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FORWARD OSMOSIS: INFLUENCE OF SUCROSE AND SODIUM CHLORIDE AS DRAW SOLUTIONS ON PROCESS PERFORMANCE

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Riassunto

La scarsità d'acqua è un problema che interessa molti Paesi. Nonostante la superficie terrestre sia coperta per circa il 70% da acqua, il 97.5% è composto da acqua salata e solo il 2.5% è composto da acqua fresca. Gran parte dell'acqua fresca direttamente accessibile viene impiegata nel settore alimentare e nel settore dell'agricoltura (70%), e quest'ultimo è destinato ad un consistente aumento di domanda a causa della crescita di popolazione mondiale, stimata essere circa 9.1 miliardi nel 2050. Anche la domanda d'acqua del settore industriale che è del 20% è destinata a crescere; in tal caso è stimato un aumento del consumo di energia globale del 49% nel 2035. Nonostante la gestione dell'acqua sia sempre più efficiente, per cui nei paesi più industrializzati il consumo d'acqua pro capite è via via sempre più ridotto, la domanda è destinata a crescere a tal punto che una intensa gestione dell'utilizzo e distribuzione d'acqua non sono sufficienti. Per far fronte a questa allarmante questione, la desalinizzazione dell'acqua si è sviluppata come alternativa per accedere ad acqua potabile da mari e oceani; l'industria della desalinizzazione ha progredito esponenzialmente dalla metà dello scorso secolo fino a raggiungere una produzione globale di 66.4 milioni di metri cubi al giorno. Questa crescita esponenziale è dovuta ai significativi miglioramenti tecnologici che hanno reso i processi di desalinizzazione economicamente competivi.

Le tecniche esistenti di desalinizzazione si basano principalmente su metodi termici e su processi con membrane. I metodi termici rappresentano la tecnologia più tradizionale, che basa la desalinizzazione di acqua salina sull'allontanamento dell'acqua fornendo energia sotto forma di calore; si tratta di una tecnica molto dispendiosa, e che fu la prima a essere sviluppata. Nonostante il dispendio energetico, molti paesi tuttora affidano la produzione di acqua potabile a processi termici. Questo avviene dove è alta la disponibilità di petrolio a basso costo, come nel Medio Oriente. I metodi a membrana cominciarono a essere competitivi negli anni '70 quando i metodi termici erano già largamente utilizzati, e negli ultimi decenni la loro applicazione è aumentata grazie a membrane più affidabili e selettive. A giorno d'oggi circa il 60% della produzione globale d'acqua potabile è affidato a tale tecnica. Recentemente la ricerca si sta orientando su tecniche ibride che sfruttano energie rinnovabili, e tecniche alternative sempre basate su membrane al fine di abbassare i costi di produzione.

Una delle più promettenti di queste tecniche alternative è costituita dal processo MOD (Manipulated Osmosis Process), sviluppato dal team CORA (Centre of Osmosis Research an Application) presso la University of Surrey, e coperto da brevetto. Tale processo prevede uno step iniziale che consiste in un sistema di osmosi diretta (*forward osmosis*) e un secondo step di rigenerazione, che può essere nanofiltrazione o osmosi inversa (*reverse osmosis*). La desalinizzazione è ottenuta grazie a una soluzione osmotica che ricircola alimentando

costantemente i due processi a membrana. Tale soluzione, detta *"draw solution"*, è caratterizzata da una pressione osmotica superiore a quella dell'acqua salina, per cui nel primo step di osmosi diretta si sfrutta il gradiente di pressione osmotica delle due soluzione per estrarre l'acqua potabile dall'alimentazione. Tale fenomeno naturale avviene perché una membrana separa le due soluzioni con la peculiarità di essere permeabile al solvente piuttosto che ai soluti. La *draw solution* diluita alimenta il secondo step in cui la soluzione viene rigenerata per nanofiltrazione o osmosi inversa. In tale step viene esercitata una pressione idraulica per vincere la differenza di pressione osmotica, ma la natura e le caratteristiche di pulizia della *draw solution* permettono di rendere il processo economicamente vantaggioso, in quanto richiede pressioni minori. I principali vantaggi del processo MOD sono quindi: ridotto consumo energetico, aumento della durata della vita delle membrane e quindi riduzione dei costi di esercizio ad esse associati. Per esercire tale processo la *draw solution* deve essere selezionata in modo da assicurare un'elevata efficienza in entrambe le unità a membrana: questo vincolo rende la scelta della *draw solution* non immediata, anche perché le caratteristiche di alcuni soluti migliorano le prestazioni di una sola unità come ad esempio la dimensione della molecola disciolta. In generale una *draw solution* adatta deve rispettare molti criteri come basso costo, no tossico, alta pressione osmotica a basse concentrazioni, alta solubilità in acqua, stato solido a temperatura ambiente.

Lo scopo di questo lavoro è di testare una *draw solution* composta da saccarosio e cloruro di sodio nel processo di *forward osmosis*, in particolare miscele con diverse concentrazioni dei due soluti che contribuiscono diversamente alla pressione osmotica totale. Dapprima è stato fissato il contributo osmotico del cloruro di sodio a 10 bar variando quello dato dal saccarosio, per poi fissare a 10 bar il contributo osmotico del saccarosio variando quello dato dal cloruro di sodio. Le prestazioni del processo vengono misurate in termini di recupero d'acqua, flusso, ritenzione del soluto, consumo d'energia e *performance ratio*. Gli esperimenti sono stati svolti testando le *draw solutions* contro acqua distillata e acqua salmastra mediante un impianto pilota di osmosi diretta in cui è installata una membrana di tipo *hollow fiber* in triacetato di cellulosa. Al fine di valutare la ritenzione dei soluti sono state eseguite analisi quantitative alle alimentazioni. I risultati relativi all'analisi dei cloruri hanno mostrato una discordanza non accettabile con le concentrazioni note, rendendo il calcolo dell'indice di ritenzione poco affidabile. Una tecnica di analisi amperometrica quantitativa basata su biosensore è stata presa in considerazione per l'analisi del saccarosio come analisi alternativa all'HPLC dal momento che in lavori precedenti è stata riscontrata un'interferenza analitica del saccarosio col sale, ma senza successo. La *draw solution* con contributo osmotico del cloruro di sodio variabile fornisce indici prestazionali migliori. In particolare il flusso è maggiore dell'11% rispetto all'altra *draw solution*. L'impiego di acqua salmastra fa crollare i flussi ottenuti con acqua distillata di circa il 40% nonostante la pressione osmotica dell'alimentazione salina sia solo 4 bar. Dai valori di ritenzione si osserva una forte dipendenza dal flusso: con acqua distillata essi superano il 99.9% per entrambi i soluti, mentre con acqua salmastra la ritenzione cala al 99.5% per il saccarosio e al circa 90% per il cloruro di sodio. I fenomeni fisici responsabili dello scostamento dalla idealità del flusso di acqua sono descritti da un modello i cui parametri sono stati ricavati implicitamente dai valori sperimentali di flusso ottenendo, previa alcune assunzioni, una modellazione dei flussi dei vari esperimenti. Questo risultato viene considerato accettabile per l'intervallo di differenza di pressioni osmotiche studiato, sebbene sia consigliabile verificare le assunzioni sperimentalmente operando a portate di *draw solution* costanti. In questo modo può essere possibile trovare un profilo dei parametri in funzione della pressione osmotica che permetta di estrapolare il modello di flusso nel range non esaminato.

Le soluzioni composte da saccarosio e cloruro di sodio potrebbero rappresentare un buon compromesso per i processi costituenti il MOD, ma per poter valutare meglio il compromesso esse necessitano di essere testate per l'unità di rigenerazione, in modo da prendere in considerazione entrambi i processi nella valutazione finale.

Desidero ringraziare la Faculty of Engineering and Psysical Sciences della University of Surrey, e in particolare il Dr. Sami Al-Aibi per avermi permesso di svolgere il mio lavoro di Tesi e per il suo costante aiuto durante lo svolgimento dell'intero lavoro.

Abstract

This thesis work investigates experimentally the performance of different draw solutions on Forward Osmosis, first step of the Manipulated Osmosis Desalination (MOD) process. The research was performed by measuring the water flux and solute rejections at different draw solution concentrations in which mixtures of sucrose and sodium chloride are involved. The draw solutions were tested at constant temperature (25°C) in a trial plant in which a hollow fiber TCA FO membrane is installed. Different combinations of osmotic pressure contributions of sucrose and sodium chloride were tested: firstly fixing the sodium chloride osmotic pressure at 10 bar and secondly fixing the sucrose osmotic pressure at 10 bar; both mixtures were tested with distilled water and brackish water as feed solutions. From the experimental parameters recorded it was possible to calculate several performance indices such as recovery, water flux, solute rejection, performance ratio. The experimental data were implemented in a model able to describe the water flux through the membrane in order to obtain implicitly the model parameters which express the physical phenomena causing a non-ideal water flux.

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Introduction

Water shortage is one of the most important issues at the present time. Despite the enormous amount of water present in the Earth's surface, freshwater is not directly accessible for many countries: the people without direct access to water are 345 million in Africa, 196 million in South, West and Central Asia, 200 million in Southeast, East Asia and Oceania against only 10 million in the rest of the World (WHO/UNICEF). Freshwater, which represents the 2.5% of the world's available water, is frozen in the form of ice and snow for about 70% and stored underground for about 30% (UNEP). The water demand is expected to raise by next years because of world population growth, irrigation and food production, in fact the agricolture sector is responsible of about 70% of freshwater drawing.

Many countries in the world have already adopted desalination technology to overcome this lack in order to produce freshwater from seawater and brackish water. Desalination industry started developing in 40's and the number of plants has been exponentially increasing due to primarly technological advances which allowed to make this operation cost-competitive. The desalination processes can be divided into two main groups: thermal and membrane methods. In first case water is separated by evaporation and condensation with an operation which requires an enormous amount of energy; thermals methods represent the first technology developed and nowadays, despite representing only about 35% of the global desalination technology, is still used in Middle East areas because of large availability of oil at low cost. More than 60% of the current freshwater production relies on membrane technology, which began more competitive in the 1970s thanks to the production of reliable and more selective membranes.

Research is focusing on alternative energy sources in order to make freshwater production as much economical as possible, such as with photovoltaic cells and wind-power but the market is still marginal. One of the most promising alternatives is the Manipulated Osmosis Desalination (MOD) process, developed at the Centre for Osmosis Research and Application (CORA) at the University of Surrey. This process is based on membranes and consists of a Forward Osmosis system and a Reverse Osmosis or Nanofiltration recovery step. The process exploits a particular draw solution which feeds both steps: the high osmotic pressure of the draw solution permits to extract the water from seawater or brackish water by a forward osmosis step, afterwards the diluted draw solution is re-concentrated in a Reverse Osmosis regeneration step and recycled to the first step. The whole process permits to product freshwater at lower energy consumption, as the pressure required for the reverse osmosis regeneration step is about 65 bar in place of 85 required for a traditional seawater reverse osmosis. A suitable draw solution must be selected taking into account both MOD steps, in particular it has to minimize phenomena of concentration polarization, fouling deposition and reverse solute flux; furthermore it has to be non-toxic and available at low cost. Although many efforts are focused on membrane improvements, the selection of the draw solution plays a very important role: it must ensure a high performance in both of the process steps.

The aim of this work is to investigate the forward osmosis performance whit a mixture of sucrose and sodium chloride in the draw solution; the process performance is examined in terms of recovery, water flux, solute rejection, energy consumption and performance ratio. The mixture involved might represent a good trade-off for the forward osmosis and regeneration step. Several experiments were carried out during this study using a hollow fiber cellulose triacetate (CTA) FO membrane. Draw solutions at different osmotic pressure were tested for which the osmotic pressure contribution is given differently changing the ratio of the solutes concentrations.

Chapter 1 provides a general overview on the problem of water scarcity, followed by a description of the mainly employed desalination technologies, with a particular detail on the forward osmosis.

In Chapter 2 the experimental work is described which consists of testing different draw solutions and analysing quantitatively the solutes concentration; equipments, materials and procedures are presented.

Chapter 3 collects and discusses the results obtained.

Finally, in Chapter 4 the results are implemented in a model of the water flux in order to get the model parameters of the draw solutions.

I would like to thank the Faculty of Engineering and Psysical Sciences at the University of Surrey and, in particular Dr. Sami Al-Aibi for giving me the opportunity to do my Master Thesis and for his help throughout the work.

Chapter 1

Desalination

This chapter indroduces the problem of water scarcity that plagues many countries, which drives the desalination market. A general introduction of existing desalination processes is given, in particular their principle of working, treatments required, costs and trends, effects on the environment and future prospects.

1.1 Water issue

Despite most of the terrestrial surface is covered by water, water scarcity is a problem that affects many countries. It derives from the fact that, of the total amount of the available water, only 2.5% is freshwater and the remaining 97.5% is saltwater (UNEP). Unfortunately the directly accessible freshwater (lakes and river) is only 0.3%, while the remaining is frozen in the form of ice and snow (about 70%) or stored underground (about 30%) (UNEP). The people without direct access to water are 345 million in Africa, 196 million in South, West and Central Asia, 200 million in Southeast, East Asia and Oceania against only 10 million in the rest of the World (WHO/UNICEF). A large part of the world therefore suffers from water scarcity that involves water stress, meant as depleting of resources, and water crisis as deficiency of available water to meet the real demand. Most of the accessible freshwater available is used for irrigation and food production which are the main responsible of freshwater drawing (70%); the agriculture sector has a large water footprint expected to grow more in the years to come: in fact the world population is predicted to grow to 9.1 billion in 2050 (UNDESA,2009*a*). The industrial sector takes around 20% of freshwater that often requires some kind of treatments to reach different qualities depending on the destination: it needs drinking water for food processing, very high-quality water for pharmaceutical and high technology. Every single operation from irrigation to water supply for domestic use needs some kind of energy that cannot be considered independent of the water itself. Energy and water are intrinsically connected: all energy and electricity sources need water for many operation processes including extraction of raw materials, cooling in thermal processes, cleaning material, powering turbines. At the same time energy is required to make the water resources available for distribution, treatment, desalination and irrigation [1]. The global energy consumption is predicted to increase of around 49% from 2007 to 2035 (EIA, 2010). Despite per capita consumption of water is decreasing in the most industrialized countries because of an increasingly intense management, overall demand of water is rising and a proper management may not be enough [1]. Many countries in the world have already adopted desalination technologies that produce freshwater from seawater for human use and irrigation to overcome to this lack. The desalination industry has progressed exponentially from the middle of the last century: in 1960 there were only five units able to produce 5000 m^3/d, compared to 12,500 units operating in 2000 with a productivity of 22.7×10^6 m^3/d intended to supply more than 120 countries in the world [2]. During the last decade the desalination industry has furtherly spread, indication of risolutive reliable technology, with a current global desalination capacity of 66.4×10^6 m^3/d [3]. This increase of desalination capacity is also due to significant technological advances which have allowed to make this operation cost-competitive [4].

1.2 Desalination techniques

Any desalination process allows to obtain a stream of freshwater from a concentrated feed stream. Applying this principle to saltwater like seawater or brackish water, it is possible to recover the water isolating it from the solute, thus obtaining freshwater free of salts and a concentrated solution called brine [5]. When it comes to water desalination, the water classification is expressed in terms of total dissolved solids (TDS). The "Glossary os Salt Water" published by Water Quality Association classifies water as: fresh water <1,000 ppm TDS, brackish water 1,000-5,000 ppm TDS, highly brackish water 5,000-15,000 ppm TDS, saline 15,000-30,000 ppm TDS, sea water 30,000-40,000 ppm TDS and brine 40,000-300,000+ ppm TDS. The term TDS means inorganic salts and small amounts of inorganic matter present in the water, the main costituents are usually calcium, magnesium, sodium, and potassium cations and carbonate, hydrogencarbonate, chloride, sulfate, and nitrate anions [6].

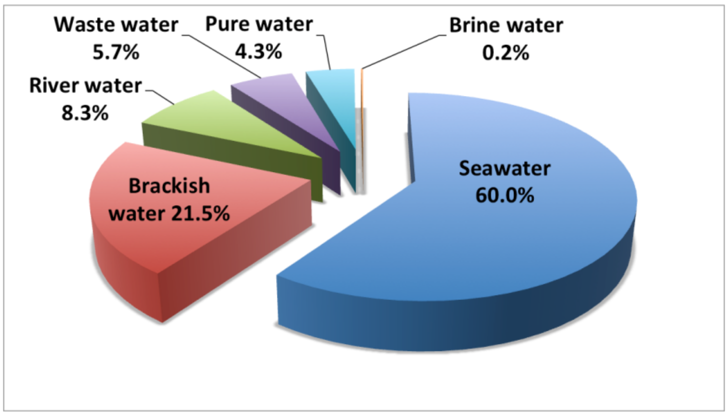


Figure 1.1 *Breakdown of water sources for global desalination processes. Source: DesalData.com*

Despite a good water, from the potability point of view, is defined between 300 and 600 mg/litre, a concentration below 1000 mg/litre is acceptable to consumers. From the plant point of view, water that has a concentration of TDS >500 mg/litre could promote a quicker limescale deposition, reducing efficiency and service life of equipment such as water pipes, water heaters, heat exchangers, boilers, kettles [6]. Figure 1.1 shows the breakdown of the water sources which feed the global desalination processes and seawater represents the majority with 60%. The main desalination process thus concerns the removal of salinity from brackish water like that found in some seas and lakes, and from seawater. Beyond the different salinity of the water feed, the typical flow diagram of the seawater desalination process is shown in Figure 1.2.

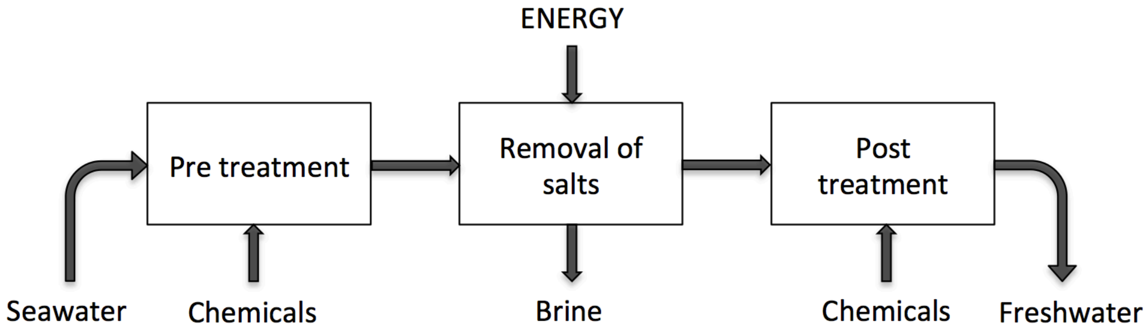


Figure 1.2 *Desalination process flow diagram.*

Focusing on the heart of the plant, several kinds of processes have been developed, mainly based on two methods: thermal and membrane separations. In the first method heat as form of energy is used so that water is removed from the feed condensing the vapour obtained by evaporation. An enormous amont of energy is required to produce the vapour. The most known thermal methods are multi-stage flash process (MSF) and multi-effect distillation (MED). Membrane methods apply an exclusion principle, allowed by a physical barrier that permits only the solvent or solute transfer. This selective crossing through the membrane is generated by a form of energy that could be electricity or pressure. The most common desalination membrane processes are reverse osmosis (RO) and electrodialysis (ED). Despite in 1999 around 78% of the world's seawater desalination capacity was made of multi-stage flash processes, whereas only 10% were represented by reverse osmosis [7], nowadays membrane methods represent the most widespread technology regarding desalination; in fact they have been successfully developed in the last years and represent the future of desalination. The desalination processes technology's spread is shown in Figure 1.3.

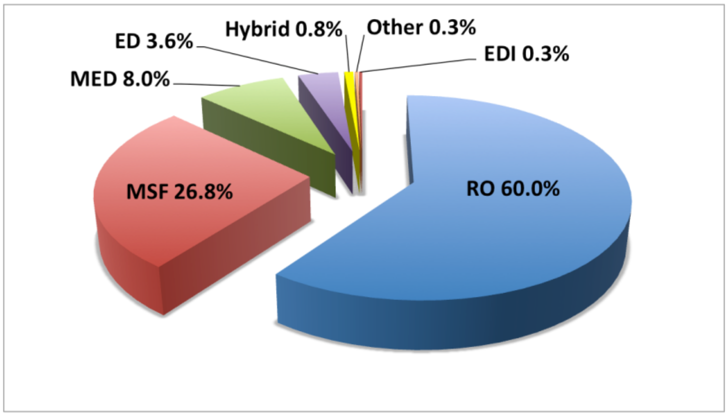


Figure 1.3 *Breakdown of installed desalination capacities by technology. Source: DesalData.com*

1.2.1 Thermal methods

They represent the first technlogy that was developed since the middle of the last century. Figure 1.4 shows the top 10 countries by total installed capacity since 1945.

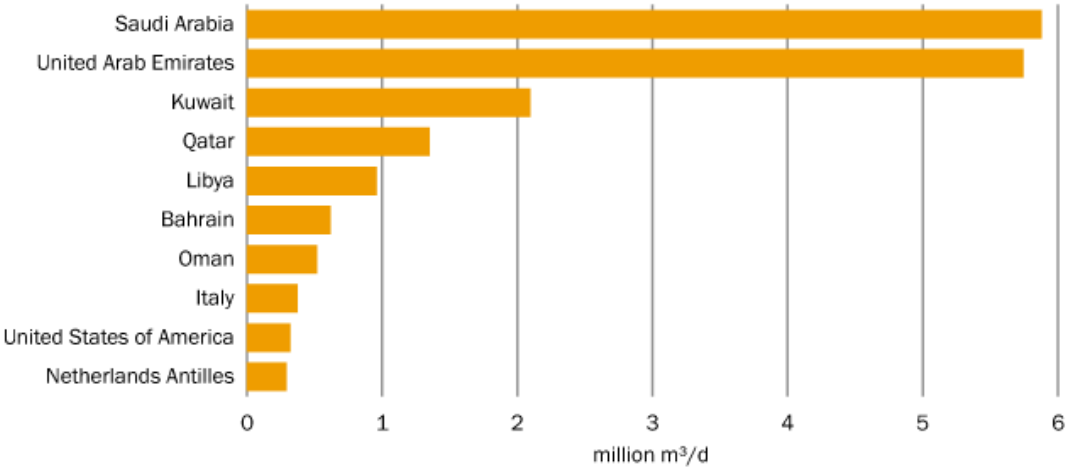


Figure 1.4 *Top 10 countries by total installed thermal capacity since 1945. Source: DesalData.com*

The gulf states keep relying on their freshwater production exploiting the large availability of oil at low cost. The phase change of water that occurs in order to remove the solvent from the solute requires enormous amount of thermal energy that makes these kind of processes expensive. The most spread thermal processes are now described.

1.2.1.1 Multi-effect distillation

The MED process, the oldest technique for seawater desalination [8], is depicted in Figure 1.5.

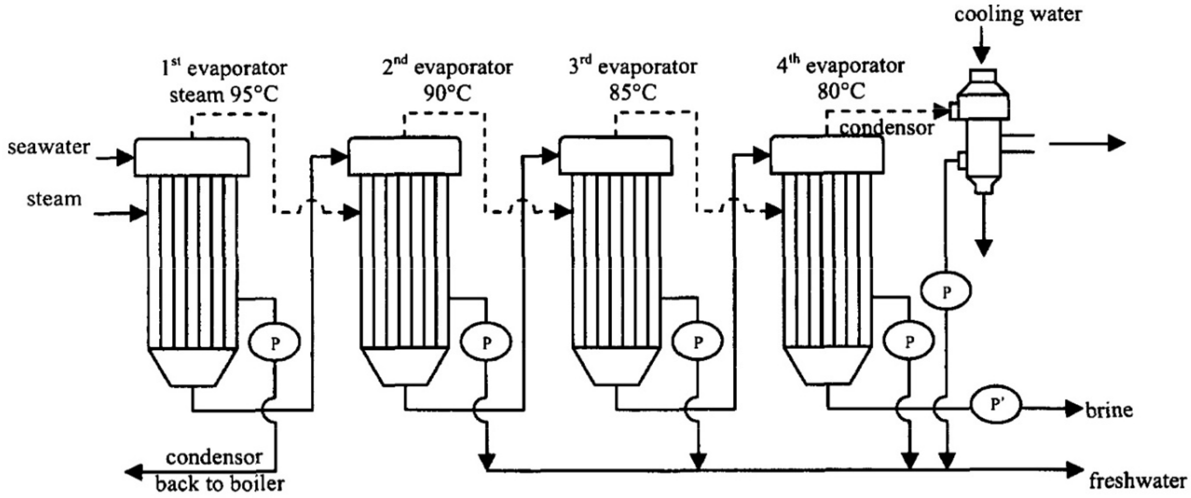


Figure 1.5 *Principle of MED process (multi-effect distillation)*

This process takes place in a series of evaporators, called effects, in which the pressure is gradually lowered [7]. In this configuration only primary steam as form of thermal energy is provided, that causes the partial evaporation of the seawater. The vapour generated from the feed causes the partial evaporation of the salt enriched seawater coming out from the first effect. A decrease of pressure is necessary to ensure the following distillation. As going toward the last effect the boiling temperature of the water decreases, and on average a minimal difference of 5°C is needed in each effect [8]. The number of effects is determinated by the maxinum temperature allowed of 120°C, that limits the risk of scaling, and the temperature of the brine in the last effect that should allow the preheating of the feed [8]. The usual number of effects is between 8 and 16 [8]. An efficient heat transfer is guaranteed by spray nozzles or perforated trays.

1.2.1.2 Multi-stage flash

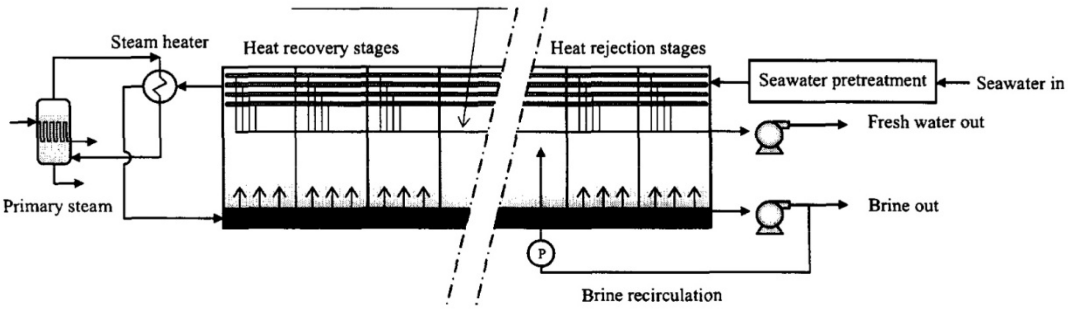


Figure 1.6 *Principle of MSF process (multi-stage flash)*

The operation of multi-stage flash process is based on a series of flash where steam is generated from saline seawater at a progressively reduced pressure (Figure 1.6) [8]. The freshwater is obtained condensing the vapour developed by flash chambers with the feed, that is in this way preheated. After it has been preheated, the temperature of the seawater is increased by primarly steam until maxinum 120°C to prevent the risk of scaling. In each stage the pressure is mantained below the saturation value corresponding to the temperature of the heated seawater flowing into it [7]. The number of multi-stages of a typical large modern plant is between 19 and 28 [7]. This process represents one of the easiest and most reliable processes between the thermal methods that have been the most used for decades since the early 1960s.

1.2.2 Membrane methods

Membrane technology began to be competitive in the 1970s, while thermal methods were already widely available [4]. In the last decades there has been an exponential growth of these methods due to the development of more reliable and selective membranes, which caused a decrease of the process costs. Figure 1.7 shows the top 10 countries by total installed capacity since 1945.

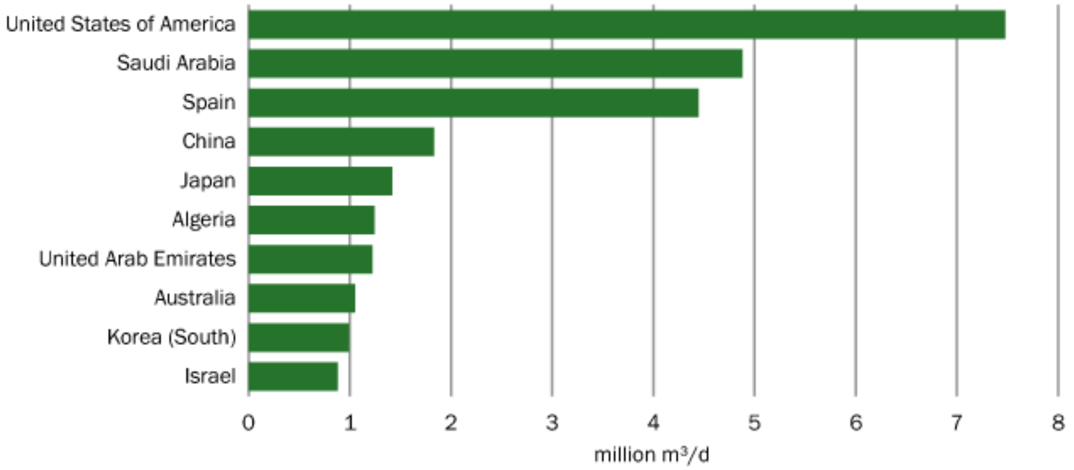


Figure 1.7 *Top 10 countries by total installed membrane capacity since 1945. Source: DesalData.com*

1.2.2.1 Electrodialysis

The process consists of separating the solute from a solution exploiting the anions and cations movement due to an eletrical potential. Referring to Figure 1.8, membranes are used to permit the transfer of the anions and cations. In this process, the semipermeable membranes are waterproof, opposite to RO membranes. The cost of desalination largely depends on the salinity of the water: for high TDS concentration the process becames not economical, while it is competitive when using brackish water.

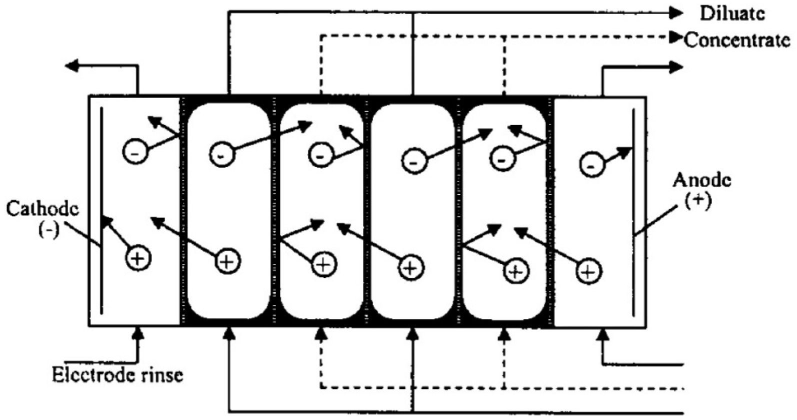


Figure 1.8 *Principle of ED process (electrodialysis)*

1.2.2.2 Reverse osmosis

The priciple on which this process is based is opposite to the natural phenomena called forward osmosis. Accordingly, if a solvent is separated by a semipermeable membrane, that permits only the solvent transfer, from a solution having the same solvent but with less solvent content, the pure solvent goes naturally to the solution due to a concentration gradient. The phenomenon stops when the pressure exerted by the solution equals a pressure called osmotic pressure, which is peculiar of the solution. In the reverse osmosis a pressure greater than the osmotic pressure needs to be applied to obtain the reverse phenomenon: the solvent from the concentrated solution goes to the other side of the membrane. If a high pressure is applied to seawater, a solution free of salts composed only by water, would be obtained. The process is driven by pressure, and at the beginning of this technology almost 120 bar were needed, but nowdays pressures around the range of 60 bar are used for seawater and 20 bar for brackish water [8]. This process needs some kinds of pretreatment to preserve the efficiency and service life of the membranes, very sensitive to fouling. Most reverse osmosis membranes are polymeric thin-film composite membranes which have to ensure low resistance against mass transport [8]. A process block flow diagram is shown in Figure 1.9.

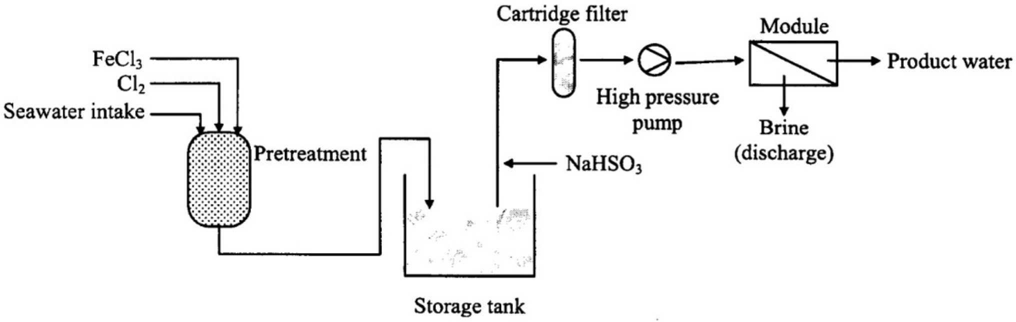


Figure 1.9 *Principle of RO process (reverse osmosis) preceded by a conventional pretreatment.*

This process and the priciples at the base of it are going to be explained in depht in §1.5.

1.2.3 Others techniques

In addition to thermal and membrane processes, other techniques have been developed with the purpouse of desalinating water. In particular, processes that combine the benefits of RO with a thermal desalination, usually MSF and also MED [8]. These hybrid systems allow operating the RO unit fed with water already partially desalinated by a thermal process, extending the membrane's service life from 3 to 5 years [9]. Replacing an existing plant with a hybrid process allows to use the same water intake and outfall facilities reducing the capital cost, and a further reduction is due to an integrated pretreatment and post-treatment which curtails the chemicals use. The hybrid MSF/RO is considered effective compared to MSF, which is decreasing, and is also considered one of the most important seawater desalination processes of the recent years [8]. Another hybrid process that has been developed is a variant of ED, combining the process with ion exchange, which is called electroionization (EDI). It allows to obtain a high purity water [10]; this process covers 0.3% of the global desalination capacity with the aim of obtaining water intended to particular industrial fields.

1.3 Desalination treatments

The seawater feed requires some treatments before being processed. Membrane methods need a more careful pre-treatment but for both methods feed pretreatment is one of most incident factor determining the success or failure of the desalination [8]. The design of the pretreatment system largely depends on the concentration of the seawater and the effects on the environment of the chemicals used [11]. Not only pretreatments are necessary to preserve the equipment, but post-treatment are also important to safeguard the water distribution systems, being the high purity water aggressive and corrosive, and to ensure a proper salt content to make the water potable [7].

1.3.1 Pretreatments of seawater

Both chemicals and physical methods are used to treat seawater from problems such as turbidity, quantity of foulants, macroparticles and macro-organism (organics, algae, particles, etc.) and oil and grease contained in the water [12,13]. Pretreatments for membrane methods are more stringent, whereas those concerning the thermal methods protect equipment from corrosion and scaling [12].

1.3.1.1 Pretreatment for thermal plant

Thermal plants require less attention compared to membrane plants. The pretreatment plant includes [12]:

- chlorination to avoid bio-fouling and acquatic organism growth in the equipment and the feed intake;
- anti-scalants to avoid scaling such as $CaCO_3$, $Mg(OH)_2$ and $CaSO_4$. Inhibitors are used such as phosphonates, polymaleic, etc. or an acid to lower the pH;
- antifoams to reduce foaming that may cause high TDS water drag;
- de-aeration to limit corrosion caused primarily by dissolved gases.

1.3.1.2 Pretreatment for membrane plant (SWRO)

Thes plants are more senvitive to contaminants present in the seawater, and an effective pretreatment must be operated to ensure a long service life of the membranes [11]. A conventional pretreatment for a seawater reverse osmosis includes:

- chlorination controlling bio-fouling and acquatic organism growth in the intake and facilities;
- de-chlorination to preserve membranes sensitive to oxydants such as polyamide using sodium bisulfite;
- coagulation and filtration to remove materials from the feed. Chemicals used are ferric chloride ($FeCl_3$) as coagulants, while micro-filtration, ultra-filtration and nano-filtration are used as physical removing;
- anti-scalants to avoid scaling using acid addition such as sulfuric acid, though it is not always required;
- filtration by cartridge filters always adopted to create a final barrier before the reverse osmosis unit.

1.3.2 Post treatments of water

The post treatment of the desalted water is called potabilization, it has the aim to reduce aggressiveness, especially for water desalted by RO, and to restore the taste [7,14]. A typical remineralization process includes addition of hydrate lime and CO_2 in order to restore pH, hardness and dissolved mineral content, chlorination with Cl_2 or $Ca(ClO)_2$ in order to disinfect the water from the bacteria, and aeration to restore the oxygen level if the water has been obtained from thermal plant [7].

1.4 Desalination and Environment

Originally desalination was only intented to those special applications which fulfill their high water demand while supporting enormous costs [5]. In subquent decades technological advances allowed to reduce the production costs which drive the desalination propagation in the world, also making the plants more environmentally friendly.

1.4.1 Environmental considerations

Aside from emissions due to energy consumption, air pollution, etc. the main desalination output is the brine made of process reject with high content of salt. In the case of RO, the brine contains almost twice the salt content of the feed, and in thermal processes around 10% more [5]. In both cases, brine discharge must not represent a hazard for the environment. Therefore, its effects on marine life could be minimized designing a proper brine discharge shape to allow a quick mixing with the water; temperature of brine discharge and chemicals level content also play an important role [5].

1.4.2 Energy considerations

Desalination costs are affected by different factors, the main of which are salinity, plant capacity, technology, energy cost and regulatory requirements. Basically materials improvement, process innovation, design optimization, energy recovery systems allowed a substantial reduction of desalination prices obtaining a water price around US\$0.50/m^3 for a large scale SWRO plants and below US\$1.00/m^3 for MSF; furthermore a reduced demand of energy makes the processes more environmentally friendly [4]. The costs of main processes and their energy demands are summarized in Table 1.1.

Table 1.1: *Water cost and energy consumption of large desalination processes [4]*

Process	*Thermal energy* [kWh/m^3]	*Electrical energy* [kWh/m^3]	*Total energy* [kWh/m^3]	*Investment cost* [US\$/m^3/d]	*Total water cost* [US\$/m^3]
MSF	7.5-12	2.5-4	10-16	1200-2500	0.8-1.5
MED	4-7	1.5-2	5.5-9	900-2000	0.7-1.2
SWRO	-	3-4	3-4	900-2500	0.5-1.2
BWRO	-	0.5-2.5	0.5-2.5	300-1200	0.2-0.4

There have been many improvements in membrane technology, particulary membrane performances and reduction in energy caused by more efficient energy recovery system: membrane performance increases life, flux capacity to work at high pressure, salt rejection and recovery ratio. A reduction of chemicals, and subsequently even of the pumping energy, occurs if a conventional pretreatment of the feed is replaced with membrane separation including micro-filtration and ultrafiltration, which faciltates the reverse osmosis inasmuch the osmotic pressure is slightly reduced [4].

1.4.3 Future prospects

Reseach is focusing on alternative energy sources in order to make the desalination process the more economical as possible. Many combinations have been suggested, such as photovoltaic cells to obtain thermal renewable energy, or wind-power to obtain mechanical renewable energy, but the market of these techniques is still marginal [8]. Another desalination technique called Manipuleted Osmosis Desalination (MOD), based on forward osmosis seems to be very promising: a draw solution having an osmotic pressure higher than the seawater is exploited to drive the water in that solution, with the peculiarity of being clean for the following regeneration process. The principle of this process will be discussed further in §1.6.

1.5 Osmosis processes

In this paragraph the osmosis principle applied to the osmosis plants existing is discussed, with particular attention the theoritical background behind reverse and forward osmosis, so as to understand in depth the working of Manipuled Osmosis Desalination, hearth of this Thesis.

1.5.1 Reverse osmosis

As already described in §1.2.2.2, reverse osmosis allows to obtain freshwater from a salted feed applying a certain pressure. This process is allowed by a membrane in which water follows a tortuous path through it to reach the permeate side. The membranes used for RO process can reject the smallest contaminants such as monovalent ions, while other membranes including micro-filtration (MF), ultrafiltration (UF) and nanofiltration (NF) allow to remove materials of increasing size. The rejection of a single membrane depends on the pore diameter which charaterizes the membrane, and on the method of separation. Figure 1.10 shows the range of nominal pore diameters for commercial membranes.

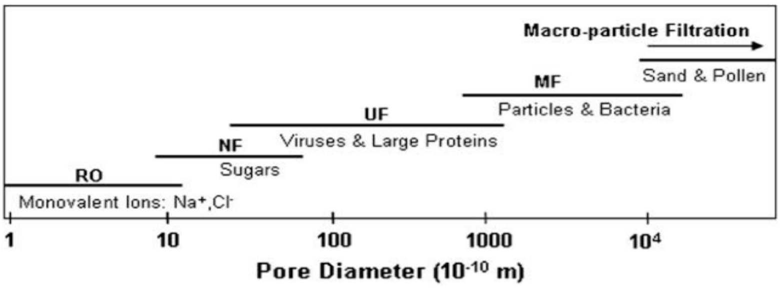


Figure 1.10 *Range of nominal pore diameters for commercially membrane [15]*

Membranes could be also categorized by their molecular weight cut off (MWCO) which refers to the lowest molecular weight solute that is 90% is retained by the membrane. Ultrafiltration and nanofiltration have respectively 2000-100,000 Da and 250-2000 as MWCO value, while that relative to micro-filtration is greater than 100,000 Da. The separation is driven by pressure and increases with decreasing pore diameter. The pressure required is low for micro-filtration and ultrafiltration (5 bar maxinum), around 20 bar for nanofiltration, and for reverse osmosis might reach 100 bar. The fluid flow through the membrane depends on some physical characteristics such as porosity and tortuosity for micro-filtration and ultrafiltration in which sieving is the separation mechanism, while concerning reverse osmosis solution-diffusion mechanism occurs, and for nanofiltration a mechanism that is a halfway between sieving and diffusion method. Membranes can be used in either dead-end or crossflow filtration: in the first case the solution flow is perpendicular to the membrane, whereas in the other the solution flow is tangential. Membrane configuration for reverse osmosis process is typically crossflow. The most used configurations are spiral wound modules, in which the membrane sheets are wound around a tube that collects the permeate, or hollow fibers which are more prone to undergo fouling. Hollow-fibre was employed by most industrial plants because it ensures a high area to volume ratio. The mechanism consists of forcing the water transfer from outside the fibre into the fibre. This configuration offers high packing density because a high number of fibres are placed in a vessel, thus providing high permeate flux per module, but at the same time the fouling phonomenon easily occurs. This drawback led to the replacement by spiral wound modules. Spiral wound is the most widely employed configuration in spite of having lower packing density, because it offers a good tradeoff between permeability, area to volume ratio, fouling and ease and simplicity of operation. Several flat sheet membranes are rolled around a central perforated permeate collector: once the pressure required is applied, the permeate channel is created in the central tube whereas the retentate leaves the module on the opposide side. Spacers placed between the sheets increase the turbulence, limiting concentration polarization as well as fouling. Commercially modules measure 8" and 4 to 8 modules are put in series inside a pressured vessel. A spiral wound module is shown in Figure 1.11.

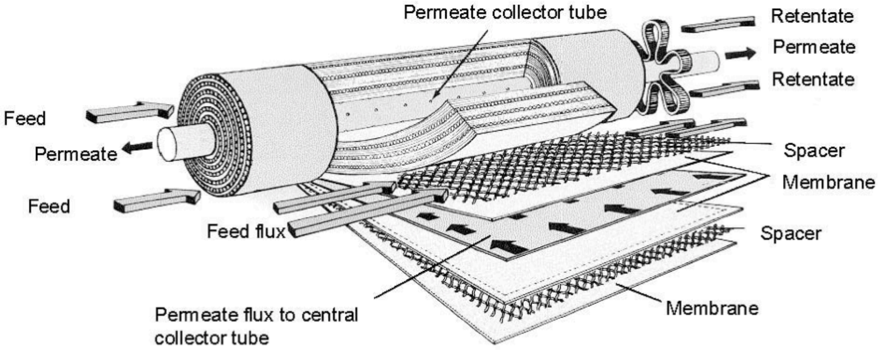


Figure 1.11 *A spiral wound module*

1.5.1.1 Transport principle

The general relation that governs the transport through the membrane can be expressed as (Bird et al., 2002):

$$J_{A,x} = \frac{\rho_A \kappa}{\mu} \frac{dp}{dx} - D_{AB} \frac{d\rho_A}{dx} \tag{1.1}$$

where $J_{A,x}$ is the mass flux of A in x-direction (orthogonal to membrane surface), ρ_A is the mass density of A, μ is the viscosity, κ is the permeability, dp/dx is the pressure gradient in x-direction and D_{AB} is the diffusion coefficient of A in the membrane. For micro-filtration and ultrafiltration the diffusive term is negligible compared to the convection term whereas in nanofiltration a combination of the two mechanisms occurs with the diffusive term that affects more. In reverse osmosis no open channel exist and the transport is controlled by diffusion. It has been termed solution-diffusion model, and occurs in three steps: absorption of the water onto the membrane, diffuson through the tickness of the membrane and desorption from the permeate the surface of the membrane. Once the water has been absorbted onto the membrane due to high pressure, it reaches the permeate side due to concentration gradient between the membrane and the permeate. A certain amount of pressure must be exerted in order to create a chemical potential difference that governs the mass transfer of the water which could be expressed as follows:

$$J_A = \mathrm{L}(\Delta p - \Delta\pi) \tag{1.2}$$

where $J_{A,x}$ is the mass flux of A, L is the permeability coefficient, Δp is the transmembrane pressure difference, and $\Delta\pi$ is the osmotic pressure difference between the two water solutions. The osmotic pressure π is a colligative property and depends on the solution concentration and solution temperature. According to the Morse equation, it derived from the Van't Hoff equation by considering dilute ionic solutions, it can be defined as follows [16]:

$$\pi = iMRT = \mathrm{i}\left(\frac{n}{V}\right)RT \tag{1.3}$$

where i is the Van't Hoff factor that indicates the number of dissociated ionic species, M is concentration of the solute expressed as molarity, R is the gas constant and T is the absolute temperature. The permeability coefficient L depends on the membrane and is described based on the solution-diffusion model of water transport across a RO membrane (Wijmans and Baker, 1995):

$$\mathrm{L} = \frac{DSV}{RTl} \tag{1.4}$$

where D is the water diffusivity in the membrane, S the water solubility in the membrane, V is the partial molar volume, R is the gas constant, T is the operating absolute temperature and l is the membrane tickness. The performance of a RO membrane or an overall RO system is given by the recovery R_W:

$$R_W = \frac{Q_P}{Q_F} \times 100\% \tag{1.5}$$

where Q_P is the permeate volumetric flow rate and Q_F is the feed volumetric flow rate. Recovery varies from 35% to 85%, depending on the feed composition, water salinity and pretreatment. Even slight changes in recovery could significantly affect the overall cost of the RO unit due to, for istance, fouling and mineral scaling. A further performance indicator is salt rejection, that for a RO membrane in crossflow operation is defined as follow:

$$R_S = \left(1 - \frac{C_P}{C_F}\right) \times 100\% \tag{1.6}$$

where C_P and C_F are the salt concentrations of permeate and feed, respectively. RO membranes achieve 98-99.8% of NaCl rejection and NF membranes values greater the 90% for multivalent ions and rejection between 60% and 70% for monovalent ions.

1.5.1.2 Limitations

Membranes life-time and flux are affected by the phenomenon of concentration polarization, as reversible effect and fouling, as irreversible. During RO operation the ions components accumulate in a thin layer at the membrane surface and their concentration is higher than the concentration in the bulk.

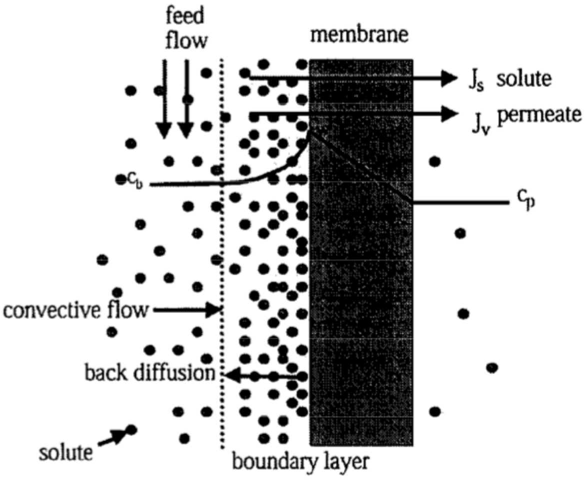


Figure 1.12 *Rapresentation of concentration polarization [17]*

As well as increasing the salt permeation through the membrane due to local higher solute concentration, for the same reason an increasing of osmotic pressure at the surface of the membrane occurs. When a RO unit is operated with high recovery this phenomenon is more severe more because the reject stream gets more concentrated. The local phenomenon is shown in Figure 1.12, in which the higher concentration of the solute at the membrane surface drives a back diffusion through the bulk. In cases of real situation in which concentration polarization occurs, the higher local osmotic pressure must be considered, thus the equation of the flux can be expressed according to Spiegler-Kedem osmotic pressure model in which Equation 1.2 becames [17]:

$$J_A = \mathrm{L}(\Delta p - \sigma \Delta \pi) \tag{1.7}$$

where σ is the reflection coefficient which represents the capability of a membrane ($\sigma = 0$ means no rejection, $\sigma = 1$ means 100% rejection). The term σ is linked to the true rejection R:

$$R = \frac{\sigma(1-F)}{(1-\sigma F)} \tag{1.8}$$

where F:

$$F = \exp\left(-J_A \frac{1-\sigma}{P_M}\right) \tag{1.9}$$

In Equation 1.9 P_M is the overall permeability coefficient. Concentration polarization is considered reversible and can be controlled by velocity adjustaments in order to reduce the boundary layer, or by pulsation, ultrasound, or an eletric field. The fouling issue is more complicated as different physical, chemical and biological effects can irreversebly occur, decreasing membrane permeability [17]. Two mechanisms of fouling can occur in membrane processes: surface fouling and fouling in pores; for RO the main mechanism occurs on the surface due to suspended particulate matter, dissolved organic matter, dissolved solids and biogenic material [15]. The fouling phenomena can be reduced by membrane pretreatment using surfactans, polymers, and enzymes, or managing the operation parameters, for example using an intermittent mode of operation [17].

1.5.2 Forward osmosis

The schematized processes of PRO and FO applied to seawater uses are shown in Figure 1.13.

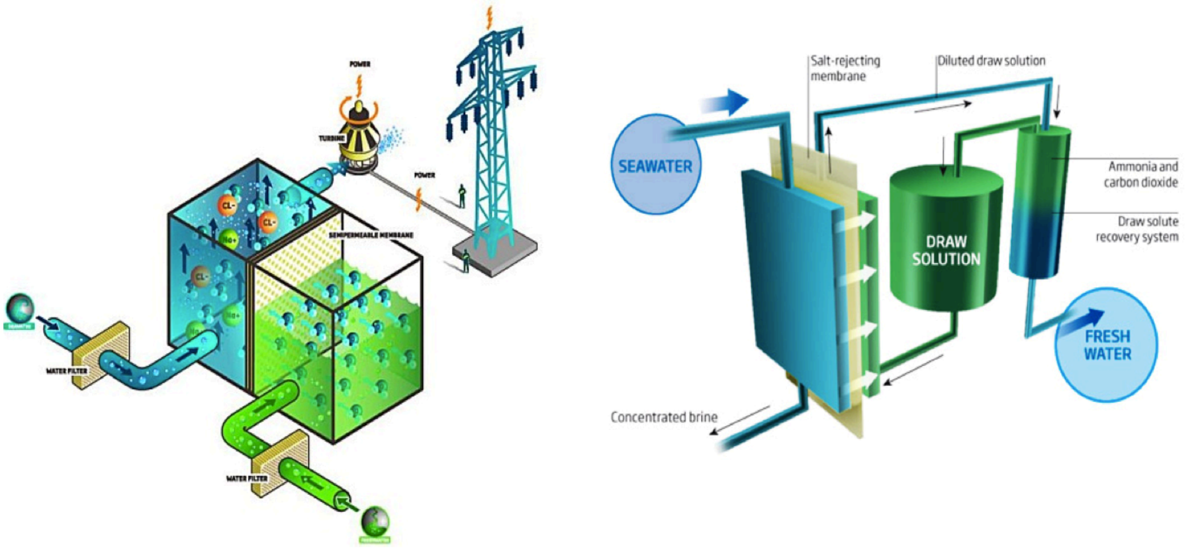


Figure 1.13 *Osmotically driven membrane processes: PRO (left) and FO (right) [18]*

Forward osmosis is a natural phenomenon occurring when the ideal semipermeable membrane allows the passagge of solvent towards a more concentrated solution called draw solution. If the physical barrier allows only the passage of solvent particles, the phenomenon occurs naturally in order to decrease the osmotic pressure of the draw solution which must therefore have a higher osmotic pressure of the feed. Despite RO is currently the most widely used technology for water production, it requires a high hydraulic pressure to overcome the osmotic pressure of the seawater; the FO technology instead needs low energy requirements, and allows high water recover rate and low fouling propensity to estract water, even though it needs a subsequent separation unit to recovery the water from the osmotic agent. The FO technology concerns applications such as concentration of digested biomass, food processing, pharmaceutical industry [18] and also power generation [16], in which the osmosis phenomenon is exploited to increase the pressure of the draw solution which is converted in electricity by a turbine (called Pressure Retarded Osmosis) [18].

1.5.2.1 Fundamentals of FO processes

In FO processes the solvent from the low concentration solution moves through a semipermeable membrane to the higher concentration solution due to the existing chemical potential difference between the two according to the 2nd law of thermodynamics. At equilibrium the chemical potentials of the solvent of the feed and draw solution are equivalent:

$$\mu_S(x_s, P) = \mu_S(x_s, P + \pi) \tag{1.10}$$

where x_s is the mole fraction of the solvent, P is the pressure and π is the osmotic pressure. This natural phenomenon is due to the difference in osmotic pressure $\Delta\pi$ and the unique charateristics of the permeable membrane which only allows solvent molecules to pass through. These membranes ensure the salt rejection by a selective layer which performs the real separation, and are made mechanically stable thanks to a porous support layer. When this coupling is used, two different configurations are possible according to the membrane orientation: pressure retarded osmosis (PRO) mode and forward osmosis (FO) mode. In PRO mode the draw solution flows against the active layer whereas in FO mode the draw solution flows against the support. Considering FO process for water desalination, the water flux through the membrane can be described by the following equation:

$$J_W = A\sigma\Delta\pi \tag{1.11}$$

where A is the water permeability coefficient, and σ is the reflection coefficient. The $\Delta\pi$ term represents the driving force of the process, hence the difference between the osmotic pressure of the feed and that of the draw solution. Generally the effective value of this term is lower and therefore also the effective flux. The reason of this is due to several complicated phenomena which occur during the process, the most influencing of which is the concentration polarization resulting in a diluitive effect of the draw solution and a concentrative effect of the feed solution [16]. Referring to Figure 1.14 it is possible to observe the real $\Delta\pi$ between the physical barrier that separates the solutions in both configurations above mentioned.

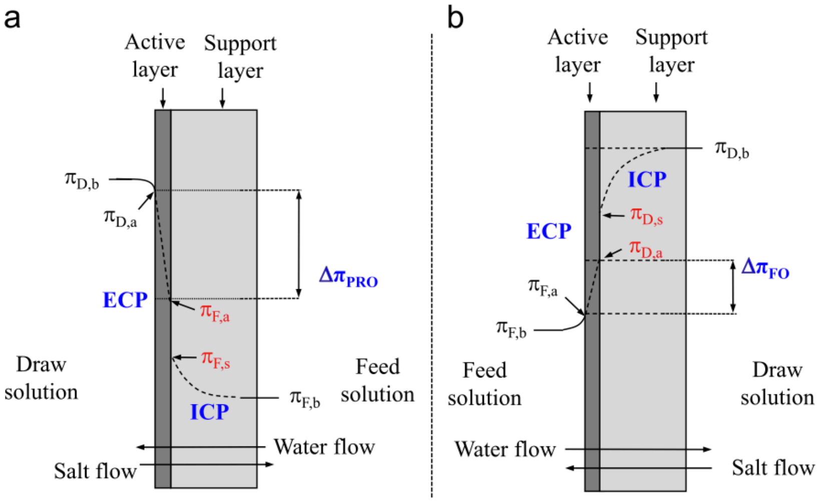


Figure 1.14 *Illustration of driving force and concentration polarization for PRO configuration (a) and FO configuration (b) [16]*

For FO mode the feed solution flows against the active layer, where a raising of the osmotic pressure occurs due to the local higher salt concentration as occurs in reverse osmosis; since the osmotic pressure depends on the solute molarity an increase of concentration in the feed side decreases the $\Delta\pi$ value. A further decrease occurs due to the decrease of solute concentration near the membrane surface in the support layer. The real driving force is that in the active layer, therefore equation for water flux through the membrane considering this phenomenon becomes [16]:

$$J_W = A\sigma\Delta\pi = A\sigma\left(\pi_{D,a} - \pi_{F,a}\right) \tag{1.11}$$

where $\pi_{D,a} - \pi_{F,a} < \pi_{D,b} - \pi_{F,b}$. Two different types of concentration polarization can be distinguished, depending on the side where it takes place: external concentration polarization (ECP) and internal concentration polarization (ICP). The first one occurs near the active layer surface and can be diluitive or concentrative depending if PRO mode or FO mode is used. External concentration polarization occurs in both pressure driven processes and in osmotically driven processes [19] and can be minimized by using crossflow filtration with hydrodynamics designed to produce sufficient turbulence in order to reduce the boundary layer [16,19]. Conversely on the porous support layer the internal concentration polarization (ICP) occurs, and it represents the most troublesome phenomenon in FO precesses because it cannot be easily eliminated, in fact it represents the main cause of water flux decline. The percentage of flux reduction can even be as high as 80% [16,19]. As for ECP, also ICP can be either a diluitive or concentrative, depending on the operating configuration (FO or PRO): dilutive ICP occurs in FO mode due to dilution of draw solute in the membrane support, whereas concentrative ICP occurs in PRO mode due to a raising of solute concentration in the support layer. In FO processes both ICP and ECP occur simultaneously, but sometimes only ICP is needed to be taken into account. In FO mode ECP can be considered negligible ($\pi_{F,a} \approx \pi_{F,b}$) while in PRO mode ICP can be considered negligible ($\pi_{F,a} \approx \pi_{F,b}$) especially when pure water is used as feed: the flux is high and reverse salt flux near zero. Nevertheless many efforts have been made to model both ICP and ECP in FO and PRO processes, and the water flux equation for both of them can be written as:

$$J_W = A\left[\pi_{D,b}\exp\left(-J_W K\right) - \pi_{F,b} exp\left(\frac{J_W}{k}\right)\right] \quad \text{(FO mode)} \tag{1.12a}$$

$$J_W = A\left[\pi_{D,b}\exp\left(-\frac{J_W}{K}\right) - \pi_{F,b} exp(J_W k)\right] \quad \text{(PRO mode)} \tag{1.12b}$$

where $\pi_{D,b}$ and $\pi_{F,b}$ are the osmotic pressures of the draw and feed solutions in the bulk, k is the mass transfer coefficient, and K is the solute resistivity. The solute resistivity K concerning the porous support is defined as follow:

$$K = \frac{t\tau}{\varepsilon\mathcal{D}} = \frac{S}{\mathcal{D}} \tag{1.13}$$

where S includes all the porous support layer physical characteristics: t, τ, and ε represent respectively tickness, tortuosity and porosity; $\mathcal{D}$ is the diffusion coefficient of the draw solute in the support layer. Investigation have shown that ICP depends on K hence on S and $\mathcal{D}$: the solute resistivity within the porous support can thus be reduced operating on the structure of the support and the draw solution trying to obtain a low S value and a high $\mathcal{D}$ value [16].

1.5.2.2 Reverse draw solute permeation

It has been seen how the phenomena which occur during forward osmosis compromise the water flux due to a reduction of driving force. The osmotic pressure difference can be further decreased by a not perfectly semipermeable membrane that could allow a flux of draw solute through the active layer from the draw solution towards the feed [16]. From a physical point of view a reverse draw solute flux increases the concentration of the feed and thus its osmotic pressure; in addition replenishment of the draw solution increases, and the nature of the solute could be harmful if the feed is reissued at sea. No ideally semipermeable membrane exists, and the high solute concentration difference between the solutions cause reduction of the flux with dramatic increase of the costs of the process if FO mode is used; the reverse flux can be expressed by Fick's Law as follows [20]:

$$J_S = B\Delta C \tag{1.14}$$

where B is the solute permeability coefficient and ΔC is the solute concentration difference. A reliable model in order to describe the reverse solute flux has been successfully developed achieving strong agreement with experimental results, in which a reverse solute selectivity term has been used to evaluate the ratio between the water flux and solute flux (J_W/J_S). The results show that the reverse solute selectivity is indipendent on the S value of the support, but only depends on the selectivity of the membrane active layer [18]. A substantial role in solute transport is given by size exclusion and electrostatic interactions, in fact investigations supported the theory for which low molar fluxes for cations like Mg^{2+}, Ca^{2+} and Ba^{2+} imply that ions with a large hydration radius and divalent charge diffuse more difficult across the active layer than monovalent ions or neutral compounds [18]. The reflection coefficient, which represents the ability of the membrane active layer to allow water flux over solute flux, must be as high as possible in order to avoid falls of driving force.

1.5.2.3 Fouling

Fouling in osmotically driven membrane processes is different from fouling in pressure driven membrane processes, but for both of them the membrane efficiency is compromised. In forward osmosis processes the fouling occurs on the surface of the active layer if the FO mode is used and on and within the support layer if PRO mode is used [18]. The deposition of retained matter such as particles, colloids and macromolecules occurs on the membrane surface and/or inside the pores; fouling can be generally classified in colloidal fouling, biofouling, inorganic fouling (scaling) and organic fouling. Fouling is a considerable problem that influences the economics of the operation and reduces the membrane water flux either temporarily and permantely if the membrane material is chemically degraded. The chemical and hydrodynamic interactions between the foulants and the membrane are therefore crucial to fouling deposition. Surface modification and material choices are the main factors to focus on in order to avoid the fouling. The different fouling deposition between RO processes and FO processes is shown in Figure 1.15, in which it can be seen that the exerted pressure in RO causes a compact deposition of fouling layer which makes the fouling less reversible than in FO, where the fouling is more loose and sparse and therefore easier to remove by physical cleaning.

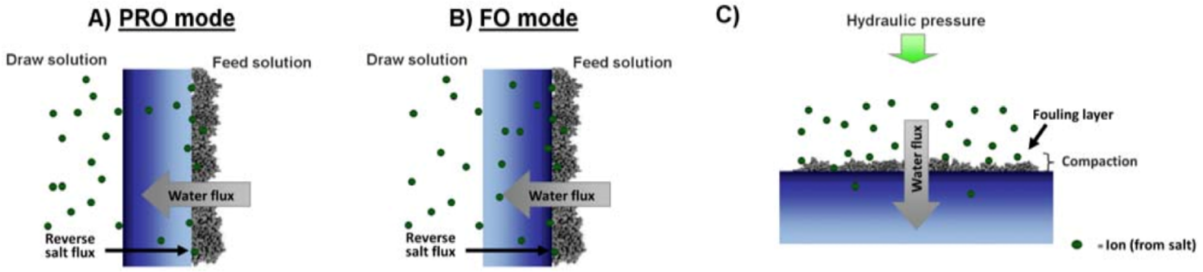


Figure 1.15 *Illustration of the fouling mechanisms in pressure driven and osmotically driven membrane processes: (A) fouling in PRO mode, (B) fouling in FO mode, (C) fouling in RO mode [18]*

Despite the fouling deposition in osmotically driven membrane processes is less compact, when a fouling layer has developed during the process, the effect of external concentration polarization cannot be considered negligible [21]. Furthermore in FO mode when a fouling layer has developed on the active layer of the membrane and a reverse draw solute occurs, the diffusion of the ions across the fouling layer is hindered and cannot be mitigated by fluid management. This phenomenon is called cake enhanced concentration polarization (CECP) and the difficult diffusion trough the fouling layer substantially increases the local osmotic pressure on the surface of the active layer, greatly decreasing the membrane performances [21,22]. Investigations confirmed the importance of reverse salt diffusion in FO fouling, confirming the strong correlation between intermolecular adhesion and fouling. It has also been demostrated that the nature of the draw solution has a great influence on the fouling behavior: different draw solutions decrease the water flux in different ways when the same fouling agent is tested [23]. In addition, investigation has demostrated that, at the same water flux level, the greatest diffusion rate was observed for a NaCl draw solution between NaCl, $Ca(NO_3)_2$, $CaCl_2$ and $MgCl_2$ draw solutions and a proper draw solution without organic fouling initiators (e.g. Ca^{2+} and Mg^{2+}) should be used [23]. The nature of the fouling phenomenon in osmotically driven processes is different from fouling in pressure driven processes and several variables influence the process and the efficiency, making the mechanism of fouling so complex. Factors such as water quality, temperature, system design, water flow, cleaning, membrane surface *ect.* need to be considered in process design and development [23].

1.5.2.4 Membrane materials

Although FO membranes are less prone to fouling than RO membranes, they are more sensitive to internal concentration polarization, which leads to the research of suitable membranes focusing not only on the active layer but also on the support layer. It is generally agreed that a small S parameter is highly preferable for the substrate in order to minimize the ICP phenomenon, and a layer with great hydrophilicity is also required to reduce the water resistance [24]. Cellulose acetate-based membranes are suitable for FO due to high hydrophilicity, wide availability, good resistance to degradation by chlorine, toughness, smoothness and low fouling propensity. The degree of acetylation affects hydrophilicity and crystallinity [18, 25]: in cellulose triacetate (CTA) only ~1% of the hydroxyl groups remain free producing a crystalline membrane. An asymmetric cellulose acetate membrane has been developed by Hydration Tecnology Innovations (HTI, Albany, OR) who has provided this kind of membranes for nearly 25 years. Commercial CA/CTA membranes present high hydrophilicity and mechanical resistance, ensuring proper wetting in order to reduce ICP [18] Most of them are prepared via conventional phase inversion using cellulose acetate as the dip-coating polymer. Research is currently focusing on others kinds of membranes, because the salt rejections achieved by cellulose acetate-based membranes are not satisfying when using NaCl, Na_2SO_4 and $MgSO_4$ as the draw solute [25]. Another cellulose acetate-based membrane has been developed in which the acetate works as hydrophilic support, while an active layer made of a polymer material is used. This thin film composite membranes (TFC) are prepared via interfacial polymerization when the active layer is synthesized over the support. A polyamide is normally used as polymer and, depending on the monomers, different properties can be obtained. The concept of interfacial polymerization is exploited: the monomers are dissolved in two immiscible liquids so that the reaction takes place at the liquid-liquid interface, the acid chloride is dissolved in an organic solvent and the amine in water. Trimesoyl chloride (TMC) is commonly used as acid chloride and several types of amine can be used: excellent flux and salt rejection properties can be achieved using m-Phenylene diamine (MPD), or higher salt rejections but lower fluxes can be achieved with p-Phenylene diamine (PPD) [18]. A support membrane is first soaked in the amine solution and subsequently soaked in a organic acid chloride solution. A TFC membrane can be developed using polysulfone (PSf), known for its good chemical resistance and good mechanical properties as support, and a polyamide as active layer where adhesion forces hold them together [18]. With regard to membrane modules, both flat sheet plate-and-frame and tubolar hollow-fiber configurations are used [26]. At the present time, only few membranes for osmotically driven processes are commercially available, and should have large water permeability (high A), low reverse solute permeation (low B) and low structure parameter (low S). Research in material choices and design strategies progress the FO technology increasing also the performance of the membranes. Nonetheless the success of a membrane greatly depends on the kind of the draw solution employed, which plays a very important role in combination with the material itself [18].

1.5.2.5 Ideal draw solution for FO process

The solute chosen for the draw solution is an important variable to be considered when a forward osmosis process has to be developed [18]; and several criteria have to be taken in account for selecting a suitable one [25]. The draw solution in fact represents the main source of driving force. Therefore, a suitable selection of the solute is important not only in combination with the type of material, but also with the global process and the all units affecting the draw solution, provinding therefore a the recovery, regeneration and recycling [18]. It is clear that a draw solution must be suitable not only to minimize the internal concentration polarization, fouling deposition, reverse solute flux and to maximize the water flux through the membrane and the osmotic pressure difference, but must also be suitable for the downstream operations such as the recovery, and economically sustainable for the regeneration. The selected draw solution may not be excellent for the single FO process, however it could be proper when the global process and all the units operations are taken into account. Focusing on the forward osmosis unit, several properties required to optimize the process are listed below:

- Osmotic pressure: the draw solution must be able to generate a high osmotic pressure in order to maximize the water flux trough the semipermeable membrane. Referring to Equation 1.3, it is possible to increase the osmotic pressure operating on the Van't Hoff factor i, the molarity M, and temperature T. Hence, to achieve a high osmotic pressure, a good solubility of the draw solute in water is required to reach high concentration values. In addition, a fully dissociated compound is preferred, so as to produce more ionic species and hence a higher Van't Hoff value, therefore multivalent ionic solutes are the most preferable. Draw solutions of NaCl and $MgCl_2$ at the same concentration extert different osmotic pressures, because the Van't Hoff factor of the fisr solution is equal to 2 and that of the second is equal to 3. Therefore compounds with high water solubility and high degree of dissociation are potential candidates as draw solutes [16]. The water flux is not linearly correlated with the osmotic pressure difference when FO mode is used, because of the ICP: water flux behavior as a function of the $\Delta\pi$ has been determined using distilled water as feed, so that the non linear behavior is attributable only to the ICP, being the ECP absent [27]. Higher draw solution concentrations produce less flux at given bulk osmotic pressure difference due to an increased degree of dilution within the porous support; tailoring the membrane for more optimal osmotic performance by making the membrane as porous and less thick as possible still remain the main task [27]. The temperature can also positively influence the osmotic pressure: an increasing of temperature leads to viscosity decrease and then the solute resistivity K is further reduced [27].

- Reverse flux and fouling: the reverse flux of the draw solution must be minimal [16]. Unfortunately, commercially available membranes are not completely ideally semipermeable, and allow a reverse flux of solute due to the large draw solute concentration difference existing. As already mentioned above, a reverse solute flux is related to fouling: could promote a deposition on the surface of the active layer with an enormous decline of the driving force due to the local increasing of the osmotic pressure. The coefficient B of the membrane plays an important role but the choice of the draw solute is fundamental: several kinds of solute such as multivalent ionic solute like Mg^{2+}, Ca^{2+} and Ba^{2+} could restrict the reverse flux, but at the same time the ICP is increased. The dimension of the ions plays a very considerable role and a trade-off must be taken between reverse salt flux, ICP and cost of the draw solute. Cations like Mg^{2+} and Ca^{2+} limit fouling propensity and limit reverse salt flux, but at the same time enhance the ICP and are more expensive; sodium based salts are cheaper and move more readily but reverse sal flux and fouling could be penalized.

A proper draw solution choice is not easy and a trade-off must be considered. However, draw solutions with small molecular weight and low viscosity in its acqueos solution are preferred; the ICP is an inevitable phenomenon but can be reduced operating on the diffusion coefficient of the solute ($\mathcal{D} \propto 1/PM, \mu$) [16]. The relationships between ICP, membrane fouling, reverse solution diffusion, membrane characteristics and draw solute properties are summarized in Figure 1.16 [25]. Focusing on the global process several important factors have to be taken into account:

- Regeneration: the dilute draw solution has to be concentrated again after the FO unit. Depending on the kind of process used to regenerate the draw solution, a proper solute must be chosen that makes the regenaration unit operationally feasible. The choice of a proper draw solution is then more complex, as it has to satisfy both the FO unit and the regeneration unit, which often could be RO, nanofiltration (NF), ultrafiltration (UF), membrane distillation (MD) or other thermal methods [16].
- Others features: depending on the kind of the regeneration process, a minimun percentage of draw solute should be lost during the separation. In the case of seawater

desalination to product freshwater, it is obvious that the solute must not be toxic [16]. The draw solute must also be stable to operation conditions, at solid state at ambient temperature for easy handling, and available at lowest costs as possible [16].

The proper draw solution can be chosen once the separation processes available are known; depending on them and on the kinds of membranes and technologies developed it is possible to have different draw solutions. Often, due to demanding research behind this topic, the draw solution is part of the know-how of the developer.

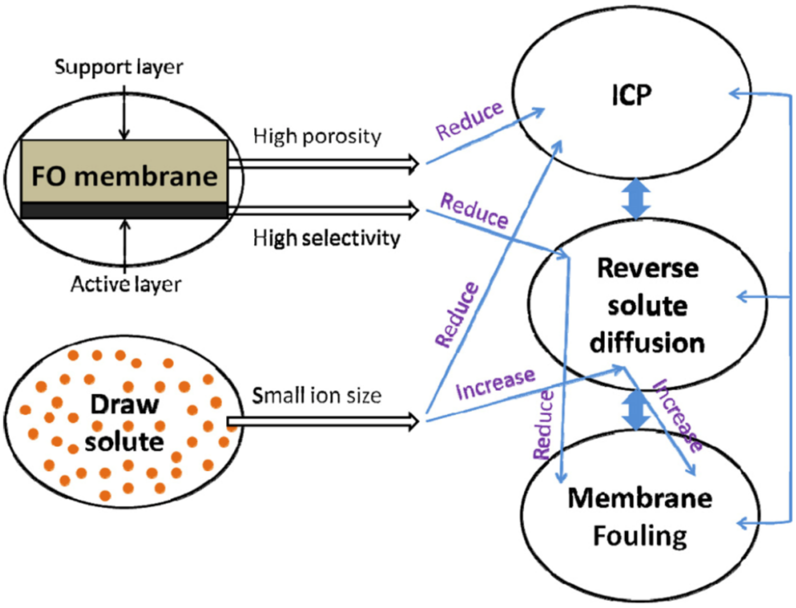


Figure 1.16 *Relationships between ICP, membrane fouling, reverse solution diffusion, membrane characteristics and draw solute properties in FO [25]*

1.5.2.6 Draw solution developments

Over the past several decades and especially during the last one, a variety of draw solutes and solutions have been investigated in osmotically driven processes [25]. Many compounds have been proposed in literature, an overview of the draw solutes, their recovery methods and possible drawbacks is summarized in Table 1.2. Draw solutes can be generically divided into commercial compounds and synthetic compounds [16]. Regarding the first category, volatile compounds have been tested in the early stages where thermal methods as recovery units were proposed. The separation of the gases from water was carried out by heating or air stripping. SO_2 has been tested by many researchers, even though precautions must be taken, being a volatile and corrosive gas and unstable in solution. Once separated the draw solutes are separated by termal methods the gases can be regenerated dissolving them back into water. However draw solutions made of volatile compounds had insufficient experimental data to demonstrate their superiority or advantages [16]. Processes using nutrient compounds have been developed over the years, glucose was first explored and afterwards fructose which has shown high efficiency.

Table 1.2: *Overview of the development and recovery approches of draw solutes used in FO technology [16]*

Year	***Researcher(s)***	***Draw solute(s)***	***Method of recovery***	***Drawbacks***
1964	Neff	Ammonia and carbon dioxide	Heating	Energy intensive
1965	Batchelder	Volatile solutes (e.g. SO_2)	Heating or air stripping	Energy intensive, toxic
1965	Glew	Mixture of H_2O and another gas (SO_2) or liquid (aliphatic alcohols)	Distillation	Energy intensive
1972	Frank	Al_2SO_4	Precipitation by doping $Ca(OH)_2$	Toxic by-products
1992	Yaeli	Glucose	Low pressure RO	Energy intensive
2002	McGinnis	KNO_3 and SO_2	SO_2 was recycled through standard means	Energy intensive, toxic
2005-2007	McCutcheon	NH_3 and CO_2 (NH_4HCO_3) or NH_4OH-NH_4HCO_3	Moderate heating (~60°C)	High reverse draw solute flux, insufficient removal of ammonia
2007	Adham et al.	Magnetic nanoparticles	Captured by a canister	Poor performance, agglomeration
2008	McCormick et al.	Salt, ethanol	Pervaporation-based separations	High reverse draw solute flux and low water flux
2010	Yen et al.	2-Methylimidazole based solutes	Membrane distillation	Material costly
2010-2011	Ling et al. Ge et al.	Magnetic nanoparticles	Recycled by external magnetic field	Agglomeration
2011	Ling & Chung	Hydrophilic nanoparticles	UF	Poor water flux
2011	Iyer and Linda	Fatty acid-polyethylene glycol	Thermal method	Poor water flux
2012	Su et al.	Sucrose	NF	Relatively low water flux
2012	Ge et al.	Polyelectrolytes	UF	Relatively high viscosity
2012	Yong et al.	Urea, ethylene glycol, and glucose	Not studied	Low water flux and high draw solute flux
2012	Bowden et al.	Organic salts	RO	Low water flux, energy intensive
2012	Carmignani et al.	Polyglycol copolymers	NF	High viscosity, severe ICP
2012	Stone et al.	Hexavalent phosphazene salts	Not studied	Not economical and practical

The use of nutrient compounds is still attracting, as even though the water flux could be penalized by the significant molecular size of sugars, it has the advange, that the following regeneration unit can be more efficient. Inorganic salts have been widely used as draw solutes because high water fluxes can be obtained. The regeneration methods can be either thermal or pressure-driven; regarding the first method an example is given by McCutcheon [16], who developed a FO process driven by a NH_4HCO_3 solution which is afterwards recovered by heating the diluted solution around 60°C: the salt decomposes into ammonia and carbon dioxide gases which can be separated from the water. However a difficult removal of the gases and a high reverse solute flux make this process unconvenient [16]. Regarding inorganic salts as draw solutes, recovered with pressure driven processes, more than 500 inorganic salts were initially considered and 14 salts remained at the end of the screened process. Draw solution containing ions such as $MgSO_4$, $KHCO_3$, $NaHCO_3$, Na_2SO_4, $(NH_4)_2SO_4$, and K_2SO_4 showed lower back reverse fluxes but none of them really represent a valid solution [16]. Organic salts such as sodium formate, sodium acetate, sodium propionate and magnesium acetate have been considered as draw solutes showing the advantage of being bigger in term of molecular size and dissociated in acqueous solution. When a RO process is being considered as regeneration of the draw solution, a lower energy consumption is required. Larger ions decrease the osmotic pressure difference but can facilitate the following recovery. Many researchers have focused also on the viability of using synthetic materials as draw solutes and some of them exhibit great potentials. Hydrophilic magnetic nanoparticles (MNPs) generated interest recently because a different recovery system is expected: the superparamagnetic nanoparticles are recovered by an external magnetic field. However although the concept is attractive, there are still not enough experimental data to demonstrate the feasibility of MSFs as draw solutions [16].

1.6 Manipuleted Osmosis Desalination

The Manipulated Osmosis Desalination process has been developed at the University of Surrey's Centre for Osmosis Research and Application (CORA), and has been made operating in industrial scale by Modern Water. The novel technology has been patented (patent number US7879243). Starting from a laboratory facility installed at University of Surrey, a trial facility has been developed at Gibraltar (in 2008) and a full-scale commercial facility is operating that provides drinking water to the residents of a village in Oman [29].

1.6.1 MOD process

The Manipulated Osmosis Process (depicted in Figure 1.17) exploits the forward osmosis to obtain freshwater from seawater. The concept is basically based on FO desalination using a proper draw solution with higher osmotic pressure, which is afterwards reconcentrated by a RO process, energetically less demanding than the conventional SWRO process. What makes the regeneration step economic is the cleaner solution which feeds the RO process, as the draw solution will be only composed by the draw solute and pure water: the RO process can operate a lower pressure being less prone to limitations which affect the conventional SWRO process. A nanofiltration can be also taken into account as regeneration step. The benefits of the MOD process are summarized as follows [29]:

- lower operating cost due to lower fouling propensity;
- energy consumption lower than conventional RO (2-3 bar instead of 60-80 bar);
- reduced membrane whole life costs;
- provision of a double membrane barrier between feedwater and desalinated water;
- significant reduction of contaminants such as boron;
- possibility to operate with lower pressure and resulting possibility to use less expensive materials for the equipments like use of the plastic.

Key variables in the system include:

- number and performance of forward osmosis membranes;
- composition, concentration and recirculation rate of osmotic agent;
- performance of regeneration system;
- temperature, composition and flowrate of feedwater.

Successful operation of the facilities depends on a suitable consideration and combination of all the above factors during design and operation, operating with the right trade-off to make the whole process as economic as possible.

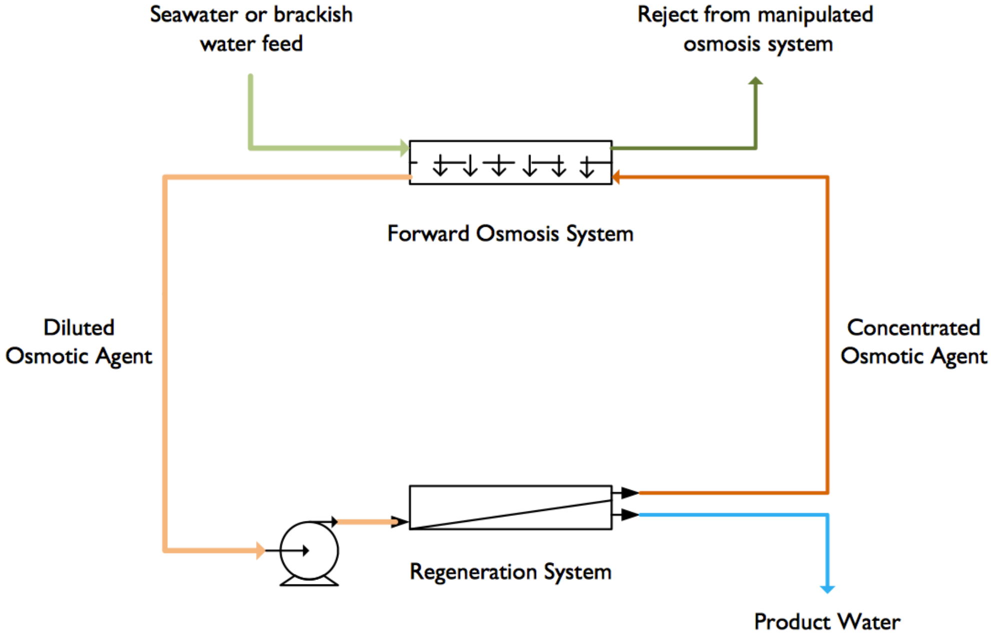


Figure 1.17 *Simplified MOD process diagram [29]*

1.6.2 MOD facilities

The reliability of the Manipulated Osmosis Desalination has been tested developing facilities from the laboratory to a commercial full-scale, passing to an intermediate trial facility installed on the Mediterranean Sea [29].

1.6.2.1 Laboratory Test Rig

A test facility has been installed at the Centre for Osmosis Research and Application (CORA) placed at the University of Surrey, UK (Figure 1.18). The CORA team investigated the performance of varius membrane units and techniques to develop the concept of MOD, together with the performance of the parameters which drive the process [29].

Figure 1.18: *Laboratory Test Rig [29]*

1.6.2.2 Trial facility

A trial plant has been commissioned by Modern Water in 2008 and located on the northern Mediterranean Sea coast at Gibraltar. The plant shares pre-treatment facility of an adjacent SWRO facility and the water produced has successfully reached the drinking water standard [29].

1.6.2.3 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 drinking water supply (Figure 1.19). This process implements a SWRO plant already existing, with which it shares both the pre-treatments and the post-treatments. Key features of the facility are [29]:

- provision for a flexible number of forward osmosis membrane elements;
- a membrane based regeneration system;
- exstensive automated measurements throughout the plant of flowrates, pressures, temperatures, pH and conductivity;
- a Programmable Logic Controller coupled with an industrial PC running SCADA software for plant control and data recording;
- membrane clean-in-place equipment;
- interconnections to external services such as filtered feedwater supply, brine discharge line, export line to permeate storage tanks.

The key objectives for the plant were [29]:

- to undertake a direct comparison between a conventional reverse osmosis process and the manipulated/forward osmosis process, utilising identical feedwater and pre-treatment;
- to demonstrate the advantages of the process;
- to reliably provide high quality drinking water for distribution to consumers in and around Al Khaluf;
- to increase Modern Water's experience of operating their facility in more challenging feedwater conditions;
- to gather operational data on the process to enhance the design and operation of future facilities;
- provide a facility on which operators can receive training.

Figure 1.19: *The freashwater production plant at Al Khaluf, including MOD plant [29]*

The FO system has been operating successfully with a seawater recovery of 35%, and the whole process ensures freshwater production which satisfies the requirements of the Omani Standard No. 8/2006. The real potential benefit associated with MOD process is the energy consumption which, compared to a conventional SWRO system, leads a saving of energy of about 40% as shown in Table 1.3.

Table 1.3: *Comparison of the SWRO and MOD process performances [29]*

Technology		***SWRO***	***MOD***
Permeate Extraction from feedwater			
Feedwater Recovery	%	25	35
Product Water Flow	m^3/d	71.4	100
	m^3/h	3.0	4.2
Feedwater Supply	m^3/h	11.9	11.9
	bar	65	4
Feedwater Pump	eff%	85	85
	kW absorbed	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 absorbed	-	18.8
Overall Plant			
Specific Energy consumption (per unit product)	kWh/m^3	8.5	4.9

Nevertheless there are still areas for improvement related to membrane technology and process optimization. The research is focusing on finding the proper draw solute which can make the process more economical and environmentally sustainable as possible [29].

1.6.3 Aim of the Thesis

The experimental work of the Thesis is based on testing the performance of sodium chloride ans sucrose draw solutions in different concentrations in the forward osmosis step of the MOD process. This research derived from some limitations encountered during the operation when using the single solutes draw solution, both in the forward osmosis unit and in the reverse osmosis unit. It is believed that a right combination of both solutes could achieve a great trade-off for both the units, improving the whole MOD process. Experimental data are implemented into a water flux model in order to obtain the parameters which describe the not ideal behavior.

Chapter 2

Experimental work

The experimental work evaluated the performances of a mixture of sucrose and sodium chloride as osmotic agents, in a FO unit at different concentrations and different kinds of feed water. The osmotic pressure is given by both of the solutes but with different contributions: first the osmotic pressure has been fixed fixed at 10 bar for the sodium chloride and changed for the sucrose, and secondly the opposite has been done; many parameters have been measured as a function of the osmotic pressure difference such as recovery rate, water flux, energy consumption. In this chapter the procedure of the experimental work is presented as well as the equipment and materials, initial calculations and qualitative analysis.

2.1 Laboratory equipment

The experimental work has been carried out using the forward osmosis trial plant shown in Fig 2.1, whose schematic flow diagram is presented in Fig. 2.2.

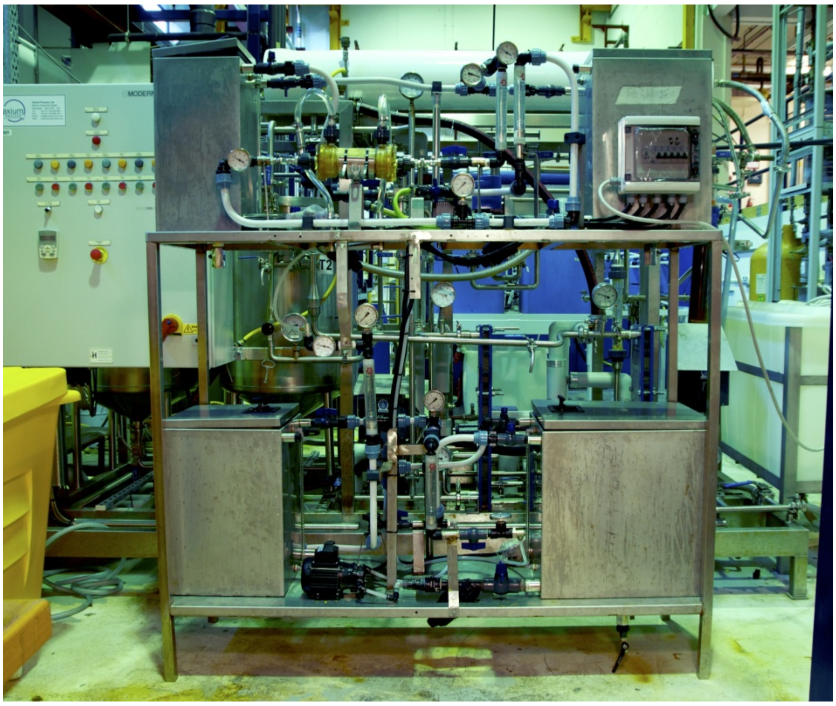


Figure 2.1: *Forward osmosis trial plant*

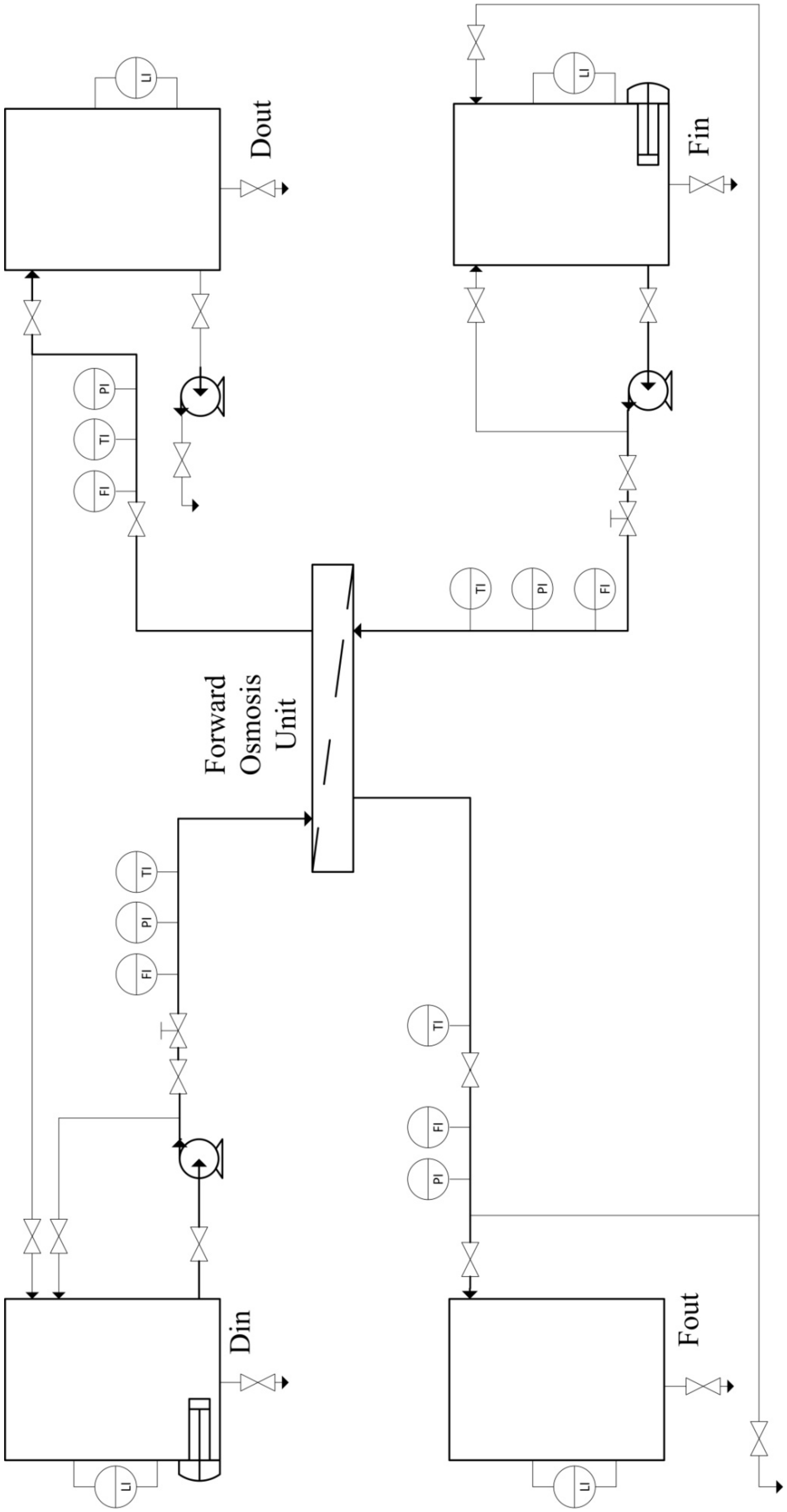


Figure 2.2: *Schematic Flow Diagram of the forward osmosis trial plant*

The plant mainly consists of two feed tanks in which draw solution and feed water are loaded, and two collecting tanks; all of them have a visual level indicator graded one tenth of a centimeter. From the reading of the levels it is possible to obtain the corresponding volume by calibrating each tank in order to have a linear function depending on the volume; the calibration has been performed by adding known volumes recording the corresponding levels so as to obtain a linear function easily implementable on an electronic spreadsheet for the corresponding calculations. The tanks D_{IN}, F_{IN}, D_{OUT} and F_{OUT} have respectively a volume of about 30, 100, 60 and 60 litres. Each stream is equipped with a termometer, pressure gauge and a flowmeter which give a rough indication on how the process is running. Even though the feed tanks are fitted with heaters, these have not been used to control temperature for safety reasons. The plant has been designed to operate with recirculation, but this kind of operation has not been taken into account. The forward osmosis unit is characterized by a hollow fiber membrane put in with the configuration shown in Fig. 2.3: the draw solution flows horizontally through the fibers whereas the feed water is placed ensuring a good covering of the whole surface available.

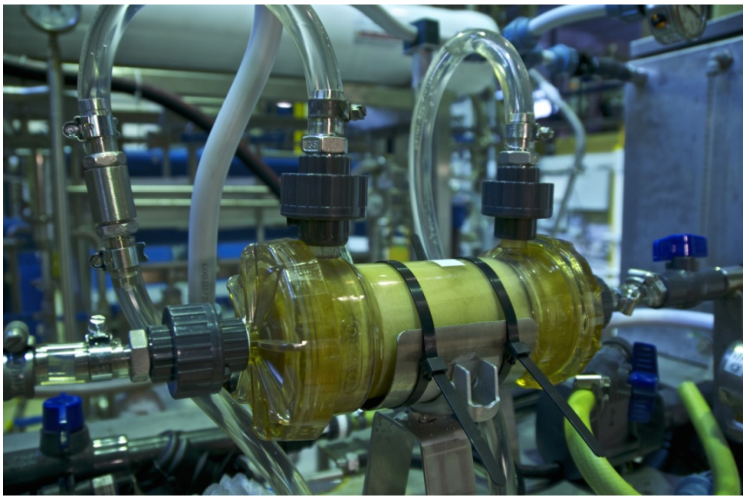


Figure 2.3: *Detail of the membrane unit connected to the streams.*

2.2 Materials

In this paragraph the characteristics of the materials involved in the experimental work are briefly presented. The osmotic agents characteristics and the specifications of the membrane are given.

2.2.1 Osmotic agents

Two different solutes have been tested as osmotic agents together with different concentrations among them. The solutes used and their physical properties are summarized below:

- **Sodium Chloride** is an inorganic salt whit chemical formula NaCl. In aqueous solution it is completely dissociated and its Van't Hoff factor is equal to 2. The main characteristics are summerized in Table 2.1.

Table 2.1 *Sodium Chloride properties*

Property	Value
Chemical formula	NaCl
Molecular Weight	58.44 g/mol
Density (25°C)	2.165 g/cm^3
Solubility in water (25°)	359 g/L

- **Sucrose** is a disaccharide composed by α-D-glucose and β-D-fructose as monosaccharides with chemical formula $C_{12}H_{22}O_{11}$, commonly known as table sugar. The Van't Hoff factor is equal to 1 because, unlike sodium chloride, it does not dissociate in aqueous solution. The main characteristics are summerized in Table 2.2.

Table 2.2 *Sucrose properties*

Property	Value
Chemical formula	$C_{12}H_{22}O_{11}$
Molecular Weight	342.30 g/mol
Density (25°C)	1.587 g/cm^3
Solubility in water (25°)	2074 g/L

As described in §1.5.2.5 both solutes satisfy most of the required features, primarily the low cost, zero toxicity and high solubility. The experimental work has not been carried out using analytical high purity compounds but commercial compounds, easily obtainable at low costs: sea salt produced in Israel has been used as sodium chloride and granulated sugar by Whitwhorts as sucrose. The osmotic pressures of the solutes have been evaluated by using OLI Analyzer's software, setting the same process conditions as in the experiments. The output data can be compared to the ideal data given by Van't Hoff equation (1.3), the difference between the two situations is shown for each solute in Figure 2.4.

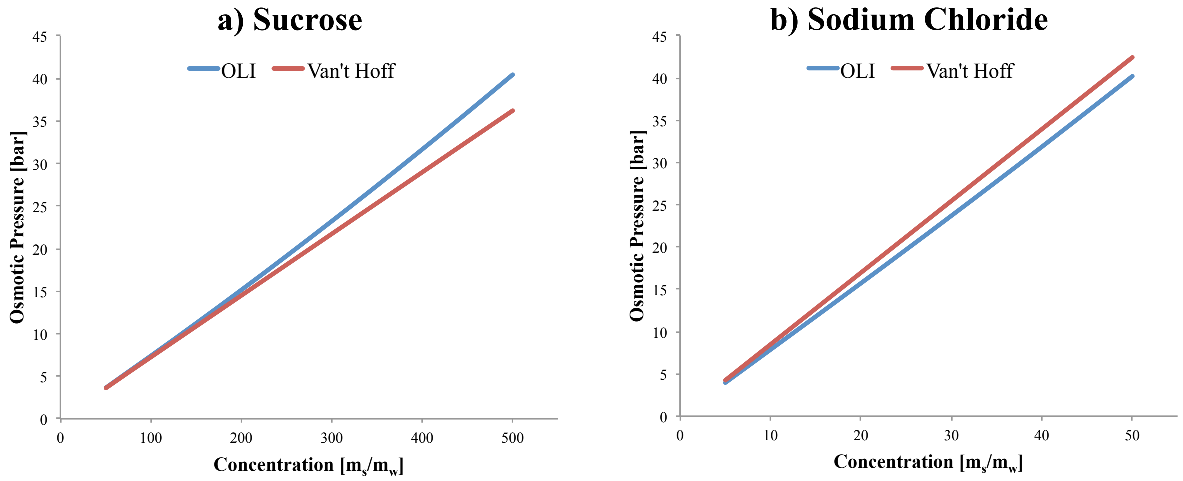


Figure 2.4: *Osmotic pressure of Sucrose and Sodium Chloride as function of the concentration for values calculated at 25°C by Van't Hoff equation and by OLI Analyzer sofware (OLI System Inc., 2006)*

From Figure 2.4 it is observed that to reach a certain value of osmotic pressure, an amount of solute of almost ten times is necessary when using sucrose, compared to sodium chloride. This fact would suggest that the sugar is not really a proper osmotic agent but, as stated before, this research is not limited to the performance of the single FO process but a global vision is taken into account, considering also the regeneration step of the draw solution. A mixture of sucrose and sodium chloride has been insvestigated as preliminary study with the prospect of testing it in the regeneration step in a future work.

2.2.2 Membrane

A membrane producted by Toyobo Co., Ltd (Japan) has been used and the specifications are summarized in Table 2.3.

Table 2.3 *Specifications of the hollow fiber DURASEP® membrane producted by Toyobo Co., Ltd (Japan).*

Type of membrane		Hollow fiber, FO
Membrane chemistry		Cellulose triacetate
Housing material		Polysulphide
Operating pressure	**Shell side**	6 bar
	Fibers side	<1 bar
Allowable pH		3÷8
Membrane area		4,5 m^2
Rejection		96%÷98%

2.3 Experimental procedure

The experimental work was aimed at testing the performance of the forward osmosis process with a sucrose and sodium chloride draw solution at different concentrations using different feeds water. The experiments have been designed thinking of a brackish water desalination, thus the osmotic pressure of the draw solutions will not overcome 40 bar and the salinity of the feed water will not exceed the 5000 ppm of sodium chloride, typical value of TDS for this kind of feed (§1.2). The range of osmotic pressure of the draw solution is between 20 bar and 40 bar; the draw solutions have different concentrations of solute, in such a way that for the first draw solution the concentration of sodium chloride is fixed in order to contribute as much as 10 bar compared to the overall osmotic pressure.

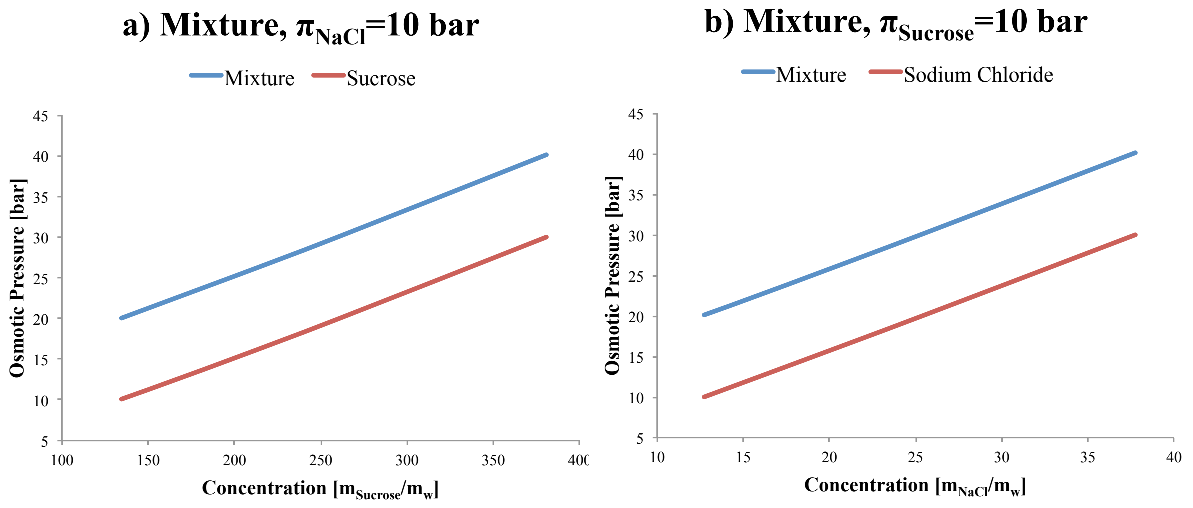


Figure 2.5: *Osmotic pressure of Sucrose and Sodium Chloride solutions for both cases analyzed: a) Sodium Chloride concentration fixed and Sucrose concentration changeable, b) Sucrose concentration fixed and Sodium Chloride concentration changeable. All values have been calculated at 25°C by OLI Analyzer sofware (OLI System Inc., 2006)*

For the second draw solution the opposite happens, the concentration of sucrose being fixed in order to give a 10 bar contribution of the overall osmotic pressure. In doing so for both cases, the increase of osmotic pressure is given by only sucrose or sodium chloride respectively. The contributions given by the solutes at the same osmotic pressure are different and a different behavior in both cases is expected. First the osmotic pressure of the single solutes have been evaluated, and secondly that of the mixtures. For an ideal solution the total osmotic pressure is given by the sum of the single osmotic pressures calculated for each single solute: for sucrose-sodium chloride solution this situation is verified even if a slight change occurs. Figure 2.5 shows the osmotic pressure of the solutions in both the cases above mentioned, in which the contributions of the changeable solutes are enhanced. For each mixture the experiments were carried out using either distilled water and brackish water. The plan of the experiments is summarized in Table 2.4.

Table 2.4 *Table of the experimental work: different combinations between sucrose and sodium chloride concentrations are tested*

Osmotic pressure [bar]			***Concentration*** [m_s/m_w]		***Feed water***
Total	Sucrose	NaCl	Sucrose	NaCl	
20	10	10	134.20	12.73	Distilled water, Brackish water *5000 ppm*
25	15	10	198.29	12.73	
30	20	10	260.66	12.73	
40	30	10	380.66	12.73	
20	10	10	134.20	12.73	Distilled water, Brackish water *5000 ppm*
25	10	15	134.20	19.08	
30	10	20	134.20	25.38	
40	10	30	134.20	37.75	

2.3.1 Procedure

The experimental runs have been carried out at a temperature as much possible close to 25°C, temperature which was used to evaluate the osmotic pressure in OLI Analyzer. The procedure followed during the experimental work is the following:

- Preparation of the plant carefully cleaning the tanks, first with tap water and secondly with distilled water, in order to remove all the salts and traces of solutions previously used which might contaminate the experiment and the sampling. The process is runned with only distilled water first, in order to ensure a complete cleaning of the whole pipelines network and primarly of the membrane unit; tap water must be avoided because of its hardness. The indication of complete cleaning of the membrane is given by the pressure drop between the draw solution inlet and outlet: the viscosity of sugar solution plays an important role in a capillary fiber, even if the concentration is very low. The membrane is considered cleaned and ready to use when the relative pressure indicated by the pressure gauge in the inlet is 0.40 bar. The pressure drop in the feed water shell of the membrane is always 0 bar; since only distilled and brackish water are used as feed water, substantial fouling phenomena do not occur and increasing flowrate by completely opening the control valve is enough to easily remove the salt from the brackish water side and the solutes from the draw solution due to reverse flux. According to §1.5.2.3 physical operations in forward osmosis are possible to clean and prevent fouling: at this cleaning stage a completely open control valve provides higher flowrate and higher turbulence in the feed shell.

- Preparation of the draw solution and the feed water. Because of the heat-labile nature of sucrose, the draw solution cannot be heated by using the available portable resistance heater, thus the water must be heated before making the solution. The temperature has been kept at 25°C as much as possible for both feeds. The feed water tank (F_{in}) is filled with distilled water which temperature was raised to about 26-27 °C by soaking a portable resistance heater. A certain volume of warm water is used to accurately make a solution with the solutes previously weighted (balance used specifications: scale capacity of 5 kg and sensitivity of 0.001 kg). 20 or 25 L of water have been used as draw solution solvent depending on the osmotic pressure and on the time expected for the experiment in order to minimize the chemicals use. After adding solutes and solvent in a separate tank, a submersible pump has been used to mix the phases and facilitate solubilization. After this step the temperature of the solution is expected to decrease to about 25°C due to the endothermic solubilization process and the cooling due to the pump use. Further desalinated water at room temperature is added to the feed water tank in order to cover the lack of water previously taken for the mixture, so that a volume about 80-85 L is restored and the temperature corrected at about 25°C. If a brackish water is used, at this step a certain amount of salt must be added depending on the volume of water. From the reading of the level indicator the volume in the tank can easily be evaluated by using the calibration of the tanks mentioned in §2.1 and 5 g per litre are mixed. For the brackish water preparation 5000 ppm are required, the volume change given by the mixture has not been taken into account, being considered negligible.
- The process requires around 30-60 seconds of running before starting the experiment in order to fill the whole pipeline network and the membrane with draw solution and feed water. The outlet tanks need emptying before running the experiment in order to remove the feeds collected. The process is run for a time between 28 to 32 minutes depending on the performance.
- At the end of the run all the tanks are emptyed and the plant is cleaned.

2.3.1.1 Parameters of the process

Before and during the process certain parameters are observed:

- The levels are the most important parameters since from the readings at t=0 and t=fin it is possible to evaluate the volumes and subsequentely the performance of the process. The duration of the experiment depends on the levels, in fact the process runs as much as at least one level is not readable anymore; for all the experiments the reading of the F_{out} drives the duration.
- The pressure gauge positioned in D_{in} stream just before the membrane indicates the pressure drop of the membrane (capillar fiber side) and is the most important pressure

value of the process also because it is the only one that can be changed. As the concentration of the draw solution increases the pressure drop of the membrane increases as well; the pressure gauge is rather sensitive (0.05 bar) with a scale capacity of 1 bar (relative pressure).

- The flowrates give a rough indication on how the process is running and if any problems are present. The value are recorded anyway but without being taken into account for elaborating.
- The densities of the solutions before and after the experiment are of the highest importance for the mass balance calculation; having to do with solutions highly concentrated the density cannot be considered unitary. A portable density meter (Anton Paar® DMA 35 with infrared interface) has been used to record the densities of the solutions at t=0 and t=fin, with a sensitivity of 0.0001 g/cm^3. Being the density a function of temperature, also the temperature values of the solutions have been recorded in order to check and possibly mantain the temperature around 25°C. A key aspect of the density is evaluating the concentrations of the solutes in the solutions. The OLI Analyzer software used for calculating the concentrations corresponding the desired osmotic pressure values requires the amount of water and the amount of the solutes expressed in mass as input. The concentrations are expressed as m_s/m_w, even if in this way the preparation of the solution is easier, only a known value of the density of the solution makes possible a transformation in a conventional concentration where the volume expressed is not the solvent, but the solution. The concentration values in g/L will be therefore less than the ones in m_s/m_w, and this is important for the evaluation of the concentrations of the solutes: to analyze the samples it is always required to know which analysis method to use and the concentrations range has to be known. Knowing the concentrations is also a good comparison method with the analysis results. Using the density values is also useful to transform the concentrations of the outlet draw solution from g/L to m_s/m_w: in this way it is possible to obtain the input required by OLI Analyzer to calculate the osmotic pressure, necessary for a future reverse osmosis experimental work in which the same solutions are involved.

2.3.1.2 Sampling

For each experiment samples of draw solution in, draw solution out, feed water in (when brackish water is used) and feed water out are taken. For each solution 3 sampling tubes are filled, of which one is sent to sodium chlorine analysis, one to sucrose analysis and one held as a precaution. All the samples must be stored in refrigerator at 4°C in order to inhibit bacterial growth for a maximum of 30 days.

2.4 Quantitative analysis

As mentioned above, the samples need quantitative analysis both for sodium chloride and sucrose. The analysis results are necessary to calculate the reverse flux due to non-ideality of the membrane that causes a diffusion of the solutes to the feed water.

2.4.1 Sodium chloride analysis

The concentration of sodium chloride has been analyzed by Ion-Exchange Chromatography; the methos is based on the measure of the chlorine anion, as it is easy that sodium cation is included in the solution by contaminations. The analysis have been performed by University of Surrey's Chemistry Department. The samples have been analyzed by a Dionex IC5000 ion chromatograph after diluting 100 times with deionized water.

2.4.2 Sucrose analysis

In previous works based on sucrose solutions, the quantitative analysis of the solute was successfully carried out by High-Performance Liquid Chromatography, but an interference in the sucrose analysis by HPLC has been observed when sodium chloride is also present in the solution. Accordingly, the search for a reliable method has shifted towards other techniques. For this thesis an Amperometric Bioanalysis using a Glucose Biosensor based on Glucose Oxidase has been used. The optimization of the apparatus and the conditions have been conducted at the University of Surrey's Chemistry Department's Biomaterials Laboratory with the aim to find a proper procedure to reliably analyze the sucrose concentration in a mixture that contains sodium chloride.

2.4.2.1 Introduction

Enzymatic reactions can be used for the determination of sucrose based on enzyme electrode [30]. These sucrose electrodes were constructed with glucose oxidase, mutarotase and invertase co-immobilized in a membrane. The reactions which occur in the membrane are summarized as follows [31]:

$$\text{sucrose} + H_2O \xrightarrow{invertase} \alpha\text{-D-glucose} + \beta\text{-D-fructose} \tag{2.1}$$

$$\alpha\text{-D-glucose} \xrightarrow{mutarotase} \beta\text{-D-glucose} \tag{2.2}$$

$$\beta\text{-D-glucose} + H_2O + O_2 \xrightarrow{glucose\ oxidase} \text{gluconic acid} + H_2O_2 \tag{2.3}$$

In the absence of mutarotase enzyme that allows the mutarotation of the α-D-glucose, the reaction 2.2 can be accelerated by phosfate ions in solution. The mutarotation reaction (2.2) can be rewritten as equilibria [30]:

$$\alpha\text{-D-glucose} \overset{\xrightarrow{phosphate\ ions}}{\longleftarrow\!\!\!-\!\!\!-\!\!\!-} \beta\text{-D-glucose} \qquad (2.4)$$

In both cases a breakdown of the sucrose and oxidation of the β-D-glucose occurs. The production of hydrogen peroxyde allows the electrochemical measurement of the oxidation current producted following an anodic potential [32]:

$$\mathrm{H_2O_2} \overset{Pt}{\rightarrow} \mathrm{O_2} + 2H^+ + 2e^- \qquad (2.5)$$

The standard procedure proposed is based on immobilazing the three enzymes between two membrane layers which are positioned on the platinum electrode. The membrane sandwich separates the electrode from the solution in which sucrose is present; an equilibrium occurs due to the diffusion of the disaccharide through the outer membrane. Whitin the sandwich reactions 2.1, 2.2 and 2.3 take place quickly giving an immediate current response, proportional to the sucrose concentration. The aim of this research is finding a proper procedure in order to analyze with a certain accuracy the sucrose concentration without using the mutarotase, as it is not easily available on the market. The basic idea is using free invertase in order to have the sucrose breakdown and exploiting the equilibrium between α-D-glucose and β-D-glucose. The process depends on several parameters and on the basis of this procedure an optimization has been carried out; the main factors to be taken into account are the amount of invertase for a complete breakdown for all the concentration range covered by the samples, enzymatic reaction time, phosphate concentration.

2.4.2.2 Apparatus

A first-generation glucose biosensor has been used. It relies on the use of the natural oxygen cosubstrate and generation and detection of hydrogen peroxide. The biocatalytic reaction involves reduction of the flavin group (FAD) in the glucuse oxydase enzyme by reaction with β-D-glucose to give the reduced form of the enzyme ($\mathrm{FADH_2}$) [32]:

$$\mathrm{GOx(FAD)} + \mathrm{glucose} \rightarrow \mathrm{GOx(FADH_2)} + \mathrm{gluconolactone} \qquad (2.6)$$

followed by reoxydation of the flavin by molecular oxygen to regenerate the oxidized form of the enzyme GOx(FAD) [32]:

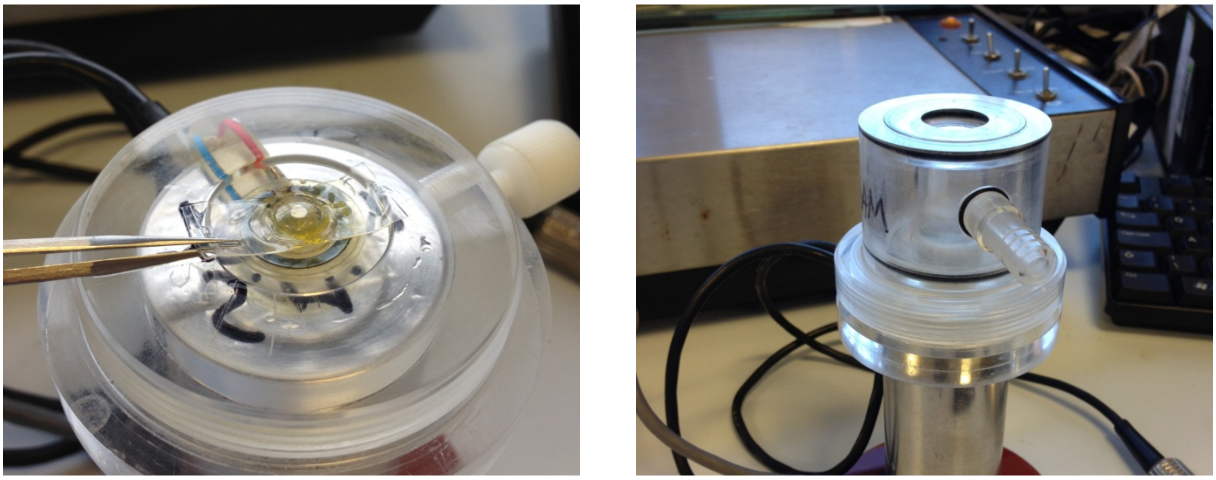
$$\mathrm{GOx(FADH_2)} + \mathrm{O_2} \rightarrow \mathrm{GOx(FAD)} + \mathrm{H_2O_2} \qquad (2.7)$$

The gluconolactone formed in Reaction 2.6 is hydrolised in gluconic acid when water is present. Measurements of peroxide formation have the advantage of being simpler, especially when miniaturized devices are concerned [32]. This measurement is carried out on a platinum electrode at anodic potential of +0.65 V (vs Ag/AgCl). An EmStat producted by Palm Instruments BV has been used as elettrochemical sensor interface (current ranges from 1 nA to10 mA; current resolution of 1 pA; accuracy ≤0.2%) and PSTrace as software.

2.4.2.3 Materials

Glucose oxidase (EC 1.1.3.4) from *Aspergillus niger* (Gox, 100-250 U mg^{-1}); Invertase (EC 3.2.1.26) from baker's yeast (Inv, ≥300 U mg^{-1}); α-D-glucose anhydrous (96%); sucrose (≥99.5%); bovine serum albumin (≥96%); glutaraldehyde solution (Grade II, 25%) were purchased from Sigma-Aldrich. Phosphate buffered saline (Sodium chloride 8.0 g/l; Potassium chloride 0.2 g/l; Di-sodium hydrogen phosphate 1.15 g/l; Potassium dihydrogen phosphate 0.2 g/l), pH 7.3 ± 0.2 at 25°C was purchased from Oxoid. Dialysis membrane was purchased from The Scientific Instrument Centre Ltd.

2.4.2.4 Biosensor preparation



(a) **(b)**

Figure 2.6: *(a) Detail of the sandwich laid on the platinum electrode; (b) electrode complete with the solution compartment.*

The glucose oxidase enzyme is immobilized by cross-linking between the two membranes layer. The method consists of using a cross-linker able to immobilize the enzyme in the sandwich. A solution of glucose oxidase is prepared dissolving 15 mg in 50 μL of a 100 mg/L BSA (bovine serum albumin) aqueous solution which acts as protein feeder increasing the immobilization efficiency. The cross-linker used is a 2.5% glutaraldehyde solution. Around 3 cm^2 of general purpose dialysis tubing membrane is used for each layer for preparing the sandwich. After positioning the lower layer on a microscope slide, 3 μL of 2.5% glutaraldehyde solution are added with 6 μL of glucose oxidase/BSA solution. The upper layer is positioned over the lower one, and a further microscope slide laid on with a moderate load in order to distribute homogeneously the liquid in the sandwich which should harden rapidly in around 5 minutes. Three drops of PBS (phosphate buffer solution) at pH=7.3 are added on the platinum electrode and afterwards the sandwich is positioned over, after being trimmed off from the excess membrane. The membrane is fixed with an O-ring and the overlying part which will contain the solution is screwed. The solution compartment screwed to the base electrode presents a hole which permits the contact of the solution to the biosensor (Figure 2.6). Whitin the compartment a certain volume of phosphate buffer solution will be filled, and a good mixing is ensured using a magnetic stirrer at constant speed. The sofware used to manage the process requires the anodic potential (that was be set at +0.65 V), time of run and time interval (5 minutes). After switching the electrochemical sensor on, the current is plotted as a function of time. The analysis consists of adding a certain volume of samples in a known volume of PBS and obtain the unknown concentration by the current variation recorded by the electrochemical sensor; each sample is analyzed adding a certain volume one after the other and the current gradient indicates the concentration gradient between one adding and the following. Before analysing unknown samples, a calibration must be carried out using a standard solution in order to find proportional relation between the concentration and the current and to indentify the linear range. Before each operation, a chemical equilibrium must be reached in which the current value approches to zero, a point from which it is possible to start increasing the concentration; during this operation, which takes average 15 minutes, it is important to wash the electrode removing the PBS and adding fresh solution back. The biosensor is ready for the measure and the membrane can be used several times providing that an accurate washing is ensured; the enzyme immobilized acts as catalyst and after every reaction is available again for the following analysis. The membrane can be stored in the fridge at 4-5 °C between every analysis even if a preparation from scratch is recommended.

2.4.2.5 Biosensor calibration

The biosensor needs calibrating and the linear range must be indentified. A standard α-D-glucose solution has been preparared dissolving 18 mg of solute in 1 mL of PBS for a final concentration of 100 mM. This solution has been used to identify the linear current response 60 minutes after being prepared. An exact volume of PBS of 3 mL is added after washing the biosensor; adding known volumes of standard solution is possible to calculate the concentration of the solution and create a calibration trend. For each 3 μL of standard solution added, a 0.1 mM difference in the concentration happens due to the dilution in the 3 mL volume. The linear response has been identified between 0 and 4 mM. The calibration procedure has been repeated with the same solution after 24 hours after being left overnight in the fridge at 4-5 °C. Best results have been observed for the second case because of the long time waiting and the low temperature. The results are shown in Figure 2.7.

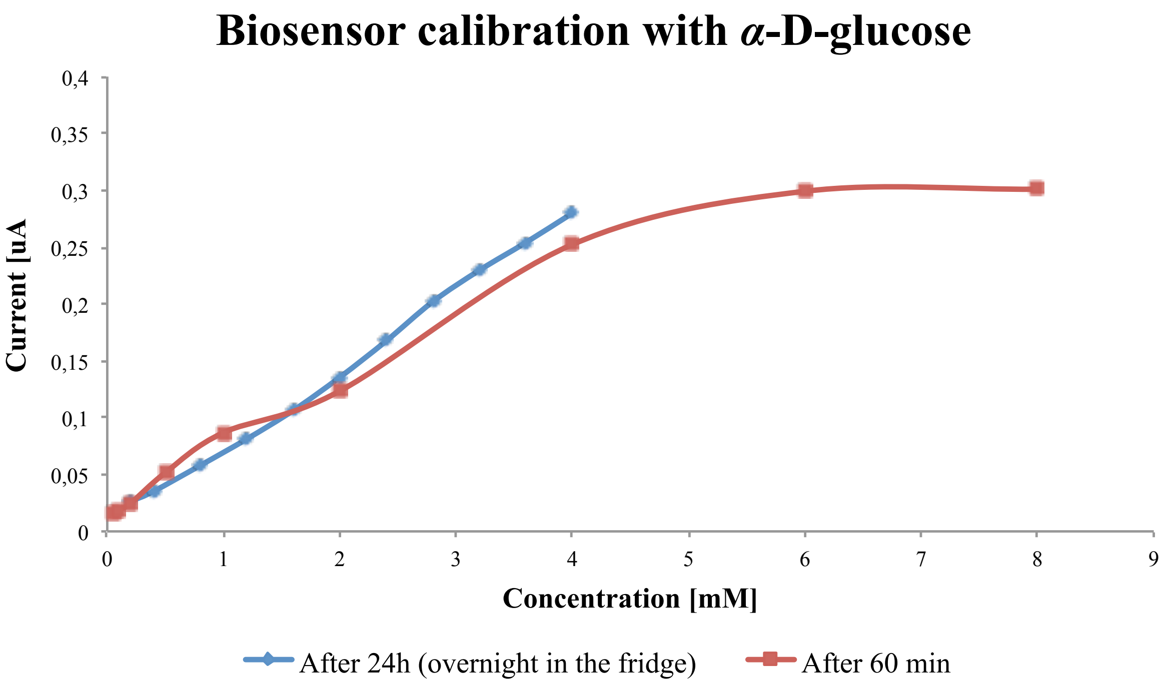


Figure 2.7: *Linear current response range identification with a 100 mM α-D-glucose/PBS solution for two different cases. More linearity is observed after having left the standard solution 24 hours.*

The better results obtained leaving the standard solution in the fridge overnight could suggest that equilibrium reaction 2.4 is slightly improved by a longer waiting time and low temperature. The electrochemical sensor response as a function of time is shown in Figure 2.8: each current step represents the addition of a certain known amount of standard solution, and each dot in Figure 2.7 represents a step in Figure 2.8.

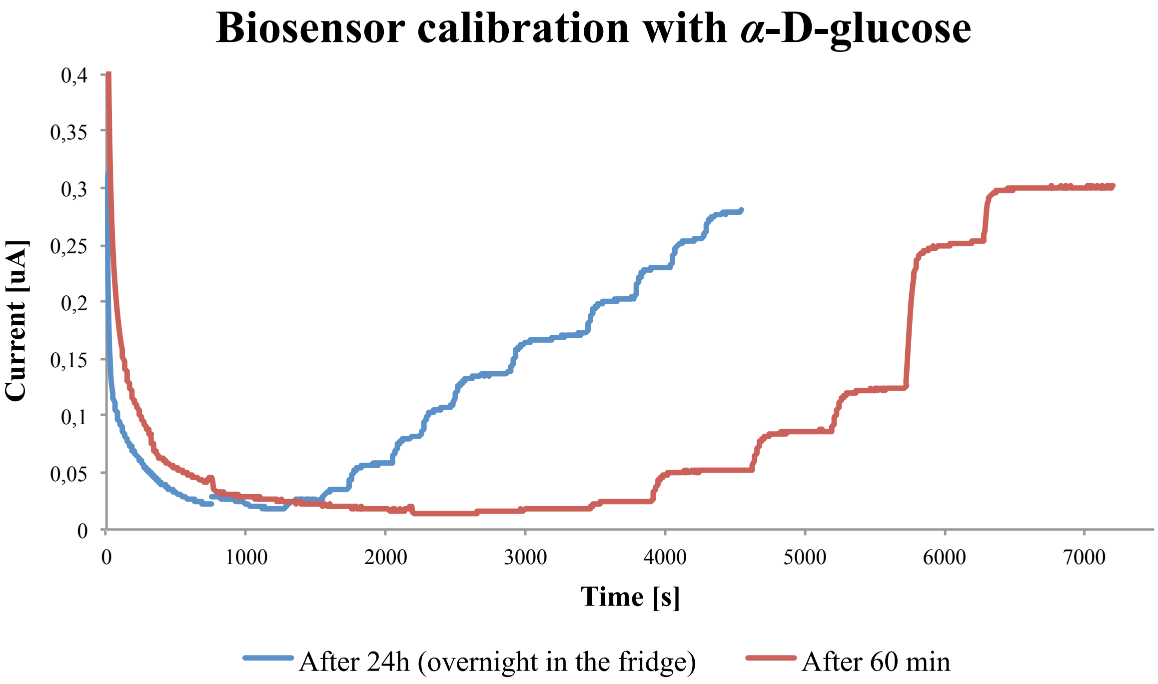


Figure 2.8: *Time dependent current response depending on 100 mM α-D-glucose/PBS solution additions.*

From Figure 2.8 it is possible to observe the time that is necessary to wait before calibrating. The discontinuities of the function in the first 1000-1500 seconds represent the washings of the biosensor with PBS. The two tests have been carried out preparing a new membrane sandwich every time. The average time needed for calibrating is 75 minutes.

2.4.2.6 Optimization procedure

When sucrose instead of α-D-glucose is used the amount of enzyme must be defined that ensures a complete breakdown of the sucrose for all the samples concentration range. A solution of invertase has been prepared dissolving 15 mg of enzyme in 50 µL of PBS. Using free invertase without immobilizing it in the membrane, the optimal ratio between sucrose solution and enzyme solution volume must be found; the only way to define it is comparing a calibration trend made using sucrose solution to the calibration trend obtained previously using α-D-glucose. A 3:1 ratio has been found covering all the concentration range. The calibration trend obtained with α-D-glucose could be used during the analysis, but a sucrose solution is preferable in order to create a real situation when sucrose samples will be used. A 1 M aqueous solution of sucrose has been prepared which should represent a likely sample. Many attempts have been done in order to obtain the same results given by α-D-glucose use:

1. Adding invertase solution to a certain volume of sample maintaining the optimal ratio, leaving overnight at room temperature. The current signal does not reach a steady state and increases costantly. This suggested that the equilibrium drived by phosphate ions is estabilising in the electrode, making the current response unstable.

2. Adding invertase solution to a certain volume of sample maintaining the optimal ratio, diluiting with PBS in order to reach the equilibria in the sample before being analyzed, leaving overnight at room temperature. The calibration trend presents the same no linearity given by α-D-glucose calibration after 60 minutes (Figure 3.2). This result suggested that leaving the samples overnight in the fridge could improve the linearity.
3. Adding invertase solution to a certain volume of sample maintaining the optimal ratio, diluiting with PBS in order to reach the equilibria in the sample before being analyzed, leaving overnight in the fridge. Compared to the second attempt, the situation slightly improved, but the procedure was still not reliable by the time really not accurate results have been reached analysing samples at known concentration. This result suggested that the different dilutions made for the samples and the standard solution could have affected the phosphate concentration and the pH.
4. Adding invertase solution to a certain volume of sample maintaining the optimal ratio, diluiting with PBS in order to reach the equilibria in the sample before being analyzed, correcting the dilution of the PBS given by the water in the samples with a PBS ten times more concentrated, leaving overnight in the fridge. No improvement has been observed, instead the situation got worse: a steady state current is not reached, and the signal increases with constant slope.
5. Same sucrose and sample solutions preparation done in the third attempt, leaving 24 hours at room temperature and 24 hours in the fridge. The linear concentration range is still between 0 and 4 mM but the current response increases: this is due to the badly defined current steps. The lack of a steady state current means that the method is unreliable, because the additions of the sucrose solution and samples are subjective, not being the steps well defined. The current slope keeps increasing when the concentration increases; better results are obtained if the linear calibration range is narrowed between 0 and 1 mM, range in which the steps are a bit more well defined even if the method is still not accurate. The trend of current as a function of time obtained with the calibration is shown in Figure 2.9.

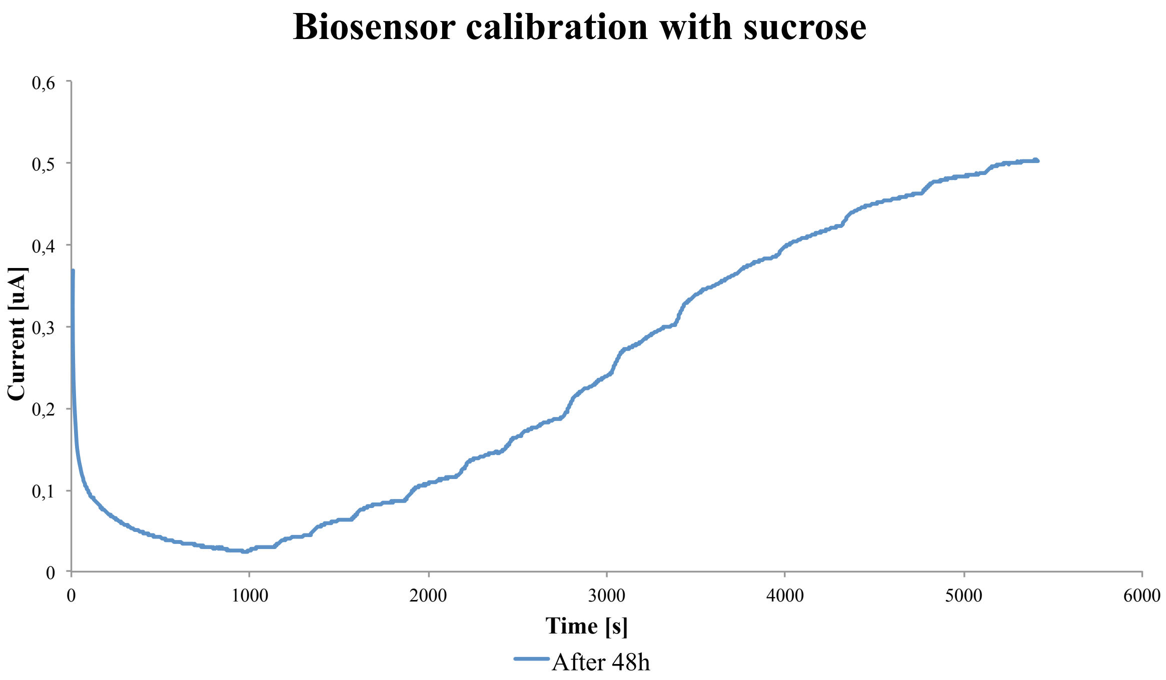


Figure 2.9: *Time dependent current response depending on 60 mM sucrose solution additions (Solution: 48 μL of 1 M sucrose aqueous solution, 16 μL of invertase solution, 736 μL of PBS); after 24 hours at room temperature and 24 hours in the fridge.*

2.4.2.7 Discussion and conclusions

The substantial difference between the α-D-glucose PBS solution and the sucrose solution diluted with PBS is the total phosphate concentration, which is less when the sucrose is used by the time the sucrose solution prepared is aqueous. This gap has been attempted to be sorted out adding concentrated PBS in order to re-estabilish the phosphate concentration with no improvement. The reason of current instability when sucrose solution is used could be attribuited to the invertase dissolved in the solution, being it the only compound not present in the α-D-glucose solution previously used; the enzyme catalyzes the sucrose breakdown without consuming and its presence could somehow affect the equilibria. No attempt was successful, and from the tests carried out it seems that the use of the free invertase without the mutarotation catalyst is not the proper procedure. Before rejecting the procedure other attempts are better be done. Being the enzymatic activity dependent on the pH a sensitivity study could be done changing the pH, of the buffer solution in order to find for which value the current response of the electrode is maximum; at that pH the response could be improved and the steps well defined. It has been demostrated how the use of a membrane based on $\mathrm{PVF^{+}ClO_4^-}$ as redox polymer gives interesting electrochemical results when used as layer on platinum surface; the phosphate ions in the matrix and those in the solution can act as accelerators for the mutarotation reaction in absence of mutarotase. An optimization of a biosensor based on this kind of membrane could significantly improve the quality of the analysis procedure.

2.4.2.8 Alternative analysis

As an interference between sodium chloride and sucrose was noticed in a previous work by using HPLC, this technique must be avoided for accurate results. Anyway, HPLC has been used for analysing the sucrose amount in the feed water outlet samples, in which only a little amount of sodium chloride is present if distilled water is used, and a concentration around 5 g/L when brackish water is used. Due to the low concentration compared to that of the draw solutions mixture, it was assumed that the interference is negligible. The analysis have been conducted by University of Surrey's Chemistry Department. The samples have been analyzed as supplied by a Varian 920-LC HPLC instrument with a Varian 385-LC light scattering detector.

Chapter 3

Results and discussion

In this chapter the results of the analysis and their elaboration are presented. Several performance indices have been plotted by using the analysis results and the parameters recorded during the experiments.

3.1 Quantitative analysis considerations

The quality of the analysis results is not good considering the comparison between the concentrations found and the samples with known concentration (D_{IN}, F_{IN}) in the case of chloride analysis. For mainly economic reasons only one analysis for each sample has been carried out and the quality of the results depends also on the number of the analysis carried out. In order to obtain more rigorous results it would be recommended to analyze at least three samples of the same solution and afterwards take an average value so as to increase the accuracy and limit some errors which could be made during the dilutions. Furthermore, the calibration data range should be narrowed in order to obtain a more accurate calibration line for the whole concentration range of the samples. The calibration curves for sucrose and chloride analysis are shown in the Appendix (Annex B) with the related table of the concentrations (Annex C). For both solutes the concentrations given by the analysis of the F_{OUT} have been taken into account in order to calculate, by using the known concentrations, the concentrations of the D_{OUT}; in this case the mass balances based on the solutes are substantial.

3.2 Experiments consistency

To elaborate the parameters recorded in each experiment and the analysis results, an Excel spreadsheet has been used. In order to verify the validity of the experimental data the mass balance has been calculated; the volumes derive from the calibration trends obtained for each tank and the densities are measured as described in §2.3.1.1. The model equation is:

$$V_{D_{IN},t=0}\rho_{D_{IN}}+V_{F_{IN},t=0}\rho_{F_{IN}}=V_{D_{IN},t=t_{fin}}\rho_{D_{IN}}+V_{F_{IN},t=t_f}\rho_{F_{IN}}+V_{F_{OUT}}\rho_{F_{OUT}}+V_{D_{OUT}}\rho_{D_{OUT}} \quad (3.1)$$

Where V and ρ are the volume and density of the relative feeds at the beginning ($t=t_0$) and at the end ($t=t_f$). The percent errors have been calculated as:

$$e_{\%} = \frac{m_{t=0} - m_{t=t_f}}{m_{t=t_f}} \cdot 100 \tag{3.2}$$

The calculated errors are limited in a range $|e_{\%}| < 0.4\%$ with an average value of 0.28%.

3.3 Performance indices

Several performance indices have been obtained through the processing of experimental data. In this paragraph the calculation and the results are presented.

3.3.1 Water recovery

The volume of the draw solution increases due to the dilution caused by the water passed through the membrane. The difference of volumes should match with the mass of water transferred from the feed water. The water mass can be rigorously calculated from the dilution as:

$$m_{water}^{D} = \mathrm{V}_{\mathrm{D}_{\mathrm{OUT}}}\rho_{\mathrm{D}_{\mathrm{OUT}}} - \Delta\mathrm{V}_{\mathrm{D}_{\mathrm{IN}}}\rho_{\mathrm{D}_{\mathrm{IN}}} \tag{3.3}$$

The mass of the water calculated this way can be compared to the mass difference of the feed water:

$$m_{water}^{F} = \Delta\mathrm{V}_{\mathrm{F}_{\mathrm{IN}}}\rho_{\mathrm{F}_{\mathrm{IN}}} - \mathrm{V}_{\mathrm{F}_{\mathrm{OUT}}}\rho_{\mathrm{F}_{\mathrm{OUT}}}{}^{1} \tag{3.4}$$

The percent error has been calculated as:

$$e_{\%} = \frac{m_{water}^{D} - m_{water}^{F}}{m_{water}^{F}} \cdot 100 \tag{3.5}$$

The calculated errors are limited in a range $|e_{\%}| < 6.5\%$ with an average value of 3.2%. For data processing the mass of water calculated with Equation 3.3 has been taken into account, as the D_{IN} and D_{OUT} tanks are smaller than F_{IN} and F_{OUT} tanks, and the error due to the level reading is limited; being the variation of the volume sensitive to the level. Furthermore the mass of water found with Equation 3.3 almost perfectly matches the variation in the volume. Using the mass of water transferred the water recovery is calculated as:

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[1] When brackish water is used as feed water the density increases due to the water removal. For this case the density change is supposed to occur for such concentration and not for solute flux from the draw solution. When distilled water flows against the membrane, the solute flux is still not taken into account and the density values are 1000 g/L for both F_{IN} and F_{OUT}.

$$\text{Recovery}_{\%} = \frac{V_{water}}{\Delta V_{F_{IN}}} \cdot 100 = \frac{(V_{D_{OUT}}\rho_{D_{OUT}} - \Delta V_{D_{IN}}\rho_{D_{IN}})/\rho_{water}}{\Delta V_{F_{IN}}} \cdot 100 \tag{3.6}$$

The recovery trends versus the osmotic pressure gradient regarding the two mixtures, with distilled water and brackish water as feed water, are shown in Figure 3.1.

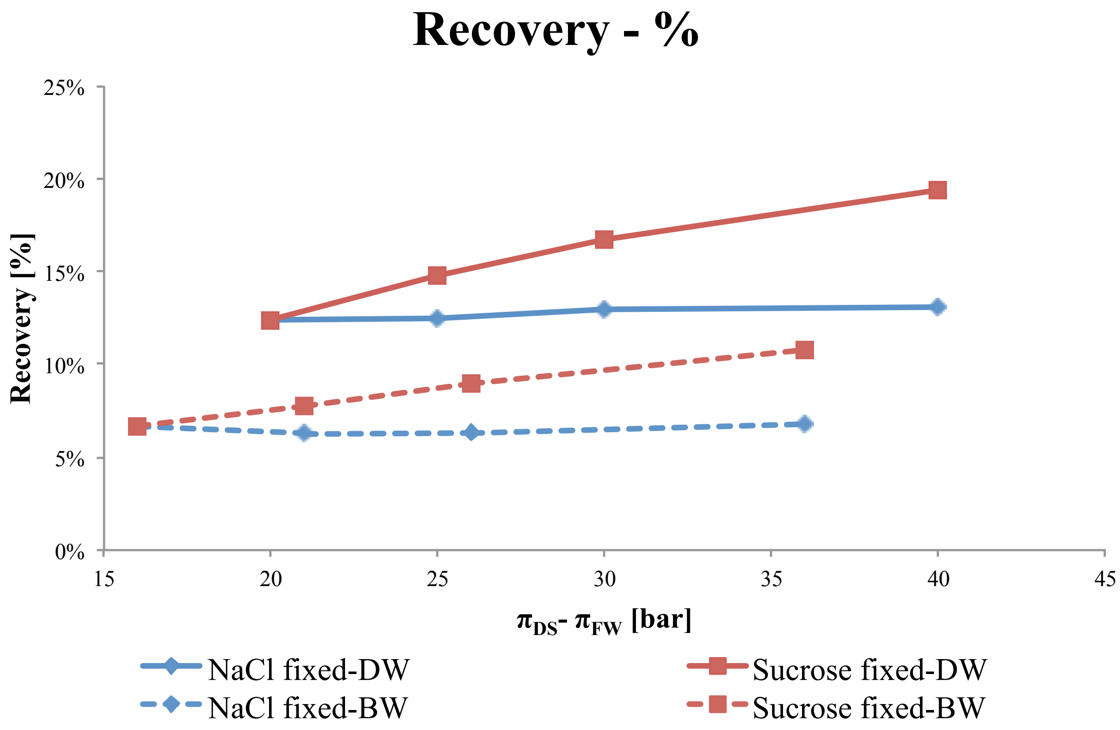


Figure 3.1: *Water recovery percentage for different feeds when NaCl osmotic pressure contribution is fixed at 10 bar (blue trends) and when sucrose osmotic pressure contribution is fixed at 10 bar (red trends).*

Figure 3.1 shows the significant recovery increase when the osmotic pressure of the sucrose is fixed at 10 bar, whereas the recovery function for the other solution is almost stationary. When brackish water flows against the membrane the osmotic pressure gradient decreases by 4 bar (which is the osmotic pressure of the ~5 g/L brackish water), and the water recovery decreases by about 50%.

3.3.2 Water Flux

The water flux which crosses the membrane surface can be calculated as:

$$J_W = \frac{V_{water}}{A_m \cdot t_{exp}} = \frac{(V_{D_{OUT}}\rho_{D_{OUT}} - \Delta V_{D_{IN}}\rho_{D_{IN}})/\rho_{water}}{A_m \cdot t_{exp}} \tag{3.7}$$

where A_m is the membrane surface area and t_{exp} is the duration time of the experiment. These results are shown in Figure 3.2.

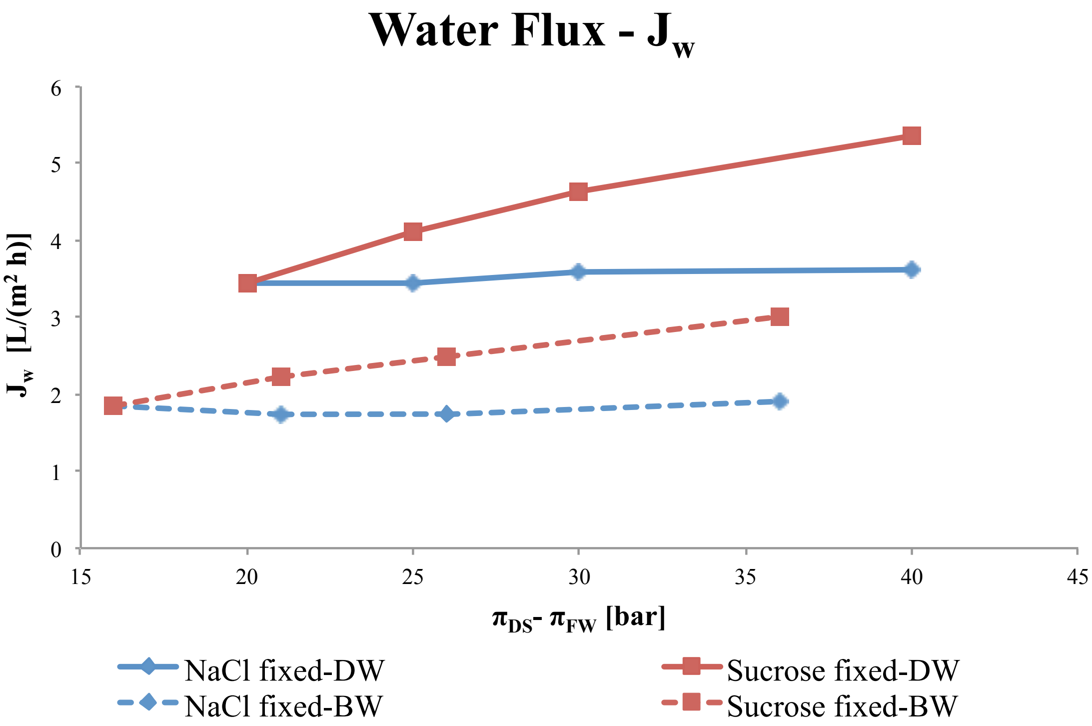


Figure 3.2: *Water flux for different feeds when NaCl osmotic pressure contribution is fixed at 10 bar (blue trends) and when sucrose osmotic pressure contribution is fixed at 10 bar (red trends).*

These trends completely match the previous ones related to the water recovery.

3.3.3 Solutes rejection

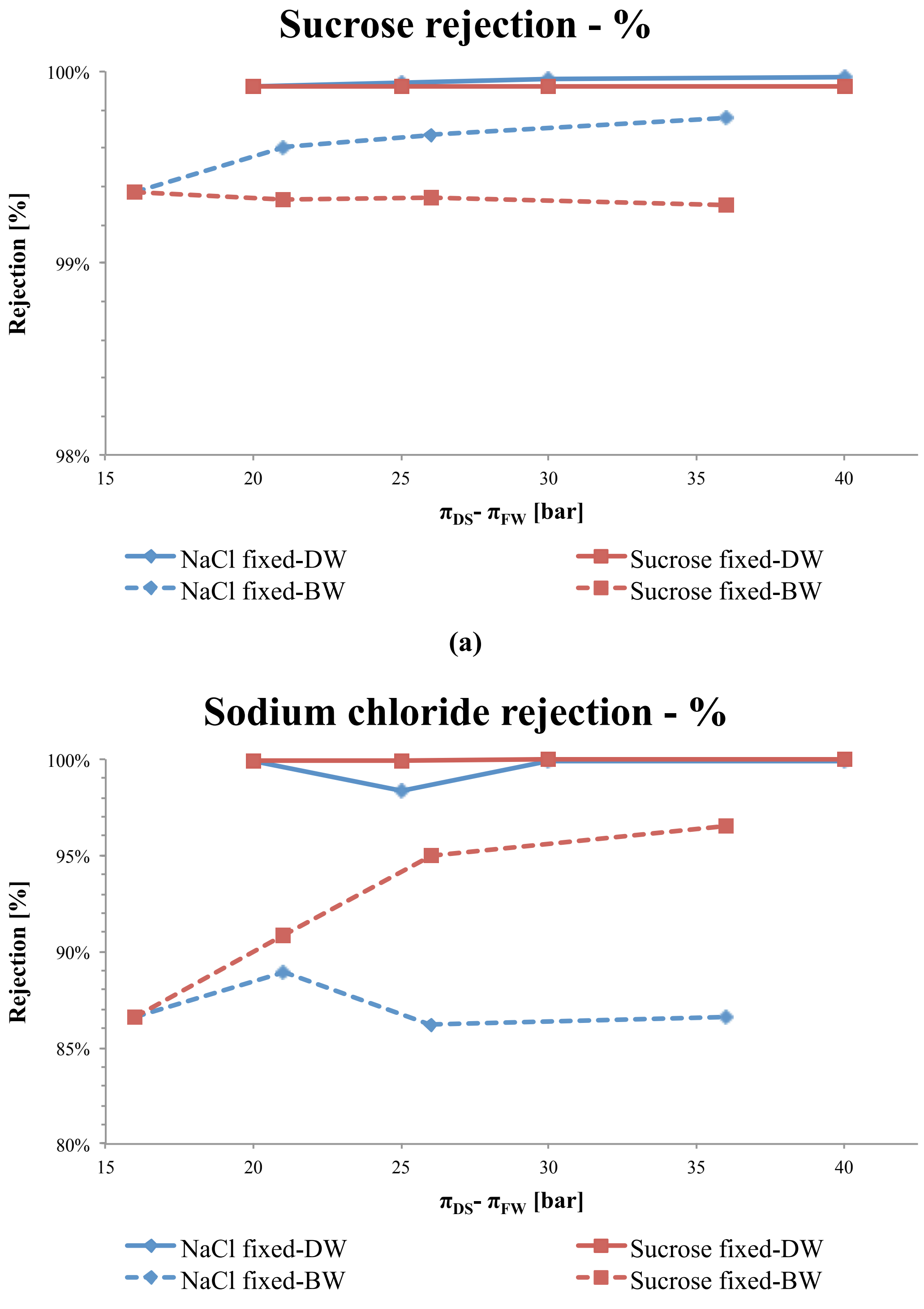
The solute rejection is defined as:

$$Rejection_{\%} = \left(1 - \frac{c_{S,F_{OUT}}}{c_{S,D_{IN}}}\right) \cdot 100 \tag{3.8}$$

where $c_{S,D_{IN}}$ and $c_{S,F_{OUT}}$ are respectively the solute concentrations of the inlet draw solution and in the outlet feed water. According to §3.1 only the solutes concentrations given by the analysis of the outlet feed water have been used. When brackish water is involved, sodium chloride rejection is defined as:

$$Rejection_{\%} = \left[1 - \frac{c_{S,F_{OUT}} - c_{S,F_{IN}}\left(\dot{V}_{F_{IN}}/\dot{V}_{F_{OUT}}\right)}{c_{S,D_{IN}}}\right] \cdot 100 \tag{3.9}$$

where $c_{S,F_{IN}}$ is the sodium chloride concentration of the inlet brackish water (~5 g/L), $\dot{V}_{F_{IN}}$ and $\dot{V}_{F_{OUT}}$ are respectively the volumetric flowrates of the inlet feedwater and of the outlet feed water. The numerator of the ratio in the square brackets represents the concentration increase given by the reverse flux. The results for both sucrose and sodium chloride are shown in Figure 3.3.



(a)

(b)

Figure 3.3: *Sucrose rejection (a) and sodium chloride rejection (b) for different feeds when NaCl osmotic pressure contribution is fixed at 10 bar (blue trends) and when sucrose osmotic pressure contribution is fixed at 10 bar (red trends).*

From the analysis results, when distilled water is used. sucrose has not been detected in the feed water outlet; the concentration has been claimed lower than 0.1 mg/mL. In Figure 3.3a the sucrose rejection trend calculated with 0.1 g/L as concentration is depicted, it presents an average value of 99.85% which could be considered the minimum limit of the range in which the real rejection is included. For both graphs a decrease of rejection occurs when brackish water is used as feed. An explanation could be that in the case when distilled water is used, the solute reverse flux through the membrane is limited by the high water permeability, even if the concentration gradient which should drive this solute flux is higher. From Figures 3.3a and 3.3b the decrease due to different feed water is highlighted. Nonetheless it is not recommended to rely completely on the rejection functions based on the results found because of the poor quality of the analysis.

3.3.4 Net Driving Pressure

The osmotic pressure which drives the forward osmosis process can be calculated taking into account average values of osmotic pressure of the draw solution and feed water. The $\Delta\pi = \pi_{DS} - \pi_{FW}$ represents the osmotic pressure gradient between the solutions fed to the membrane unit. The osmotic pressure of the draw solution decreases whitin the fibers because of the dilution, reaching the osmotic pressure of the outlet draw solution. Instead, the osmotic pressure of the feed water increases, even if slightly, because of solvent removal and solute reverse flux. The net driving pressure is a parameter that takes into account average values of osmotic pressure and average values of hydraulic pressure, and can be calculated as:

$$NDP = \Delta\pi - \Delta P = \left[\frac{\pi_{D_{IN}} + \pi_{D_{OUT}}}{2} - \frac{\pi_{F_{IN}} + \pi_{F_{OUT}}}{2}\right] - \left[\frac{P_{D_{IN}} + P_{D_{OUT}}}{2} - \frac{P_{F_{IN}} + P_{F_{OUT}}}{2}\right] \quad (3.10)$$

The osmotic pressures have been calculated using the solutes concentrations from quantitative analysis and mass balance using OLI Analyzer and the densities. For simplicity the osmotic pressures of the feed water have been calculated considering the g/L concentration as m_s/m_w concentration, thus neglecting the volume change because of the very low concentrations. The hydraulic pressure term is almost irrelevant, by the time the only pressure to be changeable is P_{DIN} with a range between 1.45 bar and 1.65 bar. As much the draw solution is diluted by the transferred water, as much the osmotic pressure output decreases and thus the average osmotic pressure of the draw solution is the rather influential in Equation 3.10. The calculated Net Driving Pressures are shown in Figure 3.4.

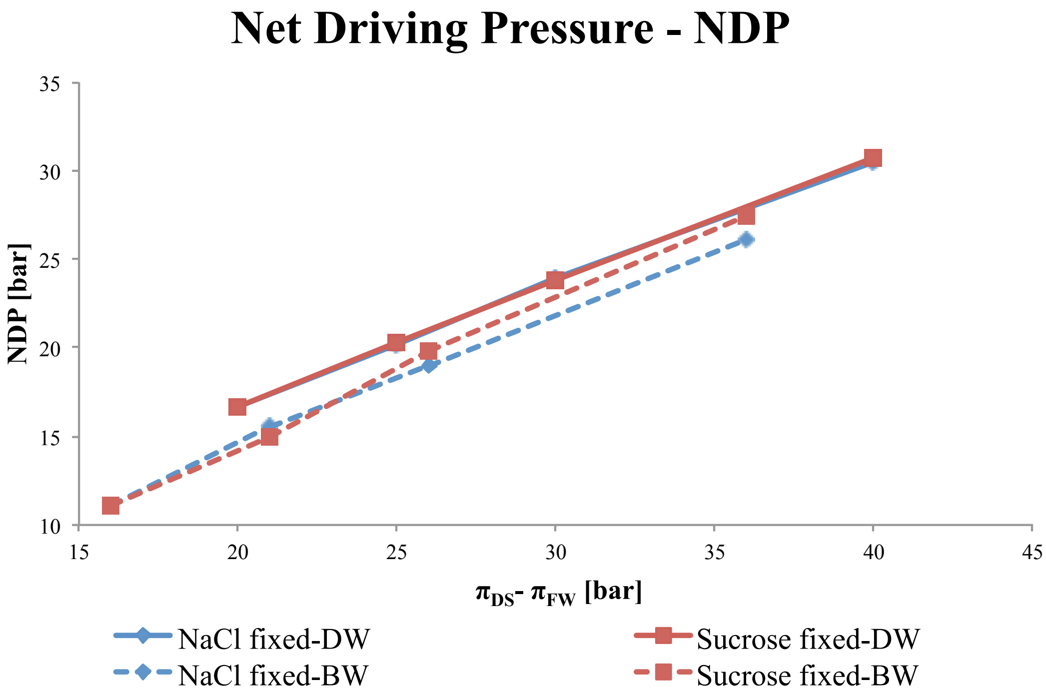


Figure 3.4: *Net Driving Pressure for different feeds when NaCl osmotic pressure contribution is fixed at 10 bar (blue trends) and when sucrose osmotic pressure contribution is fixed at 10 bar (red trends).*

From Figure 3.4 the trends of the two draw solutions seem to coincide when distilled water is used. At constant $\Delta\pi$ the net driving pressure is lower when brackish water flows against the membrane, which can be translated into lower water flux. The net driving pressure gap between the two processes is due to the physical phenomenon caused by a solute presence in the feed water (external concentration polarization). Furthermore the slope of each stroke decreases slightly. Although it seems that the water flux is responsible of the NDP gap between the two processes, it does not seem to be so when the two mixtures are compared against the same feed water. The continuous lines and the dashed lines seem almost to match among them despite a remarkable gap of water flux exists as previously shown in Figure 3.2. So, when the feed water is the same, the two mixtures get diluted almost equally despite the water flux calculated is substantially different, especially when distilled water is used. The draw solution flowrate generally decreases as the concentration increases, especially when the sodium chloride massive concentration is fixed and the sucrose concentration is changed. This is due to the pressure drop of the membrane in the fibers shell: increasing concentration also increases density and viscosity, which substantially influence the process. In Figure 3.5 the draw solution flowrates are shown as function of the draw solution osmotic pressure.

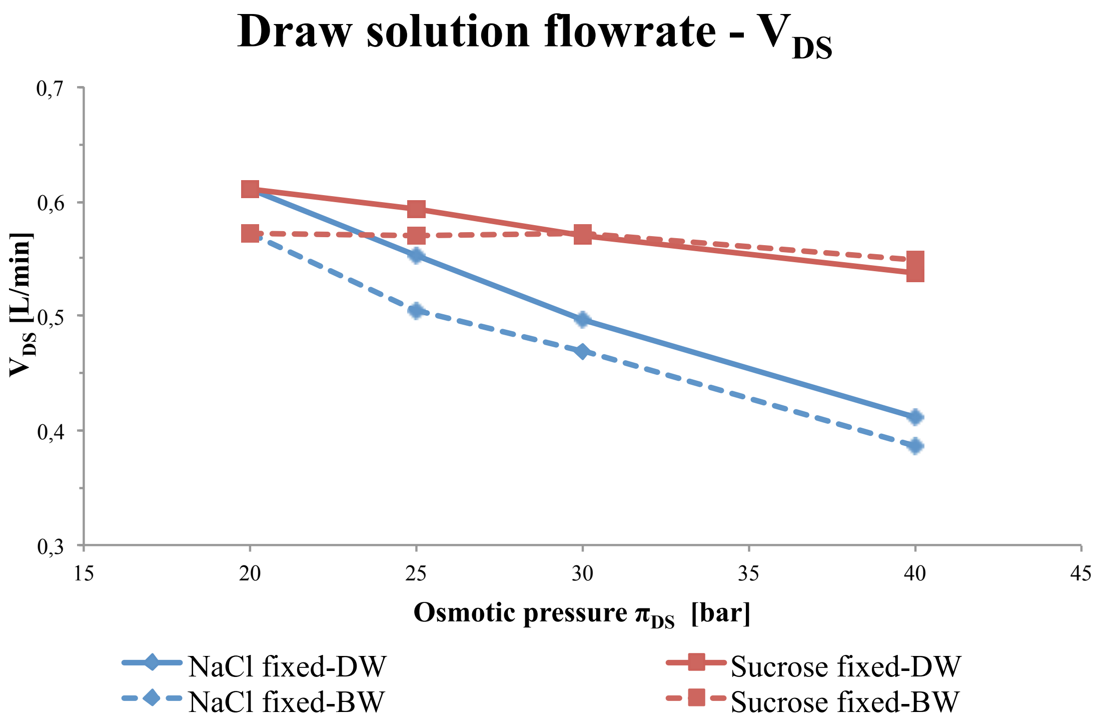


Figure 3.5: *Draw solution flowrate for different feeds when NaCl osmotic pressure contribution is fixed at 10 bar (blue trends) and when sucrose osmotic pressure contribution is fixed at 10 bar (red trends).*

When the sodium chloride concentration is varying, the flowrate of the draw solution is pretty constant or slightly decresing (red trends), while the sucrose concentration changes significantly the flowrate instead. For different feeds water the trends are maintained but furtherly decresed.

3.3.5 Specific Water Flux

From the considerations made so far, a specific flux must be calculated in order to make each different case comparable. The ratio between the water flux J_W and the draw solution flowrate could be considered and expressed as:

$$SWF = \frac{J_W}{\dot{V}_{DS}} \tag{3.11}$$

where $\dot{V}_{DS}$ is the volumetric flowrate of the draw solution. The calculations relating to the specific water flux are shown in Figure 3.6.

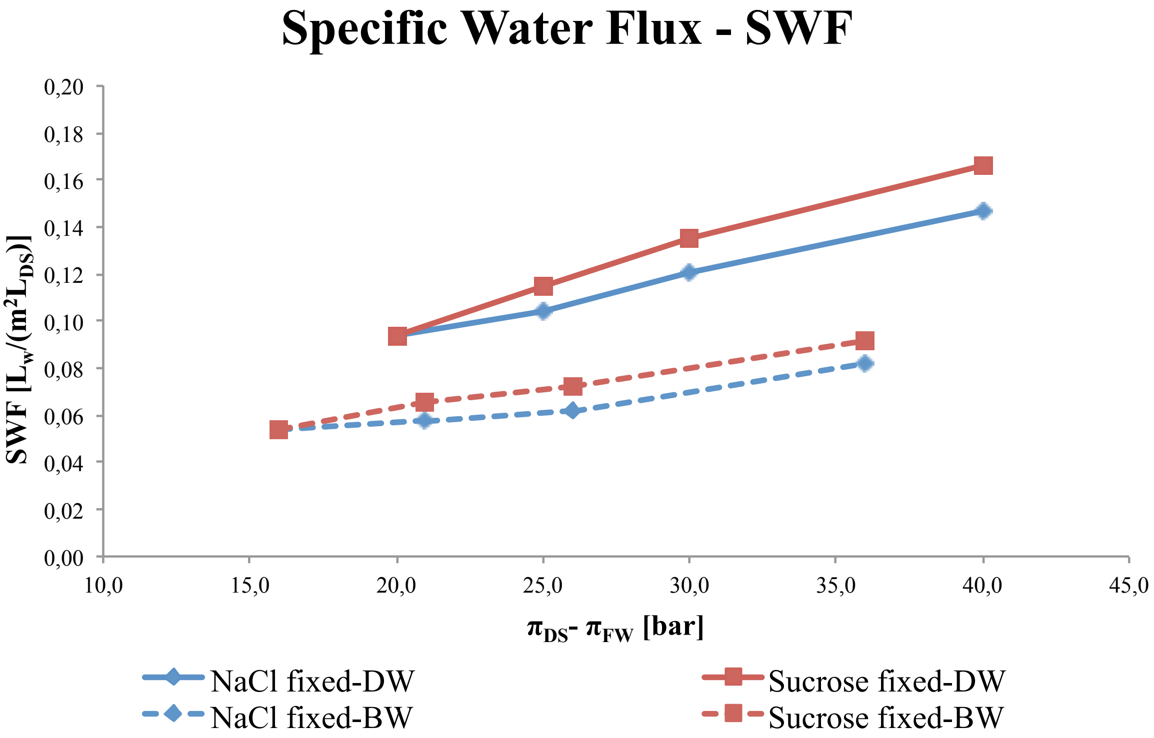


Figure 3.6: *Specific water flux for different feeds when NaCl osmotic pressure contribution is fixed at 10 bar (blue trends) and when sucrose osmotic pressure contribution is fixed at 10 bar (red trends).*

The result is significant for the mixture with the sodium chloride osmotic pressure fixed. If the trends are compared to the trends in Figure 3.2 a remarkable increase of the slope of each stroke is observed; in Figure 3.2 the water fluxes are compared, but the draw solution flowrates are different, making the comparison not rigorous. The use of draw solution with sodium chloride osmotic pressure fixed decreases the specific water flux by about 11%.

3.3.6 Specific Energy Consumption

The specific energy consumption can be calculated as:

$$SEC = \frac{\dot{V}_{DS}P_{DS}+\dot{V}_{FW}P_{FW}}{J_W A_m} \tag{3.12}$$

where $\dot{V}_{DS}$ and $\dot{V}_{FW}$ are respectively the inlet volumetric flowrates of draw solution and feed water, P_{DS} and P_{FW} are the hydraulic pressures of the respective feeds and the term $J_W A_m$ represents the volumetric flowrate of water transferred through the membrane. The trends obtained as a function of the $\Delta\pi$ are shown in Figure 3.7.

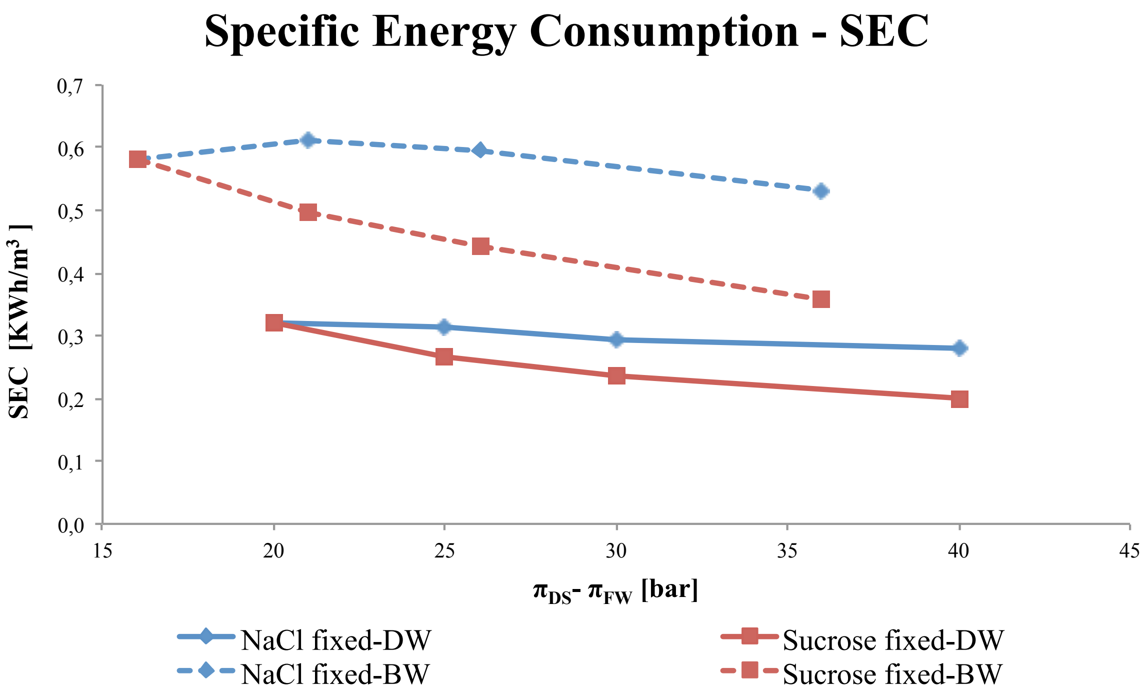


Figure 3.7: *Specific energy consumption for different feeds when NaCl osmotic pressure contribution is fixed at 10 bar (blue trends) and when sucrose osmotic pressure contribution is fixed at 10 bar (red trends).*

Each trend tends to decrease as much the $\pi_{DS} - \pi_{FW}$ increases. The term $\dot{V}_{FW}P_{FW}$ is almost constant by the time the feed water shell does not cause pressure losses, while the term $\dot{V}_{DS}P_{DS}$ globally decreases. By the time the water flux increases the specific energy consumption decreases.

Chapter 4

Process modeling

In this chapter it is described the procedure with which the model parameters were obtained for the forward osmosis process with to the draw solutions studied in this work.

3.1 Parameters determination

In the forward osmosis processes with a FO membrane configuration the water flux can be described as mentioned in §1.5.2.1:

$$J_W = A\left[\pi_{D,b}\exp\left(-J_W K\right) - \pi_{F,b} exp\left(\frac{J_W}{k}\right)\right] \tag{1.12a}$$

where $\pi_{D,b}$ and $\pi_{F,b}$ are the osmotic pressures of the draw and feed solutions, k is the mass transfer coefficient, K is the solute resistivity and A is the water permeability [27]. Equation 1.12a provides the water flux if the values of parameters A, K and k are available. They can be obtained by using experimental data of water fluxes. The water permeability is a peculiarity of the membrane and does not depend on the draw solution; not being available from the membrane specification, it was necessary to find its value in order to complete Equation 1.12a.

4.1.1 Water permeability

The equation which describes the ideal water flux is:

$$J_W = A\Delta\pi \tag{4.1}$$

If the water flux was represented as function of osmotic pressure gradient, A would be the slope of the straight line. From experimental data of water flux it is possible obtain the water permeability by calculating the first derivative of the water flux function when $\Delta\pi \rightarrow 0$. In order to do that, experimental data obtained by testing only sodium chloride as draw solution against distilled water, with the same membrane mentioned in §2.2.2 have been used. The experiments have been carried out by Saleh O. M. Al Aswad (University of Surrey UK, 2014) and the results obtained are shown in Figure 4.1.

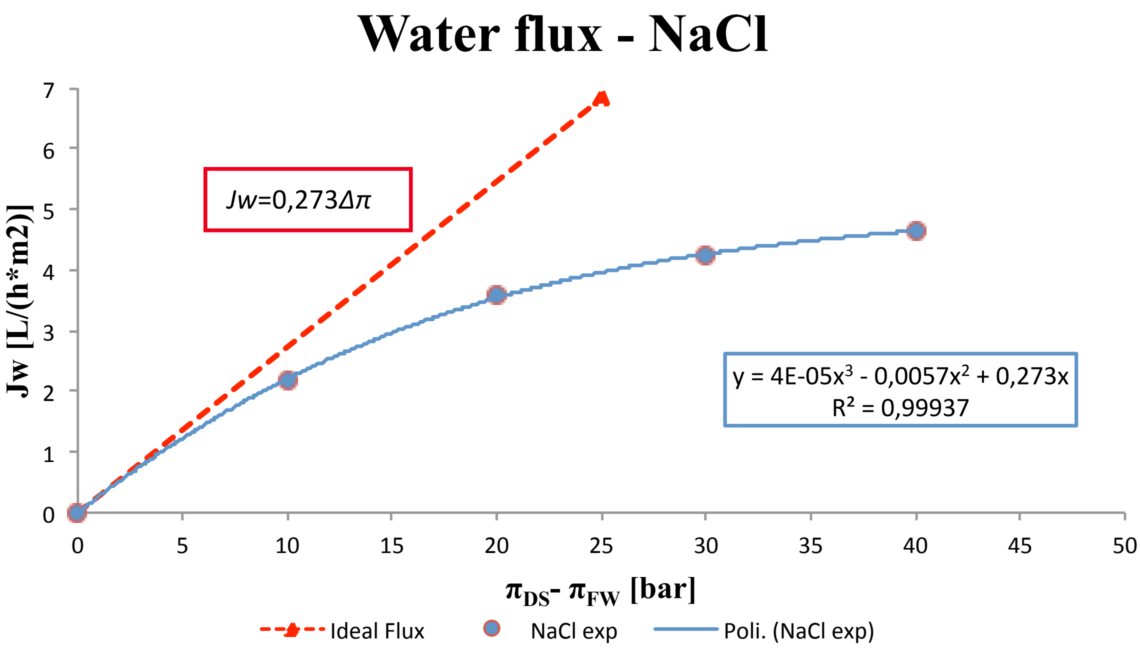


Figure 4.1: *Water fluxes with sodium chloride as draw solution and distilled water as feed water for ideal and real situation (T=25°C)*

The experimental data from Figure 4.1 have been elaborated by using the procedure described in §2.3.1 and §3.2.2. Although the flowrate of the draw solution decreases slightly (range between 0,60 and 0,52 L/min) the water permeability has been calculated neglecting this change. The derivative of the trend line concerning the experimental data can be solved for *x=0* giving the value of the water permeability which is $A = 0{,}273\ L/(hm^2 bar)$.

4.1.2 Solute resistivity

The solute resistivity K describes the water flux reduction due to the internal concentration polarization (ICP). The parameter can be expressed as:

$$K = \frac{t\tau}{\varepsilon\mathcal{D}} = \frac{S}{\mathcal{D}} \tag{1.13}$$

where S includes all the porous support layer physical characteristics, which t, τ, and ε representing respectively tickness, tortuosity and porosity; $\mathcal{D}$ is the diffusion coefficient of the draw solute in the support layer. The value of parameter K relative to the two draw solutions can be found using experimental data for which only distilled water is involved. In this case external concentration polarization does not take place because $\pi_{F,b} = 0$ and thus Equation $1.12a$ becomes :

$$J_W = A\left[\pi_{D,b} \exp\left(-J_W K\right)\right] \tag{4.2}$$

Equation 4.2 can be implicitly solved for the experimental water fluxes values of the draw solutions, and the results are shown in Figure 4.2.

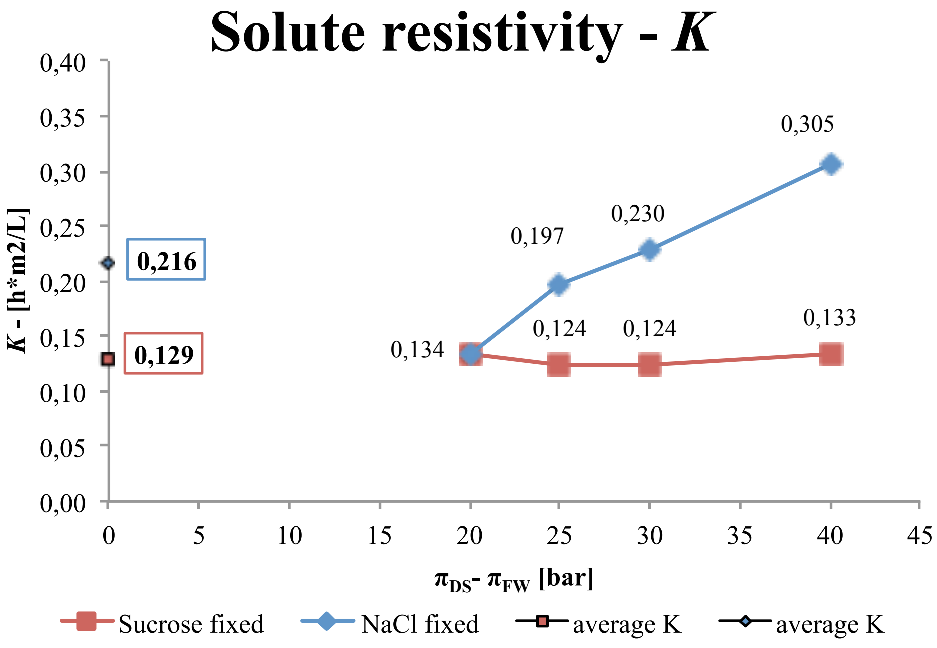


Figure 4.2: *Solute resistivity K of the draw solutions: when NaCl osmotic pressure contribution is fixed at 10 bar (blue trends) and when sucrose osmotic pressure contribution is fixed at 10 bar (red trends).*

The red curve in Figure 4.2 refers to the draw solution with constant massive concentration of sucrose; the blue one with fixed concentration of salt. Clearly, in the first case a constant value of K is obtained, while in the second case it significally increases. The term S in Equation 1.13 is fixed because it is peculiar of the membrane, and the term $\mathcal{D}$ should be approximately constant, even if the draw solution is a mixture with a different ratio between the solutes for each data point. The cause of the significant increase of K for the blue trend is the constancy of the water flux. The relative flux observable in Figure 3.2 assumes a value almost constant and thus K must increase when $\pi_{D,b}$ increases according to Equation 4.2.

4.1.2.1 Water flux correction

The constancy of the water flux is due to the draw solution flowrate which is not constant, as already observed in §3.3.4 and §3.3.5. The water flux could be corrected by multiplying the dimensionless ratio $\dot{V}_{Din,o}/\dot{V}_{Din}$where $\dot{V}_{Din}$ is the flowrate of the inlet draw solution and $\dot{V}_{Din,o}$ is the flowrate of the inlet draw solution relative to the first data point, which represents the highest flowrate. Equation 4.2 becomes:

$$J_W \frac{\dot{V}_{D_{in},0}}{\dot{V}_{D_{in}}} = A\left[\pi_{D,b} \exp\left(-J_W \frac{\dot{V}_{D_{in},0}}{\dot{V}_{D_{in}}} K\right)\right] \tag{4.3}$$

In this way the flowrates ratio increases the fluxes. Being the decrement of draw solution flowrate linear, this modification assumes that the water flux increases linearly with the draw solution flowrate. The water fluxes have been corrected for both mixtures and the corresponding solute resistivities are shown in Figure 4.3.

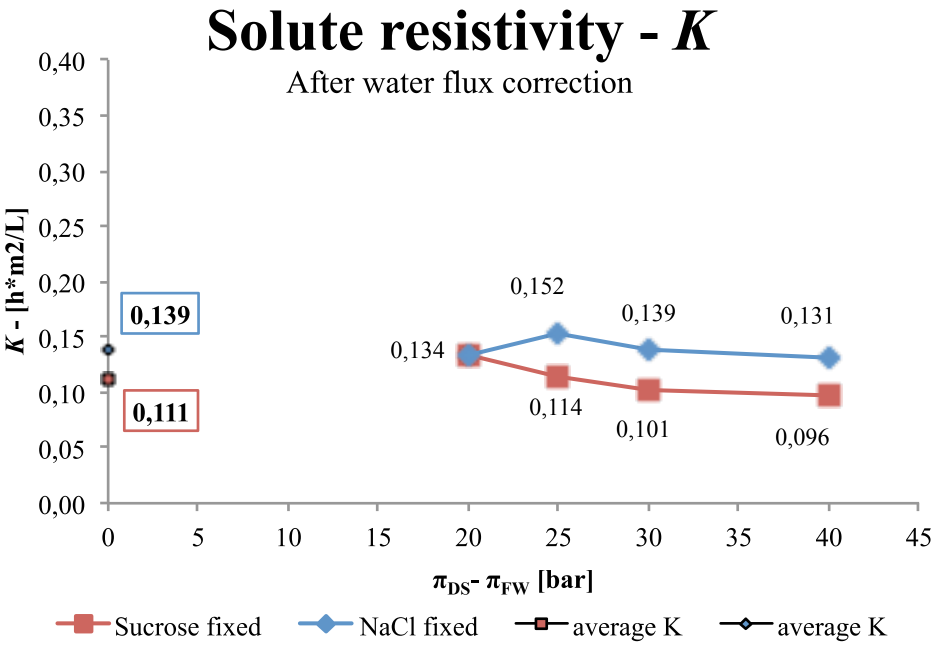


Figure 4.3: *Solute resistivity K after correcting the water fluxes of the draw solutions: when NaCl osmotic pressure contribution is fixed at 10 bar (blue trends) and when sucrose osmotic pressure contribution is fixed at 10 bar (red trends).*

The correction due to the flowrate seems to be efficient for the blue trend by the time the solute resistivity can be considered constant. Also the solute resistivity relative to the red trend has change, but it is still quite constant. The average values indicated in Figure 4.3 can be taken into account for modeling the process even if a constant value of solute resistivity would not describe rigorously the process by the time the ratio between the solutes concentrations in the draw solution change, and the diffusion coefficient $\mathcal{D}$ accordingly. Only experimental data of water fluxes obtained at constant flowrates could allow to obtain a solute resistivity trend for both draw solutions, but for this modeling it is indispensable to assume K constant. The average K values calculated can describe the water flux when the draw solution is constant. In Figure 4.4 and 4.5 the experimental water fluxes for the two mixtures involved as draw solutions, are shown, i.e. the water fluxes after flowrate correction and the water fluxes modeled mantaining the average K.

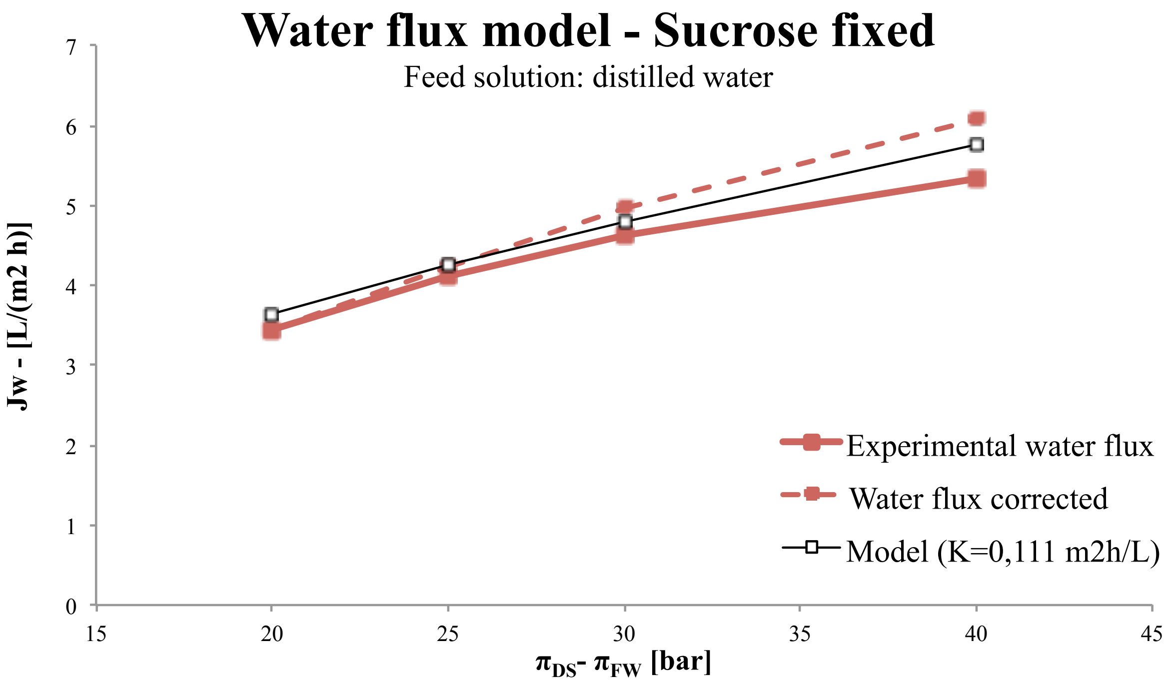


Figure 4.4: *Water fluxes of the draw solution with sucrose osmotic pressure contribution fixed at 10 bar*

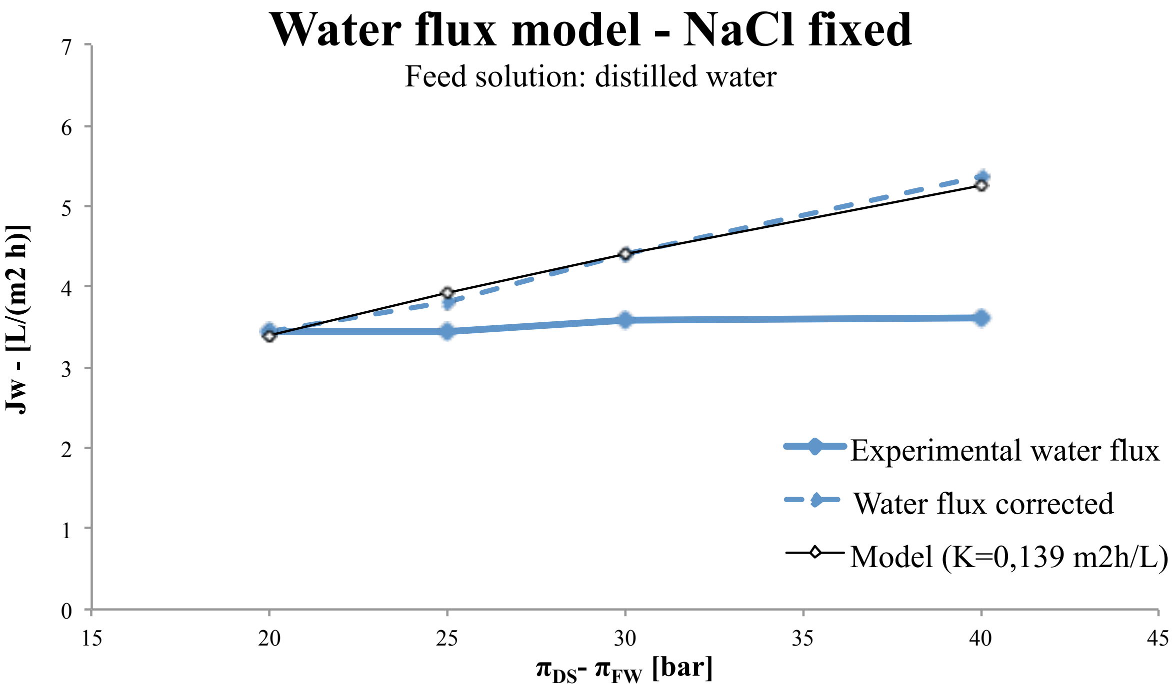


Figure 4.5: *Water fluxes of the draw solution with NaCl osmotic pressure contribution fixed at 10 bar*

With these average values the model seems to be able to well represent the water flux in both cases; the water fluxes at 20 bar should coincide, as the draw solution is the same, but assuming a constant K introduces a small error.

4.1.3 Mass transfer coefficient

External concentration polarization occurs in FO when the feed solution is placed against the active layer of the membrane. Knowing the osmotic pressure of the feed at the active layer surface is important to determine the overall effective osmotic driving force [27]. The osmotic pressure of the feed at the active layer surface can be calculated from experimental data using boundary layer film theory. The mass transfer coefficient k is used to calculate the concentrative ECP modulus [27]:

$$\frac{\pi_{F,a}}{\pi_{F,b}} = \exp\left(\frac{J_W}{k}\right) \tag{4.4}$$

where $\pi_{F,a}$ and $\pi_{F,b}$ are respectively the osmotic pressures of the feed solution at the membrane surface and in the bulk. The mass transfer coefficient is related to the Sherwood number Sh, by:

$$k = \frac{Sh\, \mathcal{D}}{d_h} \tag{4.5}$$

where $\mathcal{D}$ is the solute diffusion coefficient, d_h is the hydraulic diameter of the channel. Depending on the flow regime and the geometry of the channel the Sherwood number is defined by different equations but it is generally:

$$Sh = \propto (Re, Sc, d_h, 1/L) \tag{4.6}$$

where *Re* is the Reynolds number, *Sc* is the Schmidt number and *L* is the lenght of the channel. The parameter k can be calculated from experimental data in which brackish water is the feed solution. The average K values calculated in §4.3.1 for the corrected water fluxes are used to obtain the corresponding values of mass transfer coefficient, which are implicitly calculated by Equation 4.7 and shown in Figure 4.6.

$$J_W \frac{\dot{V}_{D_{in},0}}{\dot{V}_{D_{in}}} = A\left[\pi_{D,b}\exp\,(-J_W \frac{\dot{V}_{D_{in},0}}{\dot{V}_{D_{in}}} K) - \pi_{F,b}\, exp\left(\frac{J_W}{k}\frac{\dot{V}_{D_{in},0}}{\dot{V}_{D_{in}}}\right)\right] \tag{4.7}$$

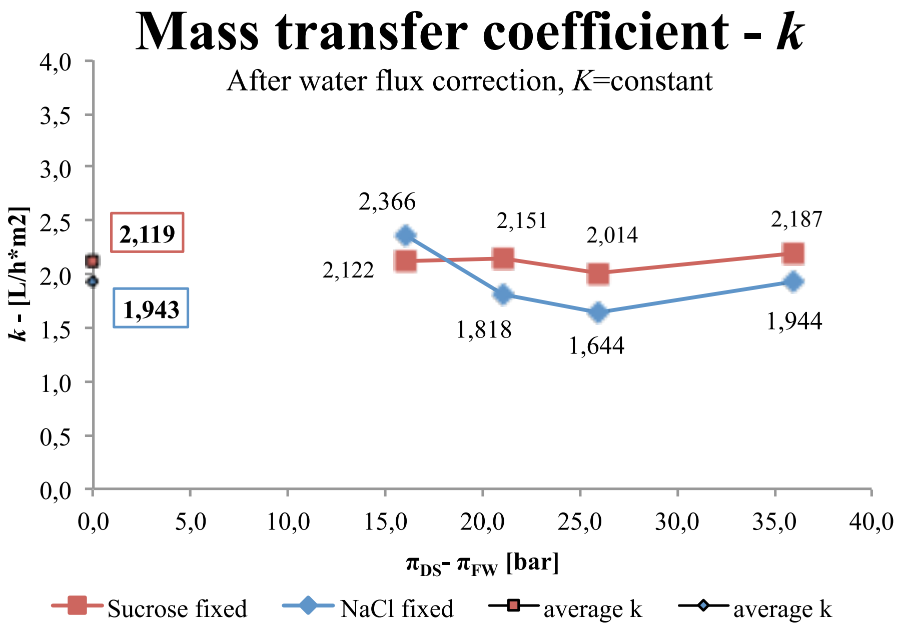


Figure 4.6: *Mass transfer coefficients k calculated for corrected water fluxes at K constant: when NaCl osmotic pressure contribution is fixed at 10 bar (blue trends) and when sucrose osmotic pressure contribution is fixed at 10 bar (red trends).*

The trends in Figure 4.6 seem to be pretty constant. Being the brackish water at fixed concentration the mass transfer coefficients have to be equal for both sistems, and the average values are in fact rather close. The water fluxes can be calculated for the average k, as reported in Figure 4.7 and 4.8.

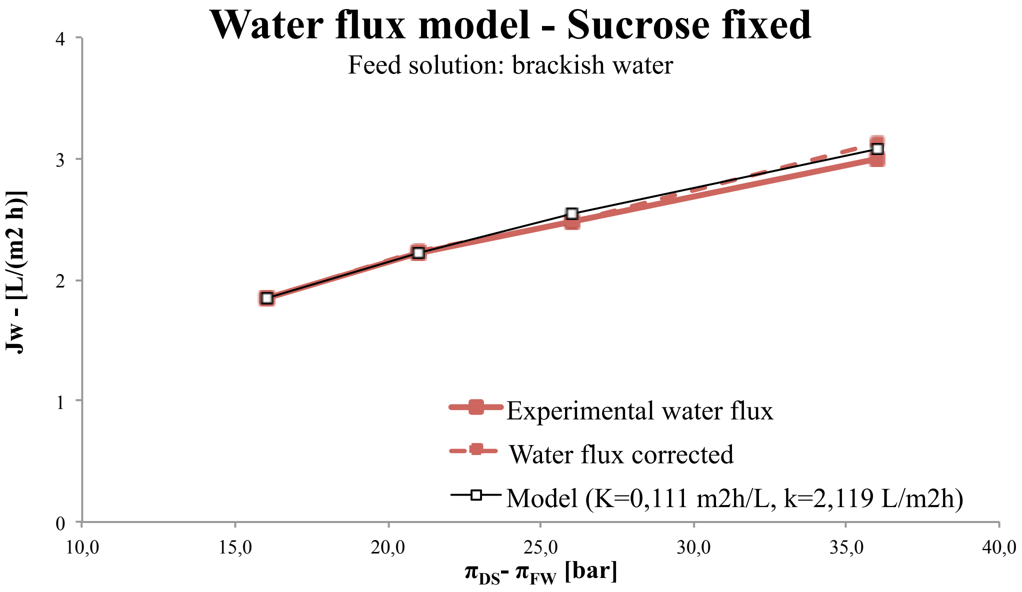


Figure 4.7: *Water fluxes of the draw solution with sucrose osmotic pressure contribution fixed at 10 bar*

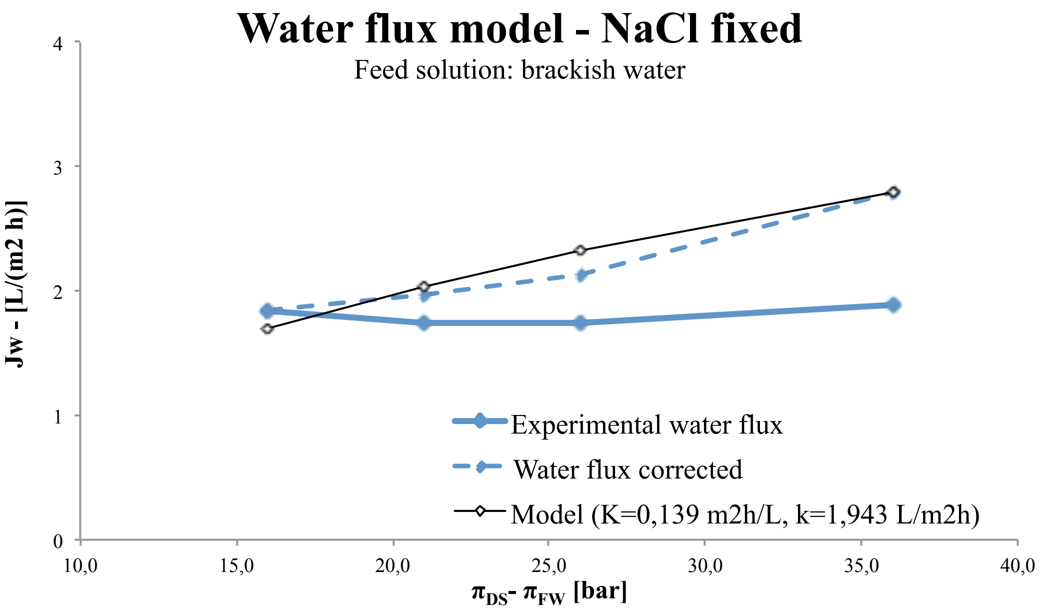


Figure 4.8: *Water fluxes of the draw solution with NaCl osmotic pressure contribution fixed at 10 bar*

The parameters seem to model reliability the water fluxes.

4.2 Water flux model

As mentioned before the mass transfer coefficients should assume the same value for both draw solutions, by the time the salinity and process conditions of the feed water are the same. For this reason an averange k can be furtherly calculated, for a value k=2,031 L/m^2 h. The water fluxes relative to the two draw solutions for both distilled and brackish water can be modeled by using the parameters previously found, which are collected in Table 4.1.

Table 4.1. *Parameters relative to the draw solutions and the membrane used in the experimental work*

Draw solution	***Water permeability*** ***A*** **[L/m^{2}hbar]**	***Solute resistivity*** ***K*** **[m^{2}h/L]**	***Mass transfer coefficient*** ***k*** **[L/m^{2}h]**
$\pi_{Sucrose}$=10 bar	0,273	0,111	2,031
π_{NaCl}=10 bar		0,139	

Figure 4.9 summarizes all water fluxes corrected taking into account the variation of the draw solution flowrate, and the relative fluxes modeled by using the parameters in Table 4.1.

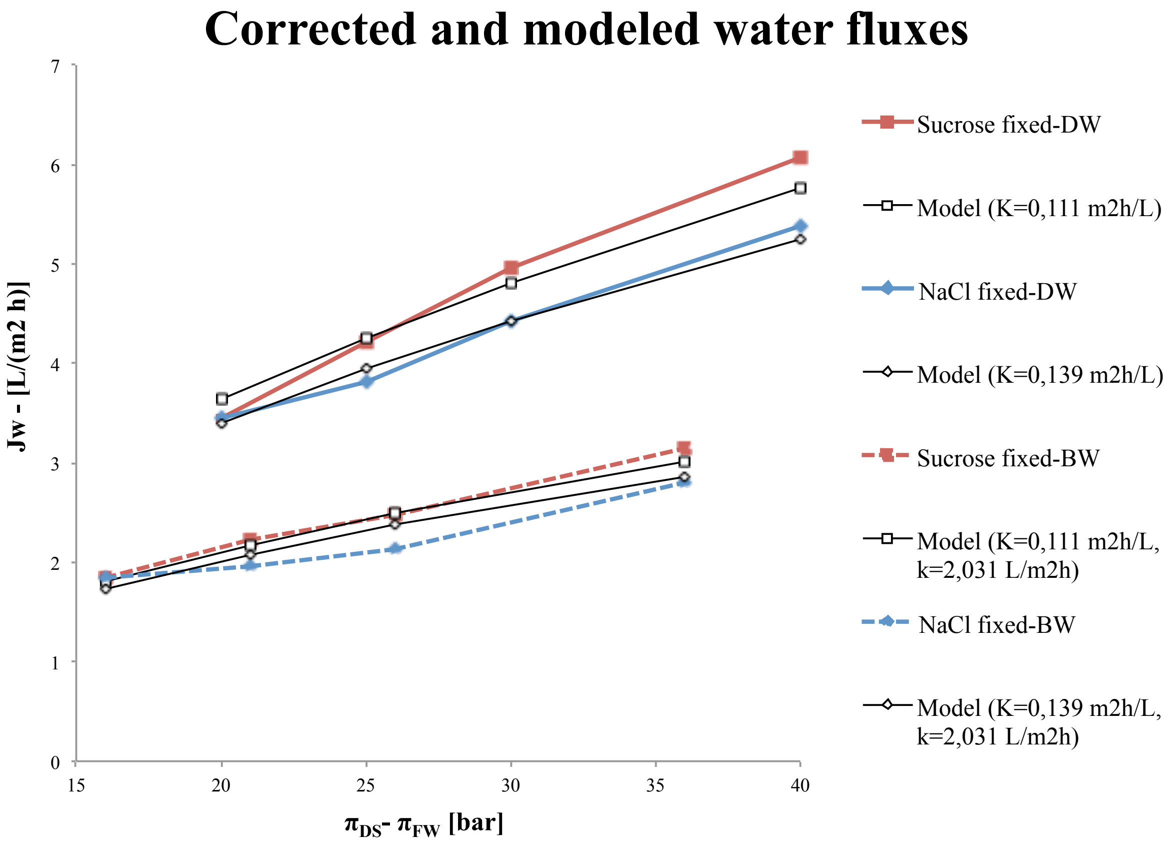


Figure 4.9: *Water fluxes for different draw and feed solutions; calculated correcting the draw solution flowrate decrease and modeling by using the parameters*

The water flux model indicating in Figure 4.9 is based on the following assumptions:

1. the water flux is corrected linearly because of the linear draw solution decrease;
2. the parameter K is considered constant for all the draw solutions.

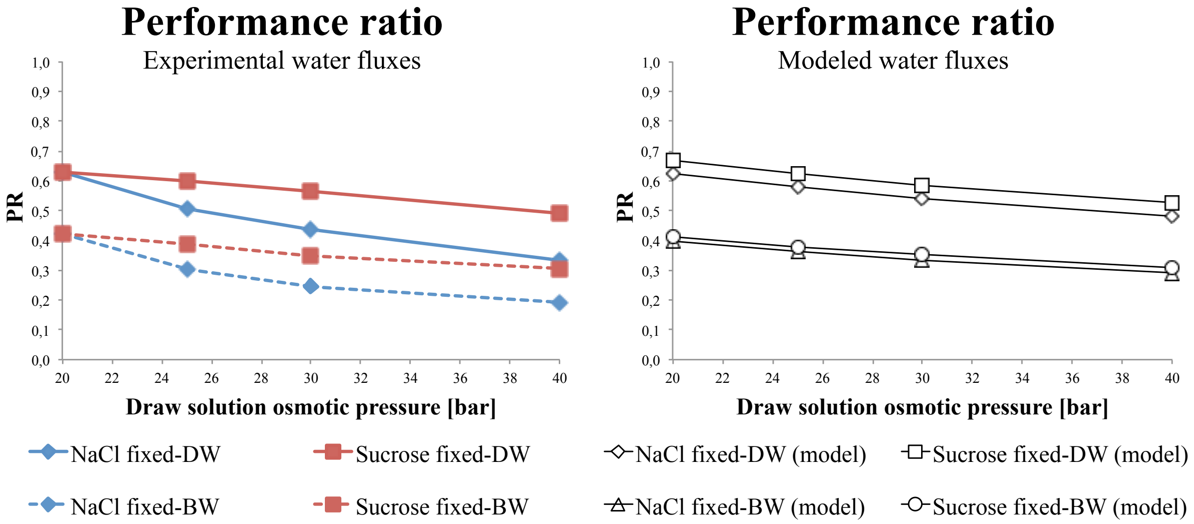
First assumption makes the parameter K almost constant as seen in §4.1.2.1 and this remark could validate the hypothesis, although it would be recommended to verify the trend experimentally. The second assumption derived from the experimental evidence. With a constant K all the modeled flux functions cross when $\Delta\pi = 0$, which is physically impossible because the experimental fluxes present equal values when the draw solution osmotic pressure is 20 bar. Extrapolating the model in the range between 10 bar and 20 bar the behavior does not represent reality: for a 10 bar osmotic pressure draw solution the flux values are given by only single solute contributions and the values for the blue curve are expected to be higher than the red ones. This demonstrates that a constant K in not a rigorous choiche, at least when the concentration of one solute tends to zero. For a higher osmotic pressure range the trend of K must be experimentally verified. Overall the model seems to describe acceptably the reality in the range of experimental osmotic pressures.

4.2.1 Performance ratio

The effects of the concentration polarization phenomena can be highlighted by calculating the performance ratio defined as [19]:

$$PR = \frac{Jw_{real}}{Jw_{ideal}} \tag{4.8}$$

The ideal water flux is calculated by Equation 4.2. In Figure 4.10*a* and 4.10*b* the performance ratios calculated for experimental water fluxes and for modeled water fluxes as real fluxes, are shown respectevely.



(a) **(b)**

Figure 4.10: *Performance ratio calculated for different real water fluxes: experimental fluxes (a) and modeled fluxes (b)*

The model developed demonstrates once again how working at constant draw solution flowrate is more convenient. The indices relative to the draw solutions against brackish water almost coincide between them. The presence of external concentration polarization decreases the performance ratio by about 40%, an effect that could be reduced operating on k, the mass transfer coefficient of the feed solute. The k parameter must be maintained as much high as possible by introducing high shear and turbulence at the membrane surface: according to Equation 4.6 a flowrate increase would make the Reynold number higher. In a scaled up process, the effects of the external CP phenomenon on driving force are minimized by using crossflow filtration with hydrodynamics designed to produce sufficient turbulence. In order to reduce the internal concentration polarization phenomenon the process conditions have to make the K parameter as much low as possible: low viscosity and dimensional size draw solutions are preferable for an high $\mathcal{D}$ with a low S support membrane.

Conclusions

The present work was aimed at investigating the performance of a mixture of sucrose and sodium chloride as draw solution on the Forward Osmosis desalination process. The process represents the first step of the Manipulated Osmosis Desalination (MOD) for which a suitable draw solution must offer a good performance for both forward osmosis and regeneration steps. The study was based on the idea that a mixture of sucrose and sodium chloride might represent a good trade-off for both steps. The experimental investigation was carried out in draw solution with different concentrations, at constant temperature (25°C), in a trial plant whose membrane unit consists of a hollow fiber CTA FO membrane. The osmotic pressures range is between 20 bar and 40 bar, and both distilled and brackish water as feed solutions were used. The water fluxes were measured and the solutes rejections were determined by sampling and analyzing: sodium chloride concentration was detected by a Dionex IC5000 ion chromatograph and the sucrose concentration by a Varian 920-LC HPLC instrument with a Varian 385-LC light scattering detector. An Amperometric Bioanalysis using a Glucose Biosensor based on Glucose Oxidase has been optimized in order to obtain reliable sucrose concentration values as analysis by HPLC was impossible in the cases considered; the optimization has not been successful. The water recovery decreased by about 50% when brackish water is tested as feed solution instead of distilled water for both draw solutions. An almost constant recovery and flux were observed for the mixture as a function of the sucrose concentration because of the draw solution volumetric flowrate decrease. The use of draw solution with sodium chloride osmotic pressure fixed decreases the specific water flux by about 11%. High rejections have been measured by both draw solutions when distilled water is used, lower values with brackish water, causing a higher reverse solute flux. From the experimental data the parameters of the water flux model have been obtained which accounts for non-ideality. For the forward osmosis of brackish water the performance ratio is 40% less than the one calculated with distilled water, as concentration polarization heavily affects the process and should be reduced increasing the shear and turbulence. A study of the performance of the draw solutions on the regeneration step is indispensable to fully evaluate if the mixture examined could represent a good trade-off, taking into account both steps of the MOD process.

Appendix

ANNEX A: Table of the experiments

Table A.1. *Table of the experiments*

N° Exp.	***Osmotic pressure* [bar]**			***Concentration* [m_s/m_w]**		***Feed water***
	Total	Sucrose	NaCl	Sucrose	NaCl	
1.1	20	10	10	134.20	12.73	Distilled water
1.2	25	15	10	198.29	12.73	
1.3	30	20	10	260.66	12.73	
1.4	40	30	10	380.66	12.73	
2.1	20	10	10	134.20	12.73	Brackish water, *5000 ppm*
2.2	25	10	15	134.20	19.08	
2.3	30	10	20	134.20	25.38	
2.4	40	10	30	134.20	37.75	
3.1	20	10	10	134.20	12.73	Distilled water
3.2	25	15	10	198.29	12.73	
3.3	30	20	10	260.66	12.73	
3.4	40	30	10	380.66	12.73	
4.1	20	10	10	134.20	12.73	Brackish water, *5000 ppm*
4.2	25	10	15	134.20	19.08	
4.3	30	10	20	134.20	25.38	
4.4	40	10	30	134.20	37.75	

ANNEX B: Quantitative analysis results

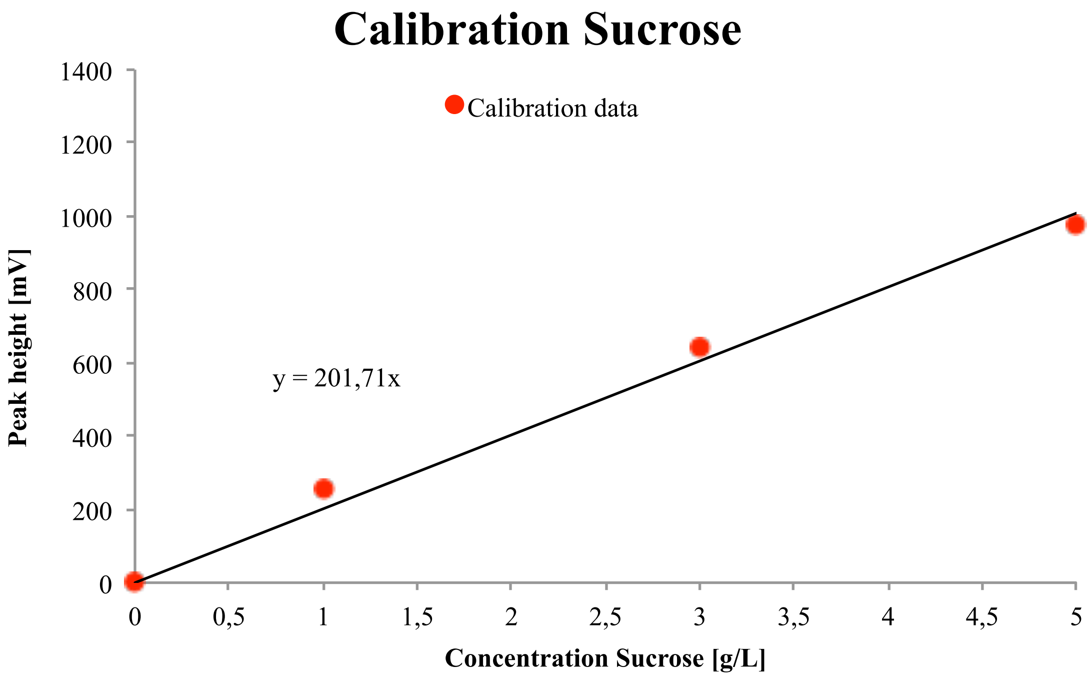


Figure B.1: *Calibration data for sucrose quantitative analysis and calibration line*

Table B.1. *Results of the sucrose quantitative analysis*

Sample	***Peak height* [mV]**	***Sucrose concentration* [g/L]**	***Sample***	***Peak height* [mV]**	***Sucrose concentration* [g/L]**
Fout 1.1	ND	ND	*Fout 3.1*	157	0.778
Fout 1.2	ND	ND	*Fout 3.2*	140	0.694
Fout 1.3	ND	ND	*Fout 3.3*	150	0.744
Fout 1.4	ND	ND	*Fout 3.4*	149	0.739
Fout 2.1	ND	ND	*Fout 4.1*	157	0.778
Fout 2.2	ND	ND	*Fout 4.2*	167	0.828
Fout 2.3	ND	ND	*Fout 4.3*	164	0.813
Fout 2.4	ND	ND	*Fout 4.4*	173	0.858

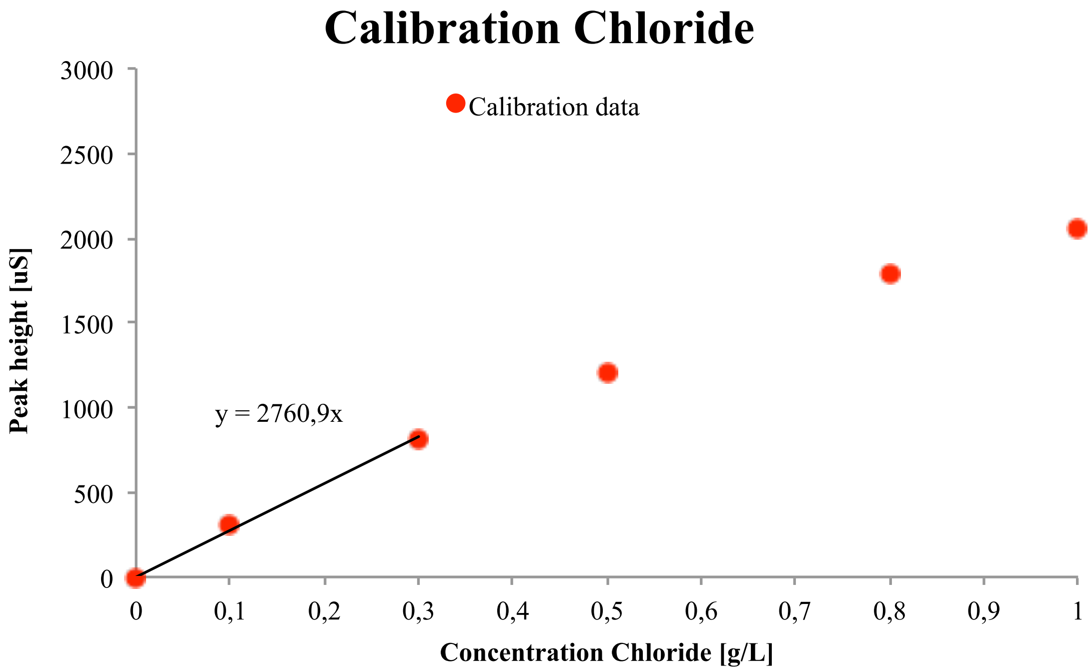


Figure B.2: *Calibration data for chloride quantitative analysis and calibration line*

Table B.2. *Results of the sucrose quantitative analysis*

Sample[2]	***Peak height* [mV]**	***Cl^- Concentration* [g/L]**	***Sample***	***Peak height* [mV]**	***Cl^- Concentration* [g/L]**
Din 1.1	237	0.0858	*Din 3.1*	257	0.0931
Din 1.2	184	0.0666	*Din 3.2*	241	0.0873
Din 1.3	206	0.0746	*Din 3.3*	229	0.0829
Din 1.4	206	0.0746	*Din 3.4*	209	0.0757
Din 2.1	237	0.0858	*Din 4.1*	257	0.0931
Din 2.2	360	0.1304	*Din 4.2*	373	0.1351
Din 2.3	479	0.1735	*Din 4.3*	494	0.1789
Din 2.4	655	0.2372	*Din 4.4*	762	0.2434
Dout 1.1	143	0.0518	*Dout 3.1*	173	0.0627
Dout 1.2	134	0.0485	*Dout 3.2*	168	0.0608
Dout 1.3	123	0.0446	*Dout 3.3*	154	0.0558
Dout 1.4	100	0.0362	*Dout 3.4*	134	0.0485

---

[2] The numbering of the samples is referred to Table A.1.

Dout 2.1	143	0.0518	*Dout 4.1*	173	0.0627
Dout 2.2	200	0.0724	*Dout 4.2*	250	0.0906
Dout 2.3	272	0.0985	*Dout 4.3*	321	0.1163
Dout 2.4	359	0.1300	*Dout 4.4*	450	0.1630
Fout 1.1	0,1	0.00004	*Fout 3.1*	113	0.0409
Fout 1.2	3	0.00109	*Fout 3.2*	108	0.0391
Fout 1.3	0.1	0.00004	*Fout 3.3*	112	0.0406
Fout 1.4	0.1	0.00004	*Fout 3.4*	110	0.0398
Fout 2.1	0.1	0.00004	*Fout 4.1*	113	0.0409
Fout 2.2	0.2	0.00007	*Fout 4.2*	115	0.0417
Fout 2.3	0.1	0.00004	*Fout 4.3*	109	0.0395
Fout 2.4	0.1	0.00004	*Fout 4.4*	111	0.0402
Fin 1.1	*na*[3]		*Fin 3.1*	107	0.0388
Fin 1.2	"		*Fin 3.2*	97	0.0351
Fin 1.3	"		*Fin 3.3*	107	0.0388
Fin 1.4	"		*Fin 3.4*	105	0.0380
Fin 2.1	"		*Fin 4.1*	107	0.0388
Fin 2.2	"		*Fin 4.2*	100	0.0362
Fin 2.3	"		*Fin 4.3*	104	0.0377
Fin 2.4	"		*Fin 4.4*	108	0.0391

The conversion formula for Cl$^-$ concentration is:

$$c_{NaCl} = c_{Cl^-} \frac{MM_{NaCl}}{MM_{Cl}} DF \tag{B.1}$$

where MM_{NaCl} and MM_{Cl} are the molar masses of sodium chloride and chlorine respectively and DF is the dilution factor.

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[3] Not analyzed (distilled water).

ANNEX C: Table of concentrations

Table C.1. *Table of the sucrose and sodium chloride concentrations: the calculated concentrations derived from known concentration solutions (D_{IN} and F_{IN}) or from mass balance calculation (D_{OUT}). Only F_{OUT} analyzed concentrations are taken into account for the solutes mass balances (Legend: na: not analyzed, nc: not calculated, nd: not detected)*

		D_{IN}					D_{OUT}		
		[g/L]					**[g/L]**		
N°	**Sucrose**		**Sodium chloride**		**N°**	**Sucrose**		**Sodium chloride**	
exp	**Calculated**	**Analyzed**	**Calculated**	**Analyzed**	**exp**	**Calculated**	**Analyzed**	**Calculated**	**Analyzed**
1.1	123.28	*na*	11.70	14.15	*1.1*	86.63	*na*	8.21	8.54
1.2	175.78	″	11.26	10.99	*1.2*	119.62	″	7.26	8.00
1.3	223.42	"	10.97	12.30	*1.3*	144.68	"	7.09	7.34
1.4	306.83	"	10.32	12.30	*1.4*	184.29	"	6.18	5.97
2.1	123.28	"	11.70	14.15	*2.1*	86.63	"	8.21	8.54
2.2	123.14	"	17.54	21.49	*2.2*	81.10	"	11.53	11.94
2.3	122.94	"	23.27	28.60	*2.3*	76.39	"	14.45	16.24
2.4	122.51	"	34.46	39.11	*2.4*	70.16	"	19.72	21.43
3.1	123.34	"	11.76	15.34	*3.1*	97.14	"	5.80	10.33
3.2	175.77	"	11.35	14.39	*3.2*	137.51	"	5.85	10.03
3.3	223.30	"	10.96	13.67	*3.3*	172.13	"	4.42	9.19
3.4	305.79	"	10.28	12.48	*3.4*	220.46	"	3.29	8.00
4.1	123.34	"	11.76	15.34	*4.1*	97.14	"	5.80	10.33
4.2	123.13	"	17.53	22.27	*4.2*	92.93	"	9.83	14.93
4.3	122.90	"	23.29	29.50	*4.3*	90.58	"	15.22	19.17
4.4	122.41	"	34.48	40.12	*4.4*	84.61	"	22.13	26.87

		F_{IN}					F_{OUT}		
		[g/L]					**[g/L]**		
N°	**Sucrose**		**Sodium chloride**		**N°**	**Sucrose**		**Sodium chloride**	
exp	**Calculated**	**Analyzed**	**Calculated**	**Analyzed**	**exp**	**Calculated**	**Analyzed**	**Calculated**	**Analyzed**
1.1	0	*na*	0	*na*	*1.1*	*nc*	*nd*	*nc*	0.006
1.2	0	″	0	″	*1.2*	″	″	″	0.179
1.3	0	"	0	"	*1.3*	"	"	"	0.006
1.4	0	"	0	"	*1.4*	"	"	"	0.006
2.1	0	"	0	"	*2.1*	"	"	"	0.006
2.2	0	"	0	"	*2.2*	"	"	"	0.012
2.3	0	"	0	"	*2.3*	"	"	"	0.006
2.4	0	"	0	"	*2.4*	"	"	"	0.006

3.1	0	"	5.05	6.39	*3.1*	"	0.78	"	6.75
3.2	0	"	5.05	5.79	*3.2*	"	0.69	"	6.45
3.3	0	"	5.05	6.39	*3.3*	"	0.74	"	6.69
3.4	0	"	5.04	6.27	*3.4*	"	0.74	"	6.57
4.1	0	"	5.05	6.39	*4.1*	"	0.78	"	6.75
4.2	0	"	5.05	5.97	*4.2*	"	0.83	"	6.87
4.3	0	"	5.04	6.21	*4.3*	"	0.81	"	6.51
4.4	0	"	5.04	6.45	*4.4*	"	0.86	"	6.63

The D_{IN} concentrations were calculated as:

$$c_{Sucrose,D_{IN}} = \frac{m_{Sucrose}}{(m_{Sucrose}+m_{NaCl}+m_{water})/\rho_{exp}} \tag{C.1}$$

$$c_{NaCl,D_{IN}} = \frac{m_{NaCl}}{(m_{Sucrose}+m_{NaCl}+m_{water})/\rho_{exp}} \tag{C.2}$$

where $m_{Sucrose}$, m_{NaCl} and m_{water} are the masses of sucrose, sodium chloride and water respectively, and ρ_{exp} is the draw solution experimental density.

The F_{IN} concentration was calculated as:

$$c_{NaCl,F_{IN}} = \frac{m_{NaCl}}{V_{F_{IN},t=0}} \tag{C.3}$$

where m_{NaCl} is the mass of sodium chloride, and $V_{F_{IN},t=0}$ is the initial feed water volume.

The D_{OUT} concentrations were calculated depending on the feed water as:

$$\text{Distilled water: } c_{Sucrose,D_{OUT}}{}^{4} = c_{Sucrose,D_{IN}} \frac{\Delta V_{D_{IN}}}{V_{D_{OUT}}} \tag{C.4}$$

$$c_{NaCl,D_{OUT}} = \frac{c_{NaCl,D_{IN}} \cdot \Delta V_{D_{IN}} - c_{NaCl,F_{OUT}} \cdot V_{F_{OUT}}}{V_{D_{OUT}}} \tag{C.5}$$

$$\text{Brackish water: } c_{Sucrose,D_{OUT}} = \frac{c_{Sucrose,D_{IN}} \cdot \Delta V_{D_{IN}} - c_{Sucrose,F_{OUT}} V_{F_{OUT}}}{V_{D_{OUT}}} \tag{C.6}$$

$$c_{NaCl,D_{OUT}} = \frac{c_{NaCl,D_{IN}} \cdot \Delta V_{D_{IN}} + c_{NaCl,F_{IN}} \cdot \Delta V_{F_{IN}} - c_{NaCl,F_{OUT}} \cdot V_{F_{OUT}}}{V_{D_{OUT}}} \tag{C.7}$$

Equations C.4, C.5, C.6 and C.7 represent mass balances based on sucrose and sodium chloride at $t=t_f$, in which only F_{OUT} analyzed concentrations appear.

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[4] Concentration calculated with a 100% sucrose rejection because of not detected concentrations

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