containing Calcium ions, at the fixed initial water flux of 15 LMH and 30 LMH, respectively. Fig. 5.4 and 5.6 were repeated in the same way, but with a feed water without calcium content.

The flux decline observed with $CaCl_2$ as draw solute was moderate, followed by Na_2SO_4 and $MgCl_2$, and lower with NaCl as draw solute.

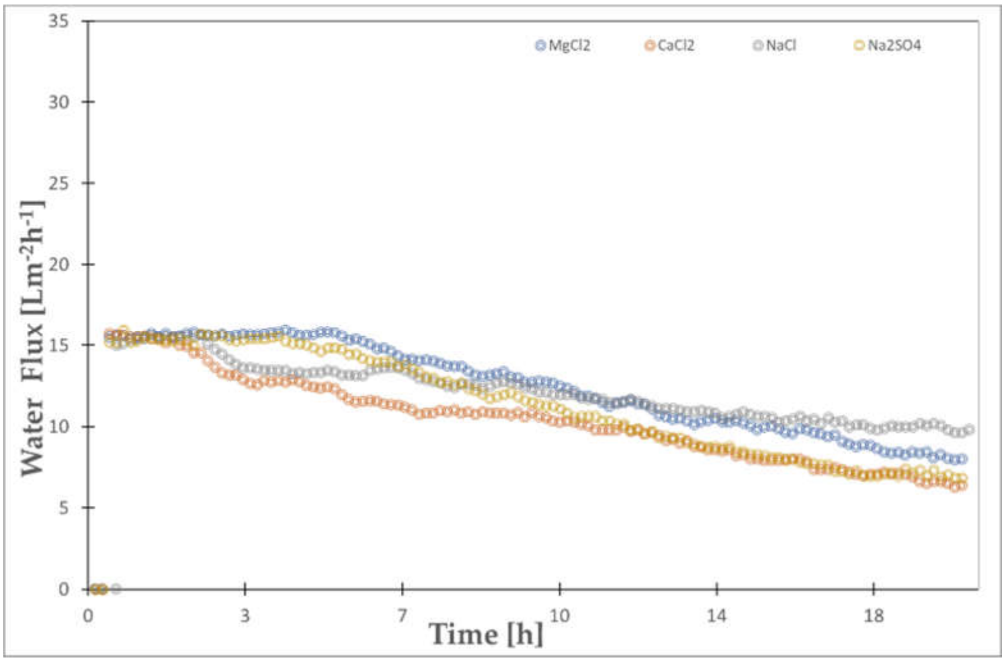

Figure 5.3: Results of the fouling tests performed at 15 LMH, with different draw solutions and with a feed water containing Calcium ions. The flux decline was respectively 50% for $MgCl_2$, 37% for NaCl, 58% Na_2SO_4 and 56% $CaCl_2$.

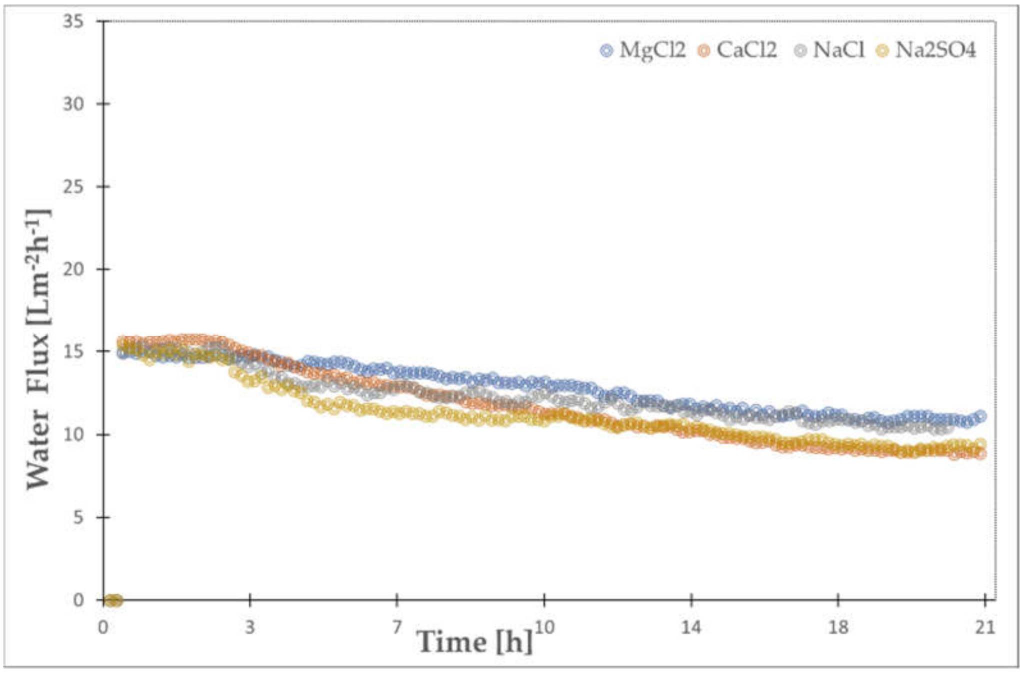

Figure 5.4: Results of the fouling tests performed at at 15 LMH, with different draw solutions and with a feed water without calcium ions. The flux decline was 30% for NaCl, 25% for $MgCl_2$, 42% for $CaCl_2$ and 39% Na_2SO_4.

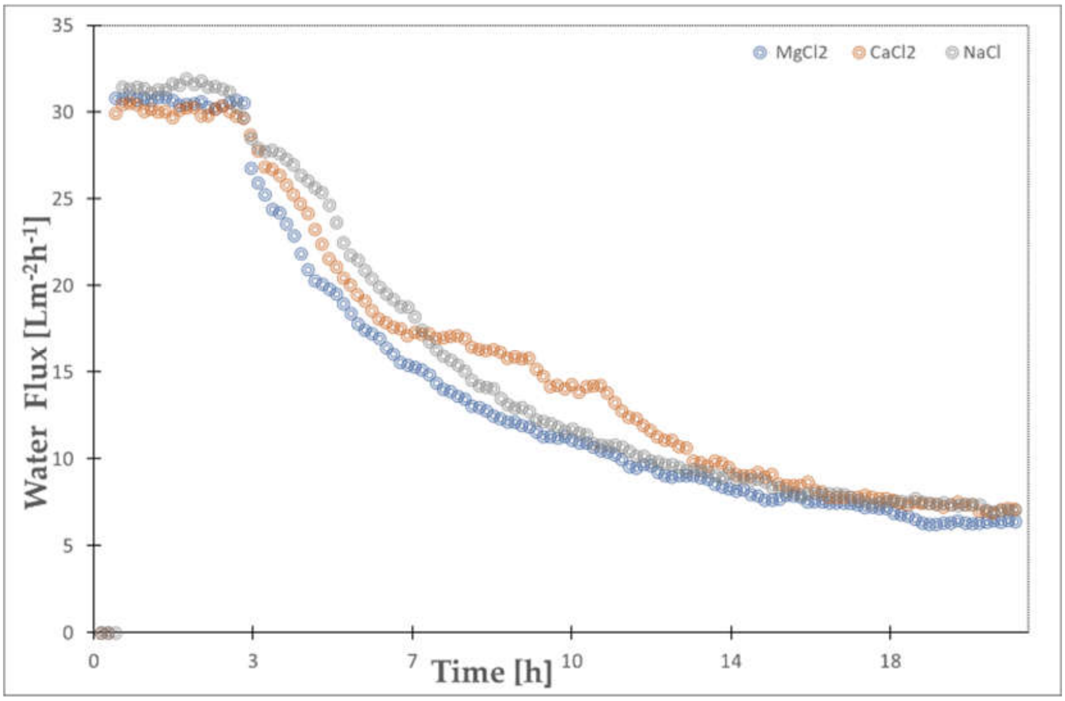

Figure 5.5: Results of the fouling tests performed at 30 LMH with different draw solutions and with a feed water containing Calcium ions. The flux decline was respectively 79% for $MgCl_2$, 78% for NaCl and 76% $CaCl_2$.

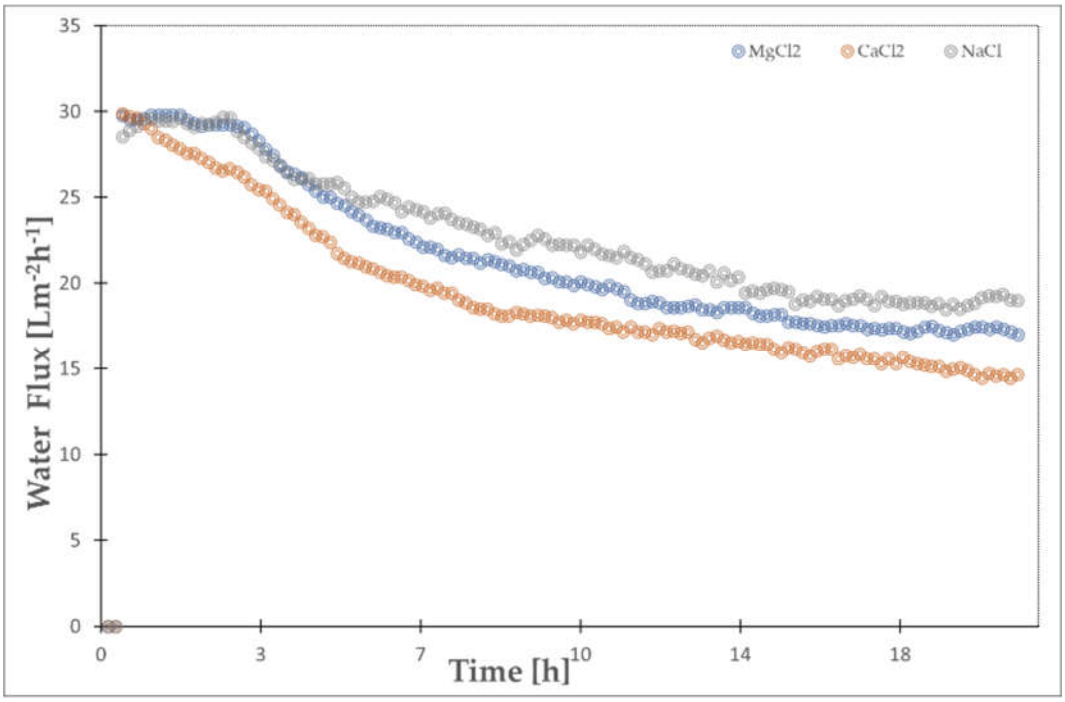

Figure 5.6 Results of the fouling tests performed at 30 LMH, with different draw solutions and with a feed water without Calcium ions. The flux decline was 34% for NaCl, 42% for $MgCl_2$, 51% for $CaCl_2$.

As previously said, since the draw solution can pass on the feed side, it can interact with the compounds of the feed solution. The extent of the interaction depends on the nature of the solute and its Reverse Solute Diffusion. The result suggests a role of divalent cations, such as Ca^{2+} and Mg^{2+} in promoting fouling more than monovalent ions such as Na^{+}. This chemical interaction has been extensively confirmed by previous literature reports. [29, 40]

$CaCl_2$ is more prone to this interaction, due to its Calcium ions. This is in accordance with previous studies, discussing the role of Ca^{2+} in binding with organic foulants and form bridges between other molecules, leading to a cross-linked gel layer that increases adhesion on the membrane surface. [29, 31] $MgCl_2$ can also enhance fouling, but it has slightly less affinity to the organic matter than $CaCl_2$.

Meanwhile, Na_2SO_4 exhibits a larger decline with the feed water containing Calcium, compared to the one without Calcium ions. This might arise from the fact that the ion sulphate can interact with the calcium present in the water, precipitating and creating gypsum.

Although the monovalent NaCl has high rate of diffusion, it is not likely to interact with the organic matter, leading to less fouling in presence of this draw solute.

All the set of results indicate that for initial fluxes of 15 LMH, the behaviour due to the draw solute can be clearly differentiated, since , the type of draw solution determines dissimilarity in the trend of each curve. This is because Reverse Salt Diffusion plays an important role in FO fouling. At higher fluxes, contrariwise, (fig. 5.5) the trends tend to collide to similar behavior.

A different trend can be observed between the feed water with Calcium and the one without. Feed water containing Ca2+ ions would be associated with larger membrane fouling, possibly due to the bridging with other foulants in the feed stream. [29]

With an initial flux of 30 LMH, the flux decline for the feed water without Calcium exhibits the same behaviour as the one at 15 LMH, while this is not true for the feed water containing Calcium.

In absence of calcium, both Reverse salt flux and advective transport cause the decrease in flux. The effect of the different draw solutes can be clearly identified for higher fluxes as well, because it is not attenuated by the presence of Calcium in the feed. Advective transport seems rather to prevail in the runs with feed water containing Calcium, at initial flux of 30 LMH, and the disparity due to draw solutes cannot be regarded.

Finally, all the sets of results indicate that the characteristics of the feed water are prevalent, and the presence of Calcium ions is significant. Therefore, Calcium, when present in the feed water, prevails over other mechanisms, covering the differences in behavior due to other mechanisms.

Subsequently, preliminary RO fouling tests were performed with the same conditions used in FO, at initial fluxes of 15 and 30 LMH. (fig. 5.7)

Like in FO, the initial flux has some influence on the extent of fouling, since the rate of flux decline is higher for higher initial fluxes, which in this case are due to higher applied pressure.

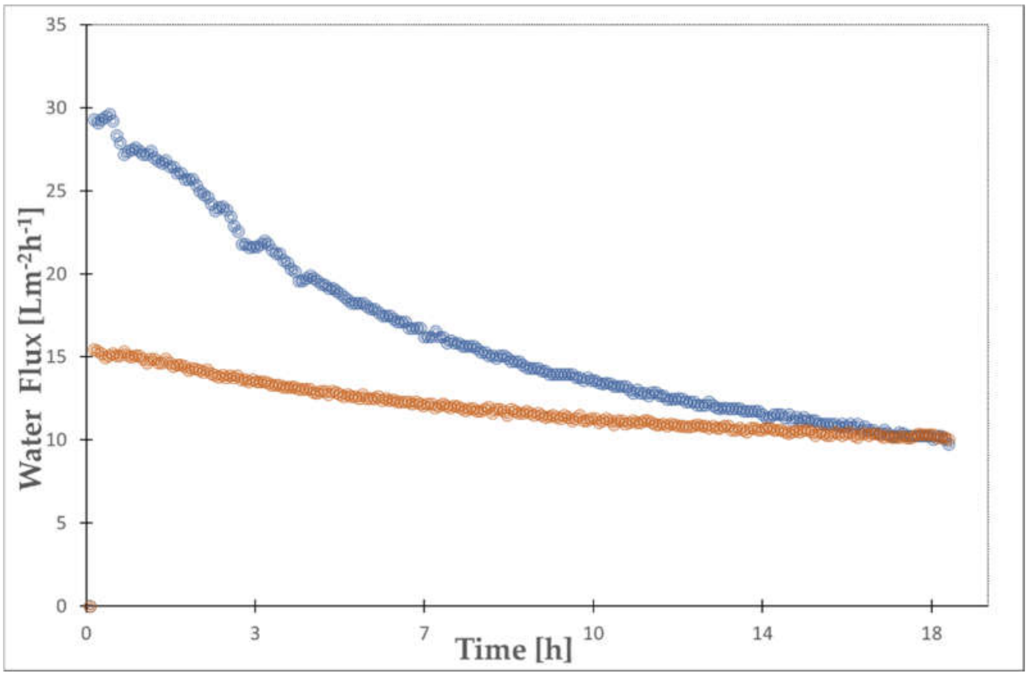

Figure 5.7:Results of flux decline in RO, at initial flux of 15 LMH and 30 LMH. The loss in flux is respectively 66% and 35%.

The leading mechanisms in RO is the flux, therefore the extent of fouling depends on the applied pressure, for these tests being 7 and 4 bar, which pushes the foulants to attach onto the membrane. At 15 LMH this effect is thus low, and since draw solute is absent, the loss due to back diffusion of salt is not significant.

In RO, water is being pressed against the membrane by a pressure that is constant, respectively, 7 and 4 bar. The compactness and the structure of the organic fouling layer depends on the applied hydraulic pressure, that forces the foulants to attach to the membrane, and to the transversal flux. [24]

In FO, the accumulation of foulants is rather due to the osmotic pressure gradient, hence the fouling layer may be more loose. [24] Fouling only occurs in the laminar layer next to the membrane, since it is not due to pressure but to chemical interactions. After this layer is filled, it is not expected to further increase. Furthermore, the foulants-foulants interactions in the feed water play an important role.

Another observation is related to the fact that FO profiles tend to reach a near stable point around the end of the runs. For this reason, studies have suggested the possibility that the fouling layer cannot be further developed after this point. [13]

This is not true for RO flux profiles. As it can be seen in fig. 5.7, in RO an increase in flux leads to an increase in fouling, but the flux trend keeps decreasing over time, even though not linearly, without reaching a stationary condition.

This result does not necessarily imply that fouling in FO is lower than RO, since the extent of fouling in FO changes according to the draw solute. Owing to the different driving force of the two processes, fouling behaviour is then presumed to be different. [42]

More in-depth fouling experiments are required to support further knowledge on fouling mechanisms in FO and RO and its reversibility. Additionally, the membranes used for this study where FO membranes. Certainly, more research with RO membranes should be conducted, to understand whether the behaviour may differ.

6 CONCLUSION AND FUTURE PERSPECTIVES

The purpose of this thesis project was to further elucidate the fouling mechanisms in Forward Osmosis, based on an experimental approach.

The extent of fouling in FO was evaluated at different concentrations, hence different fluxes, with different draw solutions and with a different composition of the feed water. Keeping the same conditions, a preliminary systematic comparison with fouling in RO was then performed.

The results suggested that the coupled effect of hydrodynamic and chemical relations is the governing factor of flux decline in FO. The nature of the draw solute plays an important role in rate and extent of fouling.

Due to transport of salt to the feed side of the membrane, fouling can be enhanced by the interaction between the draw solute and the foulants present in the feedwater.

Fouling effects would more severe in presence of Calcium ions, because it increases foulants-foulants deposition through bridging and can also bind draw solution ions, such as sulphates.

It has been seen that for higher fluxes, hydrodynamic is the key mechanisms of fouling, therefore the chemical interactions cannot be esteemed, and the trends of flux decline tend to stick to the same values.

More differences in behaviour can be seen in the curves at lower fluxes, where reverse solute diffusion is the dominating factor. When Calcium is not present, the peculiarities of chemical interactions can be displayed for high fluxes as well.

As a result, the presence of Calcium in the feed solution is overwhelming, since it shadows all other mechanisms.

When compared to RO, FO is not necessarily characterised by better fouling behaviour. The differences between the two processes arise from the different driving force, which lead to a different structure of the fouling layer. For RO, the key factor affecting flux reduction is the hydrodynamic, therefore it might experience lower fouling when the applied pressure is lower. This cannot be said for FO, since it is always present the flux decline due to the draw solute back diffusion.

Overall, these results imply that further improvements of this novel technology are needed to reach a full-scale implementation of FO. It remains of paramount importance selecting a draw solution with low reverse solute diffusion and improving the membrane selectivity, to minimize salt back diffusion.

Nevertheless, the potential of FO technology remains high thanks to its low energy requirements and the absence of applied pressure, that might make this technology competitive to other energy intensive processes.

Since RO can appropriately treat contaminated streams with salinity ranging between 5-40 mg/L, FO can be a promising technology to widen the range of application of membrane technologies, thus increasing the potential sources of drinking water. FO would be recommended to treat complex waters, having large concentrations of organic compounds.

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