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EXPERIMENTAL INVESTIGATION OF SUGAR AQUEOUS SOLUTIONS SEPARATION BY REVERSE OSMOSIS FOR THE MANIPULATED OSMOSIS DESALINATION PROCESS

Relatore: Prof. Alberto Bertucco
Correlatori: Prof. Adel Sharif, University of Surrey (UK)
Dr. Sami Al-Aibi, University of Surrey (UK)

Laureando: ELENA BARBERA

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Riassunto

Il problema della scarsità d'acqua è una delle questioni attualmente più delicate e rilevanti. Difatti, nonostante l'enorme quantità di acqua che è presente sulla superficie terrestre, più del 97% di questa è costituito da acqua salata sotto forma di mari o oceani, e soltanto una minima percentuale è disponibile come acqua fresca; inoltre, le risorse convenzionali di acqua fresca (laghi e fiumi) stanno diventando nel tempo sempre meno disponibili e più costose. Attualmente si stima che circa il 20 % della popolazione mondiale soffra di carenza di acqua potabile, e che circa un terzo viva in regioni cosiddette *water-stressed;* si ritiene che tale percentuale possa salire a due terzi, a causa dell'aumento della popolazione affiancata dal miglioramento degli standard di vita, che provocano un maggiore consumo di acqua pro capite. Per far fronte a questa attuale e allarmante questione, la desalinizzazione dell'acqua salina si è sviluppata come una preziosa alternativa per l'approvvigionamento di acqua potabile, sfruttando le quasi inesauribili riserve di acqua salata presente nei mari e negli oceani; la capacità mondiale di desalinizzazione è infatti in aumento anno dopo anno.

Esistono molte e diverse tecnologie di desalinizzazione. Le più tradizionali sono le tecniche di desalinizzazione termiche, che prevedono la fornitura di calore per consentire il passaggio di stato dell'acqua alla fase di vapore, successivamente condensato; si tratta di tecniche energicamente dispendiose, ma tuttavia largamente impiegate nelle regioni del Medio Oriente, dove la presenza di combustibili fossili rende disponibile a costi relativamente bassi l'energia necessaria per vaporizzare l'acqua. Recentemente però, soprattutto negli Stati Uniti e nelle aree europee, si sono sviluppate tecnologie di desalinizzazione tramite membrane, le quali hanno il grande vantaggio di operare a temperatura ambiente e di non prevedere un passaggio di stato dell'acqua. Tra queste, la più diffusa è la tecnica dell'Osmosi Inversa, la quale presenta numerosi vantaggi rispetto alle altre. Tuttavia, nonostante essa sia una tecnologia robusta, e numerose ricerche siano in atto al fine di migliorarne ulteriormente l'efficienza, è caratterizzata dallo svantaggio di richiedere un consumo di energia intrinsecamente elevato; si stima infatti che anche con sistemi per il recupero dell'energia efficienti al 100%, e con membrane dalla maggiore permeabilità, il consumo di energia non possa essere ridotto più del 15% rispetto ai processi termici.

Per tale motivo le ricerche si stanno indirizzando verso lo sviluppo di nuove tecnologie di desalinizzazione alternative, soprattutto a base di membrane, al fine di ridurre i consumi energetici ed abbassare i costi di produzione.

Una delle più promettenti in questo campo è costituita dal processo MOD (Manipulated Osmosis Desalination), sviluppato dal team del CORA (Centre of Osmosis Research and Application) presso la University of Surrey, e coperto da brevetto.

Tale processo è costituito da due stadi per estrarre l'acqua fresca dall'acqua salina: il primo stadio è rappresentato da un'unità a osmosi diretta (FO – Forward Osmosis), in cui l'alimentazione salina viene messa in contatto attraverso una membrana con una soluzione (*draw solution*) a pressione osmotica più elevata, causando il naturale passaggio di acqua attraverso la membrana al fine di diluire quest'ultima soluzione. La *draw solution* così diluita viene inviata al secondo stadio, caratterizzato anch'esso da un'unità a membrana (in particolare a Osmosi Inversa o a Nanofiltrazione), al fine di ottenere l'acqua pura desiderata e al contempo rigenerare la soluzione, che viene ricircolata al primo stadio. I vantaggi di tale processo sono numerosi: in primo luogo permette un ridotto consumo energetico, in quanto la *draw solution* è pulita e richiede pressioni inferiori per assicurare le stesse performance; inoltre, il minor sporcamento aumenta la durata delle membrane e riduce quindi anche i costi di esercizio ad esse associati. Nonostante gli evidenti vantaggi, il processo MOD presenta ancora due aspetti che possono essere approfonditi per migliorarne le prestazioni: in primo luogo, lo sviluppo di membrane apposite per l'Osmosi Diretta, al fine di minimizzare il fenomeno della polarizzazione interna che causa una notevole diminuzione del flusso di acqua; in secondo luogo, la scelta di una *draw solution* adatta. Tale scelta non è immediata, poiché la soluzione deve rispettare molti criteri (basso costo, zero tossicità, alta pressione osmotica a basse concentrazioni, buona solubilità in acqua), e deve inoltre garantire buone prestazioni in entrambi gli stadi.

Lo scopo di questo lavoro è stato di testare l'efficienza di rigenerazione nello stadio a Osmosi Inversa di *draw solutions* a base di soluzioni zuccherine; in particolare, si sono utilizzati glucosio e saccarosio. Tale efficienza è stata valutata in termini di flusso di permeato ottenuto, il quale è indice di produttività, e di ritenzione del soluto, che rispecchia la qualità dell'acqua prodotta. Al fine di raggiungere l'obiettivo dello studio, sono stati svolti numerosi esperimenti utilizzando un'unità a osmosi inversa da laboratorio (SpinTek Filtration, Inc.).

Per entrambe le soluzioni zuccherine sono state indagate diverse concentrazioni iniziali (pressioni osmotiche), diverse pressioni applicate (fino a 20 bar) e due tipi di membrane *flat-sheet* (in particolare, una da Osmosi Inversa e una da Nanofitrazione); per ogni condizione operativa sono stati determinati il flusso di acqua e la ritenzione dello zucchero.

I risultati sperimentali hanno mostrato che la membrana per osmosi inversa (TFC®-ULP) garantisce performance migliori in termini di permeabilità e flusso di acqua rispetto a quella da Nanofiltrazione (TFC®-SR®2) con entrambe le soluzioni zuccherine, e generalmente fornisce migliori risultati anche per quanto riguarda la ritenzione.

La *draw solution* a base di glucosio produce flussi più elevati rispetto a quella di saccarosio, ma con valori di ritenzione leggermente più bassi; in particolare, con la membrana di Nanofiltrazione, la ritenzione risulta essere troppo bassa per poter essere accettabile per applicazioni pratiche. Tuttavia, negli altri casi il valore di ritenzione risulta essere sempre maggiore del 90%. Ciò pone le basi per un approfondimento degli studi: espandere i range delle pressioni e delle concentrazioni indagate, al fine di determinarne l'effetto sui parametri di interesse in maniera più accurata; indagare altre possibili membrane, o altri zuccheri, quali fruttosio o maltosio; eseguire degli esperimenti anche riguardo allo stadio di Osmosi Diretta per valutare se le prestazioni siano soddisfacenti.

La parte finale del lavoro riguarda lo sviluppo di un modello per la simulazione dell'intero processo MOD, e la determinazione dell'influenza che alcune variabili di progetto hanno sulla pressione necessaria da applicare, e dunque sul consumo energetico. Tale modello si basa sui dati sperimentali raccolti per quanto riguarda lo stadio di osmosi inversa, sebbene essi non siano in numero sufficiente per garantirne l'accuratezza; relativamente allo stadio di osmosi diretta, in carenza di risultati sperimentali, si è fatto riferimento a dati di letteratura e assunzioni specifiche. Nonostante le forti limitazioni di tale modello, i risultati ottenuti sono verosimili, ed esso può essere usato come base di partenza per lo sviluppo della tecnica MOD una volta ottenuti dati sperimentali adeguati a supportarlo.

Desidero ringraziare la Faculty of Engineering and Physical Sciences della University of Surrey, e in particolare il Prof. Adel Sharif per avermi dato la possibilità di svolgere il mio lavoro di tesi magistrale in un ambiente così attivo e stimolante. La più sincera gratitudine va al Dr. Al-Aibi per il suo costante supporto durante lo svolgimento dell'intero lavoro.

Abstract

This research project has investigated the recovery efficiency of different sugar draw solutions, such as glucose and sucrose, using Reverse Osmosis as a regeneration step for the Manipulated Osmosis Desalination (MOD) process. The research was performed by several experiments at different sugar feed concentrations and feed pressures at room temperature in a Reverse Osmosis (RO) laboratory cell. Two commercial kinds of flat sheet membranes (TFC®-ULP and TFC®-SR®2) were used in this investigation. Results show that TFC®-ULP gives better performances in terms of permeability compared to TFC®-SR®2, and generally higher rejection values. Furthermore, it has been seen that glucose draw solutions produce a higher permeate flux than sucrose ones, at the same operating conditions (same feed applied pressure and feed solution osmotic pressure), with both membranes. On the other hand, sucrose draw solutions achieve slightly higher rejection values compared to glucose ones. Nonetheless, excluding glucose experiments with TFC®-SR®2, where rejection values are too low (between 70% and 80%), they result to be always >90%, proving that the chosen materials may be feasible enough to be used in the MOD process.

The results obtained have been used to develop a simple approximate model for the entire process, which could be used after gaining more experiments to validate it or make it more accurate.

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Introduction

The problem of drinking water shortage is one of the most alarming issues at the present time. In fact, despite the huge amount of water on the Earth's surface, only a small percentage is available to produce fresh water, and the conventional resources are starting to become more and more expensive and unavailable. Nowadays, it is estimated that about 20% of the entire world population suffers of lack of drinkable water, and approximately one third lives in water stressed countries. This percentage is thought to increase up to two thirds in the years to come, due to increases both in population and lifestyle standards, which results also in higher per capita consumption. To face this relevant and current issue, desalination of seawater and brackish water has developed as a precious alternative to provide fresh water in a reliable way, exploiting the enormous amount of salt water available on Earth. In fact, the worldwide desalination capacity is increasing year by year.

Many and different technologies are already available to obtain pure water from seawater, in both traditional thermal distillation processes which are mainly employed in the Middle East areas, and membrane-based processes, which have been developed later and are largely used in the United States and Europe. Among all, the most widely applied desalination technology is Reverse Osmosis, which has lately overtaken other processes because of the numerous advantages it offers compared to them. Nonetheless, despite being a robust technology with a lot of researches going on that aim at further improving its efficiency, it has the major disadvantage of requiring intrinsically high energy consumption; as a matter of fact, it is estimated that energy consumption, even with 100% efficiency energy recovery devices, cannot be reduced of more than 15% with respect to thermal methods.

For this reason, novel desalination technologies, especially those involving membranes, are being investigated in order to reduce the energy consumption required and subsequently lower the process overall costs. One of the most promising alternatives is the Manipulated Osmosis Desalination (MOD) process, developed at the Centre for Osmosis Research and Application (CORA) at University of Surrey. This process consists of two steps for extracting fresh water out of seawater: a first Forward Osmosis step to obtain pure water flux from the salt water feed to a specifically tailored "draw solution"; and a second Reverse Osmosis or Nanofiltration recovery step to obtain the desired product (fresh water) and re-concentrate the draw solution to be recycled back to the first step. The selection of the most suitable and appropriate draw solution is not straightforward, as many are the criteria it must obey, and it has to show good performance both in the FO and in the RO recovery steps.

The aim of this work is to investigate the regeneration efficiency of different sugar types draw solutions such as glucose and sucrose; this efficiency is examined in terms of pure water flux obtained, which determines the productivity, and solute rejection, which influences the product quality.

In order to get the aim of this study, several experiments are carried out using a SpinTek RO laboratory cell. For each sugar draw solution, different concentrations, different feed pressures applied (up to 20 bar), and different types of flat-sheet membranes (in particular, one RO and one NF membrane) are tested, and in each experiment both pure water flux and sugar rejection percentage are determined.

Chapter 1 provides a general overview on the problem of water scarcity, followed by a description of the most employed desalination technology, with particular emphasis on Reverse Osmosis.

The Manipulated Osmosis Desalination process is fully described in Chapter 2, where its principle and development are presented, followed by a direct comparison with an existing RO technology, highlighting the advantages of the former.

Chapter 3 is a detailed description of the equipment, materials and procedure that have been used to carry out the bench-scale experimental work.

The results obtained and the discussion that follows are presented in Chapter 4.

Finally, in Chapter 5 a model for the simulation of the entire MOD process is proposed, based on the experimental results that were obtained for the RO regeneration step.

The author would like to thank the Faculty of Engineering and Physical Sciences at the University of Surrey and, in particular Prof. Adel Sharif for giving me the opportunity to do my master thesis work in such a stimulating and challenging place. Deepest gratitude goes to Dr. Al-Aibi for his constant presence and help throughout the work.

Chapter 1

Desalination: general aspects and main technologies

This chapter gives a general review about desalination and its importance to face the problem of water scarcity around the world. A brief introduction is presented, followed by the description of the main traditional technologies developed over the years, with particular attention on membrane processes and Reverse Osmosis (RO).

1.1 Water scarcity

On all Earth, water covers 70% of the entire surface. Unfortunately, of this huge amount 97% is present as salt water, and 80% of the remaining is frozen as permanent snow or glaciers; thus, only 0.5% of the entire amount is available as fresh water([1]). Table 1.1 shows how water is stocked on Earth surface:

Table 1.1 *Major stocks of water on Earth*([2])

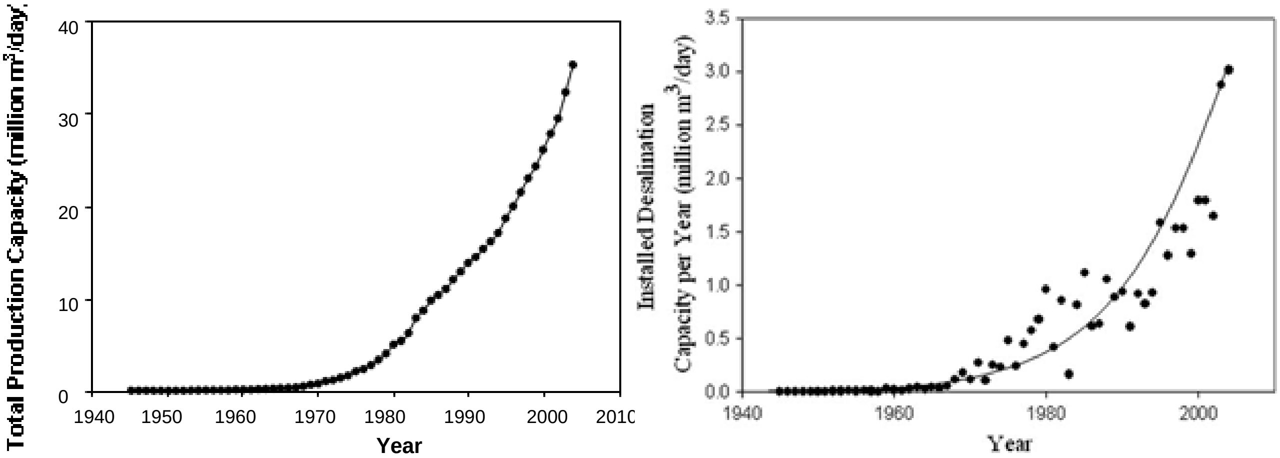
Location	Amount (10^5 km^3)	Percentage of World Water
Ocean	1338.0	96.5
Glaciers and permanent snow	24.1	1.74
Groundwater (brackish or saline)	12.9	0.94
Groundwater (fresh)	10.5	0.76
Ground ice/permafrost	0.30	0.022
Freshwater lakes	0.091	0.007
Freshwater stream channels	0.002	0.0002

The short amount of fresh water is not evenly distributed, ad is not always available where or when it is needed. At present, 40% of the world's population is suffering from serious water shortages, and by 2025 this percentage is expected to increase to more than 60%([1]).

The main cause of this phenomenon is the increasing population, which is expected to grow to up to 8,000,000,000 by 2025; this, together with changes and improvements in lifestyle, increased economic activities and reduction of natural sources results in a decrease of the average per capita water availability.

Renewable groundwater resources alone would be sufficient to cover only 33% of the current municipal domestic water consumption(3); moreover, these conventional water supplies are becoming increasingly expensive and unavailable. For these reasons, desalination, converting the almost inexhaustible supply of seawater and brackish water into fresh water, has proved to be a valid contender, and in the years to come it will probably be the only solution to provide water for many countries around the globe.

Desalination plants have been built since 1960s – 1970s, but historically costs were too high and the technologies could be used only under certain circumstances. Reduction in costs and improvements in technologies have made it possible and available for different countries, even though more developments are necessary to further lower the costs and allow poorer countries to benefit from desalination. Presently, the worldwide capacity for desalination is greater than 37,000,000 m^3/day(2), the majority of which is concentrated in the Middle East and Saudi Arabia, followed by USA, Japan and Europe (mainly Spain and Italy). Recently, countries in North Africa (Algeria, Tunisia) and South America (Chile) as well as Australia have been implementing large desalination plants(4).



(a) **(b)**

Figure 1.1 *a) Total worldwide desalination capacity since 1945, including plants that are operating, built but not operating, and built but shut down; b) New installed desalination capacity each year worldwide from 1945*

These plants provide water for municipal, industrial and agricultural applications, among others.

1.2 Main desalination technologies

Water can be classified according to its TDS (Total Dissolved Solids): seawater has an average TDS of 34,000 ppm, but ranges between 33,000 - 37,000 ppm depending on the location, reaching up to 50,000 ppm in the Arabian Gulf([1,2]); brackish water has a TDS between 1000-30,000 ppm. Fresh water has been defined to have less than 1000 ppm TDS; above this value, properties like taste, odour and colour may be adversely affected. Despite this, different countries have adopted different standard limits: the World Health Organization (WHO) has established a limit of 1000 ppm for drinkable water, while the Environmental Protection Agency (EPA) has fixed a maximum value of 500 ppm([4]).
Desalination is the separation of salted water into two streams: freshwater and a concentrated stream also known as brine. In order to do so, some form of energy must be provided, and different technologies have been developed over the years, but they share some common features:

- Feed-water intake: desalination facilities require a reliable supply of feed-water. Seawater intakes are divided into two major categories: surface and subsurface intakes. The former, also called open intakes, are located above the seafloor; water is taken directly from the sea or ocean, through the use of submerged devices. Usually, large desalination plants employ this type of water intakes, with the addition of screens to limit the amount of marine organisms entrained with water.
  Subsurface intakes are instead located below the ocean floor, thereby using sand and sediments as natural filters. Better quality water is obtained, requiring less intensive pre-treatment, especially for membrane-based desalination systems([2]).
- Pre-treatment: this is a very important step for all desalination processes. It is necessary in order to preserve the desalination facility’s performance, and is particularly critical for membrane-based processes, whose successful operation depends on its efficiency. As stated above, the quality of the feed-water affects the extent of pre-treatment needed. The principal aim of this step is that to avoid scaling of mineral salts, especially calcium, which tend to precipitate during operation because of progressive elimination of water; in order to do that, chemical anti-scalant are employed for pH control.
  In particular, for membrane processes pre-treatment is fundamental to prevent membrane fouling, and thus enhance their lifetime. Conventional methods such as coagulation and sedimentation are still widely used, though recently membrane pre-treatment (like Micro and Ultrafiltration) has proved to be much more effective([2]).

- Desalination processes: the actual desalination process is represented by the removal of solutes from the feed-water to obtain the desired product water. Many and different technologies have been developed to accomplish this objective, and the most commonly known will be briefly described in the following pages.
- Post-treatment: water coming out from the desalination process has very low salt content and hardness, thus it must be re-mineralized in order to prevent corrosion of pipes, which could reduce the lifetime of the infrastructure and also introduce metals into drinking water. This is a bigger issue for thermal processes, where temperatures are higher, while membrane processes work at ambient temperature. For this purpose, lime and limestone are added to product water([2,5]). In addition, water must be disinfected in order to protect consumers from pollution that may be introduced: the most commonly diffused disinfection method is chlorine treatment([5]).

  Another important issue regarding the post-treatment step is boron removal: it has been found to be dangerous for human health, causing birth defects and fetal abnormalities, as well as harmful to crops when water is used for irrigation purposes. Therefore, the WHO has fixed a limit for boron content in water of 0.5 mg/L. In seawater its concentration is of 4.5-7 mg/L, present as boric acid and thereby dissociated; if a RO process is employed, its rejection is favoured by high pH values([5]).
- Concentrate management: at the end of the process, the concentrated brine must be disposed of; this represents an important and delicate step because of its environmental impacts. There are several options for brine disposal, but the less expensive and most commonly used is discharge into the open sea. The major problems related to this procedure are: the higher brine density compared to that of seawater, which causes it to sink towards the seabed; its higher temperature if it comes from thermal processes; the high osmotic stress to which marine organisms are exposed.

  In order to reduce the environmental impacts, measures can be adopted on the discharge system, such as multiple diffusers placed along the end of the outfall which increase the volume of seawater in contact with the brine, therefore enhancing dispersion([5]).

The main traditional and diffused desalination processes can be divided into two big categories: thermal and membrane processes. A brief discussion of the various technologies of both the aforementioned categories is hereafter presented, followed by a comparison between them all.

1.2.1 Thermal processes

They are also called distillation or phase-change processes. These processes are very energy intensive, as they require thermal energy in order to evaporate water and subsequently separate it from the solution. The energy required is expressed in terms of Product Ratio (PR = units of water produced per units of steam consumed). Despite being the first technologies to be developed, they achieve high salt rejection and are still the preferred choice in the Middle East, where seas are very hot and saline, and the energy cost is low due to the presence of fossil fuels. Besides, this technology is well suited for coupling with power plants for the co-generation of steam and electricity. The most employed thermal processes are presented in this paragraph.

1.2.1.1 Multi-Stage Flash (MSF)

This is probably the most robust desalination technology, and is capable of large production capacities. In this operation, seawater passes through the different stages (counter-current with respect to the evaporating solution) for a pre-heating, and then into a final heat exchanger where its temperature is risen to saturation. Then, it is fed into the first vessel which is at lower pressure thus causing water to flash out of the solution. The water vapour produced is condensed by the contact with the feed-water pipe (energy recovery) and collected. A typical process has 14-20 stages, and the maximum PR is equal to 13, even though in reality values of 8-10 are achieved([6,7]). A scheme of the process is presented in Fig. 1.2.

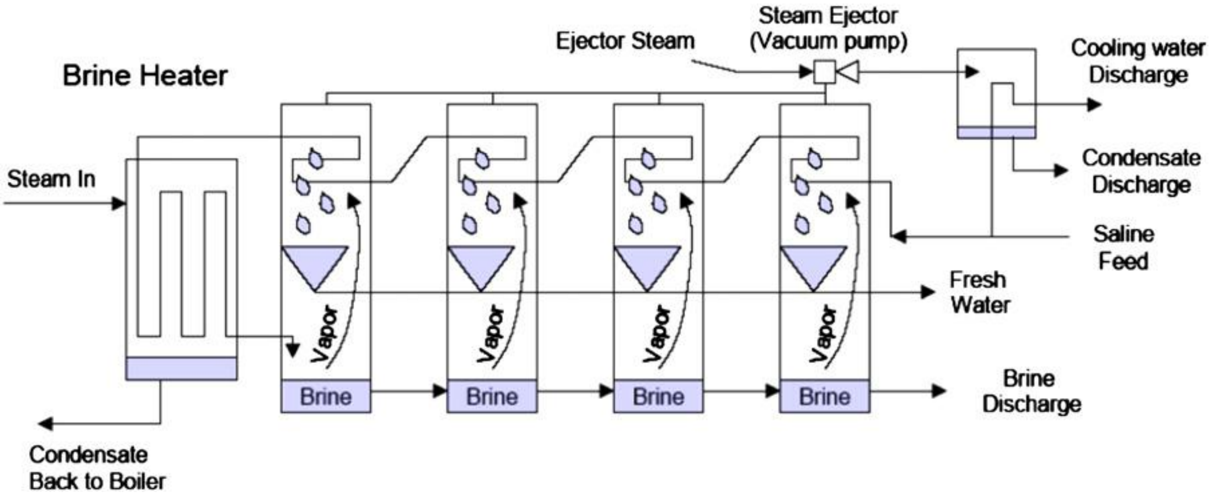


Figure 1.2 *Principle of Multi-Stage Flash desalination (MSF)*([8])

1.2.1.2 Multiple Effect Distillation (MED)

This process involves spraying or distribution of feed-water in a thin film onto the evaporator surface of different chambers (effects) in order to promote evaporation, after it has been preheated. The first effect requires steam to cause water to evaporate, but then the vapor hereby produced is used to provide heat for evaporation in the second effect, which is at lower temperature and pressure, while condensing(8). Thus, steam is needed in the first effect only. The number of effects is between 8 and 16, and the vapor produced in the last effect is condensed in a final condenser. MED has a higher PR (12-14) and thermal performance with lower capital costs and power requirements with respect to the previous MSF(7). Fig. 1.3 shows a scheme of MED process.

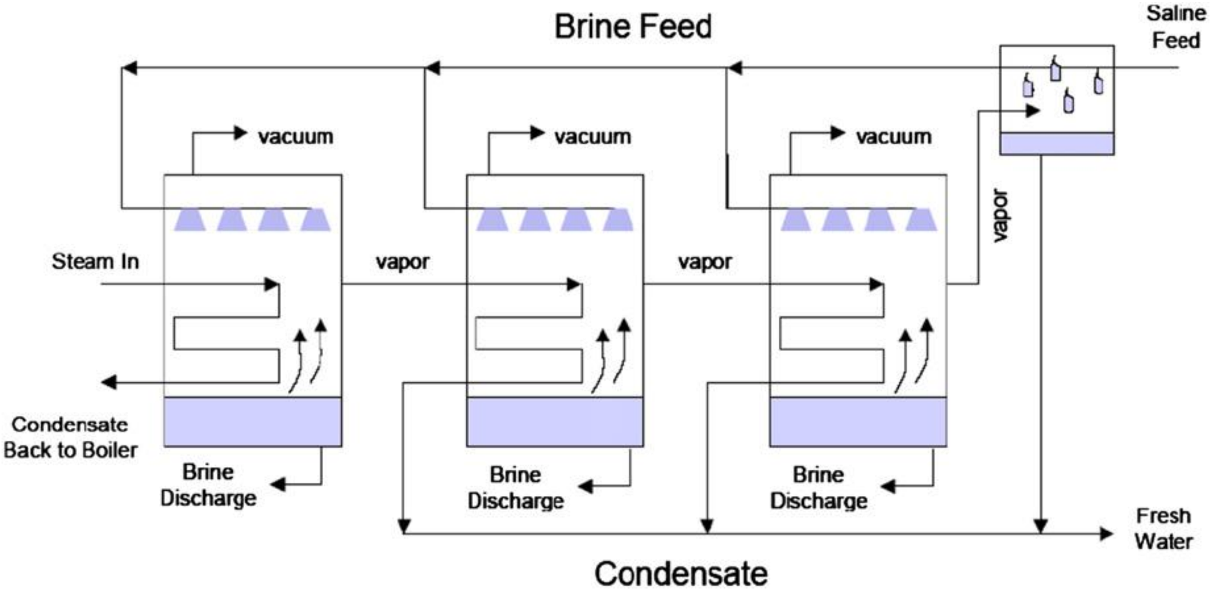


Figure 1.3 *Principle of Multiple Effect Desalination (MED)*(8)

1.2.1.3 Vapor Compression (VC)

Vapor Compression is different from the previous thermal processes, which involve heating and then cooling: in fact, VC compresses the vapour produced with the evaporation in order to condense it, and the temperature rise caused by the compression is used to heat the feed-water(7). These plants are meant for low capacities (typically up to about 3000 m^3/day), and when steam and cooling water are not easily available(7,8). The principle of VC is schematized in Fig. 1.4.

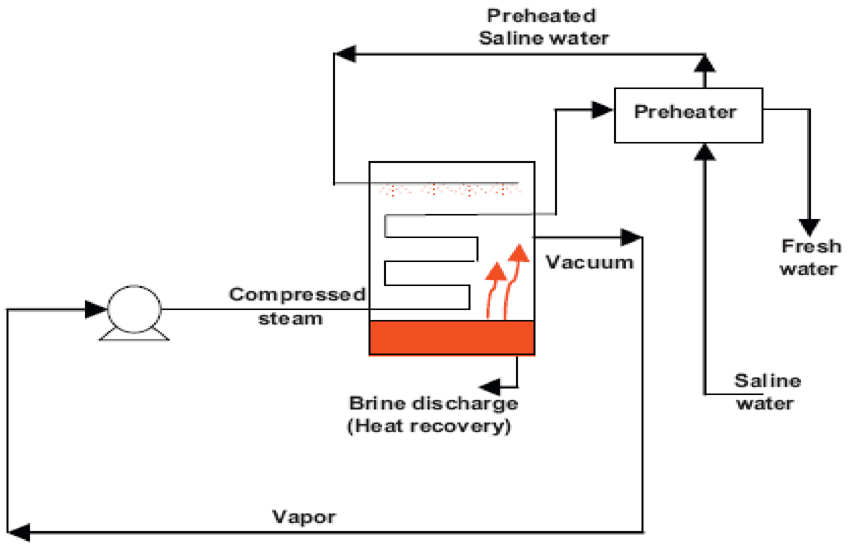


Figure 1.4 *Single stage mechanical vapor compression process*(8)

1.2.2 Membrane processes

Membrane processes do not involve a phase change, but use a membrane as a physical barrier between seawater and fresh water, so they require much less energy compared to thermal processes. They operate at room temperature, thus also the effect of corrosion is much reduced, and metal alloys can be substituted with polymeric materials(6).

These processes are power consuming, so the energy requirement is expressed as kWh/m^3 of water produced. Commercially available membrane technologies for desalination are represented by Reverse Osmosis (RO) and Electrodialysis (ED) or Electrodialysis Reversal (EDR), thus a brief description of them is presented hereafter.

1.2.2.1 Electrodialysis (ED)

This is an electrically-driven process in which, under the application of an electrical potential, ions are induced to move towards the electrodes, passing through ion-selective membranes: cations (Na^+) move towards the cathode, while anions (Cl^-) are attracted by the anode, therefore leaving unsalted water in the middle of the selective membranes(7). A simple representation of the process is illustrated in Fig. 1.5.

Electrodialysis Reversal (EDR) is a variation of this process in which polarity is periodically reversed in order to reduce fouling.

These processes are only used to desalinate brackish water (up to 7500 mg/L), otherwise the cost becomes too high(2).

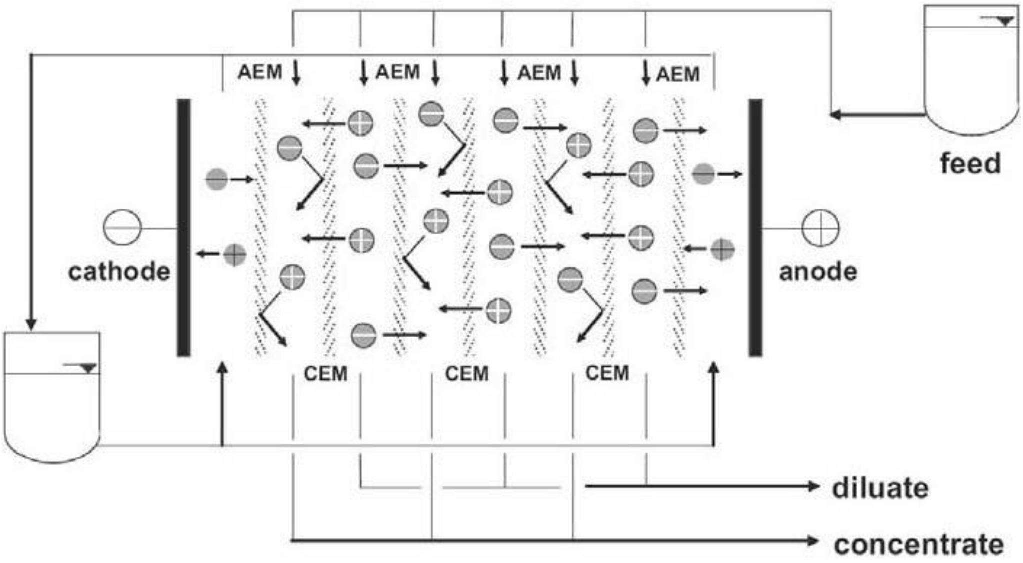


Figure 1.5 *Principle of Electrodialysis (ED) process*(^{5})

1.2.2.2 Reverse Osmosis (RO)

This is a pressure-driven separation process in which, under the application of a pressure higher than the osmotic pressure of the solution, water flows through a semi-permeable membrane, leaving rejected salts behind. Pressurizing the saline water accounts for most of the energy consumed by RO, which is of 3-5 kWh/m^{3} for plants with energy recovery devices. The operating pressure for seawater systems ranges between 50-80 bar (the osmotic pressure of seawater with 35,000 TDS is about 25 bar)(^{8}).

Reverse Osmosis has widely spread all over the world, due to its numerous advantages compared to thermal processes; nonetheless it has many limitations that brought to the concept and development of the Manipulated Osmosis Desalination (MOD) process, which will be described in Chapter 2.

For better understanding the advantages brought by MOD, traditional Reverse Osmosis process is fully described in §1.3

1.2.3 Comparison between thermal and membrane processes

Choosing the most suitable process for desalination is of crucial importance, as it represents a fundamental source of fresh water, but is not inexpensive.

The selection of the most appropriate technology depends on several parameters, the most relevant of which is the quality of feed-water, in particular its salinity: for distillation processes, salt content has very little effect on the overall energy consumption, while membrane processes costs are directly and strongly related to it(^{2,7}); for this reason, thermal processes are usually employed for high salinity feed-water, RO is used over a wide range of salinity from brackish water to seawater, while ED is suitable only for low salinities (brackish water)(7).

Another important parameter to be considered is plant size, which is normally dictated by the entity of the water demand. MSF, being the most robust and one of the oldest desalination technologies, can be used for very large scale applications (10-60,000 m^3/day); MED capacity reaches up to 20,000 m^3/day, while VC is employed only for small scale applications. Membrane processes, due to their modularity, can be applied in a wide range of sizes, from very small to very large(7).

Table 1.2 sums up the characteristics of the predominant seawater desalination processes:

Table 1.2 *Comparison of Predominant Seawater Desalination Processes*(2)

	Seawater RO	MSF	MED (with TVC)	MVC
Operating temperature (°C)	<45	<120	<70	<70
Pre-treatment requirement	High	Low	Low	Very low
Main energy form	Mechanical (electrical) energy	Steam (heat)	Steam (heat and pressure)	Mechanical (electrical) energy
Heat consumption (kJ/kg)	NA	250-330	145-390	NA
Electrical energy use (kWh/m^3)	2.5-7	3-5	1.5-2.5	8-15
Current, typical single train capacity (m^3/d)	<20,000	<76,000	<36,000	<3,000
Product water quality (TDS mg/L)	200-500	< 10	< 10	< 10
Typical water recovery	35-50%	35-45%	35-45%	23-41%
Reliability	Moderate	Very high	Very high	High

In conclusion, thermal processes are more energy intensive compared to membrane processes, even though they are capable of using low-grade heat(2); nonetheless they deal more easily with high saline and hot water, like that present in the Middle East. For this reason, together with the availability of energy at low cost due to the presence of fossil fuels, these technologies (MSF among all) are the preferred choice in these regions, which account for almost 50% of the global desalination capacity(5).

On the other hand, RO is the most widely used technology in the area around the Mediterranean Sea and in the US, surpassing thermal processes in new plants installations (75% of new production capacity)(4).

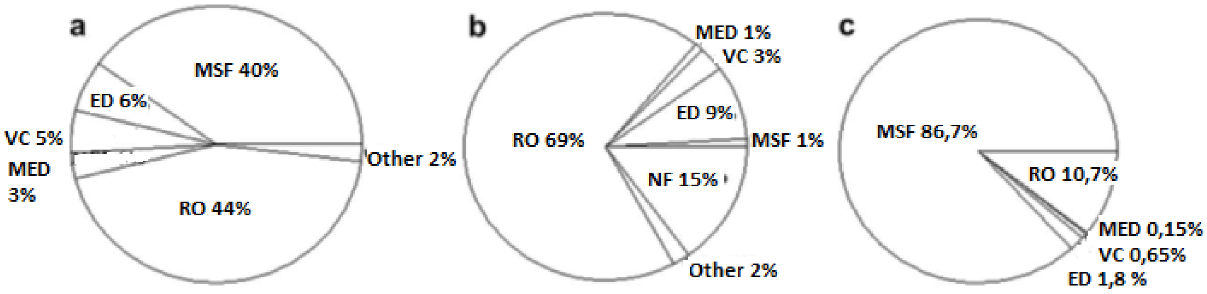


Figure 1.6 *Distribution of desalination production capacity by process technology for: a) the world; b) the United States; and c) the Middle East*

1.2.4 New processes development and investigation

Even though the traditional processes described in the previous paragraphs are robust and well operated, there is still space for further improvements, regarding simplification and optimization of plant design, as well as construction materials or new membranes, in order to enhance efficiency and reliability, therefore reducing investment and operative costs(6).

Recently, several different approaches have been investigated in order to reduce the energy requirements for desalination. Some of them are briefly described in this paragraph.

1.2.4.1 Renewable Energy Sources (RES) processes

Numerous RES-desalination combinations have been investigated and tested by researches on innovative desalination processes. Their distribution is shown in Fig. 1.7. One that is already commercially available is Photovoltaic (PV) – RO: electricity generated by PV is clean, renewable, quiet and maintenance-free. This is considered one of the most promising desalination technologies in producing fresh water, especially for small systems located in remote areas(8).

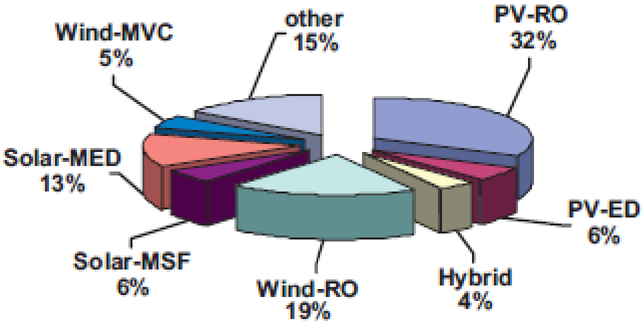


Figure 1.7 *Distribution of renewable energy powered desalination technologies*(8)

1.2.4.2 Dewvaporation

This technology is based on the fact that air can transport important quantities of water vapor. A stream of air, which is partially heated by an external source, is humidified by direct contact with a falling film of saline water. Afterwards, the humid stream is cooled in order to cause the condensation of water vapor, which is then collected as product water(2).

1.2.4.3 Freeze desalination

This method involves the passage of water from the liquid to the solid phase. As ice crystals are formed, salt is excluded from their structure and can then be washed away. This technique can lead to potential energy efficiency improvements, but has also some difficulties, such as effective washing of crystals without melting them and thus re-dissolving the salts, and the refrigeration equipment required(2).

1.2.4.4 Forward Osmosis

This is a membrane-based technique that employs the use of a "draw solution" of osmotic pressure higher than that of seawater in order to drive water flux through a semi-permeable membrane. This method has proved to be very promising, and it is upon this that the Manipulated Osmosis Desalination process is based. Therefore, it will be thoroughly discussed in Chapter 2.

1.3 Reverse Osmosis

The technology of RO has developed in the past 40 years, reaching up to 44% of the global desalination capacity and 80% of the total number of plants installed worldwide(4). At present, it is the leading desalination technology, especially in Europe and the United States, gaining a much wider acceptance compared to thermal alternatives because of its lower energy consumption.

The principle upon which the process is based is illustrated in Fig. 1.8.

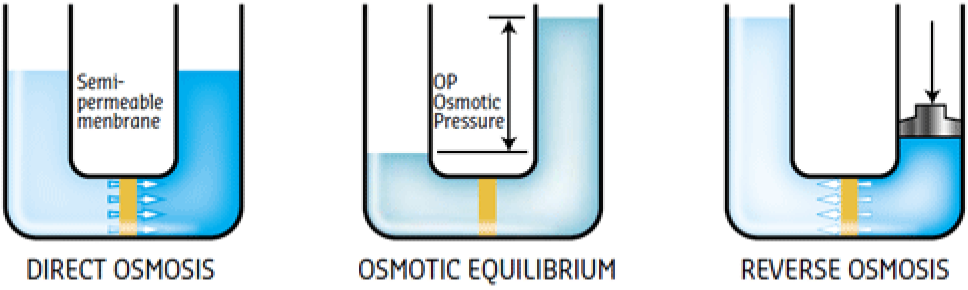


Figure 1.8 *Reverse Osmosis operating principle*

The key factor is a property of membranes called “semi-permeability”: they are in fact very permeable for water and much less for dissolved salts. When two solutions at different concentrations are separated by a semi-permeable membrane, water will naturally flow (permeate) from the dilute to the more concentrated side; this process is called Direct or Forward Osmosis. When osmotic equilibrium is reached, the flow stops, and the height difference between the two sides corresponds to the osmotic pressure. If a hydrostatic pressure higher than this value is applied on the more concentrated side, a chemical potential difference is created across the membrane that drives water flux against the natural direction of osmosis (from concentrate to dilute), while salts are retained by the semi-permeable membrane([4,5]). This process is known as reverse osmosis, and is thus a pressure-driven process, whose driving force is the difference between the trans-membrane pressure and the trans-membrane osmotic pressure ($\Delta P - \Delta\pi$).

Osmotic pressure is thermodynamically defined as:

$$\pi = -\frac{RT}{V_w}\ln a_w \ , \tag{1.1}$$

where T and V_w are temperature and solvent molar volume respectively, R is the ideal gas constant, and a_w is the activity of water([5]). For ideal (dilute) solutions, the activity coefficient is almost 1, so a_w can be substituted with the molar fraction of water x_w, leading finally to the Van’t Hoff equation:

$$\pi = \frac{n_s}{V}RT = CRT. \tag{1.2}$$

In eq. (1.2) n_s are the moles of solute, and C is therefore the solute concentration. To take into account the non-ideality of most solutions and ion dissociation, equation (1.2) becomes:

$$\pi = i\Phi CRT \ , \tag{1.3}$$

where i is the dissociation parameter, representing the number of ions per mole of solute produced by dissociation, and Φ is a correction factor accounting for non-ideality([5]).

The osmotic pressure of seawater is approximately 25-27 bar, but the hydraulic pressure that needs to be applied in industrial systems ranges between 50-80 bar, due to practical limitations that will be discussed later in this paragraph.

When speaking of membrane processes, in particular about RO, there are two important factors to measure the process performance. These are water recovery and salt rejection respectively.

They are defined as follows:

$$R = \frac{F_p}{F_f} \tag{1.4}$$

represents water recovery, where, with respect to Fig. 1.9, F_p and F_f are the permeate and feed volumetric flow-rates respectively;

$$R_s = \left(1 - \frac{c_p}{c_f}\right) \cdot 100\% \tag{1.5}$$

is salt rejection, where c_p and c_f are the solute concentration in the permeate and in the feed.

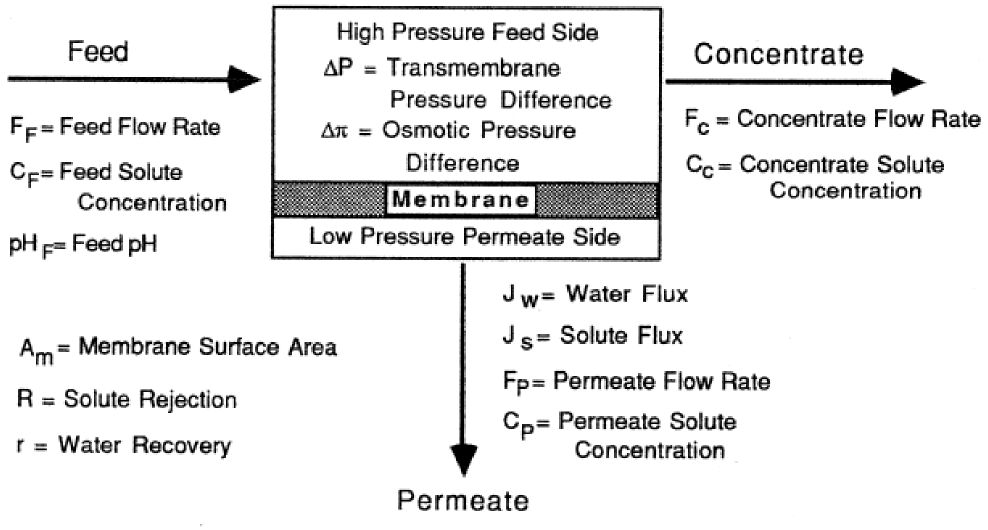


Figure 1.9 *Schematic representation of Reverse Osmosis*

1.3.1 Membranes for Reverse Osmosis

As already mentioned above, RO is a pressure-driven membrane process. RO membranes are capable of rejecting the smallest contaminants, like monovalent ions, with respect to other pressure-driven membranes used to remove materials of increasing size, such as Micro, Ultra and Nanofiltration(^{4}). These processes are briefly discussed and compared.

- **Microfiltration (MF)** is used to reduce turbidity and remove suspended particles, algae and bacteria. The separation mechanism is that of particle size-based sieving at slightly low applied pressures; the pore size of the membrane ranges between 0.03-10 µm., with a molecular weight cutoff (MWCO: molecular weight of the molecule that is 90% retained by the membrane) greater than 100,000 Daltons([2,4]).
- **Ultrafiltration (UF)** allows the removal of contaminants affecting colour, high-weight organic compounds and viruses. The mechanism is, like in MF, pressure-driven particle size sieving, with pore size ranging between 0.002-0.01 µm and MWCO of 2000-100,000 Da([2]).
- **Nanofiltration (NF)** membranes are employed for water softening and removal of organic contaminants. Here the particle size-based sieving is combined with solution-diffusion([2]). The membrane pores are smaller than 0.001 µm, and the characteristic MWCO ranges between 250-2000 Da ([4]).
- **Reverse Osmosis (RO)** membranes are capable of rejecting monovalent ions as well as larger organic contaminants, while allowing small uncharged particles to pass through. The separation mechanism is based on solution-diffusion, where water dissolves into the non-porous membrane and diffuses through it, rejecting the majority of the salts.

The properties of pressure-driven membranes are summarized in table 1.3.

Table 1.3 *Pressure-driven membrane separation processes and their properties*

Separation process	**Membrane type**	**Hydrostatic pressure difference**	**Method of separation**	**Flux range l/(m^{2}h bar)**
Microfiltration	Symmetric microporous	(0.1-2 bar)	Sieving mechanism	>50
Ultrafiltration	Asymmetric microporous	(1-5 bar)	Sieving mechanism	10-50
Nanofiltration	Asymmetric microporous	(5-20 bar)	Sieving and solution diffusion	1.4-12
Reverse Osmosis	Asymmetric non-porous	(10-100)	Solution diffusion mechanism	0.005-1.4

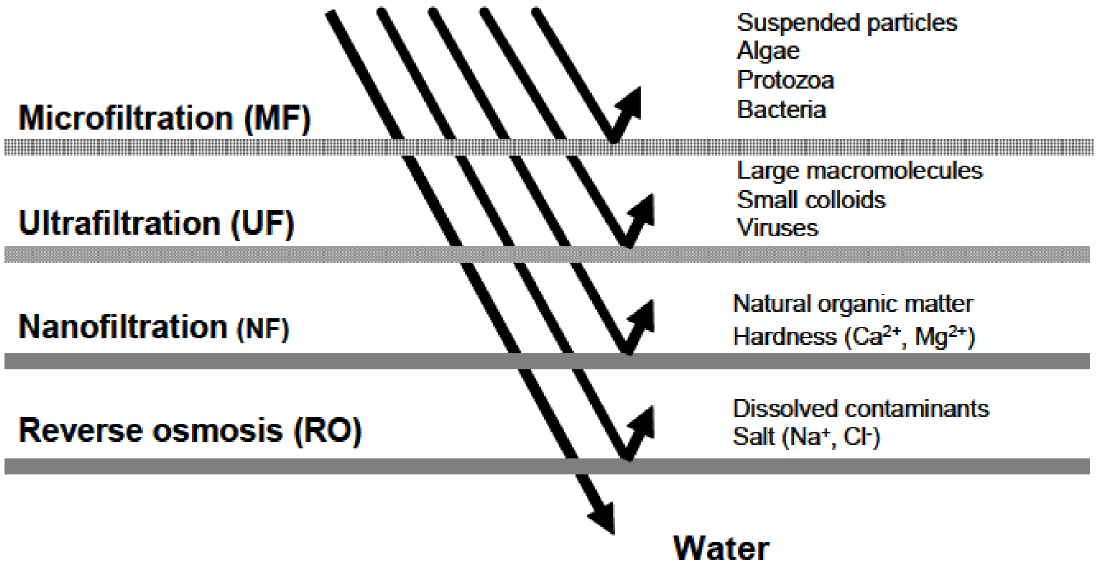


Figure 1.10 *Substances and contaminants removed by pressure-drive membrane processes*(2)

The important features that RO membranes have to guarantee are high water flux and high selectivity (resulting in high recovery and salt rejection). In order to allow high water flux, membranes must be thin, but at the same time they need to be mechanically stable in order to resist to the high pressures applied in the process. Therefore asymmetric membranes are employed for RO, made of a thin dense active-layer which provides selectivity and a porous support to give stability to pressure(5).

At the early stages, the first membranes to be developed were made of Cellulose Acetate (CA); they were produced by phase inversion. The main problem was that this material is very susceptible to hydrolysis, and thus the process had to be operated under strict pH control. CA membranes have therefore been substituted by Thin-Film Composite (TFC) membranes, which are currently still the most employed commercial membranes. They consist of a structural support made of polyestere (120-150 µm), followed by 40 µm of polysulfone microporous support (whose function is that of giving resistance to high pressures), and a 0.2 µm ultra-thin active layer made of polyamide(9). Polysulfone has been found to be very suitable as a support layer as it is not prone to compaction and allows the use of interfacial polymerization for membrane realization, as it resists to alkaline conditions. TFC membranes are more stable and no subject to hydrolysis, but at the same time are more sensitive to fouling and less hydrophilic(5,10). Their fabrication and performance have greatly improved over the years, achieving very high permeability and rejection, even though evidence suggests that permeability cannot be further improved without affecting selectivity(11); in addition, fouling remains a severe problem, and current researches aim at finding more effective and hydrophilic membranes in order to improve the process efficiency and enhance the lifetime, thus lowering the overall costs(9,12).

One of the most promising and attractive emerging alternative to polymeric materials is given by nano-structured membranes. The most studied are zeolite, carbon nano-tube and biomimetic membranes.

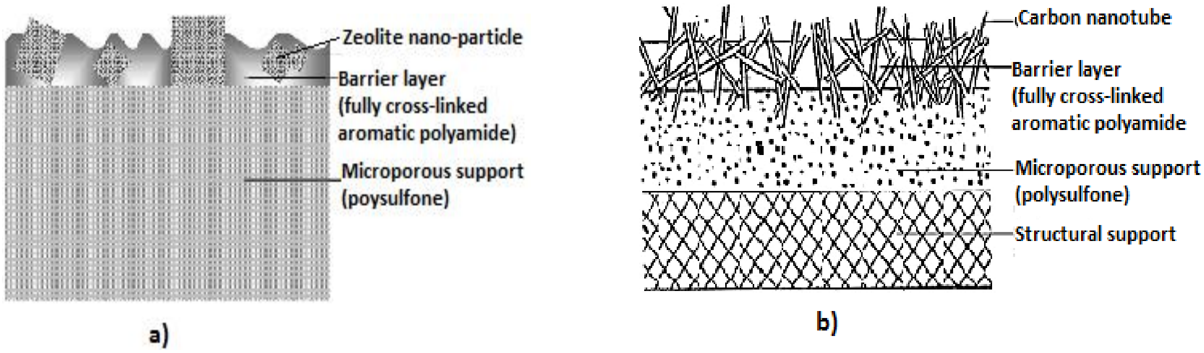


Figure 1.11 *Examples of novel nano-structured membranes: zeolite (a) and nano-tube (b)*([9])

Various scientists believe in nano-technology for RO membranes; nevertheless researches and developments are still in the initial stages, and many limitations have yet to be overcome, among all the cost of nano-materials and difficulties in scale-up for commercial industrial use([9]). Therefore they are still not employed for industrial applications, and TFC membranes are still widely leading the market.

Industrially, membranes are organized in modules as, if materials are of importance with regards to flux and selectivity, membrane packing is also an important characteristic to ensure the process feasibility([10]). The important features of a module are: high packing (area to volume ratio); mechanical stability; low pressure drops across the module as well as low concentration polarization and fouling (see §1.3.3); low costs and easy operation and replacement([10]).
The most commonly diffused module configurations are hollow fiber and spiral wound.

- **Hollow-fibre** was initially employed by most industrial plants because it offers high area to volume ratio. A large number of hollow fibre membranes, of outer diameter up to 200 μm, are placed in a pressure vessel, and water is forced to flux from outside into the fibres bore, from which the permeate is collected([5,10]). This configuration offers high packing density, thus providing high permeate productions per module, but is very prone to fouling and therefore has been substituted by spiral wound modules.

- **Spiral wound** is definitely the most widely employed configuration despite its lower packing density, because it offers a good compromise between permeability, fouling, area to volume ratio and ease of operation(^{5}). A spiral wound module is illustrated in Fig. 1.12.

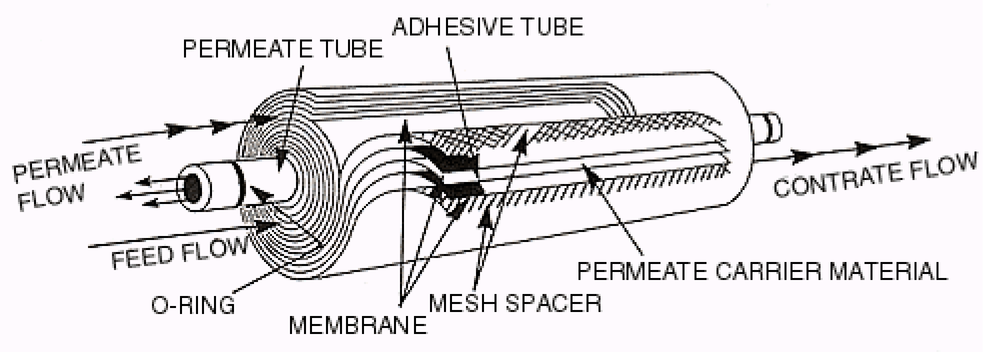


Figure 1.12 *A spiral wound module*

It is made of several flat sheet membranes rolled around a central perforated permeate collector, therefore alternate feed and permeate channels are created. The permeate is collected in the central tube, while the retentate leaves the module on the opposite side. Spacers are placed in between the flat sheets in order to enhance turbulence, that limits concentration polarization as well as fouling; at the same time they cause an increase in pressure drop across the module, so dimensions must be optimized(^{5}).

Current industrial modules measure 8”, and 4 to 8 modules are put in series inside one pressure vessel. Researches are aiming at increasing the dimensions in order to enlarge the production capacity(^{5}).

1.3.1.1 Mass transfer across membranes: the Solution-Diffusion Model

Many models have been developed to describe mass transfer across RO membranes, but the most commonly used to predict water and solute fluxes is the Solution-Diffusion Model (SDM). It is based on the following basic assumptions:

- The active layer of the membrane is dense (non-porous), and permeating species dissolve in the membrane phase;
- There is always chemical equilibrium at the interface between membrane and permeate/feed side;
- Salt and water fluxes are independent of each other;
- Water concentration and diffusion are constant along the membrane(^{5}).

The fundamental statement of SDM is that flux is due to a chemical potential gradient(^{13}). With regard to Reverse Osmosis, this results in the combination of concentration and pressure gradients. However, according to the assumption of constant concentration along the membrane, water flux is caused only by the pressure difference; for the solute on the contrary, at low concentrations, the pressure term is negligible and the flux is determined by a concentration gradient only(^{5}). The equations for water and solute flux are the following:

$$J_w = A(\Delta P - \Delta\pi)\,, \tag{1.6}$$

$$J_s = B(c_f - c_p)\quad . \tag{1.7}$$

ΔP and $\Delta\pi$ are the trans-membrane hydraulic and osmotic pressure respectively, while c_f and c_p are the solute concentrations in the feed and in the permeate. A and B are water and solute permeability coefficients, and are determined experimentally(^{5}). They are defined as follows:

$$A = \frac{D_w c_{w,m} V_w}{RTl}\ , \tag{1.8}$$

$$B = \frac{D_s}{l}\ . \tag{1.9}$$

D_w and D_s are water and solute diffusivity coefficients, $c_{w,m}$ represents water concentration on the membrane surface, V_w is water molar volume and l is finally the membrane thickness(^{5,13,14}).

The physical meaning of the Solution-Diffusion model is that transport depends not only on the kinetic properties (diffusivity), but also on equilibrium (solubility)(^{15}).

The model presents some important limitations, like the fact that it is not capable of describing high concentrated systems, as it does not consider interactions between different species(^{5}). Other proposed models are, for example:

- The Pore-Flow model;
- Coupled Models, such as the Analytical Solution-Diffusion Pore-Flow Model (ASDPF)(^{16}).

Although its limitations, however, SDM is still widely used because of its simplicity and ability to predict mass transfer to some extent of success(^{16}).

1.3.2 Reverse Osmosis plant design

In industrial applications, a typical RO plant is made of the following components:

- Water intake
- Pre-treatment
- Pumping system
- RO membrane unit
- Post-treatment
- Energy recovery(5).

As mentioned in §1.2, a proper pre-treatment is essential, as RO membranes are very sensitive to pH, oxidizers, a wide range of organic compounds, algae, bacteria, particulate deposition and fouling(8). The way pre-treatment is managed has a significant impact on energy consumption and overall costs.

High pressure centrifugal stainless steel pumps are employed to raise the feed water pressure to an appropriate value (60-80 bar depending on water TDS)(6).

With regard to the membrane unit, RO plants usually employ more than one single step: they can be configured either in passes or stages. Usually, seawater desalination is organized in passes, with the permeate of the first pass being the feed for the second pass, while brackish water plants are structured in stages, where it is the concentrate of the first stage to be fed to the second. The reason of this distinction is mainly the lower salt content of brackish water, which allows for higher recoveries(4). The two different configurations are represented in Figure 1.13.

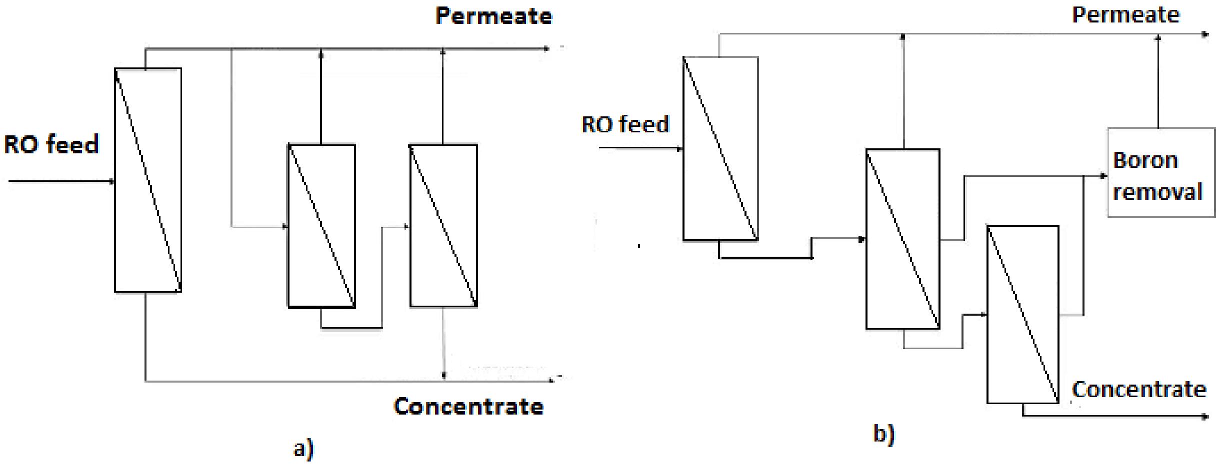


Figure 1.13 *RO plant configurations: passes (a) and stages (b)*

Energy recovery is a key element to optimize and improve the energy efficiency of RO plants: as a matter of fact, energy is one of the main cost components for this desalination technology. As the concentrated brine exits the membrane module still at a high pressure, it contains a lot of the energy previously supplied by the pumping system, and discharging it the way it is would be a tremendous waste([8]). Various technologies have been developed to achieve this objective, but they all apply the principle of exchanging energy between brine and feed water, lowering the energy consumption from 6-8 kWh/m^3 to 4-5 kWh/m^3([6,8]).
These technologies are:

- **Energy recovery turbines (ERT)**, also called Pelton wheels turbines. They convert the pressure energy of the concentrate stream to mechanical energy which is used to aid the pumping system in pressurizing the feed water.
- **Turbochargers**, which are the most applied turbines. They are similar to the previous ones, as they also convert pressure energy in mechanical energy, but here a first pump is employed to raise the pressure to a certain intermediate value, followed by a separated coupled turbine-pump system which completes the pressurization step([5]).
  Pelton turbines and turbochargers are schematized in Fig. 1.14.

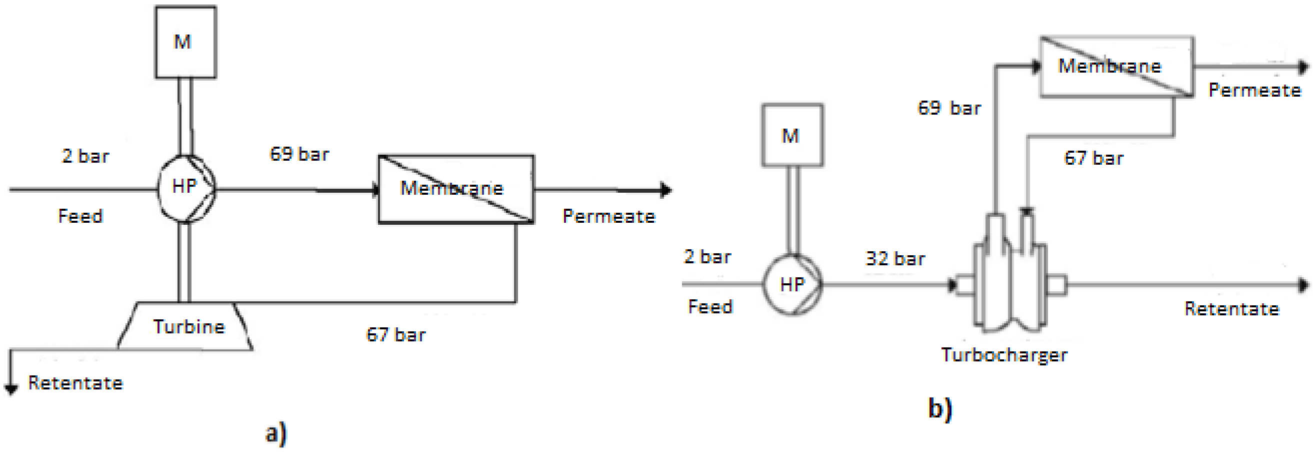


Figure 1.14 *Turbine energy recover systems: Pelton turbine (a) and turbocharger (b)*([5])

- **Pressure exchangers (PX)**, which are isobaric devices that, by the mean of a ceramic rotor, allow direct contact between feed water and the concentrate([8]): part of the feed water enters a duct, subsequently a valve is opened and the concentrate is led into the duct as well, directly transferring its pressure. High pressure feed water is then mixed with that exiting the pumping system and then fed to the membrane module([5]).
  The representation of a RO system employing a pressure exchanger is shown in Fig. 1.15.

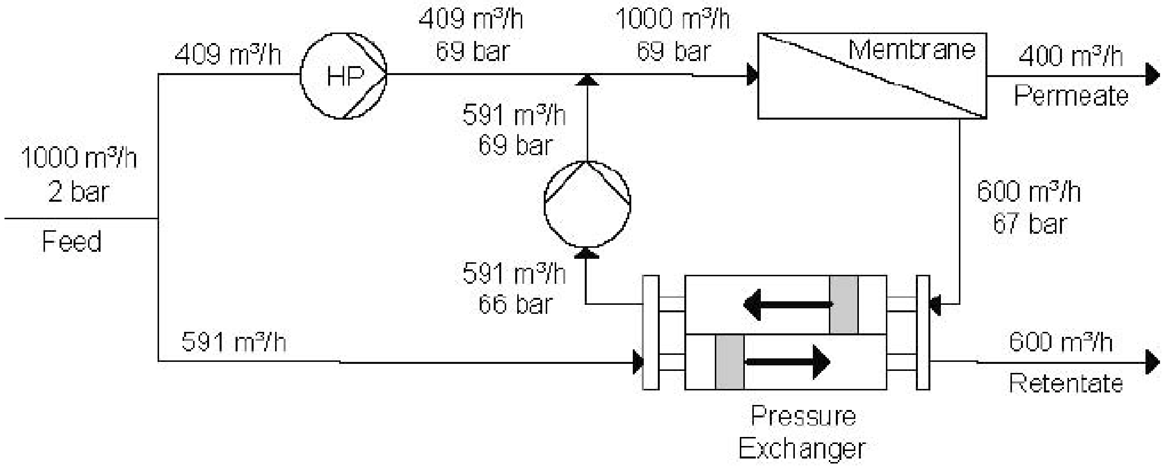


Figure 1.15 *RO process scheme with pressure exchanger*(5)

Pressure exchangers are able to achieve higher recovery efficiency (96% - 98%) compared to turbine systems, which reach values up to 90%(5). Nonetheless, the latter are the mostly used systems, because pressure exchangers have two major disadvantages: they require an additional pumping system after the energy recovery due to pressure drops, and they increase the feed water salinity because of directly putting it in contact with the brine, which results in a higher osmotic pressure and the subsequent need to provide up to 2 additional bar of pressure(5).

The importance of energy recovery in the reduction of electricity consumption can be evinced from Fig. 1.16

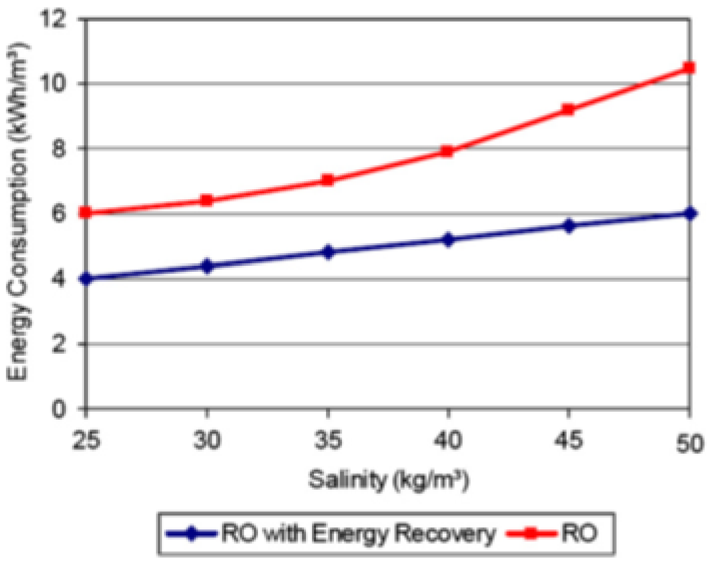


Figure 1.16 *Specific electricity consumption of RO plants with and without energy recovery systems as a function of raw water salinity*(8)

1.3.3 Limitations and problems

In the past 40 years, the amount of energy required for the operation of RO plants has dramatically declined, thanks to great improvement in the efficiency of energy recovery devices and pumping systems, along with the development of high-permeability membranes. Nonetheless, this desalination technology has several limitations that lead to an energy consumption much higher than the minimum theoretical value, calculated for a reversible thermodynamic process (1.06 kWh/m^3 for a 35,000 ppm TDS feed-water and 50% recovery)([11]).

In addition to the fact that the process is not reversible, it has already been stated that pressures much higher than the osmotic pressure of seawater are needed in order to obtain satisfactory water fluxes. This is due to two main phenomena: fouling and concentration polarization.

Fouling is due to convective and diffusive transport of colloidal and particulate matter. It has been stated in the previous paragraphs that a proper pre-treatment is fundamental in order to avoid, or limit, this phenomenon and preserve membranes as long as possible, therefore current researches are developing with regard to the pre-treatment stage. In addition, the production of more fouling-resistant and of fouling-release membranes (that are not able to avoid adhesion of foulants, but have a low surface tension active layer so that they can be easily washed away) is being investigated ([5,11]). Nonetheless, energy savings obtained by the development of these membranes are likely to be very small([11]).

1.3.3.1Concentration Polarization

The phenomenon of concentration polarization deserves particular attention. It takes place in all membrane processes, and is due to the fact that that while water penetrates the membrane, the solute accumulates on the membrane surface, resulting in a build-up layer. This leads to several negative impacts on the process efficiency:

1) Increase of salt flux because of the higher concentration at the membrane surface, which results in lower salt rejection;
2) Lower water flux due to an increase in trans-membrane osmotic pressure caused by the higher solute concentration, which reduces the mass transfer driving force;
3) Enhancement of scaling phenomena due to lower solubility, and subsequent further mass transfer reduction([5]).

For these reasons, knowledge of concentration polarization is essential for the design of RO processes and plants.

A schematic representation of the phenomenon is presented in Fig. 1.17.

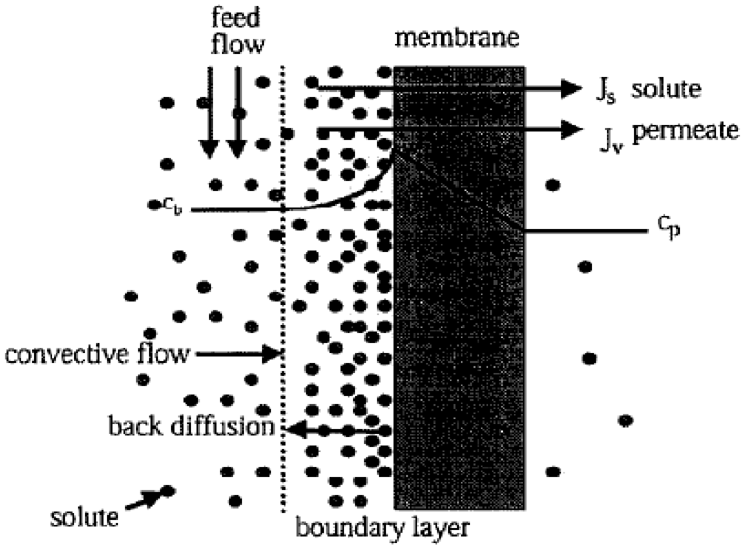


Figure 1.17 *Schematic representation of Concentration Polarization*

The simplest and most widely used model to predict CP is the Film Theory Model. It is based on the hypothesis of a uniform solute layer over the membrane surface. According to this model, water flux and concentration polarization are related through the following equation:

$$\frac{c_m - c_p}{c_b - c_p} = \exp\left(\frac{J_w \delta}{D}\right) = \exp\left(\frac{J_w}{k}\right) \quad , \tag{1.10}$$

where c_m, c_p and c_b are the solute concentration at the membrane surface, on the permeate side and in the bulk of the feed side, δ is the build-up layer thickness, D is the diffusion coefficient and k is the solute mass transfer coefficient, that can be evaluated through Sherwood-type correlations:

$$Sh = \frac{kd}{D} = a\,\mathrm{Re}^b\, Sc^c. \tag{1.11}$$

A key limitation to this model is that it does not consider the influence of permeate flux on δ(17). More accurate and complex models have been developed taking into account the coupling between permeate flux and layer thickness, together with the non-uniformity of the latter(17,18,19). Despite its theoretical limitations, the Film Theory Model has proved to be reliable.

CP has been seen to increase with increasing applied pressure and decreasing flow velocity. In order to limit the phenomenon, tangential configuration (cross-flow) is preferred, as it enhances shear at the membrane surface. In addition, turbulent vortices have proved effective in reducing Concentration Polarization;

therefore, spacers are placed in the membrane modules in order to create turbulent eddies, as previously stated with regard to membrane modules.

In conclusion, despite all the improvements made throughout the years and the researches currently working on further reducing the energy consumption of RO seawater desalination plants, a maximum limit of energy saving of 15% has been estimated([2]). Therefore, even though RO at present is still the leading desalination technology worldwide, new innovative processes are being investigated that could reduce the amount of energy needed.
One of the most promising is the Manipulated Osmosis Desalination process, whose features and advantages compared to traditional RO will be widely described in the following chapter.

Chapter 2

The Manipulated Osmosis Desalination process

This chapter contains the description of the Manipulated Osmosis Desalination process, developed at the University of Surrey's Centre for Osmosis Research and Applications (CORA) (Sharif & Al-Mayahi, 2005), its principle and its development from laboratory scale to industrial installed plant. Before that, the principle of Forward Osmosis, on which the process is based, is presented. Finally, the advantages of this process with respect to the traditional Reverse Osmosis desalination process are highlighted.

2.1 Forward Osmosis

The principle of Forward (or Direct) Osmosis, is described in this paragraph in order to better understand the MOD process, which is based on this technique. As previously anticipated, FO is a natural phenomenon that occurs when two solutions at different concentration are put in contact through a semi-permeable membrane that allows water to pass, but rejects salt and other solutes. Water will flux from the dilute side, which is at higher chemical potential, to the concentrated, low chemical potential side, until equilibrium is reached. The driving force for the process is the osmotic pressure difference between the two solutions.

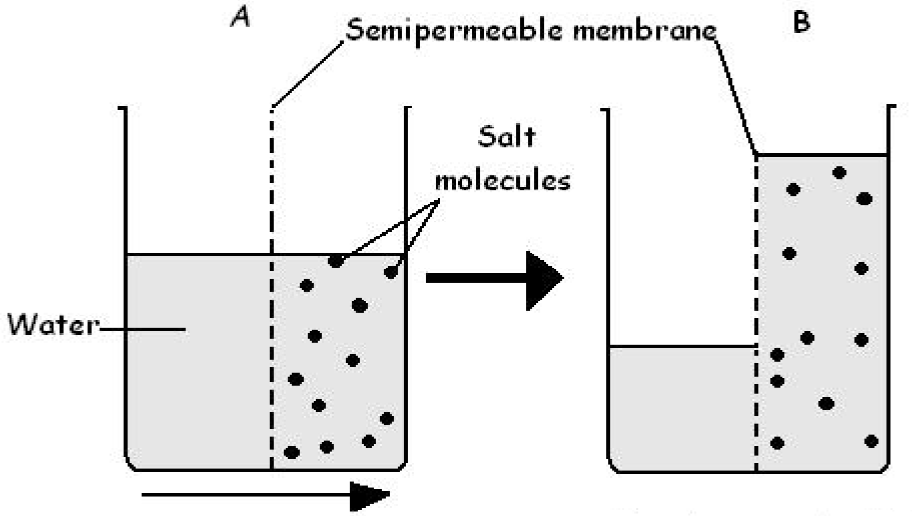


Figure 2.1 *Principle of Forward Osmosis*

FO has found various applications, from power generation (also known as Pressure Retarded Osmosis), wastewater treatment, food and pharmaceutical processes, and especially desalination([20]).

Early researches about using FO for desalinating salt water existed only in Patent form, and it is only since 2005 that technical papers began to be published. It represents a promising desalination technology due to the numerous advantages it brings, and offers a good challenge for future developments.

The process consists in putting seawater in contact with a proper draw solution of higher osmotic pressure: pure water will therefore flow from the feed water side to this solution, causing its dilution. A second step must be considered, in which the draw solution is recovered and pure product water is obtained; various are the draw solutions that can be employed and the techniques employed for their recovery([20,21]). A scheme of the process is shown in Fig. 2.2.

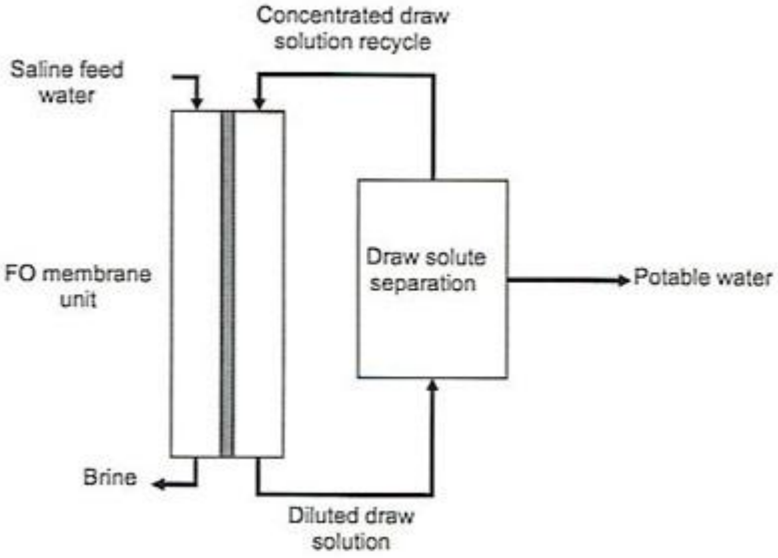


Figure 2.2 *Scheme of a Forward Osmosis desalination process*

Forward Osmosis, compared to the traditional Seawater Reverse Osmosis (SWRO) desalination technology, offers many advantages:

- Lower hydraulic pressure required by the process, as the only pressure losses are those along the membrane. This results in less energy consumption, provided that a proper draw solution as well as its re-concentration step is adopted. It is probably the main and most attractive advantage offered by FO, as it is related to lower costs.

- Lower and more reversible membrane fouling, which can be minimized by hydrodynamic optimization. Moreover, a wide variety of contaminants is easily rejected.
- Higher water fluxes accompanied by higher recovery, which represents an improvement also from the environmental point of view: in fact, higher recoveries allow a reduction in the volume of brine produced and then discharged, thus the environmental impact of the process is less compared to pressure-driven processes(20).

Despite these major and important advantages, there are still many challenges to be faced to improve the process performance and obtain satisfactory results. The key issues for the development of a FO desalination process concern finding proper high-performance membranes as well as draw solutions; the criteria that they should satisfy will therefore be presented in detail in the following pages.

2.1.1 Forward Osmosis membranes

Asymmetric membranes similar, but different from those used for RO processes are employed in FO operations. These membranes must have certain characteristics in order to limit some undesirable but inevitable phenomena which occur in the process: these are Internal Concentration Polarization, membrane fouling and reverse solute diffusion.

The phenomenon of concentration polarization is even more dramatic and severe in FO compared to pressure-driven Reverse Osmosis, as it takes place in both sides of the membrane: due to the water flux, a salt build-up layer is formed on the membrane surface in the feed side, exactly like already seen in RO processes; this is called concentrative concentration polarization, as there is an increase in salt concentration.

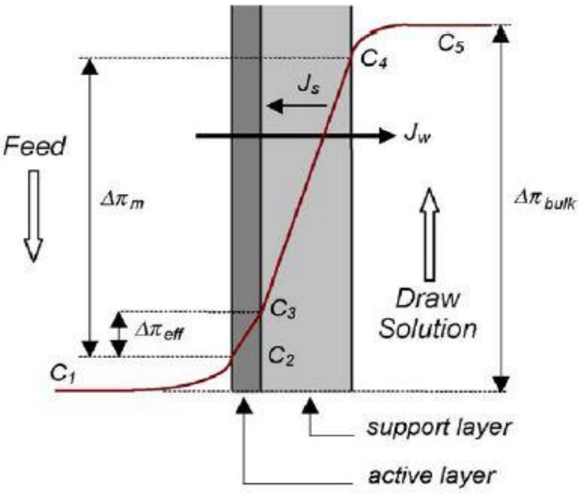


Figure 2.3 *Effect of external and internal concentration polarization on overall driving force in FO*

At the same time, on the other side (draw solution side), water flux causes a reduction of the draw solute concentration near the membrane; this is therefore known as dilutive concentration polarization. Both of them cause a decrease in the overall driving force for the process, resulting in fluxes much lower than expected([20,21]).

Moreover, in FO processes, the dense thin layer faces the feed seawater side, originating an external concentrative concentration polarization layer, which can be reduced manipulating the hydrodynamics as seen for RO processes; the porous support layer is instead placed in the draw solution side, this meaning that the dilutive effect takes place into the membrane pores (Internal Concentration Polarization, or ICP), and is therefore much more difficult, if not impossible, to limit([20,21]). ICP causes a dramatic decrease of the driving force, as can be seen in Fig. 2.3.

Membrane fouling, as mentioned above, is an inevitable phenomenon. It is different from that occurring in RO processes in that it is reversible; in addition, membrane cleaning is easier, probably because the fouling layer formed is much less compact due to the lower operation pressure. Nonetheless, it causes a reduction in the driving force, and it is therefore desirable to limit its occurrence.

Finally, reverse solute diffusion is another undesirable phenomenon that further enhances fouling. In order to limit its effect, high selectivity membrane must be employed([20]). This is one of the main challenges at the present time.

In summary, the characteristics that FO membranes should satisfy are: high density and selectivity for high salt rejection to avoid reverse flux; low support layer porosity in order to minimize the ICP effect; hydrophilicity for higher water fluxes, and low reduced membrane fouling([21]).

2.1.1.1 Membrane materials and modules

Initially, RO membranes were employed for FO processes, but recently studies on membranes specifically designed for this purpose have been conducted. Two types of membranes exist for FO; the first type are cellulosic membranes, realized through phase inversion: they are made of cellulose acetate or polybenzimidazole (PBI), and are characterized by high hydrophilicity and low fouling propensity, good mechanical strength and resistance to chlorine and oxidants([20]); at the same time, these materials are easily subject to hydrolysis and biological attack, so pH must be strictly maintained in the range of 4-6 and temperature must be up to 35°C. The second type of membranes is that of multiple layer membranes: they have an overall thickness of approximately 50 µm, and are very different from RO Thin-Composite Film membranes in that the thick polysulfone support is replaced with a polyester mesh([20]).

With regard to membrane modules, both flat sheet plate-and-frame and tubular hollow-fiber configurations have been developed. Spiral wound modules are instead not feasible to be operated in FO mode, because the draw solution cannot be forced to flow into the envelope formed by the membranes([21]). Plate-and-frame is the simplest flat sheet configuration, and can be constructed in a wide range of sizes; however, it has two main limitations: the lack of an adequate support that limits its use to low pressures operation or to applications with similar pressure on both sides; the low packing density is also a disadvantage, as it results in a larger footprint, and in higher operational and capital costs. Tubular membranes are probably the most practical configuration for FO processes: the packing density is relatively high; they can be operated at higher hydraulic pressures without deforming; besides, which is necessary in FO, they allow liquids to flow easily on both sides of the membranes, in opposition to spiral wound modules.

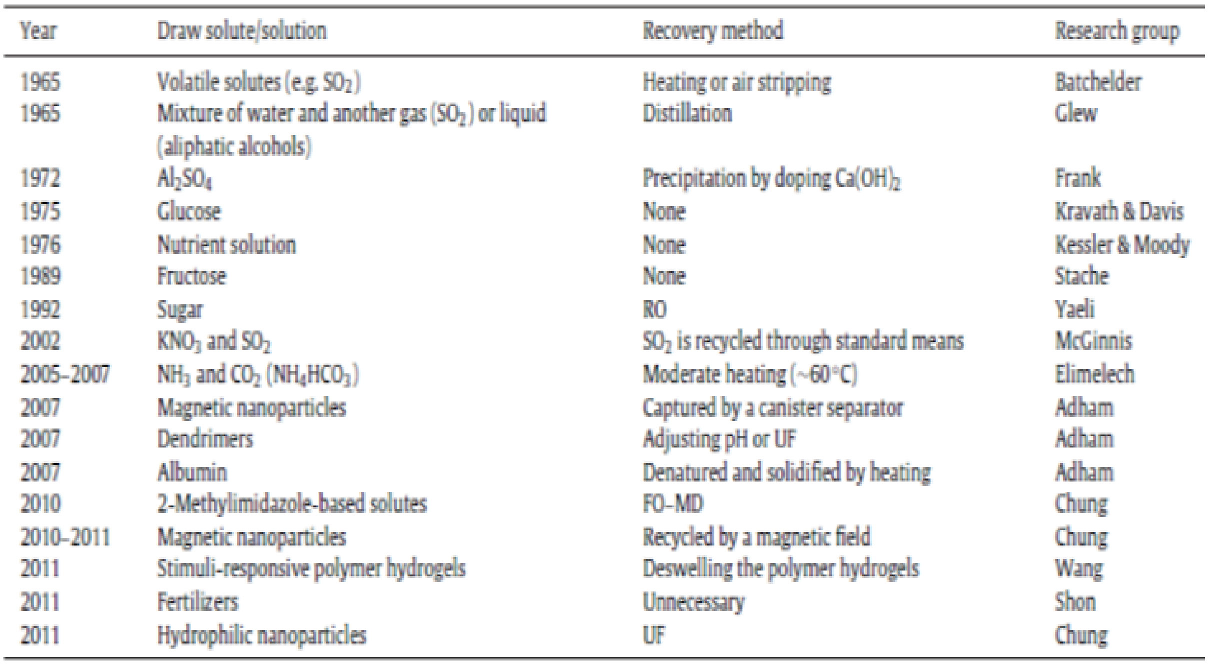
2.1.2 Draw solutions

The choice of a proper draw solution (or osmotic agent) is the second bigger issue of FO processes, together with the recovery technique employed. It is of critical importance, as it represents the source of the driving force. For a draw solution to be suitable to this purpose, it must obey certain criteria:

- The main characteristic is that it must have an osmotic pressure higher than that of seawater. It is preferable that this is obtained at low concentrations, therefore the solute should also have high solubility in water;
- It must cause minimal ICP in the process: diffusion coefficient, viscosity and molecular size all influence ICP; in particular, higher diffusion coefficients, lower viscosities and smaller molecules minimize the internal concentration polarization, even though it must be considered that the smaller the solute molecule, the more difficult is its recovery([20,22]);
- The draw solution must be easily and economically recovered or re-concentrated; two types of solute exist: thermolytic solutes, that are recovered by supplying heat to the system, and water soluble salts, recovered with different various methods.

In addition to these major characteristics, a proper draw solution must also provide low cost, low reverse solute flow, zero toxicity and stability to the operation conditions([20,21,22,23]).
A list of the previously investigated draw solutions is shown in Table 2.1.

Table 2.1 *Overview of the draw solutions/solute used in FO investigations and their recovery methods*([20])



Year	Draw solute/solution	Recovery method	Research group
1965	Volatile solutes (e.g. SO_2)	Heating or air stripping	Batchelder
1965	Mixture of water and another gas (SO_2) or liquid (aliphatic alcohols)	Distillation	Glew
1972	Al_2SO_4	Precipitation by doping $Ca(OH)_2$	Frank
1975	Glucose	None	Kravath & Davis
1976	Nutrient solution	None	Kessler & Moody
1989	Fructose	None	Stache
1992	Sugar	RO	Yaeli
2002	KNO_3 and SO_2	SO_2 is recycled through standard means	McGinnis
2005–2007	NH_3 and CO_2 (NH_4HCO_3)	Moderate heating (~60 °C)	Elimelech
2007	Magnetic nanoparticles	Captured by a canister separator	Adham
2007	Dendrimers	Adjusting pH or UF	Adham
2007	Albumin	Denatured and solidified by heating	Adham
2010	2-Methylimidazole-based solutes	FO-MD	Chung
2010–2011	Magnetic nanoparticles	Recycled by a magnetic field	Chung
2011	Stimuli-responsive polymer hydrogels	Deswelling the polymer hydrogels	Wang
2011	Fertilizers	Unnecessary	Shon
2011	Hydrophilic nanoparticles	UF	Chung

In the early stages, volatile solutes as sulphur dioxide were used as draw solutions, and could be removed by a stripping operation with heated gas([22]). Later, in 1972, an aqueous aluminium sulphate draw solution was developed, which was then separated by precipitation after the addition of salts. Various sugars, like glucose and fructose, were then investigated as they can be easily recovered with low pressure RO membranes([22]). These and other sugars are the object of the research project presented in this thesis.

In the early 2000s, Elimelech proposed a water-soluble mixture of ammonium bicarbonate, which has proved to produce high water fluxes due to its low molecular weight and high solubility; the draw solution can then be recovered by heating up to 60-65°C, causing the decomposition into ammonia and carbon dioxide([21,22]).

Recent researches are focusing on magnetic and hydrophilic nanoparticles.

As it can be inferred, the techniques employed for the recovery of the draw solutions are various and different. The Manipulated Osmosis Desalination (MOD) process, hereafter described, is based on a pressure-driven (mostly RO, but also NF) recovery step. The aim of this thesis is to test the performance of various sugars in said recovery step.

2.2 The Manipulated Osmosis Desalination process

The Manipulated Osmosis Desalination (MOD) process has been developed at the University of Surrey’s Centre for Osmosis Research and Application (CORA), and, together with Modern Water, it has been brought from university laboratory to a full-scale commercial facility. The novel technology has been patented, in order to be protected (MOD is based on Patent number US7879243, Solvent removal process([24])) and is one of the few that has become a commercial reality. The process principles and the installed facilities are presented in this paragraph, together with a direct comparison with an existing SWRO desalination plant, in order to highlight the numerous advantages offered by MOD.

2.2.1 MOD process

The MOD process is substantially based on a FO desalination step which is integrated with a regeneration step in a single cycle. The basic concept is to manipulate two fluids with different osmotic pressures (seawater and a chosen draw solution) in order to obtain a pure water flux across the selectively permeable membrane. The regeneration step is necessary to recover pure water from the osmotic agent solution([25]). A simple scheme of the process is shown in Fig. 2.4

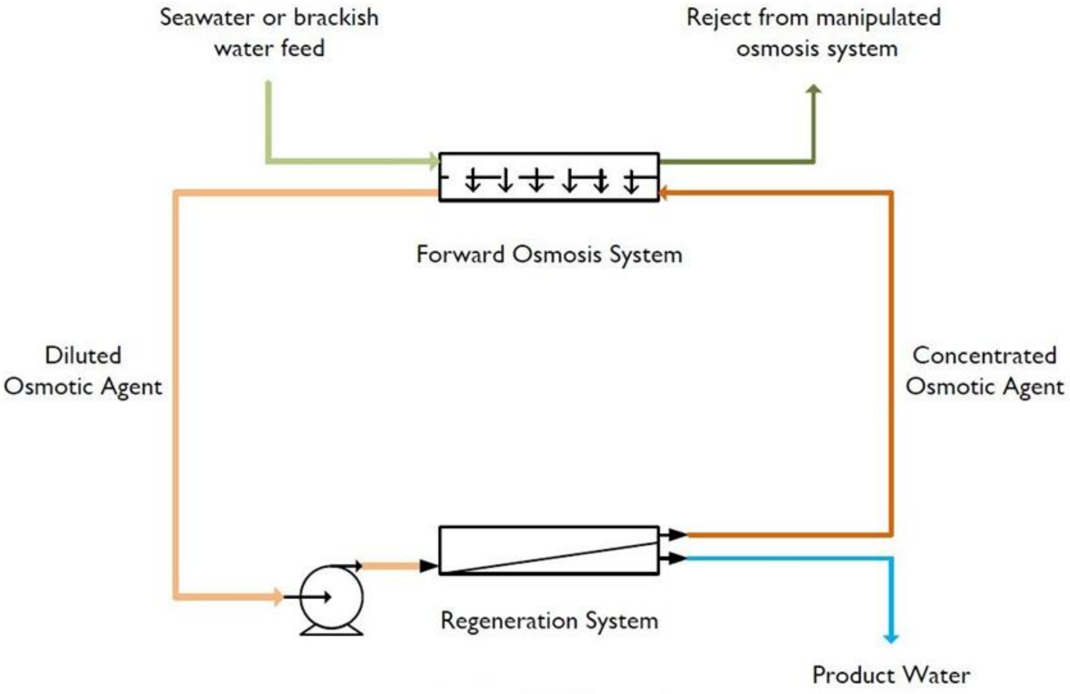


Figure 2.4 *Simplified MOD process diagram*([24])

The characteristic of this process is the regeneration step, which is also membrane-based: in particular, low pressure Reverse Osmosis or Nanofiltration. The matching of the operation of the two steps is a key factor needed to ensure a proper operation of the MOD process.

Compared to traditional RO desalination, this process has the main advantage of operating the FO step at much lower pressures (2-3 barg instead of 60-80 barg); the regeneration step does in fact consume energy, but a careful selection of the osmotic agent and of operative conditions can minimize this consumption. Besides, the efficiency of the RO recovery step is greater than that of traditional SWRO due to the fact that the composition of the draw solution is controlled, and it does not contain impurities of foulants, allowing operative conditions to be optimized([25]). In addition, other benefits shown by the MOD process are:

- Lower operating costs due to lower fouling propensity;
- Fewer membrane replacements;
- Provision of a double membrane barrier between feed-water and high quality product water;
- Significant reduction of contaminants such as boron, resulting in further reduction of capital and operative costs;
- Possibility of using low pressure (plastic) pipework and fittings, that are less expensive and easier to fabricate([25]);

The key variables to be considered for the process design and operation are:

- Number and performance of forward osmosis membranes;
- Composition, concentration and recirculation rate of the draw solution;
- Performance of the regeneration step, as the pure water recovery must be equal to the flux obtained in the FO step;
- Temperature, composition and flow rate of feed-water.

The chemistry of the membranes and of the osmotic agents specifically employed in the MOD process is commercially sensitive, and for this reason they are not presented in this work. However, they satisfy the major characteristics listed in §2.1.1 and §2.1.2.

As for the feed-water composition, it has an influence on the process performance: higher TDS may result in the need of additional FO membrane area, or higher osmotic pressure draw solution; the MOD process has a great degree of flexibility in design that allows it to adapt to the conditions required([25]).

2.2.2 MOD installed facilities

As previously mentioned, the MOD process has been developed from the laboratory to a commercial full-scale facility, passing to an intermediate trial facility installed on the Mediterranean Sea.

2.2.2.1 Laboratory Test Rig

The MOD process development began at the test facilities installed at the Centre for Osmosis Research and Application (CORA) placed at the University of Surrey, UK.

Figure 2.5 *Laboratory Test Rig*

This pilot plant has been used by the CORA team to investigate the key parameters of the process, membrane configurations, etc. to allow the following development outside the university environment(^{25}).

2.2.2.2 Trial facility

The first trial plant was built on the Mediterranean Sea, at Gibraltar, in 2008. The purpose of this facility was to test the MOD performance outside the academic environment, confirming the mathematical models accuracy, and to collect long-term operational data that could confirm the process reliability(^{25}). The plant satisfied the expectations, therefore allowing the subsequent development and installation of a production facility, installed in 2009 in the Sultanate of Oman.

2.2.2.3 Production facility

The first MOD production facility has been built in Al Khaluf, Sultanate of Oman, in July 2009, with a capacity of 100 m^3/d of drinkable water supply. The site already contained a traditional SWRO plant of the same nominal capacity, which agreed to share both the pre-treatment and post-treatment stages, allowing the possibility of a direct comparison between the two processes.

Figure 2.6 *Water production site at Al Khaluf, including containerized MOD plant*([25])

The untreated product water has typically a TDS of less than 200 ppm and boron content of 0.6 – 0.8 mg/L; with post-treatment, it fully meets the legal limits required.

The coupling with an already existing SWRO plant allows an effective comparison of the performances of the two processes, which highlighted numerous advantages of the novel MOD desalination technique. These advantages are summarized in Table 2.2.

In the particular case considered, MOD process operates at 60% of the SWRO energy consumption, and it is worth to be noted that energy recovery is not considered in the estimation, even though the MOD plant is provided with proper devices.

Apart from the lower energy consumption, another major advantage characterizing the MOD process is the longer and better membrane performance: in fact the normalized output of the permeate flow has been seen to remain relatively constant during a whole year (2010), without the need of chemical membrane cleaning, whilst the SWRO plant showed a 30% decline after only five months, despite repeated cleaning of the membranes; this results in even lower operational and capital costs for the MOD process with respect to the traditional technology.

Table 2.2 *Comparison of SWRO and MOD process performances*([25])

Technology	UoM	SWRO	MOD
Permeate Extraction from feedwater			
Feedwater Recovery	%	25	35
Product Water Flow	m^3/d	71.4	100
Feedwater Supply	m^3/h	11.9	11.9
	bar	65	4
Feedwater Pump	eff%	85	85
	kW	25.3	1.6
Osmotic Agent Regeneration			
Osmotic Agent Recovery	%	-	47
Dilute Osmotic Agent Feed	m^3/h	-	8.9
	bar	-	65
OA Regeneration Pump	eff%	-	85
	kW	-	18.8
Overall Plant			
Specific Energy Consumption (per unit product)	kWh/m^3	8.5	4.9

In conclusion, Manipulated Osmosis Desalination has proved to be a reliable process, bringing many advantages compared to traditional Reverse Osmosis seawater desalination. Nonetheless, many areas for further improvement exist, related to process optimization and membrane development for the FO step, but also to finding a more proper draw solution. The investigation of various sugars (glucose and sucrose) as osmotic agents is exactly the aim of this work, and particularly their performance in the regeneration step by RO.

Chapter 3

Experimental Work

Several experiments have been carried out in this work to investigate the efficiency of a RO recovery step. Two different types of sugar, such as glucose and sucrose, were used as osmotic agents, to evaluate their feasibility in the regeneration step of the MOD process. In addition, two different flat-sheet membranes, one for RO and one for NF, have been used in order to determine the suitable membrane type which could be applied in the regeneration step when using these two draw solutions. Also, a description of the equipment, materials and experimental procedure needed to carry out the experiments is presented in this chapter, together with the investigated ranges of feed solutions concentrations and applied pressures.

3.1 Laboratory equipment

The experimental work has been carried out using a bench-scale RO laboratory cell supplied by SpinTek Filtration, Inc. (USA) as shown in Fig. 3.1. The unit is mainly equipped with a variable speed high pressure pump with flexible connections, two pressure gauges for the feed and concentrate line respectively, a digital flowmeter, a needle valve on the concentrate line, a 4 liters capacity tank for the feed, and a flat-sheet membrane cell.

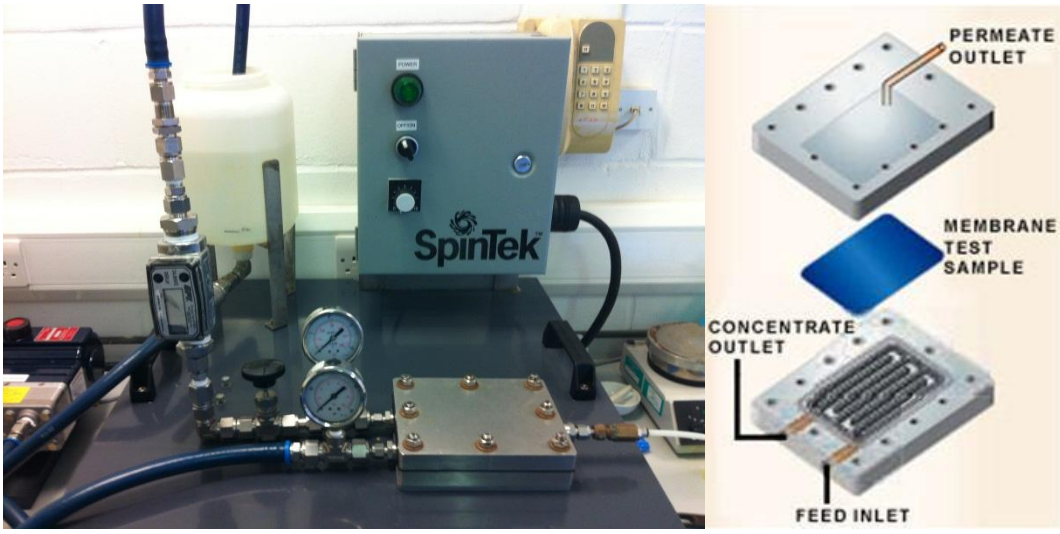


Figure 3.1 *Reverse Osmosis laboratory cell called Static Test Cell (SpinTek Filtration, Inc. (USA))*

From Fig. 3.1 and Fig. 3.2 it can be seen that the feed solution enters the lower part of the cell and goes through a zigzagged pattern, and exits through a needle valve as concentrate. The membrane, accurately shaped by cutting, is placed above the cell together with ten layers of high porosity filter paper (Whatman, type 1-Qualitative, filter speed: Medium-Fast) which have proved to be necessary in order to avoid membrane bending caused by the high hydraulic pressure, followed by a rubber gasket and a stainless wire mesh of 1 mm thickness. Everything is then secured by eight evenly positioned screws. The feed enters the cell from below, and the permeate leaves it from the above.

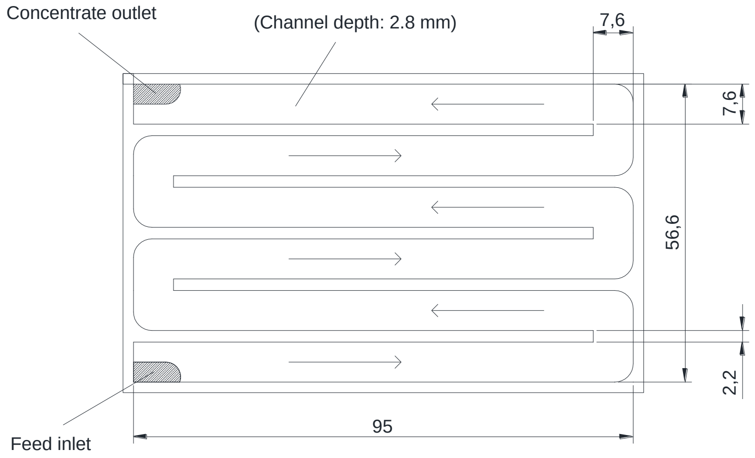


Figure 3.2 *Top view of the lower fixed part of the RO cell, showing the feed flow path. The channel cross section is about 21.3 mm^2.The dimensions are expressed in mm.*

The membrane active area is calculated from the path geometry, and results to be approximately 45 cm^2.

A schematic flow diagram of the complete unit is presented in Figure 3.3.

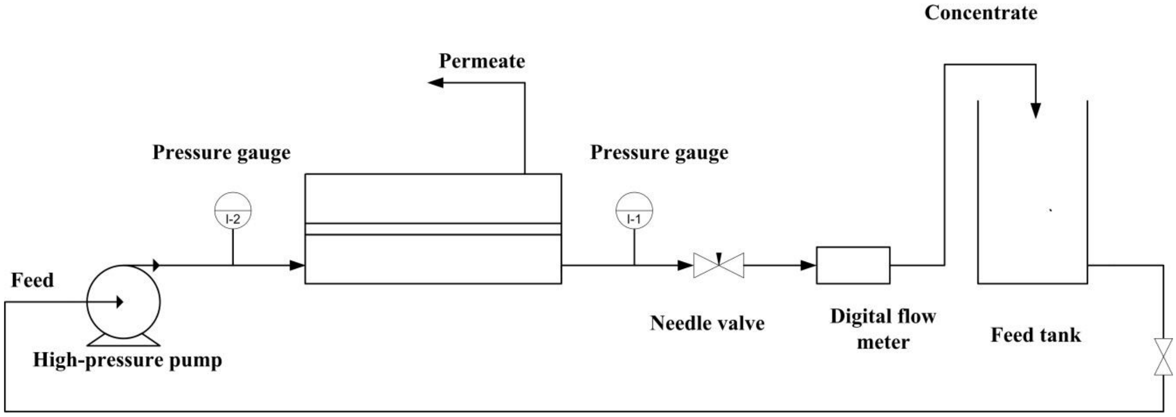


Figure 3.3 *Schematic Flow Diagram of the bench-scale Reverse Osmosis apparatus*

3.2 Materials

In this paragraph the characteristics of the materials employed in the experimental work are briefly presented. It includes a description of both the sugars used as osmotic agents and the membranes used in the experiments.

3.2.1 Osmotic Agents

Two different sugars as osmotic agents for the Manipulated Osmosis Desalination (MOD) process were used. In particular, they were glucose and sucrose.

Glucose is a monosaccharide, with chemical formula $C_6H_{12}O_6$. In aqueous solutions it is found in a cyclic form. The main properties of this sugar are summarized in Table 3.1.

Table 3.1 *Glucose properties*

Property	Value
Chemical Formula	$C_6H_{12}O_6$
Molecular Weight	180.16 g/mol
Density (25°C)	1.54 g/cm^3
Solubility in water (25°C)	91 g/100ml
Manufacturer	Sigma-Aldrich
Purity	99.5%

Sucrose is a disaccharide composed by the two monosaccharides glucose and fructose, with chemical formula $C_{12}H_{22}O_{11}$, and is most commonly known as table sugar. Its properties are listed in Table 3.2.

Table 3.2 *Sucrose properties*

Property	Value
Chemical Formula	$C_{12}H_{22}O_{11}$
Molecular weight	342.3 g/mol
Density (25°C)	1.587 g/cm^3
Solubility in water (25°C)	200 g/100ml

Both of these sugars are potentially suitable to be used as draw solutions due to the following reasons:

- high solubility in water;
- high osmotic pressure at relatively low concentration, and over a wide range of concentrations, as can be seen from Fig. 3.5 (osmotic pressures are calculated using OLI's software; for a data check, see §4.1). This makes them suitable for the FO stage;
- zero toxicity;
- relatively low cost.

Previous studies([26,27,28]) have shown that these compounds may potentially but effectively be separated by Reverse Osmosis.

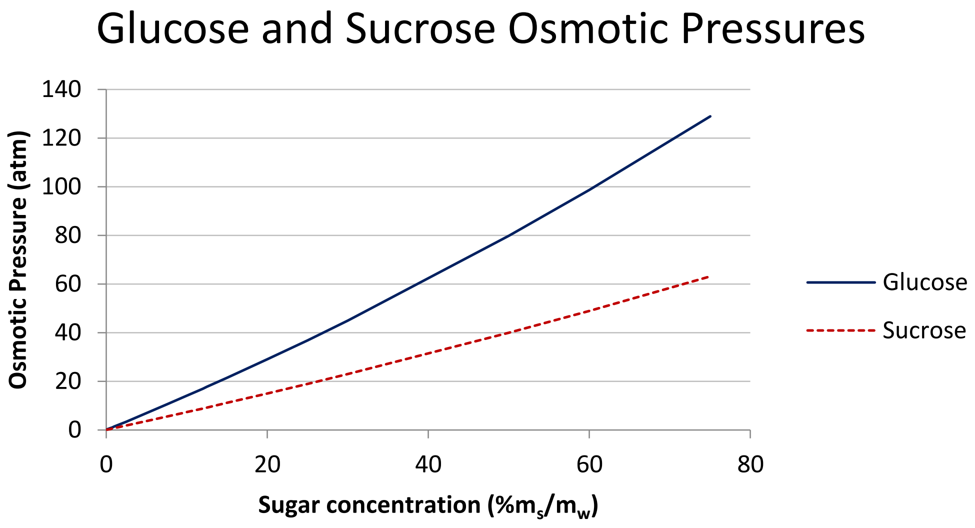


Figure 3.5 *Osmotic Pressure of glucose and sucrose as a function of concentration. Values calculated using OLI's software (OLI System Inc., 2006).*

3.2.2 Membranes

Two different flat-sheet membranes have been used in this investigation. The aim was to examine their performance in the sugars regeneration step in terms of water permeability and sugar rejection.

The first membrane used is TFC®-ULP, manufactured by Koch Membrane System Inc. (USA). It is an Ultra-low Pressure Reverse Osmosis membrane, usually employed in brackish water desalination, allowing about 20-33% lower energy consumption than traditional RO membranes. It has been commercialized since 1995 as a new generation of the TFC membranes with polyamide active layer. The membrane specifications, referred to a commercial spiral wound module, are listed in Table 3.3.

Table 3.3. *Manufacturer's operating and design data of TFC®-ULP membrane (Test conditions: 2000 mg/L NaCl solution, 8.6 bar, 15% recovery, 25°C and pH 7.5)*

Type of membrane	Ultra-Low Pessure RO element
Membrane Chemistry	Proprietary TFC polyamide
Typical operating pressure	7-12 bar
Maximum operating pressure	24 bar
Maximum operating temperature	45°C
Rejection	98.68
Flux (GFD)	29.91
Allowable pH – continuous operation	4-11
Molecular Weight Cut-Off (MWCO)	<180 Da

The Molecular Weight Cut-Off (MWCO) is defined as the molecular weight of the molecule that is 90% retained by the membrane. Commercially, the MWCO is used as an indication of the membrane's pore size. However, no industry standard exists; therefore the MWCO ratings of different manufactures are often not comparable. Furthermore, the permeability of a solute is dependent, in addition to the molecular weight, also on the shape of the molecule, its degree of hydration and its charge, and the nature of the solvent (solvent pH and ionic strength). Accordingly, MWCO should be used only as a guide, and not as an exact indicator of performance.

The second membrane used is TFC®-SR®2, manufactured by Koch Membrane System Inc. (USA). It is a Selective-Rejection Nanofiltration membrane, whose specifications, referred to a commercial spiral wound module, are reported in Table 3.4.

Both membranes have been conditioned through soaking them in de-ionized water for 24 hours prior to use in the laboratory cell.

Table 3.4 *Manufacturer's operating and design data of TFC®-SR®2 membrane*

Type of membrane	Low pressure,selective rejection,NF element
Membrane chemistry	Proprietary TFC membrane
Typical operating pressure	3.45 – 7 bar
Maximum operating pressure	34.5 bar
Maximum operating temperature	45°C
Rejection	97.53
Flux (GFD)	57.2
Allowable pH – continuous operation	4-9
Molecular Weight Cut-Off (MWCO)	300-400 Da

3.3 Experimental Procedure

The aim of the experimental work is investigating the relationship between some controlled variables and the observed response. The controlled variables are the feed flow-rate, which was kept constant, the feed solution concentration, the pressure applied to the feed and the temperature. The latter was meant to be kept constant at about 25°C, but due to the high viscosity of the sugar solutions, especially at high concentrations, an increase in the temperature has been recorded during the runs; therefore, a correction factor has been used to normalize at 25°C the flux values, which are influenced by the temperature, using the following equations:

$$J_{w,25^0C} = J_{w,T} \cdot TCF \tag{3.1}$$

$$TCF = \exp\left(2700\left(\frac{1}{T[K]} - \frac{1}{298}\right)\right) \ , \tag{3.2}$$

TCF, being the Temperature Correction Factor for the water flux. This behaviour of the flux has been verified to be consistent with the Poiseuille equation:

$$\dot{V} = \frac{32S^2\Delta P}{\pi\mu L} \ , \tag{3.3}$$

where $\dot{V}$ is the volumetric flow-rate and μ is the viscosity. Considering that μ changes with the temperature according to the following equation:

$$\mu = \mu_0 \exp\left(\frac{E}{RT}\right) \tag{3.4}$$

the expected effect on the volumetric flow-rate will be:

$$\frac{\dot{V}_{25^oC}}{\dot{V}_T}=\frac{\exp\left(\frac{E}{RT}\right)}{\exp\left(\frac{E}{R\cdot 298}\right)}=\exp\left(\frac{E}{R}\left(\frac{1}{T}-\frac{1}{298}\right)\right) \qquad (3.5)$$

in theoretical agreement with eq. (3.2)

The observed variables are the concentrate and permeate concentrations and flow-rates, and the concentrate hydraulic pressure. The data collected have been used to calculate the variables of interest for the study, these being the permeate flux (obtained dividing the amount of water collected in a certain time by the membrane area), the solute rejection (from concentration values), and the Net Driving Pressure, which is expressed as:

$$NDP=(\Delta P-\Delta\pi) \qquad (3.6)$$

where ΔP and $\Delta\pi$ are the trans-membrane pressure and osmotic pressure respectively, the latter being obtained as a function of sugar concentration using OLI’s software.

The concentrate hydraulic pressure and flow-rate were read on the pressure gauge and the digital flowmeter placed in the concentrate line respectively, after calibration of the latter, while the permeate flow-rate has been measured manually with the aid of a 10ml capacity cylinder and a digital stopwatch. As regards the concentrations of the permeate and the concentrate samples, they were determined by HPLC (High Performance Liquid Chromatography) analysis carried out by the University of Surrey’s Chemistry Department using a Varian 920-LC HPLC instrument with a Varian 385-LC light scattering detector. As the maximum concentration allowed to be analyzed by the instrument was of 10 mg/ml, concentrate and feed samples for each experimental run had to be diluted prior to analysis. The dilutions have been made using a dilution factor of 50.

Different ranges of feed solutions and applied pressures have been investigated to determine their effect on the observed variables. In order to be able to compare the performances of glucose and sucrose as osmotic agents, solutions that could give the same osmotic pressure have been prepared with the two sugars. In general, as can be evinced from Fig. 3.5, a smaller amount of glucose is required to achieve a certain osmotic pressure, with respect to sucrose. Therefore sucrose solutions had higher concentration used.

The range of concentrations and pressures investigated is summarized in Table 3.5.

Table 3.5 *Investigated ranges of feed concentration and applied pressure*

Sucrose		**Glucose**		
Concentration (g/L)	**Osmotic Pressure (bar)**	**Concentration (g/L)**	**Osmotic Pressure (bar)**	**Applied Pressures (bar)**
50	~4	-	-	10,14,18,20
-	-	45	~6	10,14,18,20
95	~8	65	~8	10,14,18,20
130	~11	80	~11	16,18,20
165	~14	95	~14	16,18,20
217	~16	105	~16	18,19,20

The maximum pressure allowed in the experimental setup was 20 bar: despite the pump itself could reach higher values (up to 70 bar) this is the limit at which the flexible pipes can be operated.

The experiments have been carried out according to the following procedure, applied to both the RO and NF membranes:

1. the membrane was cut and shaped to fit the seat and, after careful inspection to check the presence of any possible damage, soaked in de-ionized water for 24 hours; after that, it was placed in the laboratory cell and secured as described in §3.1;
2. the unit was flushed several times with de-ionized water to make sure that the pipes and the pump were clean and ready to use;
3. pure water flux has been recorded at different pressures in order to determine the membrane pure water permeability;
4. sucrose solutions were prepared pouring the calculated amount of sugar in a 5L tank, and then filling with de-ionized water until reaching the desired volume. The sugar was dissolved at ambient temperature with the aid of a magnetic stirrer.
5. the solution was poured into the feed tank, and recirculated for 5 minutes before starting the experiment, in order to homogenize the concentration;
6. a sample of the feed was taken after recirculation and before starting to run the unit;

7. after each run, the unit was flushed with de-ionized water for 10 minutes in order to clean the pipes from possible sugar residuals that could influence the concentration of the following run, and the feed tank cleaned carefully for the same reason;
8. before changing the osmotic agent, the unit was repeatedly flushed with de-ionized water, to avoid contamination of glucose by the previous sugar;
9. glucose solutions were prepared following the same procedure used for the sucrose, and the same operations were made for each experiment.

For each experiment, in addition to the feed, 6 samples of the permeate and 6 of the concentrate were taken in order to estimate the average value of both flux and concentrations.
After careful statistical considerations, some experimental data have been dropped; these data could have been affected by casual and instrumental errors, water evaporation, or unsteady state measurements.

Chapter 4

Results and Discussion

In this chapter all the results obtained in the experimental work which has been described in the previous chapter are presented and discussed. First, a comparison between the osmotic pressure values calculated by OLI's software (OLI System Inc., 2006) with experimental values found in the literature is carried out, to verify the consistency of the former. Pure water permeability is also determined. Finally, experimental results of sugar solutions regeneration are thoroughly presented and discussed. In particular, the effect of feed pressure and concentration (osmotic pressure) on water flux and sugar rejection are highlighted, followed by a comparison between the two sugars and the two membranes performances.

4.1 Osmotic Pressure calculations verification

For the purposes of this work, osmotic pressures values of the various solutions have been calculated as a function of the measured concentration through the aid of OLI's software (OLI System Inc., 2006), which predicts the properties of solutions via thermodynamic modeling based on an extensive experimental database. In order to validate OLI's calculations, a comparison is made with experimental data found in the literature, both for sucrose([29]) and glucose([30]).

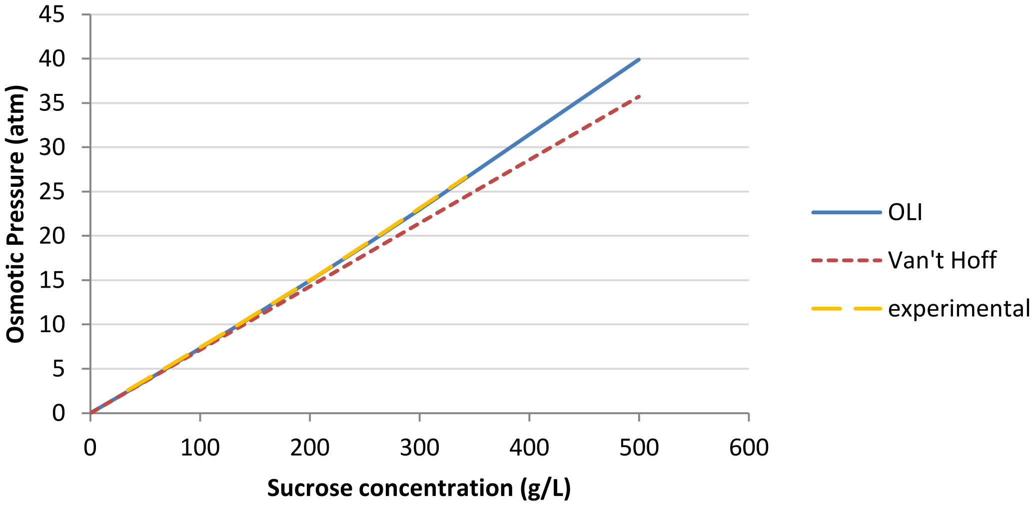


Figure 4.1 *Osmotic Pressure of sucrose as a function of concentration at 25°C and 1 atm*

Figure 4.1 shows the behaviour of the sucrose solution osmotic pressure as a function of the concentration at 25°C, 1 atm. Generally, the osmotic pressure values increase more than linearly with increasing sucrose solution concentration. Also, it is evident that osmotic pressure values data calculated by OLI's software and those obtained experimentally match very well, while values calculated using the Van't Hoff equation (eq. 1.2) are valid only for dilute solutions.

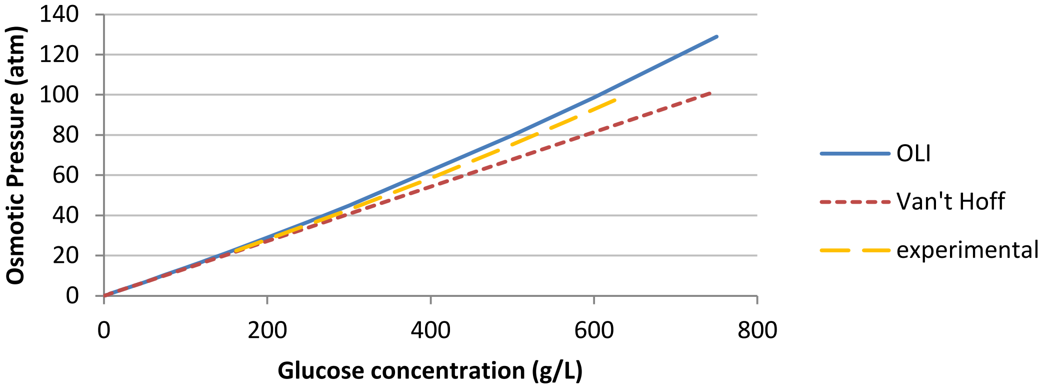


Figure 4.2 *Osmotic Pressure of glucose as a function of concentration at 25°C and 1 atm*

Figure 4.2 shows the osmotic pressure behaviour with concentration for a glucose solution. Experimental values have been calculated using eq. 1.3 from experimental data on osmotic coefficient *Φ*(30). The errors difference between OLI's calculations and experimental data are shown in Table 4.1, and calculated with the following equation:

$$e[\%] = \frac{\pi_{calc} - \pi_{\exp}}{\pi_{\exp}} \cdot 100 \tag{4.1}$$

For a concentration of 635.4 g/L the percentage error is 6.93%. That means that OLI's software is precautionary in calculating the osmotic pressure of glucose for the investigated range of concentrations.

Table 4.1 *Percentage errors between osmotic pressure values from experimental data and OLI's software for a glucose solution*

Conc [g/L]	Π_{calc} [atm]	Π_{exp} [atm]	e [%]
162	23.19	22.43	3.39
291.6	43.63	41.57	4.97
399.6	61.94	58.53	5.82
489.6	78.09	73.44	6.33
568.8	92.98	87.10	6.75
635.4	105.98	99.11	6.93

4.2 Pure water experiments

These experiments were carried out in order to determine the pure water permeability (A_{wm}) and water flux (J_w) for the two membranes. These two parameters were evaluated using the Solution Diffusion Model (see §1.3.1.1), with the following equations:

$$J_w = A_{wm} \Delta P \, , \tag{4.2}$$

$$\Delta P = \frac{p_f + p_c}{2} - p_p \, , \tag{4.3}$$

where ΔP is the trans-membrane hydraulic pressure difference averaged between inlet and outlet of the membrane module, and the subscripts f, c and p refer to the feed, the concentrate and the permeate respectively.

J_w was evaluated by dividing the measured amount of water collected in a certain time by the membrane area A_m (45 cm^2), for different values of feed applied pressure.

The pure water permeability was then calculated according to eq. (4.2) dividing J_w for the trans-membrane hydraulic pressure difference.

Figure 4.3 shows the values of water flux for both TFC®-ULP and TFC®-SR®2 as a function of ΔP.

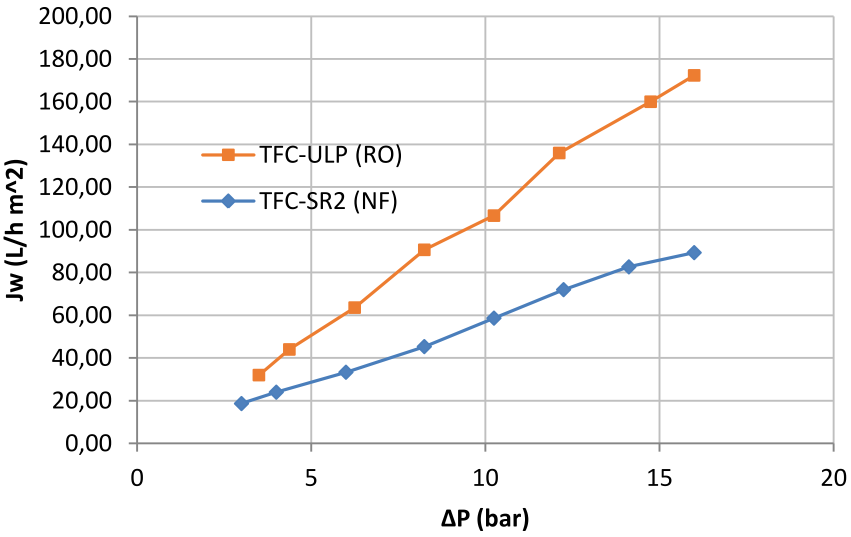


Figure 4.3 *Pure water flux J_w through TFC®-ULP and TFC®-SR®2membranes at 25°C as a function of trans-membrane hydraulic pressure*

Figure 4.4 shows the calculated values of the pure water permeability for both the membranes at various trans-membrane pressure differences.

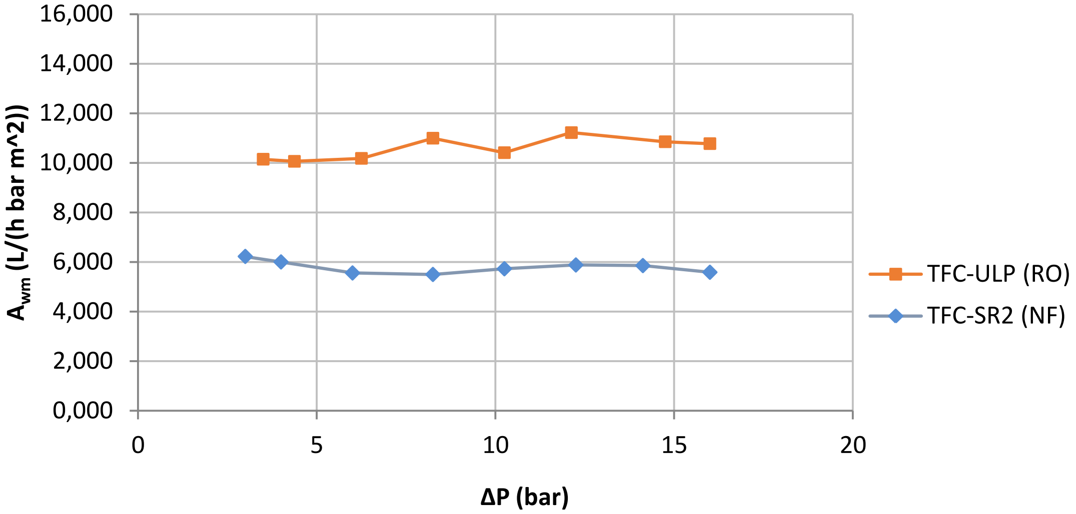


Figure 4.4 *Pure water permeability of TFC®-ULP and TFC®-SR®2membranes at 25°C as a function of trans-membrane hydraulic pressure*

As can be seen from Fig 4.3 and Fig. 4.4, the Nanofiltration membrane results to be less permeable than the Reverse Osmosis one, despite having larger pores. This may be due to the nature of the membrane surface, and its different affinity with water molecules.

4.3 Sugar solutions experiments

Several experiments using sucrose and glucose solutions have been carried out at different ranges of feed concentration and applied pressure according to the procedure described in §3.3. The main target of this study is to determine the effect of these variables on water flux J_w and sugar rejection R_s, which have been calculated using the following equations:

$$J_w = A_w(\Delta P - \Delta\pi), \qquad (4.4)$$

$$\Delta\pi = \frac{\pi_f + \pi_c}{2} - \pi_p \ , \qquad (4.5)$$

$$R_s = 1 - \frac{c_p}{c_f} \ , \qquad (4.6)$$

A_w is the overall water permeability, ΔP is the averaged trans-membrane hydraulic pressure difference (eq. 4.3), $\Delta\pi$ is the trans-membrane osmotic pressure difference, calculated with eq. 4.5, c_p and c_f are the permeate and feed concentrations, respectively.

$(\Delta P - \Delta\pi)$ in eq. 4.4 is called Net Driving Pressure (NDP), and it represents the driving force for the process.

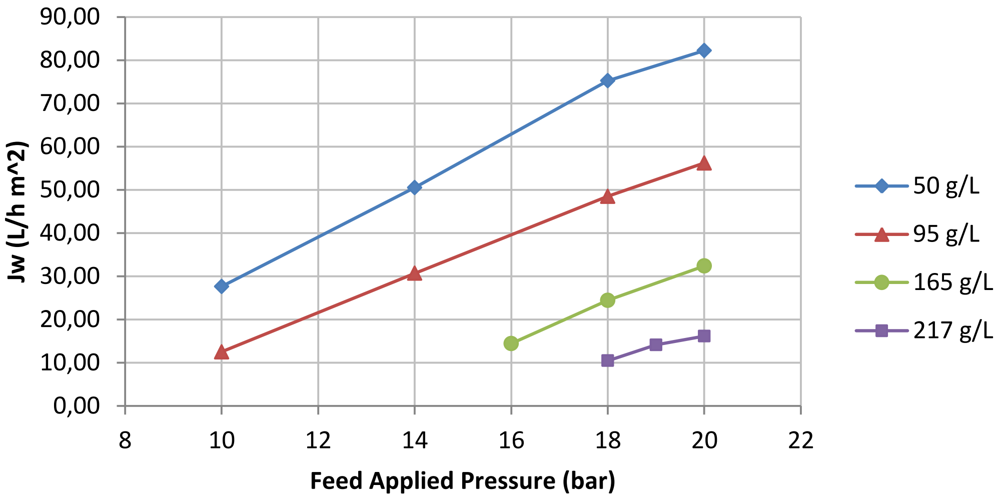
4.3.1 Effect of feed applied pressure

In this paragraph, the effect of the feed applied pressure on water flux, sugar rejection and recovery for the various set of experiments is shown.

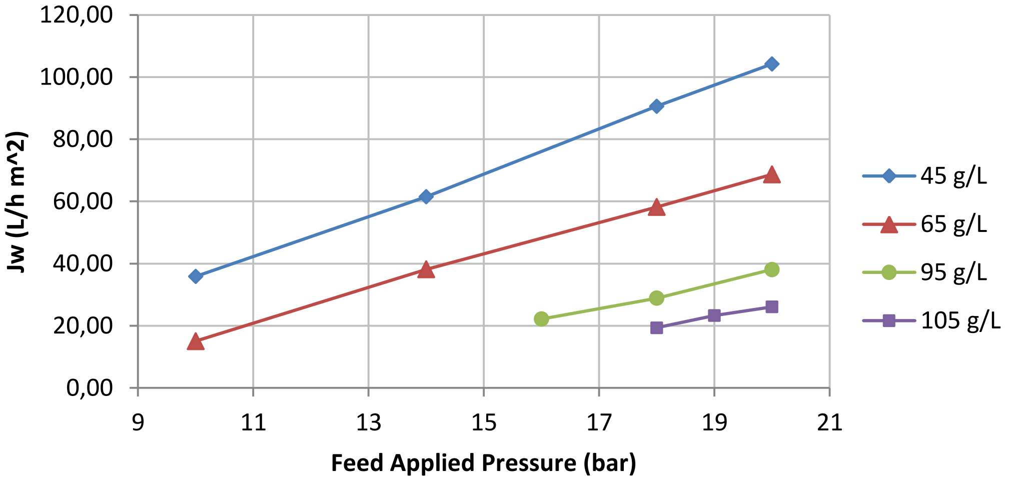
Water Flux

Figures 4.5 a), b), c) and d) display the behaviour of water flux as a function of the feed applied pressure for both sugars and both membranes employed in the experimental work, at different concentrations.

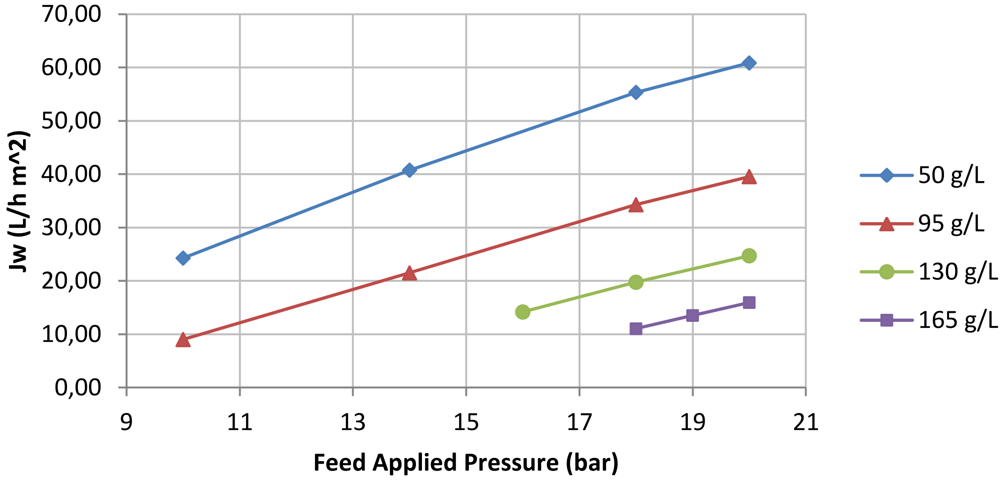
a)



b)



c)



d)

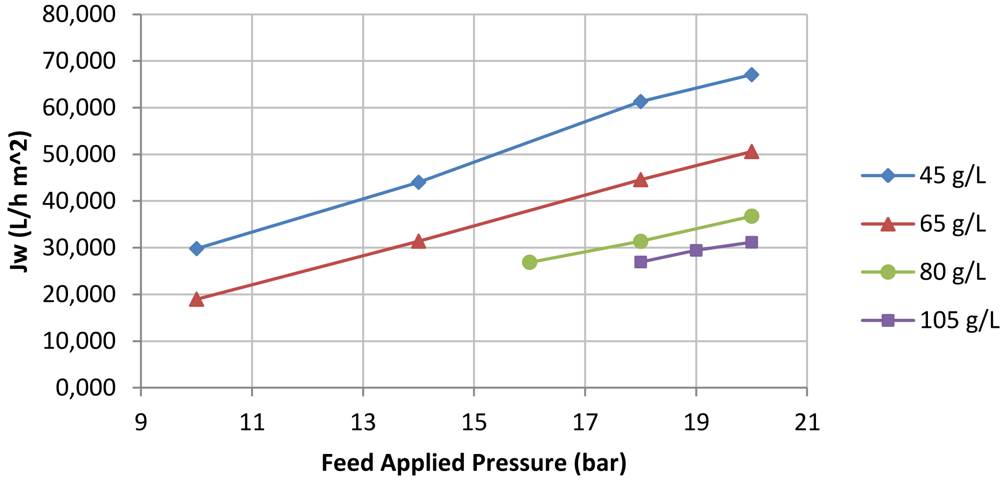


Figure 4.5 *Water Flux as a function of Feed applied pressure for TFC®-ULP with sucrose (a) and glucose (b), and for TFC®-SR®2with sucrose (c) and glucose (d)*

It can be clearly seen from the plots that an increase of the pressure applied to the feed leads to an increase in water flux; this can be attributed to an increase in the NDP. Also, the water flux decreases with increasing sugar feed concentrations.

Sugar Rejection

Figures 4.6 a), b), c) and d) show the effect of feed applied pressure on sugar rejection for both sugar types when the two membranes are employed, at different solute concentrations.

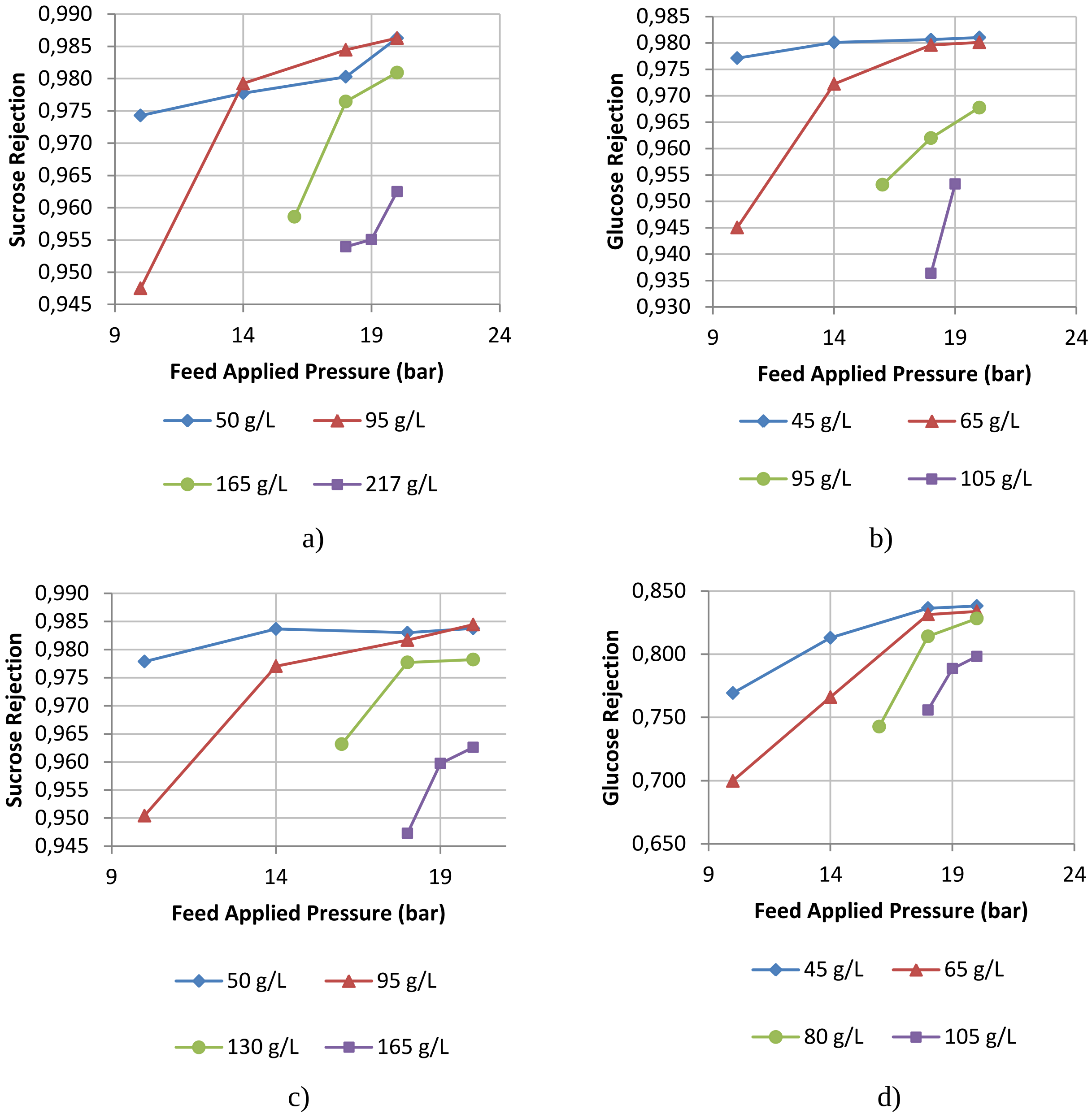


Figure 4.6 *Sugar Rejection as a function of feed applied pressure for TFC®-ULP with sucrose (a) and glucose (b), and for TFC®-SR®2with sucrose (c) and glucose (d).*

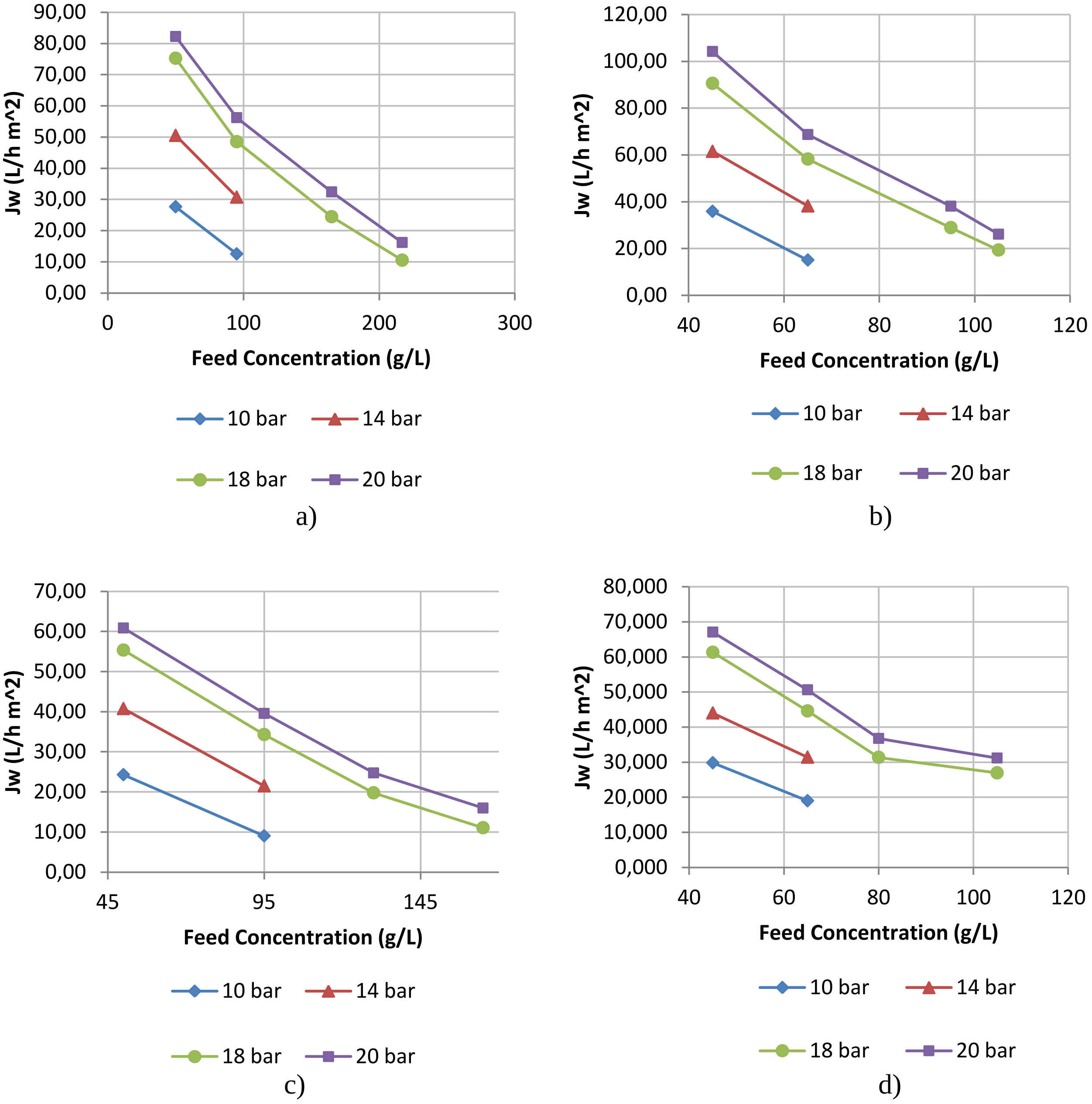
From the plots it can be evinced that sugar rejection tends to increase with increasing feed applied pressure. This behaviour is so because at higher applied hydraulic pressures, a higher water flux is obtained; therefore the sugar concentration in the permeate will be lower, as it is in fact more diluted. It can also be observed that pressure has a lower effect on rejection at lower concentrations. Moreover, beyond a certain value, pressure seems to no longer affect the sugar rejection, and this threshold value is lower for lower concentrations.

4.3.2 Effect of feed concentration

In this paragraph the effect of sugar concentration (osmotic pressure) on water flux, sugar rejection and water recovery is presented.

Water Flux

Figures 4.8 a), b), c) and d) show the behaviour of water flux J_w versus the feed solution concentrations for each set of experiments, at different feed applied pressure values.



a) b)

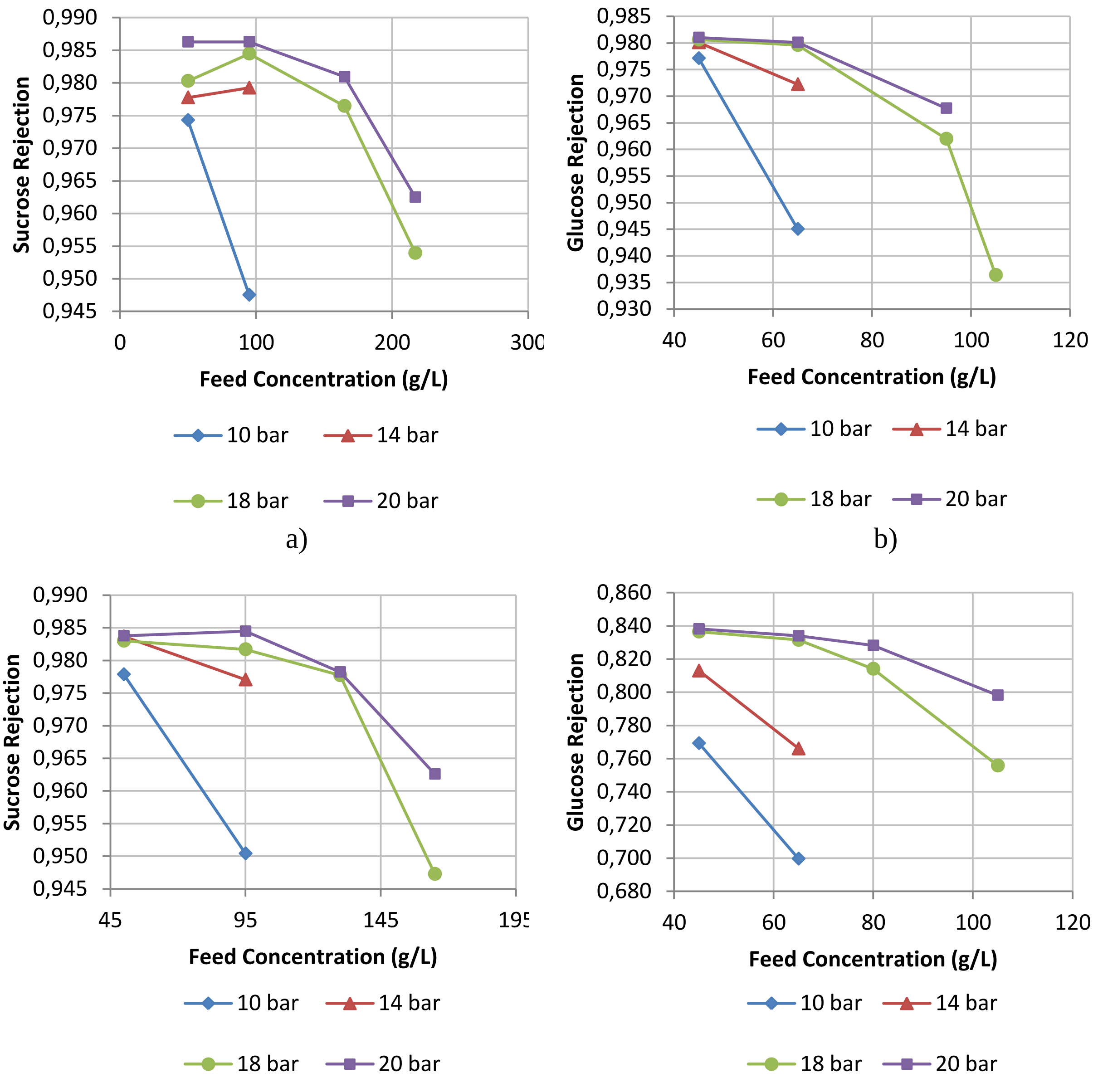
c) d)

Figure 4.8 *Water flux as a function of feed concentration for for TFC®-ULP with sucrose (a) and glucose (b), and for TFC®-SR®2with sucrose (c) and glucose (d).*

From the plots it can be seen that water flux decreases with increasing feed solution concentration, because an increase in concentration means an increase in the feed solution osmotic pressure ($\Delta\pi$), which results in a NDP decrease.

Sugar Rejection

Figures 4.9 a), b), c) and d) show the behaviour of sugar rejection as a function of feed concentration for both the sugars and both the membranes employed in the experimental study.



a) b)

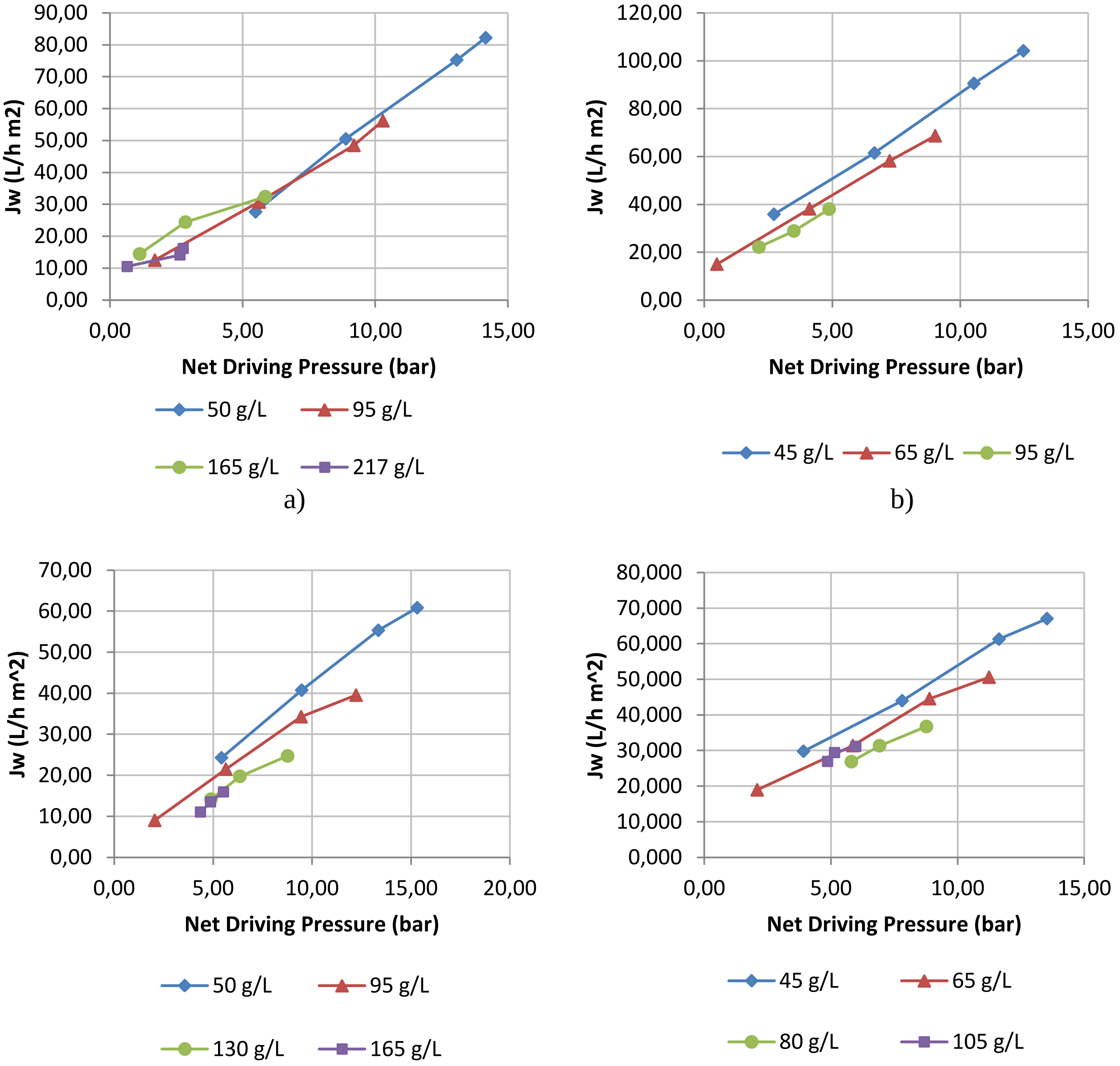
c) d)

Figure 4.9 *Sugar Rejection as a function of feed concentration for for TFC®-ULP with sucrose (a) and glucose (b), and for TFC®-SR®2with sucrose (c) and glucose (d).*

It is concluded that sugar rejection tends to decrease with increasing feed concentration, because as the feed concentration increases, water flux is decreased, and therefore the permeate will be more concentrated.

Overall water permeability

According to eq. (4.4), water flux J_w is proportional to the NDP (i.e. $\Delta P - \Delta\pi$), and the proportionality coefficient is given by the overall water permeability A_w. Figures 4.11 a), b), c) and d) show the trend of water flux as a function of NDP for both sugar solutions and both membranes, at different feed concentrations.

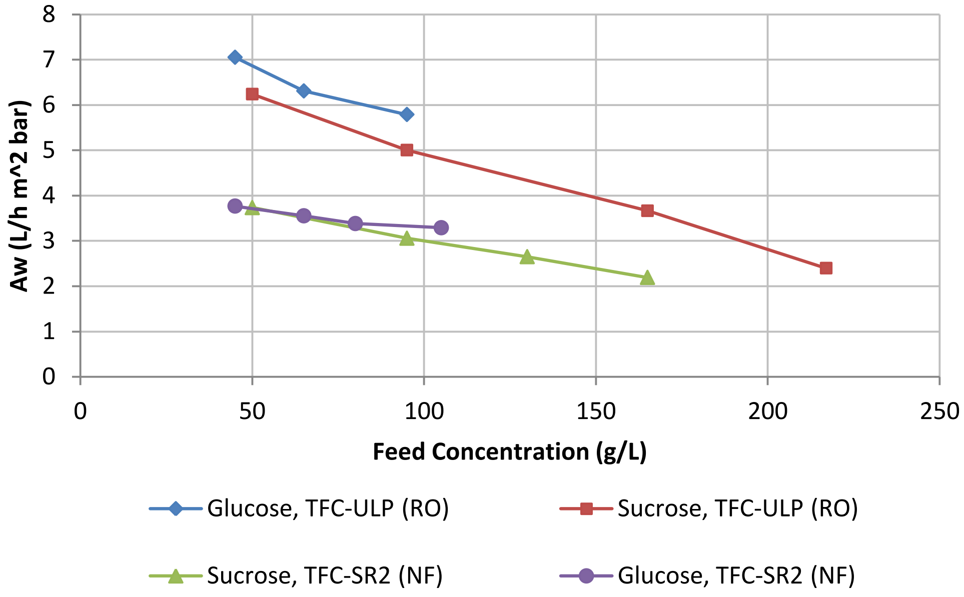


a) b)

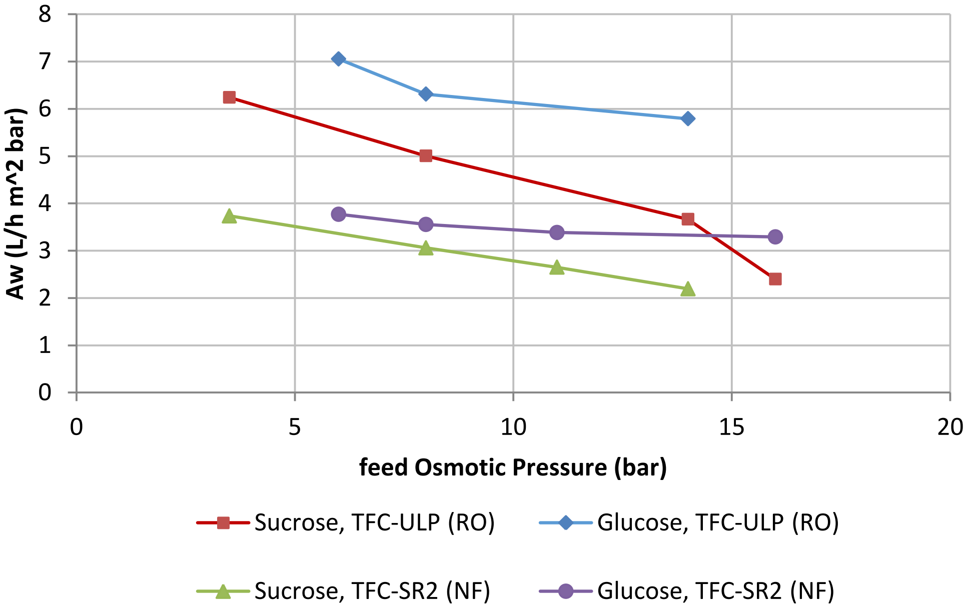
c) d)

Figure 4.11 *Water Flux J_w as a function of Net Driving Pressure for for TFC®-ULP with sucrose (a) and glucose (b), and for TFC®-SR®2with sucrose (c) and glucose (d).*

Accordingly, the overall water permeability is determined as the slope of the straight lines of the above plots. Figure 4.12 a) and b) show how A_w values change with feed concentration and feed osmotic pressure respectively.



a)



b)

Figure 4.12 *Overall water permeability A_w as a function of feed concentration (a) and of feed osmotic pressure (b), for glucose and sucrose with TFC$^{®}$-ULP and TFC$^{®}$-SR$^{®}$2*

It can be concluded that the overall water permeability tends to decrease with an increase in feed concentration and, therefore, of its osmotic pressure.

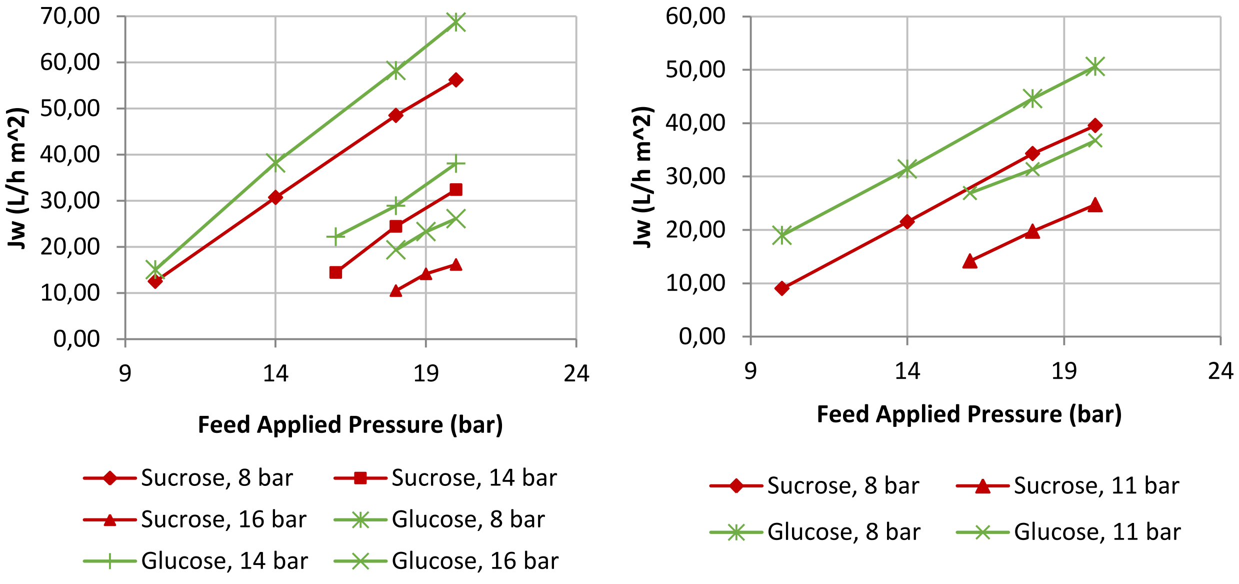
This behaviour can be due to the fact that the solute molecules form a build-up layer at the membrane surface which limits the water flux, and therefore reduces permeability. At higher concentration, this layer is thicker and subsequently the permeability is lower.

4.3.3 Comparison between sucrose and glucose

The aim of this paragraph is to compare the performances of sucrose and glucose as osmotic agents, in terms of water flux, sugar rejection, and the type of membrane.

Water Flux

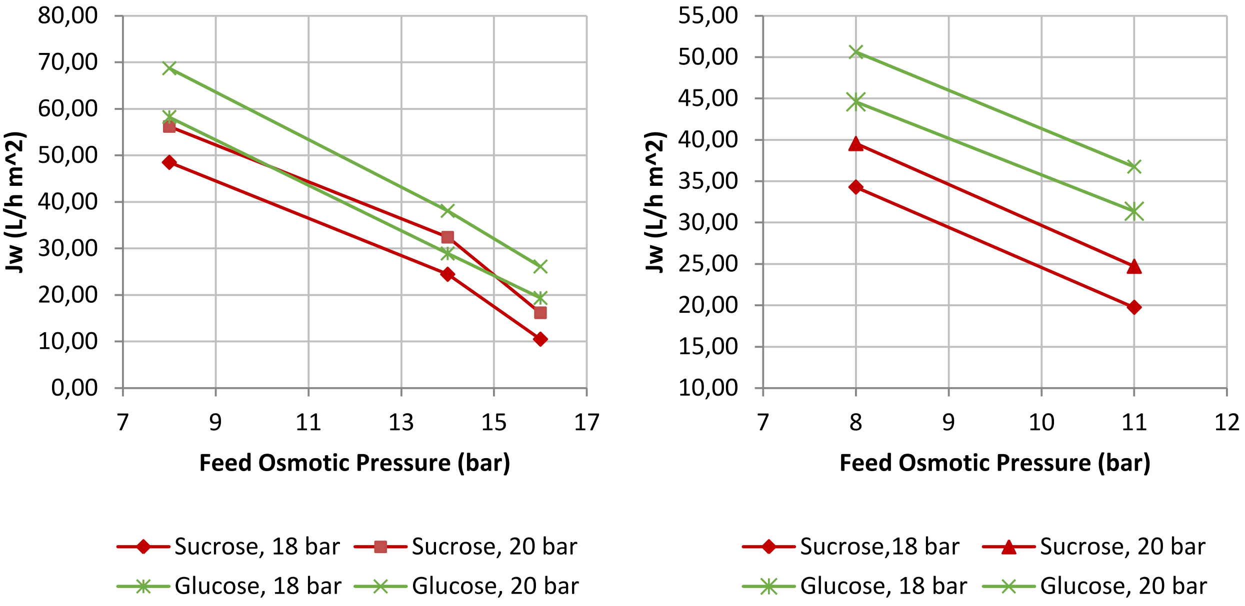
Figures 4.13 a) and b) show the comparison in water fluxes obtained when using sucrose and glucose solutions for both membranes, at the same values of feed osmotic pressure and as a function of the feed hydraulic pressure applied.



a) b)

Figure 4.13 *Comparison between water fluxes obtained with sucrose and glucose, at the same values of feed osmotic pressure, as a function of feed applied pressure, for TFC®-ULP (a) and TFC®-SR®2 (b)*

Also, Figures 4.14 a) and b) show the comparison of water fluxes obtained with sucrose and glucose as a function of the feed osmotic pressure and for different values of the feed applied pressure, both for TFC®-ULP and TFC®-SR®2.



a) b)

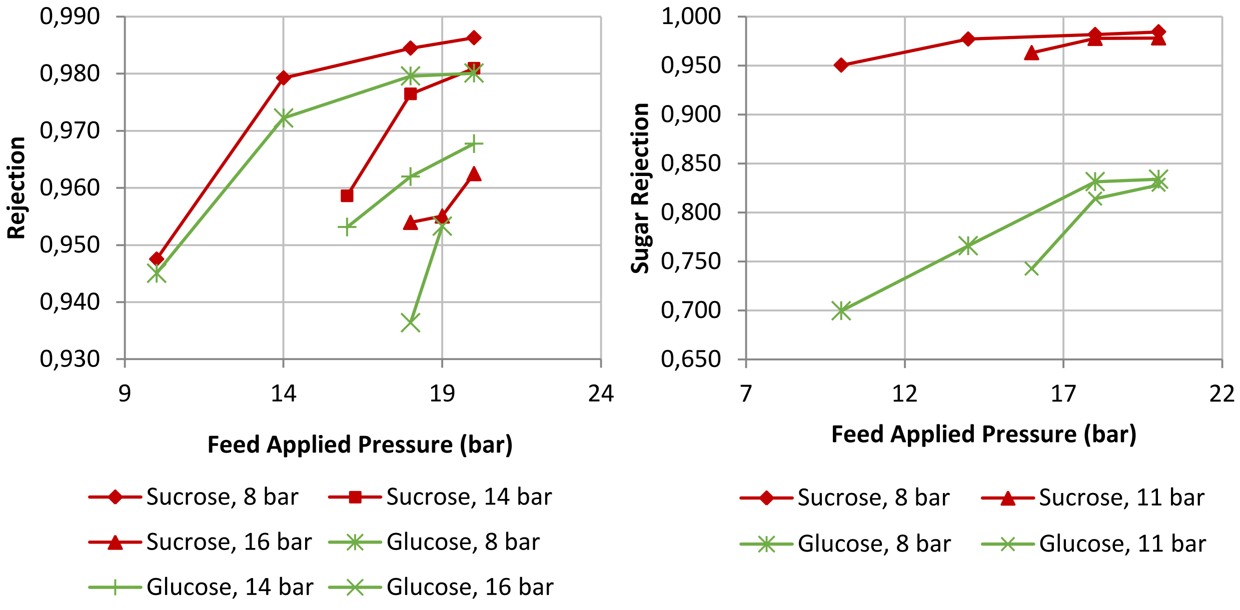
Figure 4.14 *Comparison between water flux obtained with sucrose and glucose, at the same values of feed applied pressure, as a function of feed osmotic pressure, for TFC®-ULP (a) and TFC®-SR®2 (b)*

The plots show clearly how feed solutions with glucose as osmotic agent always produce a higher water flux than sucrose solutions, despite having similar osmotic pressure and applied hydraulic pressure. This behaviour can be explained considering that glucose solutions reach a certain value of osmotic pressure at lower concentrations. This was already shown in Figure 3.5. Therefore, to get a similar effect the viscosity of glucose solutions is lower, and water diffusion is subsequently greater than in sucrose solutions; in addition, also the sugar build-up layer and the phenomenon of concentration polarization at the membrane surface are lower using glucose, i.e. less concentrated, draw solutions.

Sugar Rejection

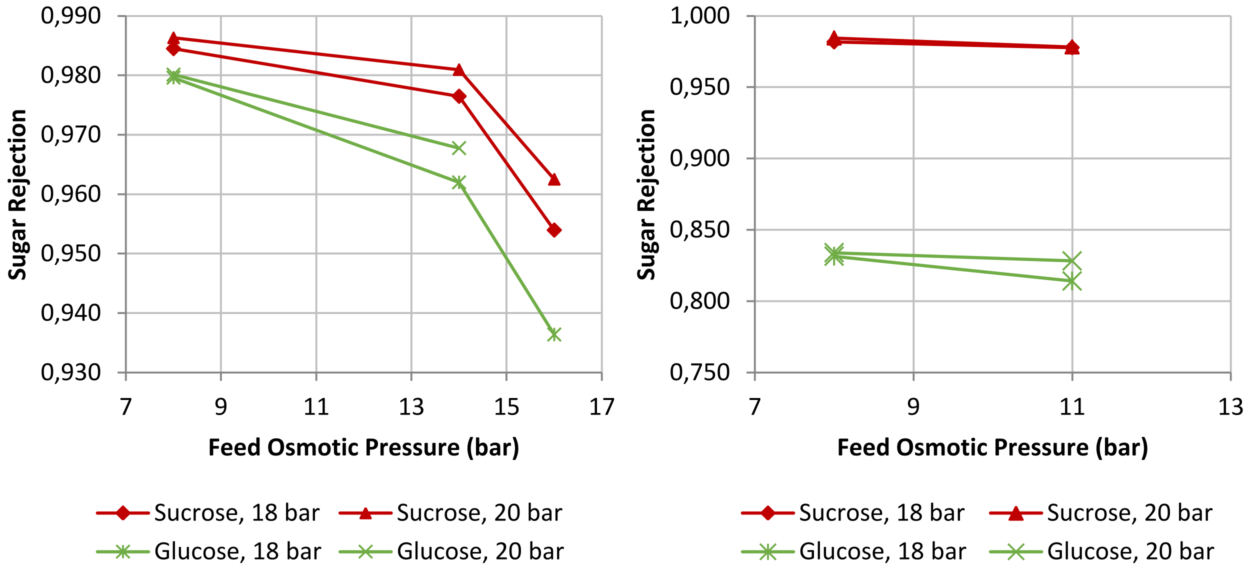
The comparison between sucrose and glucose performances in terms of solute rejection is shown in Fig 4.14 and Fig. 4.15, where it is plotted respectively as a function of the feed applied pressure (at the same values of feed solution osmotic pressure), and as a function of feed osmotic pressure (at the same values of hydraulic pressure applied), for both membranes.

Sugar rejection appears to be lower when using glucose as osmotic agent; this is due to the fact that glucose molecules are smaller than those of sucrose, the former being in fact a monosaccharide and the latter a disaccharide.



a) b)

Figure 4.15 *Comparison between sugar rejection obtained with sucrose and glucose, at the same values of feed osmotic pressure, as a function of feed applied pressure, for TFC®-ULP (a) and TFC®-SR®2 (b)*



a) b)

Figure 4.15 *Comparison between sugar rejection obtained with sucrose and glucose, at the same values of feed applied pressure, as a function of feed osmotic pressure, for TFC®-ULP (a) and TFC®-SR®2 (b)*

It is noteworthy that, while for the RO membrane TFC®-ULP the difference in rejection is evident, but limited (the highest variance being 95.4% for sucrose and 93.6% for glucose with a feed solution of 16 bars osmotic pressure), in the case of the NF membrane (TFC®-SR®2) rejection is much lower for glucose than for sucrose, with values between 70% and 83.4%, therefore too low for practical applications.

This is due to the different MWCO of the two membranes: in fact, as specified in Table 3.3 and Table 3.4, TFC®-ULP has a MWCO of 180 Da, therefore retaining both sucrose and glucose to a satisfactory extent; on the other hand, TFC®-SR®2 has a MWCO of 300-400 Da: this means that sucrose molecules (MW = 342 Da) are well retained, while glucose (MW = 180 Da) passes through more easily.

4.3.4 Comparison between TFC®-ULP (RO) and TFC®-SR®2 (NF) membranes

In this paragraph, a comparison between the two flat-sheet membranes is made, in order to determine which one gives the best performance in terms of water flux and sugar rejection, for sucrose and glucose draw solutions.

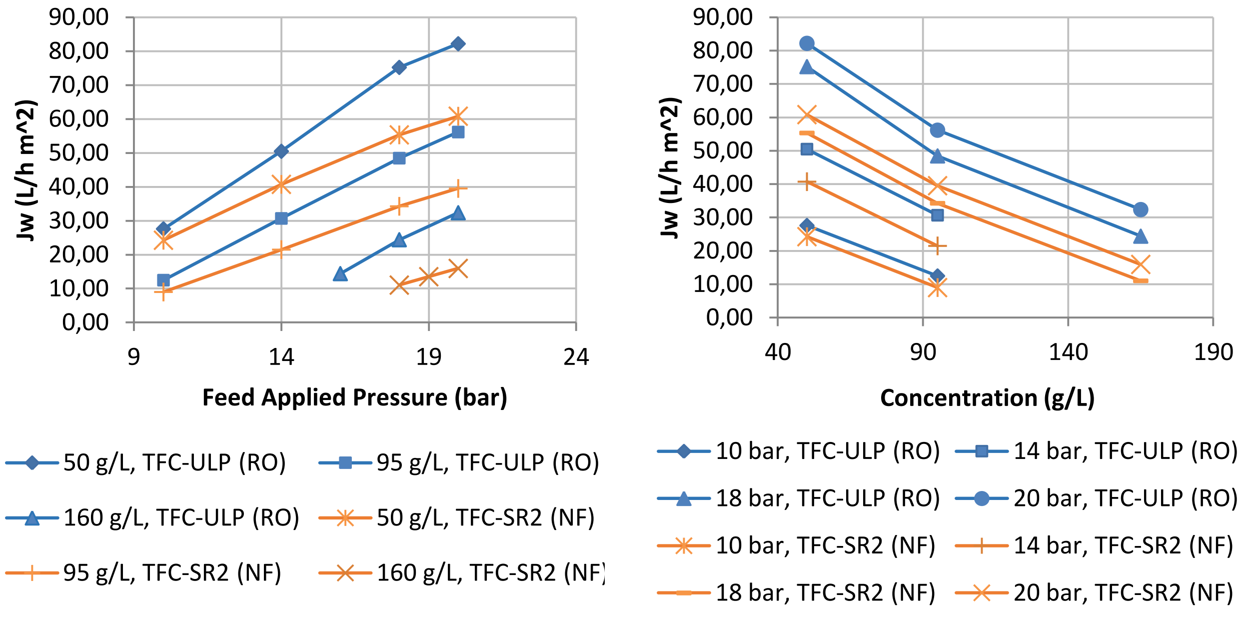
Water Flux

Figures 4.16 a) and b) show the comparison between TFC®-ULP (RO) and TFC®-SR®2 (NF) in terms of water flux for sucrose draw solutions, as a function of feed applied pressure (at the same values of feed concentration and osmotic pressure) and as a function of feed concentration (at the same values of applied hydraulic pressure) respectively.

The plots show clearly that the Nanofiltration membrane allows a lower water flux compared with the Reverse Osmosis one, the difference being greater for higher applied hydraulic pressures; the feed concentration seems not to influence this difference (Fig. 4.16 b)).

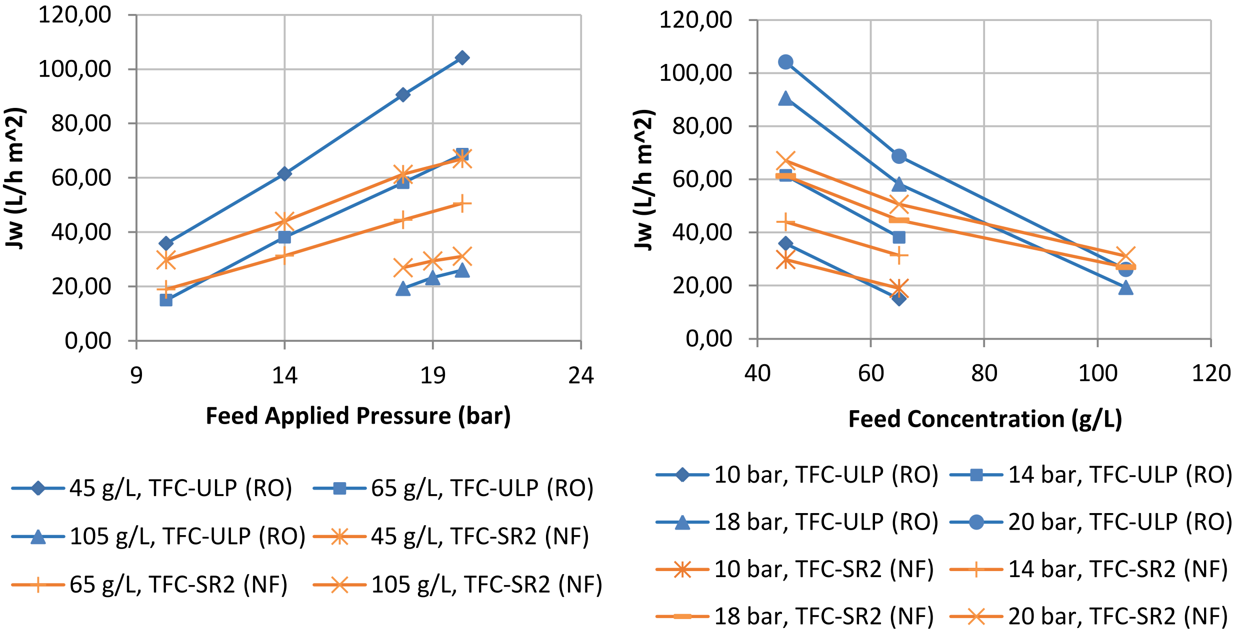
Figures 4.17 a) and b) show the comparison between water fluxes obtained with TFC®-ULP (RO) and those obtained with TFC®-SR®2 (NF) for glucose draw solutions, as a function of feed applied pressure and feed concentration respectively.

It is seen that at lower feed solution concentrations the RO membrane gives higher fluxes, but the behaviour is reversed at higher sugar concentrations, when the NF membrane becomes more permeable. This could be explained considering that, as shown in the previous paragraph, glucose is not well retained by the NF membrane; therefore, despite TFC®-SR®2 is generally less permeable than TFC®-ULP, at higher concentrations the effect of concentration polarization becomes much higher for the RO membrane, and limits the water passage as much at an extent which reverses the behaviour.



a) b)

Figure 4.16 *Comparison between water fluxes obtained with TFC®-ULP and TFC®-SR®2 for sucrose draw solutions, as a function of feed applied pressure (a) and feed concentration (b)*

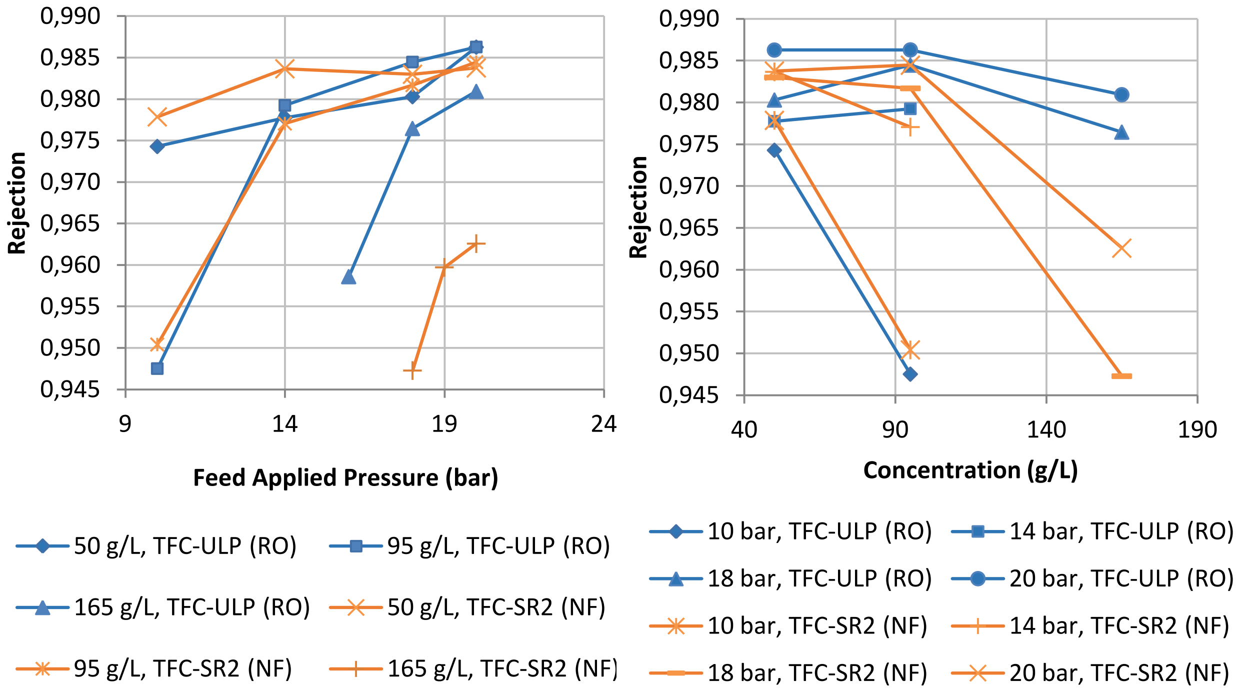


a) b)

Figure 4.17 *Comparison between water fluxes obtained with TFC®-ULP and TFC®-SR®2 for glucose draw solutions, as a function of feed applied pressure (a) and feed concentration (b)*

Sugar Rejection

The comparison between the performances of TFC®-ULP (RO) and TFC®-SR®2 (NF) in terms of sugar rejection is shown in Figures 4.18 a) and b) for sucrose draw solutions having the same values of feed concentration (and therefore of osmotic pressure), as a function of feed applied pressure and concentration respectively.



a) b)

Figure 4.18 *Comparison between TFC®-ULP and TFC®-SR®2in terms of sugar rejection for sucrose solutions, as a function of feed applied pressure (a) and feed concentration (b)*

It can be seen from the above plots that sucrose rejection appears to be higher for the NF membrane at lower feed concentrations and applied pressures, while for higher values of both concentration and hydraulic pressure the RO membrane offers a better performance.

For glucose solutions, the comparison between sugar rejections obtained with TFC®-ULP (RO) and those obtained with TFC®-SR®2 (NF) is shown in Figures 4.19 a) and b), as a function of the feed applied pressure and the concentration, respectively.

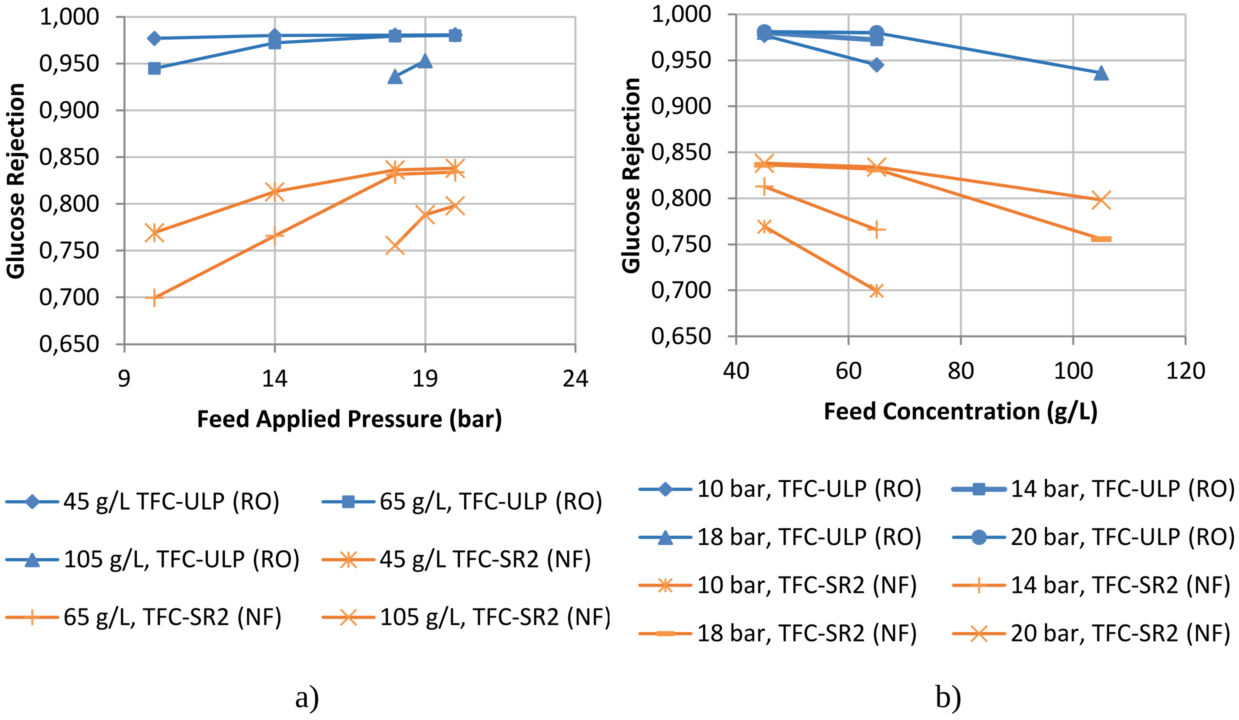


Figure 4.19 *Comparison between TFC®-ULP and TFC®-SR®2in terms of sugar rejection for glucose solutions, as a function of feed applied pressure (a) and feed concentration (b)*

As already anticipated previously, rejection values for glucose solutions are by far lower using the NF membrane, compared to those obtained with TFC®-ULP, for the reasons already explained above. As a matter of fact, these values are too low to be suitable for practical applications.

4.4 Conclusions and recommendations

The effect of feed applied pressure and concentration on water flux and rejection has been presented and discussed in the previous paragraphs, followed by a comparison between the performances of the two sugars and finally of the two membranes. The final considerations are summed up hereafter:

1. Water flux increases along with feed applied hydraulic pressure and decreases with increasing the feed concentration, as these factors influence the Net Driving Pressure, which is the driving force for the process;

   Water flux values are compatible with practical applications;

2. Sugar rejection is higher at increasing values of applied pressure, and lower for higher feed concentrations. This is a consequence of the effect that these two variables have on water flux, which causes the permeate to be more diluted in the first case, and more concentrated in the second;
3. Water flux is always greater when using glucose draw solutions. In particular, the highest flux obtained is of ~104 L/(h·m^2) for a 45 g/L feed solution (π =~6 bar) and 20 bars applied pressure, using TFC®-ULP.
4. Sugar rejection is lower for glucose solutions compared to that for sucrose. In particular, rejection values for glucose using TFC®-SR®2 (NF) membrane (which vary from 70% to 83.8%) are too low for the purposes of this study, and therefore this set is not recommended.

   Nonetheless, excluding the glucose-NF combination, sugar rejection values are always >90% (the lowest one being 93.6% for a 105 g/L glucose solution at 18 bars applied pressure), reaching up to 98%.

   It has to be considered that even if glucose shows slightly lower rejections compared to sucrose with TFC®-ULP (RO) membrane, the feed solution is less concentrated at the same value of osmotic pressure, and this is reflected in lower permeate concentration.
5. The NF membrane shows generally lower fluxes compared to the RO one, and also lower rejections at higher values of feed concentration and applied hydraulic pressure. Therefore, in this study, TFC®-ULP has been seen to give better performances, and is promising to be used in practical applications.

Chapter 5

MOD process modeling

A model for the entire Manipulated Osmosis Desalination (MOD) process is presented in this chapter. First of all, a base case is examined in order to describe the model equations; then, a sensitivity analysis is made to see how the hydraulic pressure that needs to be applied in the recovery step, and subsequently the specific energy consumption, is affected by other design specifications. The model has been solved using MATLAB (R2012b).

5.1 MOD base case modeling

The experimental results have shown that, in the recovery step, TFC®-ULP gave better performances in terms of pure water flux and, generally, of sugar rejection; furthermore, when using this membrane, glucose appeared to be a better osmotic agent compared to sucrose, allowing higher water fluxes at slightly lower, but still high, rejection values. Therefore, this configuration has been chosen to model the second step of the MOD process.

The two steps of MOD, FO and RO, have been modeled separately, and then linked together through mass balances.

5.1.1 FO model

The first step of the MOD process is Direct (or Forward) Osmosis between the saline feed-water and the glucose draw solution; this step is shown in Fig. 5.1, where W is the volumetric flow-rate and c is the solute concentration, in g/L; the subscripts s, b, d and f refer to saline feed-water, discharged brine, concentrated and dilute draw solution respectively. Because no experiments have been carried out on this step, a paper from McCutcheon and Elimelech([31,32]) has been applied in order to model the water flux.

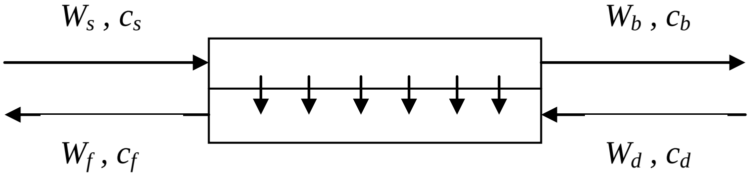


Figure 5.1 *Schematic representation of the FO step*

A first assumption is that there is no salt passage through the membrane, which is equivalent to say that salt rejection is 100%; in addition, it is assumed that there is no reverse sugar flow. Hence, the only parameter to be modelled is water flux J_w.

The driving force for osmotic processes is the difference in osmotic pressure between the draw solution π_d and feed water π_s, and ideally water flux is expressed as(31):

$$J_w = A_{FO}(\pi_d - \pi_s); \tag{5.1}$$

where the flux is expressed in [$m^3/(m^2\ s)$].

A_{FO} is the pure water permeability of the FO membrane. Nonetheless, evidence has shown that the relationship between water flux and the bulk osmotic pressure difference is not linear. This has been attributed not to changes in the membrane permeability, but to the phenomenon of concentration polarization(31,32), both external (ECP) and internal (ICP) (see §2.1.1 and Fig. 2.3), which reduces the driving force, and therefore needs to be taken into account. Eq (5.1) needs then to be modified into:

$$J_w = A_{FO}[\pi_d \exp(-J_w K) - \pi_s \exp(J_w / k_s)]; \tag{5.2}$$

6. ($-J_w K$) is the ICP modulus; the minus sign is because the effect is dilutive on the draw solution side. K is called solute resistance to diffusion, and is calculated as:

   $$K = \frac{t\tau}{D\varepsilon}\ ; \tag{5.3}$$

   in the above equation t, τ and ε are the thickness, tortuosity and porosity of the support layer, respectively, and D is the solute diffusion coefficient through the film.(31). For the purpose of this study, it has been assumed to use the same membrane that was used in the paper(32), which has a value of $t\tau/\varepsilon$ equal to $3.60 \cdot 10^{-4}$ m. The diffusion coefficient of glucose in water is of $6.7 \cdot 10^{-10}$ m^2/s (33), and therefore K results to be $5.37 \cdot 10^5$ s/m.
7. (J_w/k_s) is the ECP modulus, which takes into account the concentrative effect on the membrane active layer on the salted feed-water side. k_s is the solute mass transfer coefficient, which is calculated through Sherwood correlations, as explained in §1.3.3.1. Because it was assumed to use the same membrane investigated in the referred paper(32), the same value of k_s has been adopted ($1.74 \cdot 10^{-5}$ m/s).
8. Pure water permeability A_{FO} value has also been taken from the same work, and is equal to $3.07 \cdot 10^{-7}$ m/(s bar).

The effect of concentration polarization on water flux in the FO step is shown in Fig. 5.2, where flux has been calculated with eq.(5.1) (dotted line) and eq. (5.2) (continuous line), for a feed-water with 7 g/L of salt (π_s = 5.56 bar, calculated with OLI's software) and increasing the draw solution concentration. The feed-water concentration is kept low because glucose draw solutions are feasible only for brackish water applications, as too high concentrations give problems due to viscosity increase.

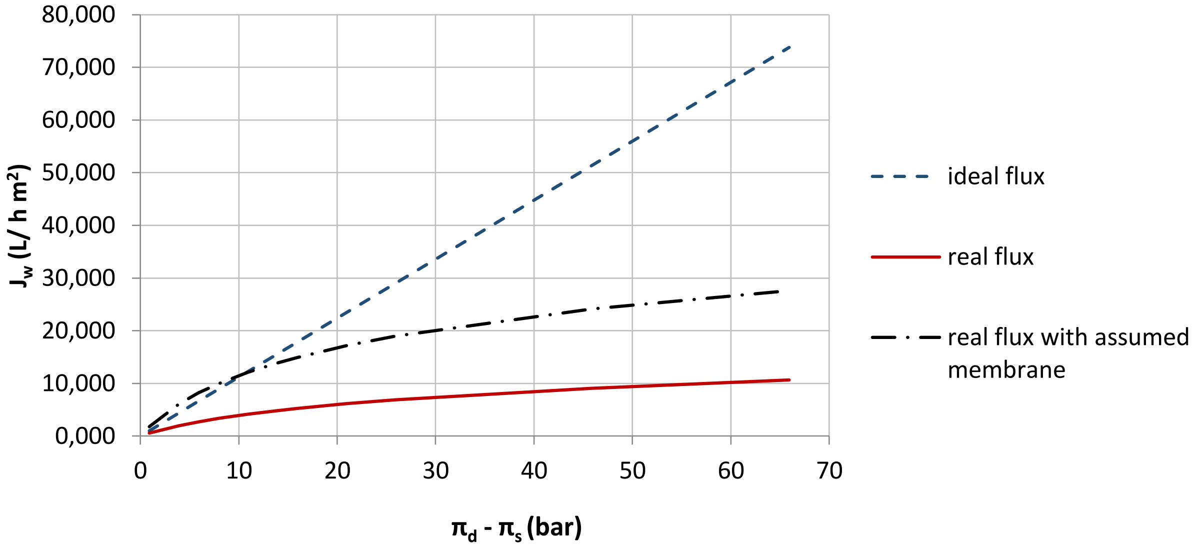


Figure 5.2 *Water flux as a function of bulk osmotic pressure difference: ideal(dotted line), real (continuous line), and with an assumed membrane (dashed line)*

It can be seen that the effect of ICP is dramatic: in fact, to achieve a typical flux of 16 L/(h·m^2)(^{31}), a much higher bulk osmotic pressure difference is required between the feed-water and the glucose draw solution with respect to the ideal case. In addition, it is worth to be noticed that water flux has a self-limiting behaviour: increasing water flux causes an increase in ECP and especially ICP, so their effect is more dramatic(^{31}).

Unfortunately, it is evident that such a membrane cannot be used in MOD, as the draw solution needs to be very concentrated (and to have a very high osmotic pressure) in order to ensure an acceptable water flux, that results in too high hydraulic pressures to be applied in the regeneration step. Therefore, for this simulation, it was assumed to use a membrane with a pure water permeability A_{FO} equal to that of TFC®-ULP, which is $2.94 \cdot 10^{-6}$ m/(s bar), and with a K value equal to half of the original one (meaning that glucose diffuses more easily in the porous support layer, either because it has a higher porosity or lower thickness and tortuosity). For a membrane with such characteristics, water flux is represented in Fig. 2.5 by the dotted (− ·) line: it allows to achieve the required water flux with an acceptable bulk osmotic pressure difference.

Please note that there is no proof that such a membrane exists in reality, and that experiments with glucose and different types of membranes should be carried out in order to validate our model; nonetheless, we think it is qualitatively valid for the purpose of this simulation.

5.1.2 RO model

The model for the RO regeneration step has been constructed based on the experimental results obtained using glucose solutions and TFC®-ULP. A schematic representation of this step is in Fig. 5.3.

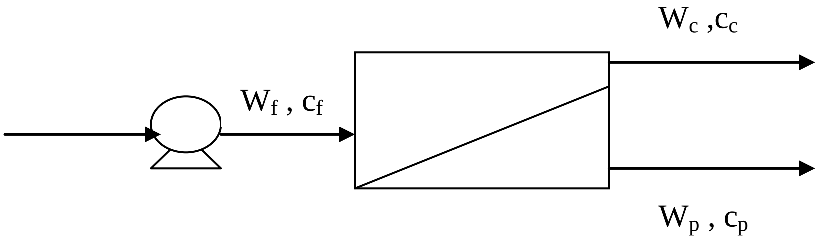


Figure 5.3 *Schematic representation of the RO recovery step*

The two parameters to be modeled are water flux and glucose rejection.
Water flux J_w has been modeled according to the Solution Diffusion Model, as described in §4.3:

$$J_w = A_w(\Delta P - \Delta \pi)\,. \tag{5.4}$$

The overall water permeability has been seen to decrease with increasing glucose concentration (§4.3.2), and this correlation has been determined by fitting the values obtained from calculations on experimental data, as shown in Fig. 5.4:

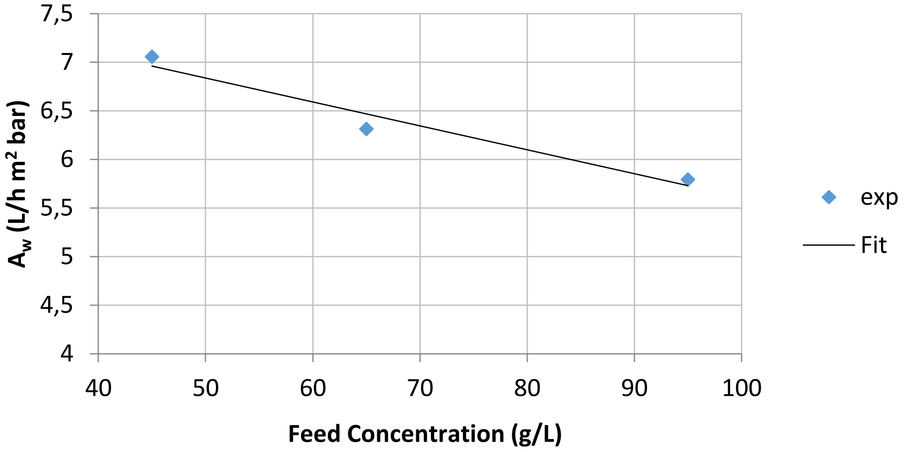


Figure 5.4 *Dependence of overall water permeability A_w from feed solution concentration*

The equation found is:

$$A_w = -0.0246 \cdot c_f + 8.0689. \tag{5.5}$$

The coefficient of determination R^2 is equal to 0.9539. The correlation has been used in the MOD model, even though it is approximate, and therefore more experimental data should be obtained in order to improve it.

Glucose rejection has been seen to depend on both the feed hydraulic pressure and its concentration (Fig. 5.5). Nonetheless, it is evident that beyond a certain value, pressure seems no longer affecting the rejection behaviour.

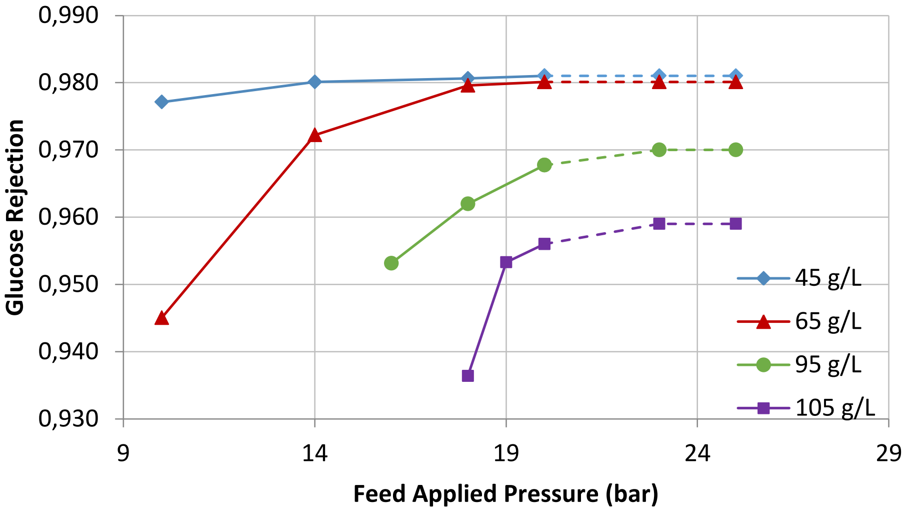


Figure 5.5 *Glucose rejection as a function of the feed hydraulic pressure: experimental values (continuous line) and extrapolation (dotted line)*

Therefore, extrapolating from the experimental results, it is possible to obtain a correlation that links glucose rejection to the feed solution concentration only, that is assumed to be valid for $\Delta P > 20$ bar, as reported in Fig. 5.6 and that was used in the MOD model. This equation is:

$$R_s = 0.9871 + \frac{0.422}{c_f - 120.0079}. \tag{5.6}$$

The coefficient of determination R^2 of this fitting is equal to 0.9981.

However, this assumption should be validated by carrying out experiments at pressures higher than 20 bars, in order to find the correct rejection limit values and improve the proposed correlation. Moreover, the fitting is only valid for the range of concentration investigated, and it should not be used outside these boundaries.

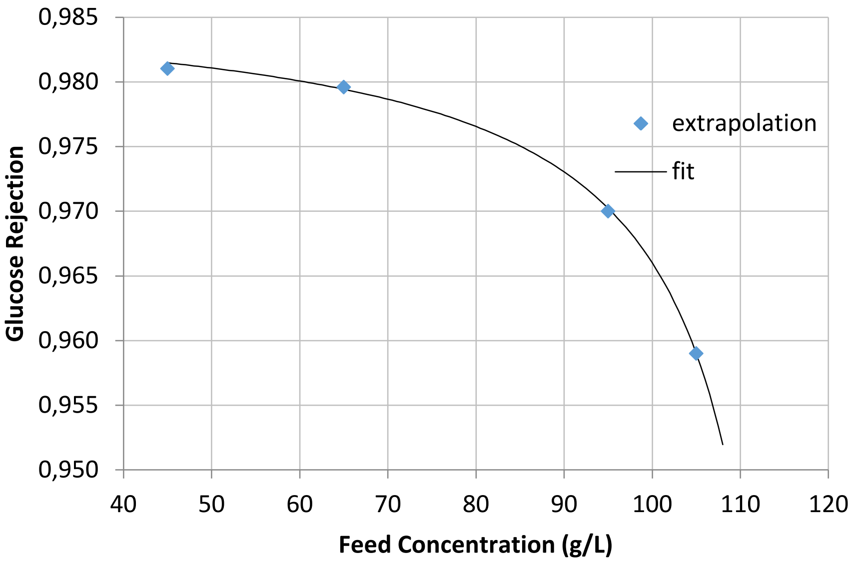


Figure 5.6 *Glucose rejection as a function of feed concentration: fit of the extrapolated values*

5.1.3 MOD model

The equations described in the previous paragraphs have then been used to construct an approximate model for the entire MOD process (Fig. 5.7).

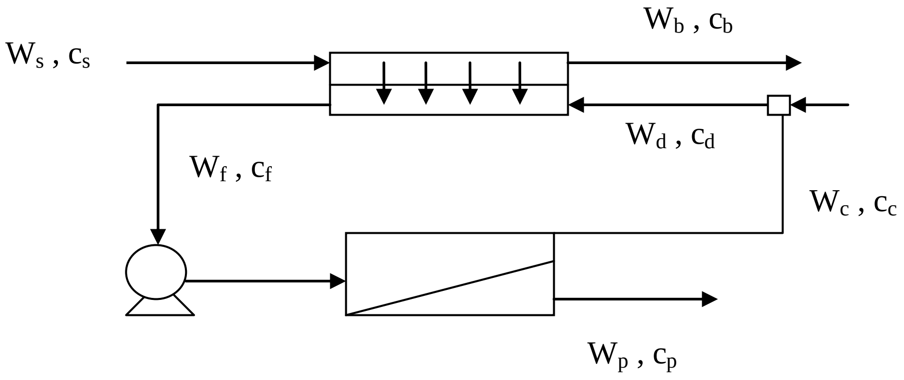


Figure 5.7 *Schematic representation of the MOD process*

The full model is reported in APPENDIX A. The major constraint that has to be obeyed is:

$$J_{w,FO} = J_{w,RO} . \tag{5.7}$$

The following specifications have been assumed:

9. $A_{membrane} = 1 \text{ m}^2$;
10. W_w (= J_w) = 16 L/h (L/h/m^2);
11. c_s = 7 g/L (π_s = 5.5621 bar);
12. c_p = 1.5 g/L; (concentration value accepted for the product water)
13. $\text{Recovery}_{,FO} = W_w/W_f = 35\%$.

The results obtained from the simulation of the model in the conditions described above are summarized in Table 5.1 .

Table 5.1 *Results of the simulation of MOD model, base case*

	s	**b**	**d**	**f**	**c**	**p**
W (L/h)	45,71	29,74	8,94	25,19	8,95	16,02
c (g/L)	7	10,76	197,78	70,19	194,93	1,5
ρ (kg/L)	1,0056	1,0079	1,2157	1,0667	1,2120	1
x (-)	0,00696	0,0107	0,1627	0,0658	0,1608	0,0015
π (bar)	5,5621	-	28,67	9,73	28,23	0,215

R_s	0,979
A_w	6,342
ΔP	21,29
R	0,35

In particular, it is found that the trans-membrane hydraulic pressure that needs to be applied for such a configuration results to be ~21 bar.

5.2 MOD sensitivity analysis

The model has been used to determine how the hydraulic trans-membrane pressure is sensitive to changes in certain process variables, such as the salinity of the feed-water c_s, and the amount of water that is required as a product, W_w (keeping a membrane area of 1 m^2).

The concentration of NaCl in the feed-water has been varied from 7 g/L to 10 g/L, because, as already mentioned in the previous paragraphs, glucose draw solutions are feasible to be used only in brackish water desalination applications, due to their excessive viscosities at high concentrations. The results of the sensitivity analysis are shown in Fig. 5.8.

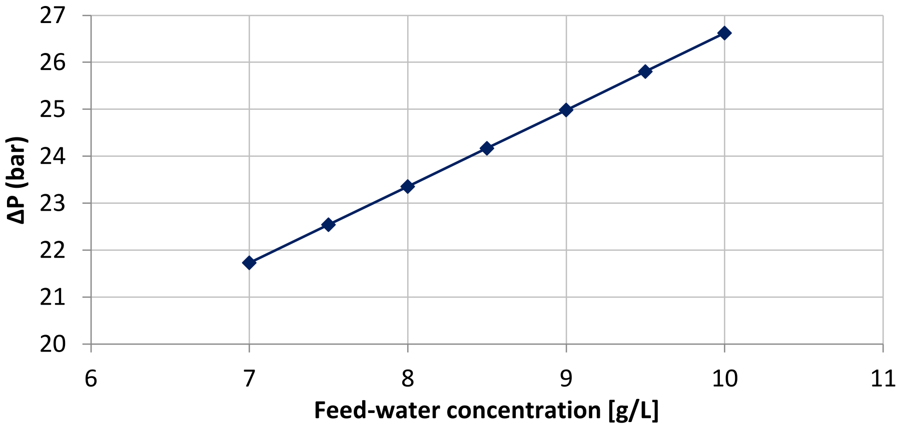


Figure 5.8 *Sensitivity analysis of ΔP to changes in the feed-water salinity. Every other specification has been maintained equal to the base case*

It can be clearly seen from the plot that ΔP increases with an increase in the feed-water salt concentration. Moreover, this increase is linear.

The volumetric flow-rate of product water W_w, and subsequently water flux J_w ($A_{membrane} = 1$ m^2), has been changed to up to 22 L/h, as typical fluxes values in RO are in that range.

As can be seen from Fig. 5.9, ΔP increases with increasing product water flow-rate (flux), and the dependence is more than linear.

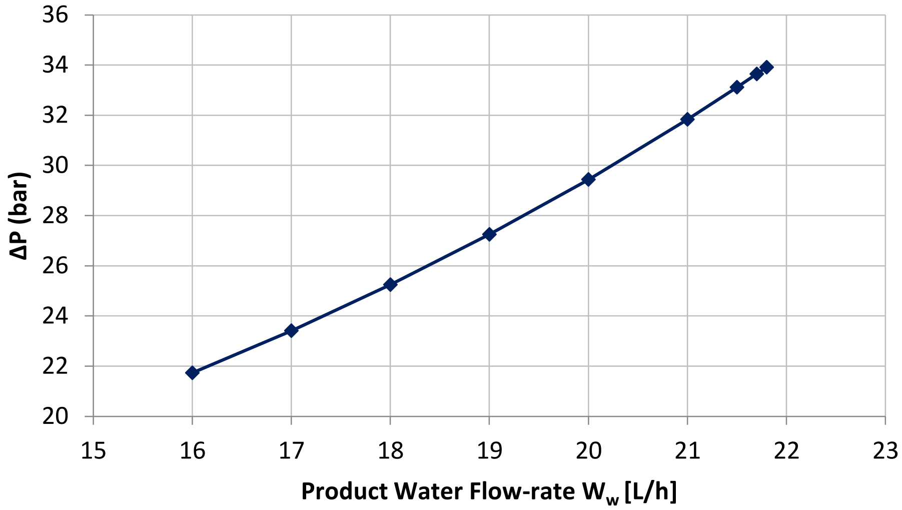


Figure 5.9 *Sensitivity analysis of ΔP to changes in the product water flow-rate (flux)*
Every other specification has been maintained equal to the base case

5.6 Conclusions and recommendations

The model described in this chapter allows to approximately simulate the operation of the MOD process working with a glucose draw solution. It also allows to see the influence of certain process variables and specifications on the trans-membrane hydraulic pressure of the RO recovery step, which determines the specific energy consumption.

The results obtained for a typical brackish water desalination case are plausible, with ΔP values of around 21 bar. Nonetheless, the uncertainty of the model is not meaningless: first, experiments should be carried out for the FO stage to verify the assumptions that were made; secondly, more experiments should be made for the RO stage also, in order to obtain more accurate correlations for the overall water permeability (A_w) and glucose rejection. Finally, it has to be pointed that if in eq. (5.2) instead of π_d and π_s the more correct average trans-membrane osmotic pressures were used ($(\pi_d + \pi_f)/2$ and $(\pi_s + \pi_b)/2$ respectively), ΔP would result to be much higher (~36 bar). To lower the value back to an acceptable result (~23 bar), the solute resistance to diffusion K of the hypothesized membrane should be equal to one third of that of the referenced paper, instead of one half.

Conclusions

The present work aimed at investigating the efficiency of the Reverse Osmosis recovery unit of the Manipulated Osmosis Desalination (MOD) process, when using sugars as osmotic agents in the draw solution. In particular, the tested sugars were glucose and sucrose, and two different kinds of flat-sheet membranes were used (TFC®-ULP as a RO membrane and TFC®-SR®2 as a NF, both manufactured by Koch Membrane System Inc.)

The experiments have been carried out using a bench-scale RO cell supplied by SpinTek Filtration Inc. (USA); different sugar feed concentrations (osmotic pressure π ranging from 4 to 16 bar) and feed hydraulic pressures (up to 20 bar) have been investigated, and for each operative condition water flux and sugar rejection have been determined. Sugar concentration in the samples has been measured by HPLC analysis using a Varian 920-LC HPLC instrument with a Varian 385-LC light scattering detector.

Results have shown that TFC®-ULP is more permeable if compared to TFC®-SR®2, and generally achieves higher rejection values. Moreover, it was seen that glucose draw solutions allow higher water fluxes than those with sucrose, with both membranes, but lower rejections. In particular, with the NF membrane glucose rejection values were between 70% and 80%, therefore too low for the purpose of this study. Nonetheless, when using TFC®-ULP glucose rejection is just slightly lower than that of sucrose, and its values are always above 90% (the smaller one being 93.6%). This suggests that glucose and sucrose are potentially good osmotic agents to be used in the MOD process, as far as the RO recovery step is concerned.

The data obtained have been used to develop a simple and approximate model for the simulation of the entire MOD process, with the aim of determining the influence that process operative conditions have on the energy consumption.

Admittedly, the study has some limitations. First of all, wider ranges of feed concentrations and pressures should be investigated in order to obtain more robust experimental data to be used for improving the model. Secondly, the effect of temperature on the parameters of interest has only partially been considered, but it may have a relevant influence. Finally, no experimental data about the Forward Osmosis step have yet been obtained, therefore the current model is based on literature data and assumptions.

Nonetheless, the promising results obtained from this preliminary study about the RO recovery step suggest that it is convenient to continue the research in this direction. More sugar types, like fructose and maltose, could be tested together with different membranes in the RO recovery step; the study should be completed with FO experiments to verify the compatibility of the two steps and to improve the model proposed.

Nomenclature

A = Solvent permeability coefficient
A_w = Overall water permeability
a_w = Water activity
A_{wm} = Pure water permeability
B = Solute permeability coefficient
c = Solute concentration [g/L]
C = Molar concentration
d = Hydraulic diameter
D_s = Solute diffusivity coefficient
D_w = Water diffusivity coefficient
i = Dissociation parameter
J_s = Solute mass flux
J_w = Volumetric Water Flux
K = Solute resistance to diffusion
k = Solute mass transfer coefficient
l = Membrane thickness
n_s = Moles of solute
P = Hydraulic pressure
R = Recovery
R = Ideal gas constant
Re = Reynolds number
R_s = Sugar Rejection
Sc = Schmidt number
Sh = Sherwood number
T = Temperature
V = Total volume
V_w = Water molar volume
W = Volumetric flow-rate
x = Weight fraction

Greek letters

δ = Build-up layer thickness
ε = Support layer porosity

μ = Viscosity
π = Osmotic pressure
ρ = Density
τ = Support layer tortuosity
Φ = Osmotic coefficient

Subscripts

b = Brine
c = Concentrate
d = Concentrated draw solution
f = RO feed (diluted draw solution)
m = Membrane
p = Permeate
s = Saline feed-water
w = Water

Acronyms

ASDPF = Analytical Solution-Diffusion Pore-Flow
CA = Cellulose Acetate
CORA = Center for Osmosis Research and Application
ECP = External Concentration Polarization
ED = Electrodyalisis
EDR = Electrodyalisis Reversal
EPA = Environmental Protection Agency
ERT = Energy Recovery Turbines
FO = Forward Osmosis
HPLC = High Performance Liquid Chromatography
ICP = Internal Concentration Polarization
MED = Multiple Effect Distillation
MOD = Manipulated Osmosis Desalination
MSF = Multi-Stage Flash
MWCO = Molecular Weight Cut-Off
NDP = Net Driving Pressure
NF = Nano-filtration
PR = Product Ratio
PV = Photovoltaic

PX = Pressure Exchangers
RES = Renewable Energy Sources
RO = Reverse Osmosis
SDM = Solution-Diffusion Model
SR = Selective Rejection
SWRO = Seawater Reverse Osmosis
TCF = Temperature Correction Factor
TDS = Total Dissolved Solids
TFC = Thin-Film Composite
ULP = Ultra-low Pressure
VC = Vapour Compression
WHO = World Health Organization

Appendices

APPENDIX A – MOD model

The equations used to model the entire MOD process are hereafter presented, based on Fig. 5.7.

$$W_{w,FO} = A_{FO}\left[\pi_d \cdot \exp(-W_w K) - \pi_s \cdot \exp\left(\frac{W_w}{k_s}\right)\right]$$

$$W_s \rho_s x_s = W_b \rho_b x_b$$

$$W_s \rho_s (1-x_s) = W_b \rho_b (1-x_b) + W_w \rho_w$$

$$W_d \rho_d x_d = W_f \rho_f x_f$$

$$W_d \rho_d (1-x_d) + W_w \rho_w = W_f \rho_f (1-x_f)$$

$$W_w = 0.35 \cdot W_s$$

$$W_f \rho_f x_f = W_c \rho_c x_c + W_p \rho_w x_p$$

$$W_f \rho_f (1-x_f) = W_c \rho_c (1-x_c) + W_p \rho_w (1-x_p)$$

$$W_w \rho_w = W_p \rho_w (1-x_p)$$

$$W_{w,FO} = W_{w,RO}$$

$$W_{w,RO} = A_w\left[\Delta P - \left(\frac{\pi_f + \pi_c}{2} - \pi_p\right)\right]$$

$$A_w = -0.0246 \cdot c_f + 8.0689$$

$$R_s = 1 - \frac{c_p}{c_f}$$

$$R_s = 0.9871 + \frac{0.422}{(c_f - 120.0079)}$$

The densities and osmotic pressures of each stream have been calculated fitting a large amount of values calculated using OLI's software for different concentrations.

For glucose:

$$\rho = 1 \cdot 10^{-6} c^2 + 0.0009c + 0.9986;$$

$$\pi = 5 \cdot 10^{-5} c^2 + 0.135c + 0.0126.$$

For NaCl:

$$\rho = 0.0006c + 1.0014;$$

$$\pi = 0.0011c^2 + 0.7263c + 0.4241$$

In addition, density ρ, concentration c and weight fraction x of each stream are related through the following equation:

$$c\left[g_{sol}/L\right]=\rho[g_{tot}/L]\cdot x[g_{sol}/g_{tot}].$$

The system of 31 equations in 31 unknowns has been solved with MATLAB (R2012b) using the *fsolve* solver.

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