HYBRID MEMBRANE SYSTEM FOR DESALINATION AND WASTEWATER TREATMENT

INTEGRATING FORWARD OSMOSIS AND LOW PRESSURE REVERSE OSMOSIS

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Cover design by: Ana Mabel López Villanueva

Last page: spring-fed pool, rancho “Ojo de Agua”, Villa Unión, Coahuila, México (Rodrigo Valladares Linares)

Printed by: Ipskamp Drukkers, Enschede (www.ipskampdrukkers.nl)

Layout: Szilárd Bucs and Rodrigo Valladares Linares

Hybrid membrane system for desalination and wastewater treatment

Integrating forward osmosis and low pressure reverse osmosis

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft;
op gezag van de Rector Magnificus Prof. Ir. Karel Ch.A.M. Luyben;
voorzitter van het College voor Promoties
in het openbaar te verdedigen op woensdag 01 oktober 2014 om 10:00 uur

door

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Acknowledgements

First and foremost, it is with immense gratitude that I acknowledge my promotors Gary Amy and Hans Vrouwenvelder for giving me the opportunity to work in such a fascinating topic leading me to the completion of this thesis. Their guidance, advice, stimulation, enthusiasm, and support made the last 3 years an extremely enriching period of my life, during which I developed as a conscious scientist.

It gives me great pleasure in acknowledging the help of the whole Forward Osmosis group under Gary’s supervision at the Water Desalination and Reuse Center (WDRC), King Abdullah University of Science and Technology, Saudi Arabia. I would like to give my most sincere gratitude to my daily supervisor Zhenyu Li. Without his continuous efforts, contributions, advice, creativity, dedication and friendship, this work would have not been possible. My deepest appreciation to my teammate Muhannad AbuGhdeeb who supported me throughout this process.

I would like to thank Victor Yangali Quintanilla, my supervisor during my Master studies, an enthusiastic and innovative person, who inspired me into science. His contributions to my professional and personal formation are invaluable. Through his knowledge, friendship, and perseverance he managed to make me jump into this adventure.

My deepest appreciation to my colleague and friend Szilárd Bucs for his support, ideas, skills and time invested in my research work. I will never forget the multiple discussions we had enjoying a cup of coffee, and I am looking forward to have more fruitful discussions and cups of coffee with him.

I am indebted to my many colleagues who supported me in the WDRC. Their experience, advice and time were essential in making progress in my research work. I would like to acknowledge the help of every person at Delft University of Technology who were involved in my doctoral education.

The financial support of GS Engineering & Construction is acknowledged for partially funding this research. I would like to thank Sarper Sarp for his enthusiastic help and contribution to this work.

This thesis would not have been possible without the support of King Abdullah University of Science and Technology, a dream that came true only 5 years ago and of which I am a proud member of the founding class.

My heartiest gratefulness to my whole family who made it possible for me to be away from home through their support and motivation: to my mom Martha, my dad Rodolfo, my twin brother Bernardo, my grandma Güels, my aunts Cary and Lissi, and my cousins Sissi, Vani, Luis and Alex for their unconditional support. I particularly dedicate my doctoral work to my uncle José Luis Rodríguez (Luigi), for his incommensurable help, advice and support.
I would like to show my gratitude to all my friends, here in the Netherlands, in Saudi Arabia and back in Mexico, my home country, for always being available and supportive during the last 3 years, during which I developed myself as an independent researcher. I start now a new chapter on this incredible journey that has changed my life.
Summary

Since more than 97% of the water in the world is seawater, desalination technologies have the potential to solve the fresh water crisis. The most used desalination technology nowadays is seawater reverse osmosis (SWRO), where a membrane is used as a physical barrier to separate the salts from the water, using high hydraulic pressure as the driving force. However, the use of high hydraulic pressure imposes a high cost on operation of these systems, in addition to the known persistent fouling problems associated with reverse osmosis (RO) membrane filtration systems.

Forward osmosis (FO) is an alternative membrane process that uses an osmotic pressure difference as the driving force. FO uses a concentrated draw solution to generate high osmotic pressure, which extracts water across a semi-permeable membrane from a feed solution. Afterwards, fresh water can be obtained when the diluted draw solution is regenerated in a second treatment step, e.g., low pressure reverse osmosis (LPRO). Research has identified the potential for hybrid forward osmosis/low-pressure reverse osmosis (FO/LPRO) systems for several applications, including seawater desalination, and to reduce the cost and fouling propensity of producing fresh water from impaired-quality water sources, compared to conventional high pressure RO systems.

One of the main advantages of FO is the limited amount of external energy required to extract water from the feed solution, using only a very low amount of energy to recirculate the draw solution on one side of the membrane, while the feed solution is passively in contact with the other side of the membrane.

The objective of this research is the evaluation of a hybrid desalination system using forward osmosis, where the feed water is a primary or a secondary wastewater effluent, and the draw solution is seawater, with the purpose of recovering fresh water from impaired quality sources with the use of minimum hydraulic pressure. This hybrid system has two clear advantages: (i) the diluted seawater resulting from the FO dilution process is further treated in a LPRO unit to produce fresh water, using less energy than conventional high pressure SWRO systems; (ii) the concentrated wastewater effluent produced by FO enables low-cost processing. The results show that forward osmosis recovers water from wastewater, rejects nutrients and micropollutants, outperforms traditional SWRO systems in terms of fouling resistance and control, having a high flux recovery when applying physical cleaning methods.

Water recovery

A study revealed the ability of a FO process to integrate seawater desalination and municipal wastewater treatment for drinking water production (Chapter 2). The FO process showed a high rejection for chemical oxygen demand, phosphate and trace metals, and moderate rejection for ammonia and total nitrogen. Organic carbon analysis revealed that the membrane tested was unable to reject low molecular weight acids and low molecular weight neutral compounds, such as sodium acetate and urea. Biopolymer-like substances played a
dominant role in the formation of fouling on the membrane surface. The study showed that FO is a reliable barrier to effectively reject most wastewater contaminants and salts from either the wastewater as feed solution or seawater as draw solution while allowing clean water to pass through, providing a possible significant energy-saving strategy to combine (integrate) municipal wastewater treatment and seawater desalination to further promote sustainable urban water management and water reuse in coastal cities. Furthermore, in another study (Chapter 3), applying practical conditions of water reuse applications, FO membranes were able to reject most of the organic micropollutants spiked in the feed water; rejections were moderate for hydrophilic neutral compounds (44 – 95%), moderate for hydrophobic neutral contaminants (48 – 92%), and high for the hydrophilic ionic micropollutants (96 – 99%). FO coupled with LPRO was effective in rejecting low molecular weight hydrophilic neutral micropollutants, with rejections exceeding 89%. For the rest of the compounds, rejections were greater than 99%. A hybrid FO/LPRO system serves as a double barrier against micropollutants, including pharmaceutically active compounds, hormones and other pollutants.

**Organic fouling and cleaning**

Characterization of the organic foulants in both wastewater and seawater was performed (Chapter 4). Organic carbon analysis (liquid chromatography coupled with organic carbon detection (LC-OCD) and three-dimensional fluorescence excitation emission matrices (3-D FEEM)) suggest that biopolymers and protein-like substances, present in the feed water, form a fouling layer on feed side of the FO membrane, reducing the water flux and thus, affecting the efficiency of the seawater dilution process. Transparent exopolymer particles (TEP) were identified in the support layer of the FO membrane in contact with the seawater, which contains a significant amount of these particles, reducing the flux of the FO membrane.

Physical and chemical methods were used and compared in an effort to set an effective protocol for FO membrane cleaning (Chapter 5). Natural organic matter fouling showed high hydraulic reversibility, up to 90% when in-situ air scouring for 15 minutes was used as a cleaning technique. Chemical cleaning with a mixture of Alconox, an industrial detergent containing phosphates, and sodium ethylenediaminetetraacetic acid (EDTA) showed to improve the reversibility further (93.6%). Osmotic backwashing using a 4% NaCl solution and deionized (DI) water proved to be ineffective to recover the flux due to the salt diffusion phenomena occurring at the active layer (the membrane separation layer). The same detergent solution used to clean the active layer was used to clean the support layer; 95% of flux was recovered, showing that the chemically irreversible fouling of the FO membrane is in the order of 5.5%, which might be associated with the adsorption of biopolymers on the active layer and some TEP residuals on the support layer. Physical cleaning (air scouring) proved to be the most effective way to control organic fouling.
The study on the influence of feed spacer thickness (28, 31 and 46 mil, 1 mil = 0.0254 mm) on performance and biofouling development on the feed side of FO membranes (Chapter 6) led to the following conclusions: (i) the biomass amount alone does not determine the flux decline: the same amount of biomass was found for all spacer thicknesses after the same run time at the same feed flow, while the flux reduction decreased with thicker spacer; (ii) the flux decline caused by biomass accumulation can be reduced by using a thicker spacer; (iii) spatial distribution of the biofilm differed with feed spacer thickness. Findings are in agreement with reported data for high pressure reverse osmosis cross-flow systems: thicker spacers reduce the impact of biofouling on performance. This result clearly contradicts observations obtained with particulate and colloidal fouling in forward osmosis.

**Outlook**

Forward osmosis (FO) is an emerging membrane technology with a range of possible water treatment applications (desalination and wastewater recovery). An overview of applications, advantages, challenges, costs and knowledge gaps is given (Chapter 7). With current commercial technology, hybrid FO systems for both desalination and water recovery applications have proven to have higher capital cost compared to conventional technologies. Nevertheless, due to the demonstrated lower operational costs of hybrid FO systems, the unit cost for each m$^3$ of fresh water produced with the FO system are lower than conventional desalination/water recovery technologies (i.e. ultrafiltration/RO systems).

There are key benefits of using FO hybrid systems compared to RO: (i) chemical storage and feed systems may be reduced for capital, operational and maintenance cost savings, (ii) reduced process piping costs, (iii) more flexible treatment units, and (iv) higher overall sustainability of the desalination process, while producing high quality water.

The major challenges of FO to be a commercially viable technology are: (i) developing a higher flux membrane, capable of maintaining an elevated salt rejection and a reduced internal concentration polarization (ICP) effect, (ii) the availability of appropriate draw solutions, which can be recirculated via an efficient recovery process, (iii) better understanding of fouling and biofouling occurrence, (iv) assuring the high quality of the water produced, (v) hybridization with other technologies that can increase the benefits of FO use (i.e. water recovery, energy production, etc.).

Numerical modeling can be a useful tool to understand biofouling in FO membrane processes and to suggest potential approaches for fouling prevention/reduction. Along with this, future experimental studies should focus on the use of modified spacers and novel cleaning strategies.

It is strongly suggested to upscale the process into a pilot scale facility in which a comprehensive evaluation of water quality and energy parameters can be done, facilitating a life cycle assessment and a cost cycle assessment of a hybrid process (i.e. FO-LPRO), which
will give important information on the direction that should be taken to develop robust low cost water treatment hybrid systems to produce high quality water.
### Samenvatting

Aangezien meer dan 97% van het water in de wereld bestaat uit zeewater, hebben ontzilingstechnologieën het potentieel om de watercrisis op te lossen. De huidige wereldwijd meest gebruikte ontzilingstechniek is omgekeerde osmose (RO), waarbij een semipermeabel membraan gebruikt wordt als fysieke barrière om zouten van water te scheiden, met als drijvende kracht een hoge hydraulische druk. Het gebruik van uitgebreide voorzuivering en hoge hydraulische druk legt hoge kosten op de toepassing van RO membraanfiltratie voor zeewaterontzouting, naast bekende RO vervuilingproblemen.

Forward osmosis (FO) is een alternatief membraanproces waarbij het osmotische drukverschil over het membraan wordt gebruikt als drijvende kracht. Het membraan scheidt de draw- van de feed-vloeistof. De draw-oplossing heeft een hoge osmotische druk (relatief tot de feed-oplossing) waardoor water door het semipermeabel membraan naar de draw-oplossing stroomt. Vervolgens kan zoet water worden verkregen wanneer de met water verdunde draw-oplossing wordt geregenereerd in een tweede behandelingstap: lage druk omgekeerde osmose (LPRO). Onderzoek heeft het potentieel geïdentificeerd van hybride FO/LPRO systemen voor diverse toepassingen, met inbegrip van het onttelen van zeewater, om de kosten en vervuilingseigenschappen in vergelijking met conventionele hogedruk RO-systemen te verlagen van drinkwaterproductie uit verontreinigde waterbronnen.

Een van de belangrijkste voordelen van FO is de beperkte hoeveelheid externe energie nodig om water te extraheren uit de feed-oplossing. Weinig energie is nodig voor het recirculeren van de draw-oplossing aan een zijde van het membraan, terwijl aan de andere zijde van het membraan de feed-oplossing passief in contact is met het membraan.

Doel van deze studie is de evaluatie van een hybride ontzilingssysteem met behulp van FO, waarbij de feed-oplossing bestaat uit primair of secundair afvalwatereffluent en de draw-oplossing uit zeewater, om zoet water te winnen uit verontreinigde bronnen zonder gebruik van hydraulische druk. Dit FO/LPRO hybridesysteem heeft twee duidelijke voordelen: (i) het door FO verkregen verdunde zeewater wordt verder behandeld met LPRO om vers water te produceren met een lager energieverbruik dan bij toepassing van een conventioneel hoge druk RO systeem, en (ii) het door FO geconcentreerde afvalwatereffluent maakt goedkope verwerking mogelijk. De studies tonen aan dat FO effectief water wint uit afvalwater, voedingsstoffen en microonreinigingen verwijdert, traditionele hoge druk RO-systemen overtreft in vervuillings-weerstand en -beheersing, en een sterk flux (water transport door membraan) herstel heeft bij toepassing van reinigingen.

### Water recovery

Een studie toonde de geschiktheid aan van FO voor integratie van zeewaterontzilting en afvalwaterbehandeling voor drinkwaterproductie (Hoofdstuk 2). Het FO proces toonde een hoge verwijdering van chemisch zuurstofverbruik, fosfaat en sporenelementen, en matige verwijdering van ammoniak en totaal stikstof. Uit organische koolstofanalyse bleek dat het geteste FO membraan effectief was in verwijdering van laagmoleculaire zuren en neutrale
Verbindingen, zoals natriumacetaat en ureum. Biopolymer-achtige stoffen speelden een cruciale rol bij de vorming van fouling op het membraanoppervlak. De studie toonde aan dat FO een betrouwbare barrière is om effectief de meeste afvalwater contaminanten en zouten te verwijderen uit zowel het afvalwater (feed-oplossing) of zeewater (draw-oplossing) terwijl schoon water het membraan passeert. Deze benadering levert een mogelijk significante energiebesparende strategie om gemeentelijk afvalwater behandeling met zeewater-ontzetting te combineren, met verdere stimulering van duurzaam stedelijk waterbeheer en waterhergebruik in kuststeden. Bovendien, in een andere studie (Hoofdstuk 3) bleek tijdens toepassen van praktische condities voor waterhergebruik dat FO membranen in staat zijn de meeste organische microverontreinigingen spiked in het feed-water te verwijderen; de verwijdering was matig voor hydrofiele neutrale verbindingen (44-95%) en hydrofobe neutrale verontreinigingen (48-92%), en verwijdering was hoog voor hydrofiele ionische microverontreinigingen (96-99%). De combinatie van FO/LPRO was effectief in verwijdering van laagmoleculaire hydrofiele neutrale microverontreinigingen, met verwijdering van meer dan 89%. Voor de rest van de verbindingen waren de verwijderingen meer dan 99%. Een hybride FO/LPRO systeem dient als een dubbele barrière tegen microverontreinigingen, met inbegrip van farmaceutisch actieve stoffen, hormonen en andere verontreinigingen.

Organische vervuiling en reiniging

Karakterisering van organische vervuilende stoffen van zowel afvalwater en zeewater werd uitgevoerd (Hoofdstuk 4). Analyse van organisch koolstof (met vloeistofchromatografie gekoppeld aan organische koolstof detectie (LC-OCD) en 3-dimensionale fluorescentie excitatie-emissie matrices (3D FEEM)) suggereert dat biopolymeren en eiwitachtige stoffen aanwezig in het feed-water, een vuillaag op de FO membraanvoedingszijde kunnen vormen, resulterend in afname van de flux en dus de efficiëntie van het FO zeewater verdunningsproces. Transparant exopolymeer deeltjes (TEP) werden geïdentificeerd in de dragerlaag van het FO membraan in contact met het zeewater, en kunnen mogelijk de water flux door het FO membraan beperken.

Fysische en chemische methoden werden gebruikt en vergeleken teneinde een effectief protocol voor reiniging van FO membranen te realiseren (Hoofdstuk 5). Vervuiling door natuurlijke organische stof vertoonde een hoge hydraulische reversibiliteit, tot 90% bij in-situ air-scouring (waterluchtwassen) gedurende 15 minuten als reinigingstechniek. Chemische reiniging met een mengsel van Alconox, industriële detergens met fosfaat en natrium-ethyleen-diaminetetra-azijnzuur (EDTA), bleek de reinigingsefficiëntie (93,6%) te verhogen. Een osmotische backwash met een 4% NaCl-oplossing en gedemineraliseerd water bleek niet geschikt om de originele flux te herstellen door zoutdiffusie verschijnselen die optraden bij de actieve membraanlaag. De reinigingsoplossing gebruikt om de activie membraanlaag te reinigen werd tevens gebruikt om de membraan-steunlaag te reinigen: 95% van flux werd teruggevonden, waaruit bleek dat de chemisch irreversibele vervuiling van de FO membraan in de orde is van 5,5%. Deze irreversibele vervuiling zou kunnen worden geassocieerd met de adsorptie van biopolymeren op de activie laag en enkele TEP residuen op de steunlaag. Fysieke reiniging (air scouring) bleek de meest effectieve manier om organische vervuiling te beheersen.
Biofouling

Het onderzoek over de invloed van spacer dikte (28, 31 en 46 mil, 1 mil = 0,0254 mm) op de ontwikkeling van membraanprestaties en biofouling (excessieve biomassagroei) aan de aanvoerzijde van FO membranen (hoofdstuk 6) heeft geleid tot de volgende conclusies: (i) de biomassahoeveelheid alleen bepaalt niet de fluxafname: dezelfde hoeveelheid massa werd gevonden voor alle spacedikten na dezelfde loop tijd op dezelfde voedingsstroom, terwijl de fluxreductie afnam met dikkere spacers, (ii) de fluxdaling veroorzaakt door biomassa-accumulatie kan worden verminderd door gebruik van een dikkere spacer, (iii) de ruimtelijke verdeling van de biofilm varieerde met de spacedikte. De bevindingen zijn in overeenstemming met gerapporteerde gegevens voor hoge druk RO cross-flow systemen: Dikkere spacers verminderen de impact van biofouling op de membraanprestaties. Ditresultaat is duidelijk in tegenspraak met waarnemingen verkregen met deeltjes en colloidale vervuiling in FO systemen.

Perspectief

Forward osmose (FO) is een opkomende membraantecnologie met een reeks aan mogelijke waterbehandelingen (o.a. ontziling en afvalwaterhergebruik). Een overzicht van toepassingen, voordelen, uitdagingen, kosten en kennishiaten is gegeven (hoofdstuk 7). Met de huidige commerciële technologie hebben hybride FO systemen voor zowel ontziling en waterhergebruik toepassingen hogere kapitaalkosten in vergelijking met conventionele technologieën. De bedrijfskosten van hybride FO systemen zijn aantoonbaar lager, waardoor de eenheidskosten per m³ geproduceerd zoetwater met een FO systeem lager zijn dan de conventionele ontziling/water terugwinningtechnologieën (bijvoorbeeld ultrafiltratie / RO systemen).

Er zijn belangrijke voordelen van gebruik van FO hybride systemen in vergelijking met RO: (i) chemicaliënopslag en wateraanvoersystemen kunnen beperkt worden, waardoor bespaard wordt op kapitaal-, operationele- en onderhouds-kosten, (ii) zuiveringsunits zijn meer flexibel, en (iii) een hogere algehele duurzaamheid van het ontziltingsproces, tijdens productie van hoge kwaliteit water.

De belangrijkste uitdagingen van FO om een commercieel levensvatbare technologie te worden zijn: (i) de ontwikkeling van een hoge waterflux membraan, in staat zijnde een verhoogde zoutverwijdering te handhaven en een verminderde interne concentratiepolarisatie (ICP) effect, (ii) in sommige toepassingen, de beschikbaarheid van geschikte draw-oplossingen, die kunnen worden hergebruikt via een efficiënt proces, (iii) een beter begrip van vervuiling en biofouling, (iv) het verzekeren van hoge kwaliteit van het geproduceerde water, (v) hybridisatie met andere technologieën waardoor de voordelen van FO gebruik kunnen toenemen (bijvoorbeeld waterhergebruik en energieproductie).

Numerieke modellering kan een nuttig instrument zijn om biofouling te voorspellen en voorkomen in FO membranen. In aanvulling hierop, wordt aanbevolen om toekomstig
experimenteel onderzoek te richten op het gebruik van gемodificeerde spacers en nieuwe reinigingsstrategieën.

Het wordt sterk aangeraden om het FO proces op te schalen naar pilot-scale, waarin een uitgebreide evaluatie van de waterkwaliteit en energieparameters gedaan kan worden en een levenscyclusanalyse en kostencyclusanalyse van een hybride proces (bijvoorbeeld FO-LPRO) mogelijk is. Dergelijk onderzoek zal informatie leveren over de te nemen richting voor de ontwikkeling van robuuste hydride waterzuiveringssystemen voor goedkope productie van hoge kwaliteit water.
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Chapter 1

Introduction
1.1 Population distribution and water scarcity

Globally, the level of urbanization has significantly increased during the last six decades. In 2010, urban areas comprised 3.5 billion people, or 50.5 per cent of the world’s population (United Nations 2011). Due to the development of coastal regions in many countries, two-fifths of cities with populations of 1 million to 10 million people are located near coastlines (Tibbetts 2002). Moreover, 14 of the largest 17 cities in the world are situated along coasts (Figure 1.1) (Creel 2003b).

Figure 1.1 | Fourteen of the world’s largest cities are located along the coast (indicated in orange), which translates into an opportunity to integrate drinking water and wastewater management, especially in water-stressed areas (Creel, 2003) (Image adapted from: NASA (2000)).

With increasing population growth, the demand for clean water is also increasing. Under an average economic growth scenario and when no efficiency gains are assumed, global fresh water demand will increase 53% from 2009 to 2030, from 4.5 trillion m³ to 6.9 trillion m³ (The Barila Group et al. 2009), with a proportionally greater deficit in many developing countries. This situation will leave between 2.4 billion and 3.2 billion people under water-scarce or water-stressed conditions by year 2025, four-folding the number of people that lived in areas with limited fresh water availability at the beginning of the 20th century. Water shortage is likely to grow especially acute in the Middle East and much of Africa (Engelman et al. 2000), as well as vast areas in Australia, China, India and Mexico (Figure 1.2), directly associated with the physical absence of additional fresh water resources to cover their demand. Besides the amount of water itself, the quality must comply with the minimum standards set by each country’s regulations to be considered as potable; diarrheal disease alone is responsible for the death of 1.8 million people every year, and it was estimated that
88% of these cases are attributable to unsafe water supply, sanitation and hygiene (Prüss-Üstün and Corvalá 2004).

![Projected global water scarcity by 2025](Image)

**Figure 1.2 |** Projected global water scarcity by 2025 (International Water Management Institute).

Human population distribution along the coasts represents a great challenge in terms of water management, due to the contamination of surface and ground water (basins, aquifers, rivers, etc.), limited fresh water sources in some areas, and more stringent environmental regulations that restrict the use of certain water resources. Therefore, a comprehensive strategy for the management of water resources is crucial for the sustainable development of these areas (Li et al. 2014).

Since more than 97% of the water in the world is seawater (Figure 1.3), desalination technologies have the potential to solve the fresh water crisis, particularly in coastal areas. The most used desalination technique nowadays is reverse osmosis, where a membrane is used as a physical barrier to separate the salts from the water, using high hydraulic pressure (Amjad 1993). Nevertheless, the use of pressure imposes a high cost on operation of these systems, besides the known persistent fouling problems associated with membrane filtration systems (Ridgway and Flemming 1996, Shannon et al. 2008, Vrouwenvelder et al. 2008).
Research has identified the potential for hybrid forward osmosis/reverse osmosis (FO/RO) systems for several applications, including sweater desalination (Choi et al. 2009), to reduce the cost and fouling propensity of producing fresh water from impaired-quality water sources (Chang et al. 2002, Achilli et al. 2009, Boo et al. 2013). Recently, studies have shown the potential of these systems to produce low cost high quality fresh water using low pressure desalination, while simultaneously recovering impaired water from a recycled feed water (Cath et al. 2009, Yangali-Quintanilla et al. 2011). Nevertheless, there are concerns about the use of FO membranes as a barrier for rejecting micropollutants and nutrients from the wastewater, besides the inevitable fouling problems that can occur during the filtration process, when the membrane is submerged in the recycled feed water, resulting in a poor water flux and an increase in the operational cost due to membrane cleaning.

1.2 Osmotic membrane processes

Osmosis is defined as the transport of water through a semipermeable membrane caused by a difference in osmotic pressure for the solutions on both sides of the membrane. The osmotic pressure is related to the concentration of dissolved ions in solution and the temperature (Cath et al. 2009).

Osmotic pressure ($\pi$) can be calculated using the van't Hoff equation (van't Hoff 1887):

$$\pi = R \cdot T \cdot \sum i \cdot M$$  \hspace{1cm} (Eq. 1.1)

where $i$ is the dimensionless van't Hoff factor for the specific ion, $M$ is the molarity of the specific ion, $R$ is the gas constant (0.08206 L·atm·mol$^{-1}$·K$^{-1}$), and $T$ is the temperature in Kelvin.

The most common applied membrane filtration processes are reverse osmosis (RO), pressure retarded osmosis (PRO) and forward osmosis (FO), also known as osmosis or direct osmosis, are shown in Figure 1.4.

RO occurs when the osmotic pressure difference between the two solutions is overcome by a hydrostatic pressure applied to the high concentration solution, reversing the osmosis.
process. PRO is an osmosis process in which there is a hydraulic pressure applied to the high concentration solution, but the osmotic pressure difference is bigger, so the water flux is opposite to the flux in RO process. When there is no hydraulic pressure applied, the osmotic process is called forward osmosis (FO), which is the natural flow of water from the low solute concentration to the high solute concentration solution to equilibrate the osmotic pressure difference.

![Osmotic processes in membrane filtration](https://example.com)

Figure 1.4 | Osmotic processes in membrane filtration. $\Delta P$ – applied hydraulic pressure; $\Delta \pi$ – osmotic pressure difference between the two solutions; $J_w$ – water flux.

### 1.3 Forward osmosis (FO)

Forward osmosis (FO) uses a concentrated draw solution to generate high osmotic pressure, which extracts water across a semi-permeable membrane from the feed solution (Mi and Elimelech 2008). As a result, the feed stream reduces in volume, increasing the salt concentration, which results in a decrease in permeate flux to the draw solution side (Choi et al. 2009).

According to Lee et al. (1981), the general equation describing water transport through the RO membrane is:

$$J_w = A (\sigma \Delta \pi - \Delta P) \quad \text{(Eq. 1.2)}$$

where $J_w$ is the water flux, $A$ the water permeability coefficient of the membrane, $\sigma \Delta \pi$ the effective osmotic pressure difference in reverse osmosis, being $\sigma$ the reflection coefficient, and $\Delta P$ the applied pressure; for FO, $\Delta P=0$; for RO, $\Delta P > \Delta \pi$ (Cath et al. 2006). This equation is not suitable for FO processes because the parameter $A$ and the reflection coefficient are calculated considering that pressure is being applied to the brine; besides, the driving force
considered is the difference between osmotic pressure and the applied hydraulic pressure (ΔP).

For FO, it is necessary to refer to the Lee’s equation for low concentration solutions in the porous substructure side of the membrane (Lee et al. 1981):

\[
\frac{J_1}{A\pi_{hi}} = \frac{1 - \left(\frac{C_{low}}{C_{hi}}\right)\exp(J_1K)}{1 + \frac{B}{J_1}\exp(J_1K) - 1} 
\]  
(Eq. 1.3)

where A is the water permeation constant for RO and B is the solute permeability coefficient for the RO, \(J_1\) is the flux measured during the experiment, \(C\) the concentration of the solutions, \(\pi_{hi}\) the osmotic pressure of the high concentration solution, and K is the solute resistivity of the membrane.

Instead, Loeb et al. derived a formula (Equation 1.4) from Lee’s equation (Equation 1.3) that can be applied to a case in which two different solutions, one with higher osmotic pressure, are kept in contact through a semipermeable membrane, making several important considerations for FO. The \(\pi_{low}\) is always considerably higher than zero; with this, A \(\pi_{low}\) and, therefore, A \(\pi_{hi}\) are much higher than B or J; the relation between the concentrations can be equal to the relation between osmotic pressures (\(C_{hi}/C_{low} = \pi_{hi}/\pi_{low}\)) when restricting the condition of appreciable osmotic pressure on both sides of the membrane.

\[
K = \frac{1}{J} \ln \left(\frac{\pi_{hi}}{\pi_{low}}\right) 
\]  
(Eq. 1.4)

where K is the solute resistivity of the membrane, \(\pi_{hi}/\pi_{low}\) the ratio between the osmotic pressure of the high concentration solution and the low concentration solution, and J the flux. The driving force in the case of FO keeps a logarithm ratio between the osmotic pressures, unlike the RO, where the driving force is the only the difference between the osmotic pressures and the pressure generated by the applied force (Loeb et al. 1997).

The main advantage of using FO is the low energy required to extract pure water from a wastewater or recycled feed, being only the energy used to recirculate the draw solution (Adham et al. 2007). A major limiting factor of FO systems performance is an eventual flux decline due to concentration polarization (Mccutcheon et al. 2005).

Many FO membrane potential applications have been studied, including desalination (Low 2009), concentration of dilute industrial wastewater, concentration of landfill leachate, direct potable reuse for advanced life support systems, food processing, pharmaceutical industry processes (Cath et al. 2006) and concentration of digested sludge liquids (Holloway et al. 2007). Because forward osmosis is gaining interest as a potential technology to reduce the cost of producing fresh water and treating wastewater effluents, a rapid increase in the number of peer reviewed publications was observed in the last years (Figure 1.5).
Figure 1.5 | Development of annual peer reviewed publications on “forward osmosis” as a keyword in the period 1994-2014 (Scopus database on: June 2014).

1.4 FO system for wastewater recovery and seawater desalination

The studies comprised in this work were based on the layout of a hybrid forward osmosis/low pressure reverse osmosis (FO/LPRO) system shown in Figure 1.6. Wastewater was used as feed water for the FO process; once concentrated, the wastewater is ready for a post-treatment step to recover energy in form of biogas. The draw solution for the FO process is seawater; once diluted, the seawater is fed into a LPRO unit to remove the remaining dissolved salts and produce fresh water.

To better understand the process, an example of FO filtration is given: using a municipal primary wastewater effluent (conductivity ≈ 2000 µS·cm⁻¹) as feed solution and Red seawater (conductivity ≈ 52000 µS·cm⁻¹) as draw solution, a 60% seawater dilution can be achieved, resulting in partially desalinated seawater (conductivity ≈ 21000 µS·cm⁻¹), which can further be treated with a LPRO system (feed pressure ≈ 20 bar), to produce fresh water (conductivity ≈ 250 µS·cm⁻¹) at a lower energy consumption than a traditional RO system (feed pressure ≈ 60 bar). The concentrated wastewater effluent can be further treated in an anaerobic bioreactor to recover biogas.
1.5 Concentration polarization in FO membranes

Concentration polarization (CP) occurs when the difference in salt concentration across the active layer is different than the difference in concentration in the bulk solutions itself (McCutcheon and Elimelech 2006). CP can refer to the formation of a concentration layer at the membrane surface, defined as external concentration polarization (ECP), or in the porous structure of asymmetric membranes, defined as internal concentration polarization (ICP); both reduce the driving force of the osmotic process, and thus, the water flow through the membrane decreases.

ECP can be controlled by several hydrodynamic techniques such as increasing the cross-flow velocity (Sabiani et al. 2001). ICP, which is one of the major drawbacks in FO, occurs within the membrane support layer (Gray et al. 2006), and thus, it is difficult to mitigate, being mainly dependent on the porous support structure.

The effects of ICP for a commercial FO membrane tested with two different orientations, one in which the active layer (dense and thin separation layer) is facing the draw solution (AL-DS), and the other one where the active layer is in contact with the feed solution (AL-FS) have been studied. After several tests, flux decline was up to 15% lower for AL-DS in comparison with the AL-FS orientation (Cath et al. 2006). ICP is very minimally affected by changing the hydraulic conditions in the membrane cell, but it is affected by the orientation of the dense layer of the membrane (McCutcheon and Elimelech 2006). Other studies refer to the overall performance of the membranes and concludes that the optimal configuration to prevent membrane damage is with the active layer facing the feed solution, reducing the ICP in the support layer, because the direction of the water flow is opposite to the concentration of the bulk draw solution into this layer; this configuration is also effective.

1.6 FO membrane fouling

Fouling is a severe problem in membranes, reducing the flux considerably, and affecting the overall performance. Fouling supposes that membrane elements have to be cleaned and eventually replaced. Biofouling has been identified as one of the major problems in spiral wound nanofiltration and reverse osmosis membrane module operation (Figure 1.7) (Winters and Isquith 1979, Paul 1991, Tasaka et al. 1994, Flemming et al. 1997, Khedr 2000, Saeed et al. 2000, Vrouwenvelder et al. 2008, van Loosdrecht et al. 2012).

In FO membrane filtration, water flux decline due to fouling is less severe than in RO, because the FO process itself does not induce suspended solids and other organic contaminants into the membrane (Holloway et al. 2007). Both reversible and irreversible membrane fouling were found to be negligible when using a FO membrane submerged in secondary wastewater effluent (Cornelissen et al. 2008). In a different study with a FO/RO hybrid system, using impaired water as feed solution, results show the low fouling propensity of the FO process, and the ability to treat large volumes of water with almost no need for physical or chemical cleaning (Cath et al. 2009). One of the few studies on biofouling in FO membrane filtration suggests that the effect of the biofilm layer is less severe than for RO processes in the same hydrodynamic cross-flow channel conditions (Yoon et al. 2013).

Fouling can change the surface characteristics of the membrane, either to improve or degrade the rejection capability and flux. Several studies show both positive and negative impacts for NF and RO membranes (Kimura et al. 2003, Bellona et al. 2004, Xu et al. 2006), but few studies have given insight on FO membranes (Cath et al. 2011, Xie et al. 2012).

Figure 1.7 | Biofouling affecting a reverse osmosis spiral wound module used in a water filtration system (photo by Johannes Vrouwenvelder).
1.7 Energy demand in desalination and water treatment processes

High energy demand for current desalination technologies has limited its use in several regions, representing more than 70% of the operating costs of the plant and up to 50% of the cost of the final product (potable water). For water treatment processes, more than 50% of the energy required is used for the activated sludge aeration; another significant fraction of the energy is used for the pumping system in all the water treatment stages (Metcalf and Eddy 2003). There are several recommendations that require implementing operational changes and retrofitting equipment to reduce the energy consumption in wastewater treatment plants as well as in desalination facilities; however, all these measures represent a significant expenditure and cannot be applied in many cases (Farooque et al. 2008).

One of the main advantages of FO is the limited amount of external energy required to extract water from the feed, only using a very low hydraulic pressure to recirculate the DS on one side of the membrane, while the feed is passively in contact with membrane on the other side (Cath et al. 2006). However, it should be noted that special attention must be taken into the water quality, because the dilution might contaminate the water and affect the downstream RO process (Shannon et al. 2008). This might turn into an energy intensive solution, having to add an advanced pretreatment process, which turns the research on contaminant removal with FO membranes critical.

1.8 Scope and outline of the thesis

The objective of this study is the assessment of indirect desalination systems using forward osmosis, where the feed water is a primary or a secondary wastewater effluent, and the draw solution is seawater, with the purpose of recovering fresh water from impaired quality sources. The studies reveal the ability of forward osmosis to effectively recover water from wastewater, reject nutrients and micropollutants, outperform RO traditional systems in terms of fouling resistance and control, having a high flux recovery when applying physical cleaning methods, and developing a less severe biofouling that can be easily controlled.

The thesis is structured in three themes studying forward osmosis: i) water recovery, ii) organic fouling and cleaning, and iii) biofouling. A layout of the structure is shown in Figure 1.8.

The first theme (Chapter 2 and 3) describes the general method and systematic studies for the assessment of a combined wastewater concentration and seawater dilution system based on a submerged FO membrane cell that concentrates a synthetic municipal wastewater using synthetic seawater as draw solution. Special attention is given to nutrients and heavy metals rejection (Chapter 2). Practical conditions (i.e. municipal wastewater effluent and Red Sea water) are used to evaluate rejection of organic micropollutants spiked in the feed water (Chapter 3).
The second theme (Chapter 4 and 5) aims to identify the main foulants of an FO membrane, responsible for the reduction of system performance. Organic foulants on both wastewater and seawater are analyzed and characterized (Chapter 4). Physical and chemical methods are used and compared to try to set a protocol for FO membrane cleaning (Chapter 5).

The last theme (Chapter 6) focuses on biofouling and its effects on forward osmosis. The influence of feed spacer on biofouling is analyzed with a cross-flow cell.

An overview is given (Chapter 7) on the possible niches in the seawater desalination and wastewater reuse industries for forward osmosis processes.

The thesis is structured as a paper dissertation, i.e. it consists of a number of scientific articles, except for the introduction chapter. Some repetitions are consequently unavoidable in individual chapters. Small adaptations have been made to improve the chapters.

References


Adham, S., J. Oppenheimer, L. Liu, and M. Kumar. 2007. WateReuse Dewatering Reverse Osmosis Concentrate from Water Reuse Applications using Forward Osmosis. WateReuse Foundation.


WATER RECOVERY
Chapter 2

Water harvesting from wastewater primary effluent using forward osmosis (FO)

Abstract

Forward osmosis (FO) presents a unique opportunity for integrated wastewater treatment and seawater desalination. This study assesses the efficiency of a submerged FO system to reduce the volume of wastewater that needs to be treated while recovering high quality water that can be further treated for sustainable fresh water production. A semi-batch operation was employed with two membrane orientations in terms of active and support layers. A change of membrane orientation could improve the flux and slightly reduce the salt leakage from the draw solution to the feed solution. The formation of fouling on the membrane resulted in a decrease of the initial flux and average flux with both membrane orientations. The fouling layer on the membrane surface was determined to be caused by biopolymer-like substances. Osmotic backwash removed almost all organic foulants from the membrane surface, but did not improve the flux. There was a moderate to high retention of nutrients (N and P), varying from 56% to 99%, and almost a complete retention for trace metals regardless of membrane orientation. However, the membrane showed a limited ability to retain low molecular weight acids and low molecular weight neutral compounds. This study identified a possible role of the FO process to integrate wastewater treatment and seawater desalination for a sustainable solution of the water-energy nexus for coastal cities.

2.1 Introduction

Under an average economic growth scenario and if no efficiency gains are assumed, global water demand will increase 53% by 2030, up to 6.9 trillion m³ per year (The Barila Group et al. 2009). Along with the growing demand for fresh water, there is also an increase in the amount of wastewater that needs to be treated adequately to meet public health and environmental discharge regulations. This problem is more significant along coastlines, where today, more than 3 billion people live, and it is likely that by 2025 this number will double (Creel 2003a). As a result of these trends, over the last two decades, wastewater recovery for direct and indirect planned reuse has become a more common practice, with an increasing number of studies that compare various technologies that can treat and recover secondary wastewater effluent (Fujita et al. 1996, Madireddi et al. 1997, Drewes and Fox 1999, Drewes et al. 2003, Melin et al. 2006). However, there are still effluents that are discharged into water bodies, which may contain contaminants that are not removed by conventional treatment processes (Levine and Asano 2004). The disposal of wastewater effluents in coastal areas poses an additional concern because of the relatively high concentration of nutrients in the treated water, i.e., nitrogen and phosphorous, which enhance eutrophication and impact the ecosystem, endangering the food source of millions of people, and disrupting the economic activities associated with coastlines, besides the public health hazards involved (Areas and Council 1993, Ng Yan Yan and Barron 2000). In addition, a significant part of the anthropogenic emissions of trace metals ends up in wastewater. The sources of these trace metals include industrial processes and/or urban runoff in combined sewers (Karvelas et al. 2003). The presence of trace metals in the influent to municipal wastewater treatment plants can adversely affect the performance of the treatment processes and quality of the effluent, and influence decisions regarding reuse (Johnson et al. 2008).

Several advanced methods have been studied for wastewater reclamation, but they all involve highly energy intensive processes, such as nanofiltration (NF) and reverse osmosis (RO) (Shannon et al. 2008, Yangali-Quintanilla et al. 2010a). A membrane bioreactor (MBR) has been considered to be a sustainable wastewater treatment process to achieve high quality effluents (Günder and Krauth 1999, Jefferson et al. 2001, Melin et al. 2006). Nevertheless, this process still involves a considerable amount of energy to extract the treated effluent through the membrane and to provide oxygen for biological degradation. To solve this problem, forward osmosis (FO) can contribute to increase water recovery at lower energy consumption, and therefore, considerable cost reduction is feasible (Cath et al. 2009, Bamaga et al. 2011). The forward osmosis (FO) process has been investigated for various applications in wastewater treatment by using different feed streams and process models including, for example, activated sludge (Cornelissen et al. 2008), anaerobic digester centrate (Holloway et al. 2007), membrane bioreactor effluent (Hancock et al. 2011b), drilling mud and fracturing wastewater from oil and gas industry (Hickenbottom et al. 2013), primary effluent (Lutchmiah et al. 2011), secondary and tertiary treated effluent (Cath et al. 2010). By an osmotic dilution process, volume-minimizing treatment of wastewater and reduction of osmotic pressure of seawater prior to RO desalination can be achieved simultaneously (Cath et al. 2010). The osmotic membrane bioreactor (OsMBR) has...
demonstrated a sustainable flux with relatively low reverse transport of solutes from the draw solution (DS) into the mixed liquor (Achilli et al. 2009). However, the energy that needs to be used for aeration (intended for bacterial growth) and air stripping (intended for membrane cleaning) is still required, and it is about 10% of total energy estimate in OsMBR while about 15% in the conventional MBR (Bharwada 2011).

On the other hand, wastewater has been considered as an energy source to produce biogas by an anaerobic process. The crucial factor for successful anaerobic treatment of wastewater with biogas production is the concentration of organic matter compounds including polysaccharides, lipids, protein, simple aromatics (Metcalf and Eddy 2003). The soluble organic fraction in wastewater cannot be concentrated easily with a low cost process, consequently becoming a barrier to the direct anaerobic treatment of wastewater (McCarty et al. 2011). In the treatment of wastewater, the idea of osmotic concentration of raw wastewaters using FO membranes has not been studied to its full extent as an alternate method to provide high organic concentration for an anaerobic process, and avoid primary and aerobic treatment of wastewater.

The objective of this research is the assessment of a combined wastewater concentration and seawater dilution system based on a submerged FO membrane cell that concentrates a synthetic municipal wastewater using synthetic seawater as a draw solution (DS). Special attention is given to nutrients removal and high recovery rates intended for optimal feed concentrations for subsequent anaerobic treatment as well as membrane fouling analysis. On the other hand, high quality water can be extracted through the FO membrane, diluting the seawater which can be utilized to produce fresh water via low-pressure reverse osmosis (LPRO) (Yangali-Quintanilla et al. 2011). This study provides insight and details into the concept of using the FO process to avoid secondary aerobic treatment of a primary wastewater effluent that has not been reported in the literature, as well as additional information on the partial desalination of seawater, including: i) the use of a submerged FO module which makes it possible to adapt the process to a primary clarifier tank, ii) analysis of the quality of the diluted seawater for further post-treatment, iii) FO rejection of nutrients and heavy metals in the wastewater, and iv) analysis of fractional organic carbon composition in the fouling layer on the FO membrane.

2.2 Experimental

2.2.1 Feed water and draw solution

Synthetic municipal wastewater containing chemical compounds, food ingredients and trace metals was prepared by a method reported previously with some modifications (Nopens et al. 2001), and used as the feed water/solution (FS) (Table 2.1). The chemical oxygen demand (COD) of the synthetic municipal wastewater was estimated to be about 360 mg-L⁻¹ before the FO process. For the DS, a solution of 4% NaCl was used to simulate Red Sea water, with a conductivity of 55±0.5 mS-cm⁻¹.
Table 2.1 | Recipe of synthetic municipal wastewater.

<table>
<thead>
<tr>
<th>Solutes</th>
<th>mg·L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical Compounds</strong></td>
<td></td>
</tr>
<tr>
<td>Urea</td>
<td>91.74</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>12.75</td>
</tr>
<tr>
<td>Sodium Acetate</td>
<td>79.37</td>
</tr>
<tr>
<td>Peptone</td>
<td>17.41</td>
</tr>
<tr>
<td>MgHPO₄·3H₂O</td>
<td>29.02</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>23.40</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>5.80</td>
</tr>
<tr>
<td><strong>Food Ingredients</strong></td>
<td></td>
</tr>
<tr>
<td>Starch</td>
<td>122.00</td>
</tr>
<tr>
<td>Skimmed Milk Power</td>
<td>116.19</td>
</tr>
<tr>
<td>Yeast extract</td>
<td>52.24</td>
</tr>
<tr>
<td><strong>Trace metals</strong></td>
<td></td>
</tr>
<tr>
<td>Cr(NO₃)₃·9H₂O</td>
<td>0.770</td>
</tr>
<tr>
<td>CuCl₂·2H₂O</td>
<td>0.536</td>
</tr>
<tr>
<td>MnSO₄·H₂O</td>
<td>0.108</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
<td>0.336</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>0.100</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>0.208</td>
</tr>
</tbody>
</table>

2.2.2 FO membrane and experimental set-up

The FO membrane was provided by Hydration Technology Innovations (HTI, Scottsdale, AZ). The FO membrane is a cellulose triacetate (CTA) layer embedded in a polyester support mesh. A layout of the experimental setup can be found in a previous publication (Valladares Linares et al. 2012). The membrane cell was a custom-made plate and frame assembly, accommodating flat-sheet membranes with a total area of 250 cm². Two orientations of the membrane were used in the experiments: active layer (AL) of the membrane facing the FS side (AL-FS mode) and active layer facing the DS side (AL-DS mode). The membrane cell was immersed in a feed tank containing FS, and connected to a receptacle containing DS. A gear pump (Cole-Parmer) was used to continuously recirculate the DS in the lumen space of the cell, extracting water from the FS into the DS reservoir. A digital balance (Sartorius AG, Germany) connected to a computer was used to measure the variation of DS weight and convert it to flux. The temperature of the FS and DS was kept constant at 20 ± 0.5 °C by using chiller/heater devices.
The experimental procedure started with 20 L of FS in the feed tank and 1 L of DS in the DS receptacle. The recirculation pump was started at a flow rate of 100 mL·min⁻¹ and dilution of the DS started, meanwhile the conductivity and flux data acquisition were also started. Since the flow rate is low, the hydraulic pressure induced by the flow in the lumen space of the cell was not detectable by the pressure gauge (1008 Ashcroft, U.S.A.) and thought to be negligible in this study. The high osmotic pressure of the DS inside the channel resulted in an extraction of clean water (permeate) from the FS to DS while most contaminants or solutes in either FS or DS were rejected by the membrane. A stirrer was used to provide mixing in the feed tank with a global velocity gradient of 50 s⁻¹. The each cycle of FO process was performed until the final volume of DS was 2 L, i.e., 1 L of permeate was extracted from FS to DS. The cycle was repeated by replacing diluted DS with fresh aliquot (1 L of 4% NaCl solution). The osmotic concentration process was terminated after 10 cycles, when FS was concentrated 50% (10 L of permeate was extracted after 10 cycles).

Osmotic backwash was used as a cleaning technique to determine its impact on flux recovery. After 10 cycles of osmotic concentration, the cell was moved to a separate tank and soaked in 4% NaCl solution while deionized (DI) water was recirculated inside the lumen space of the cell at a flow rate of 100 mL·min⁻¹. The cleaning process was performed for 12 hours. The permeability fluxes of the membrane before and after osmotic backwash were determined under the same operational condition of osmotic concentration process with DI water as feed and 4% NaCl solution as DS.

2.2.3 Analytical methods

The conductivity of the FS and DS was monitored with a conductivity meter (WTW, Germany) connected to a computer.

The salt leakage from the DS side to feed wastewater was estimated by measuring the conductivity in the DS reservoir and converting to salt amount. The loss of salt in each batch was considered to be the salt leakage to the feed tank (Equation 2.1).

\[ \text{Salt leakage} = (1 - \left( \frac{C_{DS2} \cdot V_{DS2}}{C_{DS1} \cdot V_{DS1}} \right)) \times 100 \]  

(Eq. 2.1)

where \( C_{DS1} \) and \( C_{DS2} \) are salt concentrations in the DS before and after each cycle, respectively. \( V_{DS1} \) and \( V_{DS2} \) are the volumes of DS before and after each cycle, respectively.

The trace metals (Cr, Mn, Ni, Cu, Zn and Pb) were analyzed by Inductively Coupled Plasma/Mass Spectrometry (ICP-MS 7500, Agilent, US). DOC and total nitrogen were measured by an Organic Carbon Analyzer (TOC-VCPEH, Shimadzu, Japan). COD, ammonia and phosphate were analyzed by Hach TNT reagents with a spectrophotometer (DR 2800, Hach). The proper dilution of sample was done to eliminate the possible interference caused by water salinity. Hach TNT reagent tests were performed previously with different water salinities in the samples to determine the accuracy of the method when used with concentrated FS containing leaked salts and diluted DS. All of the tests showed reliable
results due to the fact that TNT reagents chosen have been adapted to be used with saline waters samples (Boyles 1997, HACH 2012).

After 10 cycles of the osmotic concentration process and osmotic backwash, membrane samples (2×2 cm²) were cut and soaked in 15 mL DI water, and then treated by ultrasound for 30 minutes. The supernatant was collected for Liquid Chromatography – Organic Carbon Detection analysis (LC-OCD, Model 8, DOC Labor, Germany) to reveal membrane foulants. The FS and DS collected during the FO process as well as the original synthetic municipal wastewater were also analyzed by LC-OCD. All samples for LC-OCD analysis were pre-filtered by 0.45 μm pore size filter as required by the instrument.

2.3 Results and discussion

2.3.1 Flux patterns

The flux in each cycle decreased rapidly. Flux decrease is due to two reasons: i) a decrease in the osmotic pressure difference caused by the dilution of DS and concentration polarization in each cycle during a batch operation in this study, ii) fouling on the membrane surface. During a full scale application, it is possible to have a continuous supply and recirculation of DS. In such a system, the recovery rate can achieve up to 80%. The decrease of flux in the full scale application would mainly be associated with membrane fouling and fouling enhanced concentration polarization which can be demonstrated by the decrease of initial flux ($J_{ini}$) and average flux ($J_{ave}$) in each cycle of this study. Figure 2.1 shows the flux patterns for 10 cycles in terms of $J_{ini}$ and $J_{ave}$ for each mode tested. Both $J_{ini}$ and $J_{ave}$ decreased with batch number, which indicated that membrane fouling also caused a negative impact, limiting the flux in the FO process even though there was no hydraulic pressure applied. During the FO process, the fouling layer itself may not give a significant resistance to the water permeability since it was loose and easily removed by an osmotic backwash (proved in Section 2.3.3). However, fouling enhanced concentration polarization created by accumulating reversely diffused salt within fouling layer can reduce the effective osmotic driving force and, consequently, limit the water flux (Boo et al. 2012, She et al. 2012). In addition, the AL-DS mode gave a higher value of both $J_{ini}$ and $J_{ave}$. The reason is that the effect of dilutive concentration polarization at the DS side can be reduced when the AL faced the DS. The smoother and denser surface of the AL can improve the fluid shear stress near the membrane surface to reduce accumulation of salt on the membrane and diffusion of salt into the membrane, then reduce both external concentration polarization at the DS side and internal concentration polarization (Mi and Elimelech 2008, Su et al. 2010, Zhao et al. 2011).
2.3.2 Salt leakage and retention of nutrients and trace metals

Salt leakage from DS to FS was calculated through measurements of the conductivity in the DS along the dilution process. Salt leakage values ranged between 5% to 15% for both modes (Figure 2.2). The AL-DS mode showed a slightly lower salt leakage than AL-FS. In most reported studies, the salt rejection of HTI CTA membrane under various membrane orientations and operational modes was around 90% which is consistent with the result observed in this study (Cornelissen et al. 2008, Phillip et al. 2010, Yip et al. 2010, Jin et al. 2011). The remaining conductivity in the DS at the end of each cycle of both modes varied between 22.9 and 27.4 mS·cm⁻¹. The reduced conductivity indicates the reliable dilution of DS by the FO process extracting fresh water from the FS, and potential energy saving in further desalination by LPRO.

The results for the removal of trace metals are presented in Figure 2.3. Retention of all trace metals including Cr, Mn, Ni, Cu, Zn and Pb in the FS was high and stable throughout the osmotic concentration process for both modes. Most rejection rates were higher than 99%.
Figure 2.2 | Salt leakage from the draw solution to feed solution in each cycle during the treatment of synthetic municipal wastewater by forward osmosis process.

Figure 2.3 | Rejection of trace metals in synthetic municipal wastewater by forward osmosis process.

Figure 2.4 shows the average retention of nutrients in the FS. Similar to the salt leakage and retention of trace metals, there is no significant difference between the AL-FS and AL-DS mode. The highest rejection of close to 99% was observed for COD and phosphate. However, the rejection was moderate for ammonia and total nitrogen ranging from 67% to 68% and 56% to 59%, respectively, consistent with previous observations in the literature.
(Cath et al. 2006, Holloway et al. 2007). The lower rejection of ammonia might be due to its positive charge combined with its low molecular weight.

The samples of FS and DS were collected from different cycles of the process. By comparing the LC-OCD chromatograms of each component of synthetic municipal wastewater (Figure 2.5), and FS and DS (Figure 2.6), the inability of the membrane to retain low molecular weight acid compounds (sodium acetate, elution time of about 56 minutes) and low molecular weight neutral compounds (urea, elution time of about 78 minutes) in the FS can be seen.

In addition, the FS underwent some changes during the process (Figure 2.6a and 2.6b). The reduction of sodium acetate and urea can be explained by the poor rejection by the FO membrane for these compounds. The peak of skimmed milk coupled with yeast extract (elution time of about 60 minutes) disappeared while a biopolymer peak increased after 10 cycles of the process. This is probably due to the hydrolysis and coagulation of some compounds including peptone, skimmed milk, yeast extract and starch in the synthetic municipal wastewater.

Figure 2.4 | Rejection of nutrients in synthetic municipal wastewater by forward osmosis process.
Figure 2.5 | LC-OCD chromatogram of synthetic municipal wastewater and each component.

Figure 2.6 | LC-OCD chromatogram of feed solution (FS) and draw solution (DS) during treatment of synthetic municipal wastewater by forward osmosis process (a and c, AL-FS mode; b and d, AL-DS mode; FS1, FS5 and FS10, FS collected from cycle 1, 5 and 10; DS1, DS5 and DS10, DS collected from cycle 1, 5 and 10).
2.3.3 Fouling characterization and osmotic backwash

After the FO processes for 10 cycles, a thick fouling layer was observed on the membrane surface from both AL-FS and AL-DS modes. LC-OCD analysis shown in Figure 2.7a reveals the major composition of the fouling layer. For both AL-FS and AL-DS modes, only a single peak was observed at the elution time of about 35 minutes which indicated the presence of biopolymers. This is consistent with the increase of biopolymers in the feed water indicated in Figure 2.6a and 2.6b. The actual amount of biopolymer may even higher since the fractions with size larger than 0.45μm were removed by the pre-filtration in sample preparation before LC-OCD analysis. Due to its hydrophilic and gel-like character, biopolymers tend to attach to the membrane surface while other compounds in the feed water may play a minor role in the formation of the fouling layer without a hydraulic pressure in the FO process.

The fouled membranes from both AL-FS and AL-DS modes were cleaned by osmotic backwash. Almost all organic foulants, mainly biopolymers, can be removed from the membrane surface by osmotic backwash. No significant peak can be identified from LC-OCD chromatographs of osmotically backwashed membranes collected from AL-FS and AL-DS modes (Figure 2.7b).

![Figure 2.7](image)

Figure 2.7 | Foulant on the membrane surface (a, before osmotic backwash; b, after osmotic backwash).

In order to identify the performance of osmotic backwash, the fluxes of the fouled membrane before and after osmotic backwash were measured with DI water as FS and 4% NaCl as DS in both AL-FS and AL-DS modes. The AL-DS mode still showed a higher flux than the AL-FS mode regardless of the fouled or osmotically cleaned membrane (Figure 2.8). As mentioned above, this is attributed to the denser and smoother AL surface which can reduce dilutive concentration polarization at the DS side (Gray et al. 2006, McCutcheon and Elimelech 2006, Li et al. 2012a, Cath et al. 2013). However, the results also show that osmotic backwash did not result in any improvement in the DI water flux in both modes (Figure 2.8), although the membrane surface was cleaned which is proven by the results in Figure 7. The reason is probably the diffusion of salt into the FO membrane during the
osmotic backwash step (Zhao and Zou 2011). A similar result was also observed in a previous study (Valladares Linares et al. 2013b). The diffused salt remaining inside the membrane can lead to internal concentration polarization, limiting the effective osmotic pressure in the consequent FO process. This observation suggests that osmotic backwash may not provide an expected performance in the FO process compared to RO since the fouling propensity and driving force are different between FO and RO. An extended soaking of the membrane in DI water may be required to remove residual salt inside the membrane if the osmotic backwash is applied in the FO process for membrane cleaning. It is meaningful to have a systematic investigation to confirm this hypothesis and optimize the osmotic backwash procedure in a further study.

![Figure 2.8](image)

**Figure 2.8** | Deionized water flux from the membrane before and after osmotic backwash.

### 2.4 Conclusions

A submerged FO process was employed as a bridge to integrate municipal wastewater treatment and seawater desalination for drinking water. A synthetic municipal wastewater was used as FS and osmotically concentrated, while a synthetic seawater as DS was diluted. The FO process showed a high rejection for COD, phosphate and trace metals, and moderate rejection for ammonia and total nitrogen. LC-OCD analysis revealed that the membrane tested was unable to reject low molecular weight acids and low molecular weight neutral compounds, such as sodium acetate and urea in this study. A change of membrane orientation can improve the flux, but did not increase the rejection rate. Biopolymer-like substances played a crucial role in the formation of fouling on the membrane surface. Because of the absence of hydraulic pressure during the FO process, the fouling on the membrane surface at the FS side can be removed by osmotic backwash. However, due to internal concentration polarization caused by the diffusion of salts into the membrane, a single osmotic backwash cannot provide flux recovery. The present study proved that FO is a reliable barrier to effectively reject most wastewater contaminants and salts from either the wastewater as FS or seawater as DS while allowing clean water to pass through. The
concentrated wastewater can then be utilized for anaerobic treatment and biogas recovery, and the diluted seawater can be further reused in industrial/agricultural activities or desalinated with significantly reduced energy cost by LPRO to produce potable water. This study provides a possible energy-saving strategy to combine municipal wastewater treatment and seawater desalination for further promote sustainable urban water management and water reuse in coastal cities. Accompanying urbanization in coastal regions, the construction of new RO desalination plants and wastewater treatment facilities is being planned in many cities. This makes it possible to co-locate such facilities with a short distance between the desalination and wastewater treatment plants, and facilitate the application of the FO concept proposed in this study. In addition, FO membranes are being improved over the last several years by researchers and commercial vendors. However the shortage of favorable and commercially available FO membranes is still the major constrain limiting application of this FO process. More studies should be conducted to improve the process efficiency by developing novel FO membranes, and investigate the stability and sustainability of the process under long-term operation.

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Water harvesting from wastewater primary effluent using forward osmosis (FO)


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Chapter 3

Rejection of micropollutants by FO membranes

Abstract

As forward osmosis (FO) gains attention as an efficient technology to improve wastewater reclamation processes, it is fundamental to determine the influence of fouling in the rejection of emerging contaminants (micropollutants). This study focuses on the rejection of 13 selected micropollutants, spiked in a secondary wastewater effluent, by a FO membrane, using Red Sea water as draw solution (DS), differentiating the effects on the rejection caused by a clean and fouled membrane. The resulting effluent was then desalinated at low pressure with a reverse osmosis (RO) membrane, to produce a high quality permeate and determine the rejection with a coupled forward osmosis – low pressure reverse osmosis (FO-LPRO) system. When considering only FO with a clean membrane, the rejection of the hydrophilic neutral compounds was between 48.6% and 84.7%, for the hydrophobic neutrals the rejection ranged from 40.0% to 87.5%, and for the ionic compounds the rejections were between 92.9% and 96.5%. With a fouled membrane, the rejections were between 44.6% and 95.2%, 48.7%–91.5% and 96.9%–98.6%, respectively. These results suggest that, except for the hydrophilic neutral compounds, the rejection of the micropollutants is increased by the presence of a fouling layer, possibly due to the higher hydrophilicity of the FO fouled membrane compared to the clean one, the increased adsorption capacity of hydrophilic compounds and reduced mass transport capacity, membrane swelling, and the higher negative charge of the membrane surface, related to the foulants composition, mainly NOM acids (carboxylic radicals) and polysaccharides or polysaccharide-like substances. However, when coupled with RO, the rejections in both cases increased above 96%. The coupled FO-LPRO system was an effective double barrier against the selected micropollutants.

Published as: Valladares Linares et al. 2011, Rejection of micropollutants by clean and fouled forward osmosis membrane, Water Research 45:6737-6744
3.1 Introduction

Organic micropollutants, or emerging organic contaminants, are substances that include, but are not limited to, pharmaceutically active compounds (PhACs), endocrine disrupting compounds (EDCs), disinfection by-products and pesticides, that are present in the environment and, due to the increasing concentration detected in recent studies, are arising concern among researchers and regulatory agencies, because most of them are not yet regulated and their impacts on human life are not quite known (Snyder et al. 2003).

There is an urging need to understand their partitioning, accumulation and removal from water, soil, air and biota; unfortunately, there is not a clear idea of the exact risks of chronic exposure to a mixture of organic micropollutants, including quantities ingested through drinking water, leaving a big question yet to be answered (Yangali-Quintanilla et al. 2010b). There are current technologies that can remove these organic micropollutants from wastewaters, but generally they are energy intensive processes, such as nanofiltration (NF) and reverse osmosis (RO) (Kimura et al. 2003, Bellona et al. 2004). Conventional wastewater treatment plants will not remove completely these chemicals, which will partition mainly into the sludge produced and the water effluent, generating a threat for the discharge site and the downstream areas (Kümmerer et al. 2000, Snyder et al. 2003, Ternes et al. 2004).

Findings indicate that fouling significantly impacts on membrane performance and varies the removal pattern of neutral trace organic contaminants (Agenson and Urase 2007). Xu et al. found that membrane fouling facilitated the transport of hydrophobic and hydrophilic organic contaminants through a cellulose triacetate (CTA) RO membrane (Xu et al. 2006). For trace organic contaminants (hormones), colloidal fouling in an RO membrane (CTA) caused a significant increase in the permeate concentration of these substances (Ng and Elimelech 2004). Three mechanisms have been identified to govern the influence of fouling in the rejection capacity of a NF membrane: modification of the membrane charge surface, pore restriction, and cake enhanced concentration polarization (Nghiem and Hawkes 2007). Fouling can change the surface characteristics of the membrane, either to improve or degrade the rejection capability and flux of it. There are studies that can prove both situations for NF and RO membranes (Bellona et al. 2004, Xu et al. 2006, Nghiem and Coleman 2008), but there is no literature on the precise effects of organic contaminants and their rejection by FO membranes.

Forward osmosis (FO) coupled with RO membranes have been proposed in the last years to be an efficient double barrier system to reject most of emerging contaminants (Cornelissen et al. 2008, Cath et al. 2011). Cath et al. studied the removal of micropollutants by a FO-RO system using a membrane biological reactor (MBR) and the effluent from an activated sludge tank as feed waters for the spiral wound FO membrane, and synthetic seawater as draw solution (DS). They measured the concentration of the micropollutants present in the MBR and the effluent (no micropollutants were spiked in the water), varying from 2 to 400 ng∙L⁻¹ (in some cases the compounds were below the limit of quantification). The rejections were mostly high with the FO membrane, except for Bisphenol A. When the hybrid process
was considered, very high percentages of rejection (>99%) were achieved (Cath et al. 2011).

This study focuses on the study of the difference in the rejection of a cocktail of 13 micropollutants that are known to occur in aquatic environments (Heberer 2002) (5 hydrophilic nonionic, 3 hydrophobic nonionic and 4 hydrophilic ionic micropollutants) by a clean FO membrane (inorganic solution with ionic-strength used as feed) and a fouled FO membrane (secondary wastewater effluent (SWWE) used as feed). Significantly higher-than-normal concentrations of the micropollutants are used in the experiment to mainly account for membrane adsorption after steady-state saturation (Yangali-Quintanilla et al. 2009).

3.2 Materials and methods

3.2.1 FO membrane

Hydration Technology Innovations (HTI, Scottsdale, AZ) FO membranes were used for this study. The original coupons, measuring 4” X 6”, were cut into flat-sheet membranes to fit the custom-made plate and frame cell with an area of 202 cm² for each side made out of poly (methyl methacrylate), forming a channel where the DS recirculates.

3.2.2 RO membrane

The RO membrane used is an aromatic polyamide membrane produced for desalination of brackish water by Dow-Filmtec (Midland, MI, USA) under the name BW30. The RO system consists of a positive displacement pump (Hydra-Cell, MN, USA), a crossflow filtration cell accommodating a 139 cm² membrane (SEPA CF II, Sterlitech, Kent, WA, USA), needle valves, pressure gauges, a proportional pressure relief valve and stainless steel tubing (Swagelok BV, Netherlands).

3.2.3 Source waters

For the feed water of the FO process, a SWWE was used; the effluent was collected from the Al-Ruwais wastewater treatment plant in Jeddah, Saudi Arabia, after sedimentation of the effluent of the activated sludge aeration tanks (secondary treatment). The SWWE has a pH of 7.2 and a conductivity of 3300 μS·cm⁻¹. The biological oxygen demand (BOD₅) of the wastewater effluent was 20 mg·L⁻¹, and the DOC was 5 mg·L⁻¹. The effluent received no pretreatment, except that it was kept at 4°C to prevent changes in the composition.

Seawater from the Red Sea was taken from the feeding line of the desalination plant at KAUST, Thuwal, Saudi Arabia, and was used as DS for the FO process. The water has a pH of 7.8, the dissolved organic carbon (DOC) was determined to be 1 mg·L⁻¹, the total dissolved solids (TDS) are 40,500 mg·L⁻¹, and the conductivity was 57500 μS·cm⁻¹. The raw seawater was pretreated with a 0.45 μm filter.

An inorganic synthetic solution (SS) was used to simulate the ionic-strength of a wastewater effluent, avoiding the presence of suspended solids and fouling agents. It was calculated
based on the results of the analysis done to the wastewater effluent from Jeddah following the Standard Methods (Eaton et al. 2005) for common inorganic elements such as ammonium, nitrate, nitrite, total nitrogen and phosphate.

Both feed waters and the DS were kept at 20 ±0.5 °C during the FO experiments with a chilling/heating device.

For the RO experiment to be compared to FO-LPRO, the RO feed water was prepared diluting prefiltered seawater with DI water, reaching the conductivity of the diluted draw solution (DDS) after the FO process. For the FO-LPRO, the same DDS coming from the FO process with SWWE as feed water is used in the LPRO system.

3.2.4 Experimental setup and procedure

The FO membrane cell was connected, via a gear pump (Coleparmer), to the DS container. A balance (TE6101, Sartorius AG, Germany) was used as flow recorder when connected to a computer; based on the difference in weight and the effective membrane area, the flux can be calculated. The feed water tank contained 18 L of SWWE and the DS tank held 0.5 L of pretreated seawater. The recirculation flow was set at 50 mL·min⁻¹. The recording of the weight data was activated immediately after the membrane was submerged in the feed tank; at the same time the osmotic dilution process started, because the tubing system and the cell were prefilled with DS before being in contact with the feed water. A stirring device was used to create turbulence in the feed water and achieve proper mixing. A schematic is presented in Figure 3.1.

![Figure 3.1 FO-RO system layout. TC = temperature controller, GP = gear pump, CP = conductivity probe, FR = flow recorder, PDP = positive displacement pump.](image)

The dilution experiment was performed for 24 hours; the DS increased its volume due to continuous osmosis between the feed water and the DS recirculating in the cells. The dilution cycle was repeated for 5 days by replacing the fresh DS at the beginning of each new day.
The same procedure was followed with a new membrane and the SS as feed water to test the capability of the clean membrane to reject the micropollutants (no fouling agents present in the feed water).

The operating parameters for the RO system were set as follows: feed pressure of 15 bar, permeate flow of 1.6 mL·min⁻¹, concentrate flow of 80 mL·min⁻¹ and a RO flux of 7 L·m⁻²·h⁻¹. The recovery of the process was stabilized to 2%.

3.2.5 Micropollutants stock preparation and analyses

All the micropollutants were purchased from Sigma Aldrich (Munich, Germany). The list of micropollutants used to prepare the stock solutions is presented in Table 3.1. Compounds were classified according to their speciation in water as hydrophobic when the logarithm of the distribution coefficient (log D), which refers to the ratio of the sum of the concentrations of all forms of the compound in each of the two immiscible phases forming a mixture, generally water and octanol, is higher than 2.6, and hydrophilic when log D ≤ 2.6. Ionic compounds shown in the table are negatively charged at pH 7, which was determined by using ADME/Tox Web Software. Physicochemical properties were calculated using Molecular Modeling Pro.

All of the compounds, except for the 17α-ethynilestradiol, were prepared in a stock solution of 10 mg·L⁻¹ with Milli-Q water. This organic micropollutant was diluted in 1% wt. ethanol solution, and then diluted into a concentration of 10 mg·L⁻¹ with Milli-Q water.

The organic micropollutants were spiked into the SS, SWWE and RO feed from the stock solution prepared with a concentration of 10 mg·L⁻¹. The target concentration in the FO and RO feed of each micropollutant independently was 10 μg·L⁻¹. Samples of the FO and RO feed water were taken before the experiment started, and control samples were taken before the addition of the micropollutants.

For the comparison of rejections between the SWWE and the SS, the 2nd and 3rd day samples of DDS were mixed to form a composite. Afterwards, rejection over time for the SWWE was tested between 2nd and 3rd day and 4th and 5th day composites. A sample of blank DI water was taken as control.

The micropollutants in water samples were analysed by Technologiezentrum Wasser, (TZW, Karlsruhe, Germany). The information about the procedures for analyses of micropollutants in water samples were referenced in a previous study (Yangali-Quintanilla et al. 2010a). The uncertainty of measurement was ±20%, not determined for each compound individually sampled, but determined during method validation, for all of the compounds listed in Table 3.1.
Table 3.1 | Properties of the micropollutants spiked to the feed water.

<table>
<thead>
<tr>
<th>Name</th>
<th>ID</th>
<th>MW (g·mol⁻¹)</th>
<th>log Dᵃ (pH 7)</th>
<th>Mol. length (nm)ᵇ</th>
<th>Width (nm)ᶜ</th>
<th>Depth (nm)ᵇ</th>
<th>Equiv. width (nm)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-dioxane</td>
<td>DIX</td>
<td>88</td>
<td>-0.17</td>
<td>0.71</td>
<td>0.66</td>
<td>0.52</td>
<td>0.59</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>ACT</td>
<td>151</td>
<td>0.23</td>
<td>1.14</td>
<td>0.68</td>
<td>0.41</td>
<td>0.53</td>
</tr>
<tr>
<td>Metronidazole</td>
<td>MTR</td>
<td>171</td>
<td>-0.27</td>
<td>0.93</td>
<td>0.90</td>
<td>0.48</td>
<td>0.66</td>
</tr>
<tr>
<td>Phenazone</td>
<td>PHZ</td>
<td>188</td>
<td>0.54</td>
<td>1.17</td>
<td>0.78</td>
<td>0.56</td>
<td>0.66</td>
</tr>
<tr>
<td>Caffeine</td>
<td>CFN</td>
<td>194</td>
<td>-0.45</td>
<td>0.98</td>
<td>0.87</td>
<td>0.56</td>
<td>0.70</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>BPA</td>
<td>228</td>
<td>3.86</td>
<td>1.25</td>
<td>0.83</td>
<td>0.75</td>
<td>0.79</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>CBM</td>
<td>236</td>
<td>2.58</td>
<td>1.20</td>
<td>0.92</td>
<td>0.58</td>
<td>0.73</td>
</tr>
<tr>
<td>17α-ethynilestradiol</td>
<td>EE2</td>
<td>296</td>
<td>3.98</td>
<td>1.48</td>
<td>0.87</td>
<td>0.84</td>
<td>0.85</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>IBF</td>
<td>206</td>
<td>3.97</td>
<td>1.39</td>
<td>0.73</td>
<td>0.55</td>
<td>0.64</td>
</tr>
<tr>
<td>Naproxen</td>
<td>NPX</td>
<td>230</td>
<td>0.34</td>
<td>1.37</td>
<td>0.78</td>
<td>0.75</td>
<td>0.76</td>
</tr>
<tr>
<td>Fenoprofen</td>
<td>FNP</td>
<td>242</td>
<td>0.38</td>
<td>1.16</td>
<td>0.93</td>
<td>0.74</td>
<td>0.83</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>GFB</td>
<td>250</td>
<td>2.30</td>
<td>1.58</td>
<td>0.94</td>
<td>0.65</td>
<td>0.78</td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>KTP</td>
<td>254</td>
<td>-0.13</td>
<td>1.16</td>
<td>0.92</td>
<td>0.74</td>
<td>0.83</td>
</tr>
</tbody>
</table>

ᵃ. ADME/Tox Web Software; ᵇ. Molecular Modeling Pro; ᶜ. equivalent width = (width x depth)⁰.⁵

3.2.6 FO membrane characterization

An Anton Paar Zeta Potential Analyser (Austria) was used to determine the zeta potential (ZP) of the FO membrane. It uses a clamping cell where two pieces of membrane are used to create a channel of 25 mm of length and 5 mm width, with the active layers facing each other, and then the charge of the membrane in mV is measured when an electrolyte flows through it. For this analysis, two electrolytes were used, 10 mM KCl and the SWWE previously used as feed water. The ZP is measured in the pH range in which the membrane can operate (4 to 8), so the proper injection of acid (0.1 M HCl) or base (0.1 M NaOH) is added in the titration process. The results presented in this study were calculated with the Helmholtz-Smoluchowski equation.

The contact angles of clean and fouled FO membranes were measured with a goniometer CAM200 (KSV, Finland) by using the sessile drop method. The fouled membrane samples were dried for 24 hours at room temperature (20 °C) before measurements.
Confocal laser scanning microscopy (CLSM) (LSM710 upright confocal microscope, Zeiss, Germany) was used to compare the surface of the FO membrane when different feed waters were used in the FO process.

3.3 Results and discussion

3.3.1 Zeta potential and contact angle

The ZP of the new membrane (virgin membrane) and the fouled membrane (after being used in the 5-day experiment with SWWE as feed water) was determined to account for the membrane surface charge. Figure 3.2 shows the graph for the ZP in mV for each value of pH, using different electrolytes. The new membrane has a negative charge for the experiments carried out in this study, because the pH of the SWWE is 7.6, compared to the isoelectric point of the new membrane, which is below pH 3 (using the SWWE as electrolyte).

The fouling layer after the FO process increased the negative charge of the membrane. When the membrane was in contact with the wastewater effluent, the ZP was negative, which means that the ionic micropollutants were rejected due to electrostatic repulsion. This rejection was higher when the membrane was fouled; the charge became more negative due to the presence of negatively charged radicals in the foulants, mainly coming from the NOM acids (carboxylic radicals) and polysaccharides, as described in the literature (Cho et al. 1998, Fan et al. 2001, Shim et al. 2002).

There was also an increase in the hydrophilicity of the fouled membrane, based on the measurements of the contact angle of the FO membrane in both conditions, being 58.8° ±0.3 and 49° ±3 for the clean and fouled membrane, respectively. The foulants increased
the adsorption capacity of the membrane for hydrophilic compounds, and thus, the rejection of hydrophobic neutral micropollutants was higher when the membrane was fouled.

3.3.2 Rejection of micropollutants by FO

Rejections of the FO and RO membranes were calculated with Equation 3.1.

$$\text{Rejection} = \left(1 - \frac{C}{C_0}\right) \times 100$$  \hspace{1cm} (Eq. 3.1)

For FO rejection when the feed water (SWWE or SS) was spiked with the micropollutants, $C_0$ is the concentration of the feed water, and $C$ is the concentration of the DDS. For the RO rejection, the $C_0$ is the concentration of the RO feed water, and the $C$ is the concentration of the RO permeate. For the FO-LPRO process, the initial FO feed water concentration is $C_0$ and $C$ is the concentration of the RO permeate.

Figure 3.3 shows the comparison for the rejection of the 13 micropollutants by a clean FO membrane and a fouled FO membrane for the composite samples of the 2nd and 3rd day of experiments. Figure 3.4 illustrates and summarizes the rejection mechanisms of the FO membrane. It can be noticed that for the hydrophilic neutral compounds the rejection with the SS as feed water (clean membrane) is higher than the rejection when SWWE is used as feed (fouled membrane), ranging from 2% difference for Dioxane to 6% difference for Phenazone, except for Caffeine. Two hypothesis might explain these results: i) the increase in surface charge might potentially result in a higher molecular weight cut-off (MWCO) due to membrane swelling, as described by Xu et al. for NF and RO membranes, reducing the rejection of the hydrophilic neutral compounds, and ii) higher hydrophilicity generated by the fouling layer on the membrane may allow a higher amount of micropollutants to partition through the membrane, and eventually, decrease the rejection (shown in Figure 3.4a,b) (Xu et al. 2006). This hypothesis is more significant than the first one, because it is based independently from the type of membrane used and focuses on the fouling layer instead, which is certainly occurring. In the case of Caffeine, the rejection for the fouled membrane increases 15% compared to the clean membrane; this can be explained by the high hydrophilicity of the compound (log D - 0.45), being absorbed by the cake layer formed in the membrane (mainly hydrophilic) and thus, preventing the compound from partitioning through the membrane into the DS, forming a double-barrier-like system. Along with this hypothesis, the MWCO of the membrane (≈200 Da) is really close to the MW of this compound, and the fouls can be blocking the pores of the membrane, increasing the rejection of Caffeine with the fouled membrane. For the hydrophobic neutrals, the increase in rejections goes from 8.7% for Bisphenol A, to a 9.8% for Carbamazepine. In the case of the ionic contaminants, the increase goes from 0.4% for Naproxen, to 6% for Ibuprofen when the membrane is fouled.

The increment in the rejection of hydrophobic neutral compounds is due to the higher hydrophilicity of the membrane when the fouling cake layer is present; this phenomenon is also associated with an increased adsorption capacity (for hydrophilic compounds) and
reduced mass transport capacity (diffusion and partitioning) of hydrophobic compounds through the fouled membrane (Figure 3.4c,d). For the ionic compounds, the negative charge of the membrane is greater when fouled (described in section 3.3.1), increasing eventually the electrostatic repulsion (Donnan exclusion) between the negative charge of the membrane surface (Figure 3.4e,f) as mentioned by Verliefde et al. (2008) and Xu et al. (2006) and the negative charge of the compound at pH 7.3. Nevertheless, the rejection is still low for hydrophobic neutral compounds, being Bisphenol A again the lowest with 48.7% rejection with the fouling layer.

Figure 3.3 | Rejection of micropollutants by a clean and fouled FO membrane.

Figure 3.4 | Rejection mechanisms of different types of micropollutants by a clean and fouled FO membrane. a) and b) For the hydrophilic neutral substances, the fouled membrane is able to reject less efficiently the contaminants due to membrane swelling. c) and d) For the hydrophobic compounds, rejection by the fouled membrane is increased due
to reduced mass transport capacity of hydrophobic compounds. e) and f) For the hydrophilic ionic compounds, the fouling layer increases the negative charge of the membrane, increasing the rejection of these compounds.

Figure 3.5 shows images of the active layer of a FO membrane in different feed waters. Figure 3.5a corresponds to a CLSM image of the FO membrane used with SS as feed water, where the support mesh can be clearly distinguished and no fouling is present on the surface of the membrane. Nevertheless, when SWWE is used as feed for the FO process, the foulants start to accumulate on the surface of the membrane, forming a cake layer clearly identifiable in the CLSM image on Figure 3.5b, covering almost completely the support mesh. Consequently, rejection hypothesis based on the fouling layer formation are encouraged in this study.

Figure 3.6 compares the rejection percentages for the RO process and the coupled FO-RO process. For the RO process alone, the rejection of most compounds is higher than 99%, except for the two smallest micropollutants, Dioxane (67.9%) and Acetaminophen (89.4%), which have a MW lower or equal than the MWCO of the RO membrane, which can be estimated as 150Da. When the RO processes is coupled to the FO, the results for rejection can go as high as 89.1% for Dioxane, 96.3% for Acetaminophen, 98.9% for Metronidazole and for the rest of the compounds the rejection was higher than 99%.
Figure 3.6 | Rejection of micropollutants by an RO membrane and a coupled FO-LPRO system.

These results can be compared with the results presented by Cath et al. (2011) described in section 3.1. In the case of the experiments mentioned in the present study, the concentrations of the spiked MPs were in the range of 1 to 10 μg·L⁻¹, at least 2 orders of magnitude higher than those used by Cath et al., and there was no crossflow velocity on the feed side, which means a higher concentration polarization effect, leading to the accumulation of micropollutants in the membrane surface; thereby, the rejections achieved from the single FO process were lower. Nevertheless, when the coupled process was considered, the results of this work and that of Cath et al. were similar, achieving very high percentages of rejection (>99%).

Figure 3.7 shows the rejection of micropollutants for a composite sample of the 2nd and 3rd day DDS of the FO process with SWWE as feed, and the rejection percentage for a composite sample of the 4th and 5th day DDS with the same feed water. Figure 3.7a shows the hydrophilic neutral pollutants; note that for all of them, excluding Acetaminophen, the rejection decreases over time due to the formation of the fouling layer, which increases the hydrophilicity of the surface and promotes partitioning of these contaminants into the DS side. For Figure 3.7b, rejection of hydrophobic neutrals decreases over time, even for Carbamazepine, which can have the same decreasing tendency once the experimental error is considered. The cake layer formed in the surface of the membrane increases the effect of external concentration polarization (ECP), and even though the rejection of the 4th and 5th day composite is still higher than the rejection of the clean membrane (SS as feed water), ECP plays an important role in the reduction of rejection over time for the hydrophobic neutral compounds. Figure 3.7c shows an increase in the rejection for hydrophilic ionic micropollutants over time, which was expected due to the formation of the fouling layer in the membrane and the change in the surface charge over time.
Rejection of micropollutants by FO membranes

Figure 3.7 | Rejection of micropollutants on the 2\textsuperscript{nd} and 3\textsuperscript{rd} day and rejection on the 4\textsuperscript{th} and 5\textsuperscript{th} day of the FO process. a) Hydrophilic neutrals, b) hydrophobic neutrals, and c) hydrophilic ionic.

3.4 Conclusions

- Hydrophilic ionic compounds were rejected more effectively when the FO membrane was fouled due to the higher negative charge of the fouled membrane, due to the presence of negatively charged radicals in the foulants. Hydrophobic neutral compounds had higher rejections with the fouled membrane due to the higher hydrophilicity induced by the fouling layer, and the increase in adsorption capacity of hydrophilic compounds reducing passage of hydrophobic compounds. Rejection of hydrophilic neutral compounds decreased an average of 5% with the fouled membrane, caused by membrane swelling which results in a higher MWCO, and the increased adsorption capacity for hydrophilic compounds.
In real conditions of water reuse applications, using SWWE as feed and seawater as DS, FO membranes were able to reject most of the micropollutants; rejections were moderate for hydrophilic neutral compounds (44 – 95%), moderate for hydrophobic neutral contaminants (48 – 92%), and high for the hydrophilic ionic micropollutants (96 – 99%).

FO coupled with LPRO was effective rejecting low molecular weight hydrophilic neutral micropollutants, with rejections that went beyond 89.1%. For the rest of the compounds, rejections were greater than 99%. Therefore, the coupled FO-LPRO system proves to be an effective double barrier against the 13 micropollutants tested.

References


ORGANIC FOULING AND CLEANING
Chapter 4

Identification of organic fouling in FO membranes

Abstract

The study of forward osmosis (FO) membranes has increased due to the already demonstrated advantages compared to high-energy membrane processes such as reverse osmosis (RO). This research focuses on characterization of the natural organic matter (NOM) fraction causing fouling on the active layer (AL) of a FO membrane in a novel plate and frame module configuration, facing secondary wastewater effluent as a feed solution (FS) and seawater used as a draw solution (DS). In addition, transparent exopolymer particles (TEP) were observed on the support layer (SL) of the membrane in contact with the DS. The NOM fouling layer, after characterizing the water samples and membranes used, was found to be composed of biopolymers and protein-like substances, which adversely affect the flux of water through the FO membrane. However, NOM fouling showed high reversibility, up to 90% when air scouring for 15 minutes is used as a cleaning technique. The irreversible fouling in this work was found to be 8.2% after chemical cleaning. On the support layer of the membrane, TEP formed clusters clearly identifiable with an optical microscope and a TEP-specific dye. Chemical cleaning with 1% NaOCl for 10 minutes proved to be the most effective method to remove TEP.

Identification of organic fouling in FO membranes

4.1 Introduction

Forward osmosis (FO), an osmotic-driven membrane process, has been gaining attention for being a low-energy alternative for several applications usually performed by pressure-driven membranes, such as reverse osmosis (RO) and nanofiltration (NF). Recent studies have focused on the use of forward osmosis (FO) membranes for oil/gas drilling wastewater reclamation, landfill leachate treatment (Lambert and Lampi 2010) and water desalination (Cath et al. 2010).

Natural organic matter (NOM) found in water has been shown to be a serious fouling agent for RO and NF membranes (Hong and Elimelech 1997, Cho et al. 2000, Lee et al. 2004, Lee et al. 2010a). Holloway et al. (2007) compared the fouling behavior of FO and RO for wastewater concentrate treatment, and demonstrated a slower flux decline rate in FO than in RO (Holloway et al. 2007). Mi et al. (2010) studied organic fouling of FO membranes caused by sodium alginate (simulating polysaccharides in wastewater). They showed that for osmotic pressure processes, where there is no hydraulic pressure, fouling is highly reversible using a cleaning solution of deionized (DI) water with 50 mM of NaCl as feed water and 4 M NaCl as draw solution (DS); it was even suggested that chemical cleaning is not needed (Mi and Elimelech 2010). High recovery of permeate fluxes was also demonstrated in Lee's et al. (2010) research, using mainly an increased crossflow velocity in the feed stream to clean the organic fouling (composed of alginate, humic acid and bovine serum albumin) of a FO membrane, without employing chemical cleaning (Lee et al. 2010a).

Transparent exopolymer particles (TEP) are deformable, gel-like, transparent particles of acid mucopolysaccharides suspended in the water mass that appear in many forms and are ubiquitous to freshwater and marine environments. TEP can be divided according to its size as particulate TEP (>0.4 μm) and colloidal TEP, usually in a range of 0.05 to 0.4 μm (Villacorte et al. 2009). TEP are among the biopolymers that might be associated with fouling on the support layer (SL) of an FO membrane in a configuration of active layer facing the feed solution (AL-FS) when using seawater as a DS; several studies suggest that these particles are responsible for biofouling of membranes (Bar-Zeev et al. 2009). Significantly larger concentrations of TEP are found in seawater compared to wastewater effluents and diverse raw fresh waters (Villacorte et al. 2009, Berman et al. 2011). Therefore, we may hypothesize that TEP fouling of the FO membrane can occur when seawater is involved.

There has been a significant amount of research regarding chemical cleaning of RO and NF membranes. Experiments performed by Hong and Elimelech (1997) identified that ethylenediaminetetraacetic acid (EDTA) treatment of NOM-fouled NF membranes improves the cleaning efficiency significantly (Hong and Elimelech 1997). In another study, bovine serum albumin (BSA) fouled membranes were treated with as solution of NaOCl (100 ppm), effectively removing the protein (Kuzmenko et al. 2005). Unfortunately, there are no studies that refer to such processes applied to an FO fouled membrane; this is particularly important when referring to TEP fouling, which cannot be easily controlled by feed water disinfection or microfiltration (Bar-Zeev et al. 2009, Villacorte et al. 2009, Berman et al. 2011).
This research is focused on identification of the NOM fractions that might cause fouling of the active layer of a FO membrane used in an AL-FS configuration, fed with a secondary wastewater effluent (SWWE), using seawater as DS. Additionally, the study proved the presence of TEP fouling on the support layer of a FO membrane. A comparison of cleaning techniques was performed for both sides of the membrane, determining the reversibility of the fouling on the active layer (AL) of the membrane, and cleaning performance for the SL.

4.2 Experimental

4.2.1 FO membranes and cell configuration

The FO membranes used in this study were provided by Hydration Technology Innovations (HTI, Scottsdale, AZ). The HTI membrane was originally received as flat sheet coupons, each one measuring 4” × 6”, and then cut into the proper size for the membrane cell. The FO membrane is made of cellulose triacetate (CTA) embedded in a polyester mesh support, with a thickness of 30 to 50 μm (Tang et al. 2010), making it thinner than a thin-film composite (TFC) with porous support layer membrane (NF/RO) (approximate thickness of 125 μm (Yip et al. 2010)), which provides the membrane with a higher flux in FO mode. The structural parameter S, defined as the relation between the support layer thickness (t_s) and the tortuosity (τ) over the porosity (ε) of the membrane (S = t_sτ/ε), is significantly higher for a TFC-NF/RO membrane (S = 2,155 μm) compared to the HTI FO membrane (S = 595 μm) (Yip et al. 2010); this difference translates into a significantly higher resistance to mass transfer for the former one, reducing the flux of water through the membrane, leading to a higher performance of the HTI FO membrane.

The membrane cell was a custom-made plate and frame assembly made of poly (methyl methacrylate) (PMMA). The cell can hold two flat-sheet membranes, each with an area of 202 cm², forming a channel with a cross section of 1.5 cm width x 9 cm height. No spacer was used in the experiments. The recovery of the FO process for these experiments was 7%, however, recovery can be further increased (~50%) by changing the configuration of the feed water tank or increasing the number of cells immersed.

The AL of the membrane was facing the FO feed, leaving the support side in contact with the high osmotic pressure solution (seawater, DS). This configuration (AL-FS) has been proven to be the most effective in preventing fouling of an FO membrane (Cornelissen et al. 2008, Mi and Elimelech 2008, Wang et al. 2010c).

4.2.2 Water samples

The feed for the FO process was a SWWE from the Al-Ruwais wastewater treatment plant in the city of Jeddah, Saudi Arabia, which uses activated sludge aeration tanks after primary treatment. The biological oxygen demand (BOD₅) of the wastewater effluent was 20 mg·L⁻¹, the chemical oxygen demand (COD) was 20 mg·L⁻¹, the total organic carbon (TOC) was 4.60 mg·L⁻¹, the pH was 7.3, the conductivity was 2087 μS·cm⁻¹ and the osmotic pressure was
0.35 bar. The total suspended solids (TSS) and volatile suspended solids (VSS) of the effluent were 2.4 and 2.1 mg·L⁻¹, respectively.

For the high osmotic pressure solution or DS, pre-filtered (0.45 μm pore size) Red Sea water was used as filtered seawater (FSW); seawater was obtained from the seawater pipeline of the RO plant operating at KAUST. The value for total dissolved solids (TDS) was 40,500 mg·L⁻¹, the conductivity was 54,300 μS·cm⁻¹ and the osmotic pressure was 30.3 bar. The pH of the water was 7.8 and the dissolved organic carbon (DOC) was 1.12 mg·L⁻¹. Both the SWWE and the FSW, as well as the diluted draw solution (DDS) characterization can be found in Table 4.1.

Table 4.1 | Wastewater effluent, filtered seawater and diluted seawater characteristics

<table>
<thead>
<tr>
<th></th>
<th>SWWE</th>
<th>FSW</th>
<th>DDS</th>
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</tr>
<tr>
<td>Barium (mg·L⁻¹)</td>
<td>0</td>
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</tr>
</tbody>
</table>

4.2.3 FO membrane fouling procedure

The FO membrane cell was immersed in a feed tank, connected with tubing to the DS container; this DS was recirculated by a gear pump (GP) (Coleparmer) inside the cell formed by the membranes and frame. Figure 4.1 shows a detailed scheme of the setup.
At the beginning, 500 mL of seawater were poured in the DS tank; at the same time, the FO feed tank was filled with 18 L of SWWE. The two flat sheet FO membranes were set in the membrane cell, which was then immersed in the FO tank. The recirculation pump was started at a flow rate of 50 mL·min⁻¹ (transverse velocity for the DS of 0.06 cm·s⁻¹), along with the recording devices for flow and conductivity. This transverse flow inside the channel allowed the DS water to extract water from the feed, a process driven only by osmotic difference; no negative pressure inside the cells was observed during the time of recirculation of the DS. The dilution process took 24 hours, increasing the level in the DS tank, while the SWWE was concentrated (volume decreased). A stirring device was used to create turbulence in the feed water and achieve proper mixing with a velocity gradient of about 50 s⁻¹. The temperature of both FO feed and DS was maintained at 20±0.5 °C using a temperature controller (TC) with submergible stainless steel coils.

Figure 4.1 | FO system layout.

A balance (TE6101, Sartorius AG, Göttingen, Germany) was used as flow monitor (FM) when connected to a computer, for the purpose of comparing the flux recovery obtained with the different cleaning techniques implemented. This was done by measuring the difference in weight for the DS tank over an interval of time, resulting in the flow of water through the membrane. As the total area of the membrane used is known, flux can readily be calculated.

An evaporator (Rotavapor R-210, Buchi, Switzerland) was used to concentrate SWWE at 30°C without involving a membrane process, in order to identify and analyze the difference in concentrated feed water (CFW) resulting from the FO process (sample taken on the last day of FO operation) and the evaporation process, and further determine which fraction of the NOM contributed to the fouling. This sample was referred to as evaporated wastewater effluent (EWWE).

4.2.4 NOM characterization

A Liquid Chromatograph coupled with Organic Carbon Detection analyser (LC-OCD) (Model 8, DOC LABOR, Germany) was used to analyse the organic carbon content of the water samples, following the procedure established by Huber et al. (2011). The process consists of
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size-exclusion chromatography columns which separates the organic carbon into several fractions based on size and hydrophobic and ionogenic characteristics. 1000 μL of wastewater effluent samples are used with a dilution of 4:1. For seawater samples, the amount of water is usually 2000 μL, with no dilution factor (1:1). Results were calculated using peak area integration.

The recommended DOC concentration for any sample injected into the LC-OCD analyzer should not be higher than 5 mg·L⁻¹. In this case, a target of 2 mg·L⁻¹ of DOC was used for all of the samples, based on previous analyses of TOC and DOC.

An ultrasonic (US) bath was used for 30 minutes to extract the NOM fraction that was attached to the surface of a 2 cm × 2 cm sample of fouled membrane. The same US procedure was followed for a new FO membrane that was used as control, as well as for the SWWE and DS (filtered seawater).

3-Dimensional Fluorescence Excitation Emission Matrixes (3-D FEEM) were obtained with a Fluoromax-4 Spectrofluorometer (Horiba, USA) for the different water samples. The preparation of the samples consisted only in the filtration of the water with a 0.45 μm filter. The results are interpreted based on the identification of DOC fractions in previous spectrofluorescence studies (Amy et al. 2010). No pH adjustment was necessary because all of the samples tested were in a narrow pH range (7.3 to 7.8).

The fouling on both sides of the FO membrane surface was visually analyzed by Scanning Electron Microscopy (SEM) (Nova NanoSEM, FEI, USA).

In order to analyze the presence of TEP on the FO membrane, Alcian Blue dye was used to stain the particles and make them visible by microscopy. The Villacorte et al. (2009) protocol for preparing the cationic dye Alcian Blue was employed (Villacorte et al. 2009). An Olympus BX61 Motorized Transmitted and Reflected Light Research Microscope (Japan) was used with different objectives (60x and 100x) to take images of a fouled membrane after the 10-day cycle FO process.

The cut pieces of membrane were submerged in a petri dish with DI water to rinse for 2 minutes; afterwards, the pieces were immersed in a solution of Alcian Blue for 10 minutes to allow the dye to be absorbed by the TEP; finally, a second rinse was made with DI water to remove excess stain before putting the samples under the microscope.

A qualitative analysis of the images was realized; a quantitative analysis based on grayscale images was not possible because of the interference of the support mesh (dark color) with the stained TEP cluster.

4.2.6 FO membrane cleaning

4.2.6.1 Air scouring cleaning
Cleaning with air scouring was performed for 15 minutes with two air-stone diffusers (one on each side of the cell), at a cross flow rate of 4,166 mg·L⁻¹ in the feed water tank, resulting in 3.13 liters of air per liter of feed water. This flow rate was considered to prevent damage of the membrane and, at the same time from previous trials, to remove macroscopic fouling deposited on the surface of the membrane. Two different conditions were tested to determine the reversible fouling of the FO membrane with air scouring. First, the membrane was cleaned inside the CFW; afterwards, a second cleaning was done with DI water as feed and the flux was measured again. Both were in situ cleaning techniques.

4.2.6.2 Chemical cleaning

For the active layer of the membrane, which was in contact with the SWWE, the washing solution contained 0.8% sodium ethylenediaminetetraacetic acid (EDTA) and 1% Alconox, a detergent composed of sodium dodecylbenzenesulfonate (10-30%), sodium carbonate (7-13%), tetrasodium pyrophosphate (10-30%) and sodium phosphate (10-30%), adapted from cleaning protocols for ROGA RO spiral wound elements with CTA membranes. The cleaning was performed in situ, leaving the membrane cell immersed for 5 minutes on each side in the solution and rinsing both the tank and the cell with tap water; meanwhile, DI was recirculated instead of DS to prevent membrane drying. The pH of the solution was set to 8.0 to prevent membrane damage (hydrolysis of CTA) based on manufacturer specifications.

The cleaning potential of the two solutions was tested to analyze the best option for TEP removal on the support side of the FO membrane; this cleaning was not performed in situ. The first solution (Solution 1) had the same composition as the one used for the chemical cleaning of the membrane fouling on the active layer. The second one contained 1% aqueous solution of NaOCl (pH 7.6) (Solution 2). The membrane was submerged in a petri dish with cleaning solution before staining the TEP with the dye, using two pieces of the fouled membrane, one for each solution. After being submerged for 10 minutes, a quick 1-minute rinse with DI water was done before the dyeing process.

4.3 Results and discussion

4.3.1 FO membrane process

Figure 4.2 shows representative results for the normalized flux of the FO membrane process for each cycle (day) of an experiment. The membrane was tested with DI as the feed and pre-filtered seawater as DS for the first day. After this, SWWE was used as feed, running the experiment for 11 days (day 2 to 12 in Figure 4.2) with a recovery of 7% per cycle, before the first cleaning (membrane cell submerged in the CFW) with air scouring for 15 minutes (day 13). The next day (day 14), the feed water was changed to DI water, and air scouring was performed again for the same period of time. Chemical cleaning was made with the cleaning solution described in section 4.2.6.2 (day 15), after which a test with DI water as feed was made to determine the flux recovery.
After 11 days of experiment with the SWWE as feed (day 2 to 12 in Figure 4.2), the fluxes of the FO process varied between 7.2 and 2.0 L·m⁻²·h⁻¹. The draw solution was diluted, on average, from 51,500 μS·cm⁻¹ to 22,500 μS·cm⁻¹ in one cycle (1 day). The average flux was 3.42 L·m⁻²·h⁻¹. The flux decline of the FO process after 11 days was 25%, sufficient to start the cleaning process discussed in section 4.3.4.

![Figure 4.2](image-url) Flux decline of the FO process.

The driving force for the FO process was determined for the first day of this 11-cycle experiment (day 2 in Figure 4.2), considering the osmotic difference of the feed water and the DS, which was 29.95 bar. The driving force at the end of day 2 was only 9.05 bar, which explains part of the flux decline observed. The values for the ideal flux were calculated considering the internal concentration polarization (ICP) model used by Gray et al. (2006), assuming a resistance of solute diffusion for the seawater (K) of 10.26 d·m⁻¹ obtained from a previous work using the same DS (Yangali-Quintanilla et al. 2011), and water and solute permeability coefficients of the active layer of the membrane A and B of 0.027 m·atm⁻¹·d⁻¹ and 0.011 m·d⁻¹, respectively. The results for the modelled and the observed flux vary significantly (up to 22%), showing that fouling is responsible for a fraction of the reduced flux. Therefore, upon further analysis, calculations for recovery can be related to the flux decline resulting from fouling, not taking into consideration the loss of osmotic pressure difference, which is present in all of the FO cycles.

### 4.3.2 Fouling of the active layer of FO membrane

Figure 4.3a shows the chromatograms for a sample of CFW and EWWE, and Figure 4.3b for a sample of DS and DDS. The peak in the organic carbon curve representing biopolymers (polysaccharides and proteins) is larger in the EWWE than in the CFW, suggesting that these...
compounds are not present in the feed water remaining after the FO process. The chromatograms for the DS and DDS samples show that there is no transport of biopolymers through the membrane from the feed to the DS. There is a significant difference in concentration for the biopolymers comparing the CFW and the EWWE, but not for the remainder of the CDOC fractions. For the CFW, the biopolymers were present at 1.44 mg·L⁻¹, while the corresponding peak for the EWWE showed 2.52 mg·L⁻¹. The humic substances were present at concentrations of 5.40 and 5.25 mg·L⁻¹, respectively; building blocks were also similar in concentration for both samples, with 2.64 and 2.51 mg·L⁻¹, accordingly; and so are the low molecular weight (LMW) neutrals (2.29 and 2.37 mg·L⁻¹, respectively). These fractions show a slight increase in the CFW because of the volume of effluent concentrated by the FO process in relation to the evaporated volume (EWWE). The DDS showed a low concentration of biopolymers compared to the DS, 0.05 mg·L⁻¹ and 0.08 mg·L⁻¹, respectively, supporting the hypothesis that biopolymers were not transported through the membrane, and thus only the original concentration of biopolymers in the seawater was being diluted when the FO process took place. However, for the LMW neutrals, the concentration in the DDS is considerably higher than the concentration in the DS (0.74 to 0.11 mg·L⁻¹), because this CDOC fraction is transported from the feed water through the membrane due to the size of the compounds, which are smaller than the molecular weight cutoff (MWCO) of the membrane, established in previous studies as 200 Da (Valladares Linares et al. 2011).

Figure 4.3c shows the organic carbon curve after the extraction of the foulants from the membrane with an ultrasonic bath, comparing it with the control samples (new piece of membrane, SWWE and DS). A single biopolymers peak can be observed for the curve of the fouled membrane extraction sample, supporting the hypothesis that these substances were forming a fouling layer which attached to the surface membrane. The rest of the chromatogram is very similar to the new membrane control sample, which confirms that the remainders of the CDOC fractions have little or no impact on the fouling layer formation. Moreover, the new FO membrane releases LMW neutrals as seen in the control curve, even after being submerged and washed with DI water; these are presumably preservatives which are released to the DDS and thus are not present in the fouled membrane extraction sample.
Figure 4.3 | LC-OCD chromatograms for a) CFW and EWWE; b) DS and DDS; c) fouling extraction of the used FO membrane compared to a virgin FO membrane, feed water and draw solution.
Figure 4.4 shows the 3-D FEEM resulting from the analysis of the SWWE, CFW and EWWE on the same intensity scale, which corroborates the results previously obtained with the LC-OCD analysis. Likewise, the 3-D FEEM show a peak in the protein-like substances (emission range 320-350 nm, excitation range 270-280 nm (Amy et al. 2010)), which is likely associated with biopolymers, in the EWWE that is not detectable in the CFW, suggesting that this NOM fraction is not present in the feed water, and it is not being transported through the membrane to the DS (based on LC-OCD results). Therefore, biopolymers (protein-like substances) are likely responsible for the FO membrane fouling.

The results from the LC-OCD analysis combined with the 3-D FEEM evidence suggest that biopolymers and protein-like substances are accumulating on the active layer of the membrane, thus being partially responsible of the fouling of the FO membrane when SWWE is being fed to the process. Figure 4.5a,b show a SEM image of the active layer of the fouled membrane, where a uniform fouling layer is covering the surface, composed of bacteria as well as biopolymers and protein-like substances. These DOC fractions have been previously reported to be good predictors of fouling in low and high pressure membranes (Lee et al. 2004), and have also been identified as important foulant agents in RO (Li et al. 2007) and membrane bioreactor (MBR) systems (Wang and Li 2008).
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4.3.3 Fouling of the support layer of FO membrane

TEP analysis was made on both the active and support layer of the membrane with microscopy and proper dyes. Figure 4.6a shows a picture of the support layer of a used FO membrane after the dyeing process (protocol in section 4.2.5). Clusters of TEP were identified as foulants on this side of the membrane; there were large concentrations of these particles accumulating on the support side. This observation is consistent with the SEM images in Figure 4.5c,d, which show the support layer of the fouled membrane covered with bacteria and gel-like substances. The mechanism of TEP fouling may involve the adhesion of these particles to the membrane surface due to the stickiness of the substances forming TEP: polysaccharides, proteins, and nucleic acids; this mechanism may be coupled with bridging of TEP and calcium ions found in the seawater. Previous studies have confirmed that TEP presence is enhanced by silica deposits on the surface when the membranes are in contact with seawater (Li et al. 2012a).

For the active layer, there was no attachment of TEP to the surface (Figure 4.6b), suggesting that the SWWE does not contain a significant amount of these particles or that they might not be depositing on the membrane surface. Based on this observations and the fact that the support layer is facing the DS (AL-FS orientation), the identified TEP was derived from the seawater, similar to other TEP studies mentioned in the literature (Villacorte et al. 2009).

Figure 4.5 | SEM images of a fouled FO membrane. a) and b) NOM fouling on the active layer; c) and d) TEP fouling on the support layer.
Problems associated with TEP fouling of either filtration or RO desalination membranes are attributable to these particles, rather than from bacteria in the water, meaning that disinfection of the feed water would not be useful to prevent TEP from causing fouling (Bar-Zeev et al. 2009, Berman et al. 2011), and microfiltration would not significantly remove colloidal TEP (Villacorte et al. 2009). Consequently, section 4.3.4 describes the results obtained for the two cleaning solutions proposed for TEP removal.

Figure 4.6 | Bright light microscopy images of a fouled FO membrane stained with Alcian Blue dye. a) TEP fouling on the support layer (60×); b) active layer (60×); c) support layer of a cleaned FO membrane (100×) with Solution 1; d) support layer of a cleaned FO membrane (60×) with Solution 2.

4.3.4 Cleaning of the FO membrane – active layer

Equation 4.1 was used to determine flux recovery:

\[
\text{Flux recovery (\%)} = \frac{J_f - J_i}{J_i} \times 100
\]

where \(J_i\) is the average flux recorded for the initial or referential cycle and \(J_f\) is the average flux recorded for a cycle run after a certain cleaning technique was used. The flux recovery for the air scouring realized within the CFW (day 13 in Figure 4.2) was 90.8%. For the air scouring cleaning with DI water, the recovery was 88.9% (day 14 in Figure 4.2). It is important to note that the initial flux (\(J_i\)) for the CFW cleaning was obtained with SWWE as feed (day 2 in Figure 4.2); on the other hand, the initial flux (\(J_i\)) for the DI cleaning was obtained with DI as feed (day 1 in Figure 4.2), hence, the difference in recovery. Nevertheless, both results indicate a high reversibility of the NOM fouling. This high reversibility may due to the lack of hydraulic pressure on the FO process which results in the
formation of a loose foulant layer on the surface of the membrane, which was also described by Mi et al. (2010) in a previous study (2010).

The increase in flux recovery after the chemical cleaning (DI as feed) was less than 3% of the original flux, revealing that the hydraulically reversible fouling represented 90.8% and the chemically reversible fouling 91.8% of the total NOM-biopolymers fouling of the FO membrane. Therefore, the flux that could not be recovered, or the irreversible fouling considering cleaning of the active layer, accounts for only 8.2%, which may be attributed to TEP fouling of the support layer.

4.3.5 Cleaning of the FO membrane – support layer

As mentioned before, existing pretreatment against TEP fouling in water systems is generally ineffective (Villacorte et al. 2009), thus, the effectiveness of two cleaning solutions was compared.

Figure 4.6c shows the FO membrane support layer after chemical cleaning with Solution 1. The solution removed the large TEP clusters from the membrane, segregating the clusters into small particles, cleaning most of the observed membrane specimen. For Solution 2, almost no TEP could be found on the membrane (Figure 4.6d). Note that, unlike Solution 1, in this case there are no small particles left after the cleaning, suggesting that the effectiveness of Solution 2 is greater.

TEP fouling, taking into consideration the results for reversible and irreversible NOM-biopolymers fouling, was equal to or less than 8.2% of the total fouling of the FO membrane. After the membrane was cut for TEP identification and cleaning, flux recovery tests could not be performed. Future studies should determine the effectiveness of the chemical cleaning supported with flux decline and recovery experiments.

4.4 Conclusions

LC-OCD chromatograms and the 3-D FEEM images suggest that biopolymers and protein-like substances, present in the feed water (SWWE), are forming a fouling layer in the thin film of the FO membrane, reducing the flux and thus, affecting the efficiency of the seawater dilution process. TEP was identified in the support layer of the FO membrane in contact with the seawater, which contains a significant amount of these particles, reducing the flux of the FO membrane. After cleaning of the active layer, the flux recovery when air scouring is used for 15 minutes (membrane cell submerged in SWWE) is around 90%; similar results can be obtained when the membrane cell is immersed in DI water. Chemical cleaning of the active layer will barely increase the flux recovery by 3%, narrowing the irreversible fouling to 8.2%. Chemical cleaning of the support layer with a solution of 1% NaOCl during 10 minutes proved to be effective in removing the TEP when the membrane is detached from the frame.
Chapter 4

References


Chapter 5

Effect of cleaning methods to remove organic fouling

Abstract

Forward osmosis (FO) is an emerging technology which can be applied in water reuse applications. Osmosis is a natural process that involves less energy consumption than reverse osmosis (RO), and therefore can be applied as a dilution process before low pressure RO; it is expected to compete favorably against current advanced water reuse technologies that use microfiltration/ultrafiltration and RO. The focus of this research was to assess the efficiency of different cleaning procedures to remove fouling from the surface of a FO membrane during the operation of a submerged system working in FO-mode (active layer (AL) facing feed solution) intended for secondary wastewater effluent (SWWE) recovery, using seawater as draw solution, which will be diluted and can further be fed to a low pressure RO unit to produce fresh water. Natural organic matter (NOM) fouling was expected to affect the AL, while, for the support layer (SL), transparent exopolymer particles (TEP) were used as indicators of fouling due to their stickiness and propensity to enhance the attachment of other foulants in seawater on the membrane surface. The composition of the NOM fouling layer was determined after proper characterization with a liquid chromatograph coupled with organic carbon detection (LC-OCD), showing biopolymers and protein-like substances as the main constituents. NOM fouling showed high hydraulic reversibility after a 25% flux decline was observed, up to 89.5% when in situ air scouring for 15 minutes was used as a cleaning technique. Chemical cleaning with a mixture of Alconox, an industrial detergent containing phosphates, and sodium EDTA showed to increase the reversibility (93.6%). Osmotic backwash using a 4% NaCl solution and DI water proved to be ineffective to recover flux due to the salt diffusion phenomena occurring at the AL. Part of the flux that could not be recovered is attributable to TEP fouling on the SL, which forms clusters clearly identifiable with an optical microscope and TEP-specific dyeing/staining of the membrane. Two solutions were tested to clean in-place the SL: a 1% NaOCl solution and the same detergent solution used to clean the AL. The former agent compromised the integrity of the FO membrane, as proved with flux and conductivity measurements; 94.5% of flux was recovered with the latter agent, showing that the chemically irreversible fouling for the FO membrane is on the order of 5.5%, which might be associated with the adsorption of biopolymers on the AL and some TEP residuals on the SL. Physical cleaning (air scouring) of the AL proved to be the most effective way to control fouling.

Published as: Valladares Linares et al. 2013, Cleaning protocol for a FO membrane fouled in wastewater reuse, Desalination and Water Treatment 51:4821-4824
5.1 Introduction

Membrane processes are now commonly used in water reuse and seawater desalination. Forward osmosis (FO) represents a new opportunity to solve the global water crisis because of its low-energy requirement compared to high-energy processes, such as reverse osmosis (RO) or nanofiltration (NF). Previous studies investigated fouling in FO membranes (Shibutani et al. 2011, Yangali-Quintanilla et al. 2011), showing that for low pressure osmotic processes, fouling is highly reversible. Previous work by Zhang et al. (2006) has determined that extracellular substances (EPS) are the first step of fouling, comprising polysaccharides and proteins mainly, and are considered to be precursors of transparent exopolymer particles (TEP). TEP fouling cannot be controlled by feed water disinfection or microfiltration (Bar-Zeev et al. 2009, Villacorte et al. 2009, Berman et al. 2011), thus the need for an effective cleaning method.

This research focuses on the cleaning efficiency of several methods to remove NOM-fouling on the active layer (AL) of a FO membrane immersed in a municipal secondary wastewater effluent (SWWE). Seawater was used as draw solution (DS). In addition, identification and cleaning of TEP on both the active and the support layer (SL) of the membrane were performed.

5.2 Materials and Methods

The FO membranes used for this study are made of cellulose triacetate (CTA) (HTI, Scottsdale, AZ, USA). The AL of the membrane was facing the FO feed, leaving the SL in contact with the DS. This configuration (FO mode) has been proven to be the most effective in preventing fouling of the FO membrane (Cornelissen et al. 2008, Mi and Elimelech 2008, Wang et al. 2010c, Zou et al. 2011). The feed for the FO process was SWWE from the city of Jeddah. For the DS, a batch of Red Sea water was used.

Figure 5.1 shows a detailed scheme of the setup to induce fouling in the membrane. This configuration has been used in previous studies with relevant results (Valladares Linares et al. 2012). The FO dilution process takes 24 hours recirculating the DS inside the cell, increasing the level in the DS tank, while the SWWE concentrates (volume decreases). The cycle was repeated by replacing the diluted draw solution (DDS) with DS every day, to ensure that a fouling layer was formed on the surface of the membrane.

An evaporator was used to concentrate the SWWE without involving a membrane process, in order to identify the NOM fraction causing fouling. This sample was referred to as evaporated wastewater effluent (EWWE), and compared to the concentrated feed water after the FO process (CFW). A liquid chromatograph coupled with organic carbon detection analyser (LC-OCD) was used to analyse the organic carbon content of the water samples, following the procedure established by Huber et al. (2011).
Two hydrodynamic cleaning procedures were used to remove fouling from the surface of the FO membrane. First, osmotic backwash was performed replacing the feed with 4% NaCl solution and recirculating DI water inside the cell. Afterwards, cleaning with air scouring was performed for 15 minutes with air-stone diffusers at a rate of 12.5 L·h\(^{-1}\) of air per liter of SWWE. This last procedure has been proved to be very effective to remove foulants in an FO membrane.

Two chemical cleaning solutions were used to clean fouling on the FO membrane after the use of hydrodynamic procedures. The first washing solution was a 1% aqueous solution of NaOCl. The second one contained 0.8% sodium EDTA and 1% Alconox (commercial detergent containing phosphates). Both solutions were tested on both the active and the support layers to remove NOM and TEP fouling.

The Villacorte et al. (2009) protocol was used to prepare the cationic dye Alcian Blue, with which the fouled FO membrane was stained in order to assess TEP accumulation (Villacorte et al. 2009). Transmitted and reflected light microscopy was used with different objectives to determine the best option for TEP removal.

5.3 Results and Conclusions

LC-OCD chromatograms of the CFW, EWWE and DDS suggest that biopolymers (protein-like substances and polysaccharides), present in the SWWE and in the EWWE, but not in the CFW or the DDS (no partitioning through the membrane is observed) were the main constituents of the fouling layer in the active layer of the FO membrane (Figure 5.2).
After achieving a flux decline of 25% cleaning was performed. Osmotic backwash did not help to recover any flux. The interaction of the salt in the cleaning solution with the foulants might have enhanced the pore blockage and thus the water flux kept decreasing. A second hypothesis is the reduction of the osmotic pressure difference due to salt accumulation in the fouling layer, which eventually reduce the flux through the membrane. Nevertheless, NOM-fouling showed high hydraulic reversibility (89.5% flux recovery) when air scouring for 15 minutes within the concentrated wastewater effluent was used as a cleaning technique. TEP forms clusters clearly identifiable with an optical microscope (Figure 5.3a and 5.3c). After a 10-minute cleaning of the FO membrane with the Alconox + Sodium EDTA solution, TEP was significantly removed (Figure 5.3b and 5.3d); nevertheless, traces of these particles can still be observed on both layers of the membrane after the cleaning.
Figure 5.3 | a) TEP fouling in the AL of an FO membrane (60×); b) AL of a chemically cleaned FO membrane (100×); c) TEP fouling in the SL of an FO membrane (100×); d) SL of a chemically cleaned FO membrane (100×).

Chemical cleaning of the AL with Alconox + Sodium EDTA proved to slightly increase the reversibility (93.6%). Chemical cleaning of the SL increased the chemically reversible fouling up to 94.5%. The irreversible fouling in this set of experiments was 5.5%, which may be attributed to biopolymers that cannot be removed from the membrane surface, along with the trace TEP left on the membrane surface.

Cleaning with a 1% aqueous solution of NaOCl compromised the integrity of the membrane as proven by conductivity and flux measurements, even though the pH of the solution was kept below 8, as recommended by the manufacturer.

References


Impact of spacer thickness on biofouling in FO

Abstract

Forward osmosis (FO) indirect desalination systems integrate wastewater recovery with seawater desalination. Niche applications for FO systems have been reported recently, due to the demonstrated advantages compared to conventional high-pressure membrane processes such as nanofiltration (NF) and reverse osmosis (RO). Among them, wastewater recovery has been identified to be particularly suitable for practical applications. However, biofouling in FO membranes has rarely been studied in applications involving wastewater effluents. Feed spacers separating the membrane sheets in cross-flow systems play an important role in biofilm formation. The objective of this study was to determine the influence of feed spacer thickness (28, 31 and 46 mil) on biofouling development and membrane performance in a FO system, using identical cross-flow cells in parallel studies. Flux development, biomass accumulation, fouling localization and composition were determined and analyzed. For all spacer thicknesses, operated at the same feed flow and the same run time, the same amount of biomass was found, while the flux reduction decreased with thicker spacers. These observations are in good agreement with biofouling studies for RO systems, considering the key differences between FO and RO. Our findings contradict previous cross-flow studies on particulate/colloidal fouling, where higher cross-flow velocities improved system performance. Thicker spacers reduced the impact of biofouling on FO membrane flux.

Published as: Valladares Linares et al. 2014, *Impact of spacer thickness on biofouling in forward osmosis*, Water Research 57(0), 223-233
6.1 Introduction

Osmosis is a natural low energy water transport process not exploited by the drinking water and wastewater industry. The use of forward osmosis (FO) to reclaim water from wastewater is known in applications for oil/gas well drilling wastewater, landfill leachate treatment and water recycling in space missions (Cath et al. 2005, Adham et al. 2007, Holloway et al. 2007, Hickenbottom et al. 2013), which are all recent technologies with only a few years of existence. More recently, the use of osmosis to reclaim treated municipal wastewater has been demonstrated in bench-scale experiments (Valladares Linares et al. 2013a, Werner et al. 2013), where wastewater recovery is integrated with seawater desalination (designated as indirect FO desalination). Osmotic membrane bioreactors have been studied as well (Achilli et al. 2009). FO is a process that increases water reuse at a lower energy consumption compared to high-energy membrane processes (i.e. reverse osmosis (RO) and nanofiltration (NF)), and therefore, a cost reduction may be feasible (Yanga-li-Quintanilla et al. 2011).

When microorganisms are present in a membrane system, biofilm formation is inevitable due to the availability of nutrients in the water flow (Flemming et al. 1997). Biofilm formation is the accumulation of microorganisms, including extracellular polymeric substances (EPS) produced by microorganisms, on a surface due to either deposition and/or growth. When biofilm formation causes an unacceptable operational problem such as pressure drop increase, flux reduction and/or salt passage increase, it is called biofouling (Characklis and Marshall 1990).

All membrane filtration processes suffer from fouling, so the membrane elements have to be cleaned and eventually replaced. Biofouling has been identified as one of the major problems in spiral wound nanofiltration and reverse osmosis membrane operation (Winters and Isquith 1979, Paul 1991, Tasaka et al. 1994, Flemming et al. 1997, Khedr 2000, Saeed et al. 2000, Vrouwenvelder et al. 2008, van Loosdrecht et al. 2012). Feed spacers, separating the membrane sheets in cross-flow systems, are essential for membrane performance and play an important role in biofouling (Vrouwenvelder et al. 2009a).

Biofouling assessment in FO membrane studies is very limited in applications involving wastewater effluents. A study by Yoon et al. (2013) investigated biofouling in the FO process compared to the RO process. The extent of biofouling, demonstrated by the permeate flux decline, was less severe in the FO process than the RO process. Zou et al. (2013) studied the use of feed spacers in forward osmosis systems when using microalgae as a foulant, showing that spacer use not only improved the initial FO flux, but also reduced membrane fouling propensity.

The objective of this study is to determine the influence of feed spacer thickness (28, 31 and 46 mil) on membrane performance and biofouling development in a cross-flow FO system. Experiments consisted of consecutive 5 filtration cycles using similar water flow conditions in parallel systems with different feed spacers. To the authors knowledge this is the first study on the impact of spacer thickness and biofouling in cross-flow FO systems.
6.2 Materials and Methods

6.2.1 Membrane, spacers and cell configuration

The FO membranes used in this study were provided by Hydration Technology Innovations (HTI, Scottsdale, AZ), made of cellulose triacetate embedded in a polyester mesh support. The FO membrane has a thickness of 30 to 50 μm and a structural parameter S of 595 μm, defined as the ratio of the support layer thickness (Ts) and the tortuosity (τ) over the porosity (ε) of the membrane (S = Ts τ/ε). A regular thin film composite (TFC) NF/RO membrane has a higher S value (S = 2155 μm), which translates into a lower water flux through the RO membrane compared to the FO membrane using the osmotic power difference as the driving force (Lee et al. 2010a, Yip et al. 2010).

The membrane cell was a custom-made cross-flow cell made of poly (methyl methacrylate) (PMMA), designed to fit a 20 cm² sized membrane sheet. All of the experiments were performed with the active layer (AL) of the membrane facing the FO feed solution (FS), leaving the support side in contact with the draw solution (DS). This configuration has been proven to be the most effective in preventing FO membrane fouling (Cornelissen et al. 2008, Mi and Elimelech 2008, Wang et al. 2010c). The layout of the FO system is described in previous studies (Li et al. 2012a). Both feed and draw solution side were operated under a negligible hydraulic pressure (<0.01 bar).

Three spacers of different thickness were used to grow the biofilm (Figure 6.1). Two DOW diamond-shaped spacers of 28 and 31 mil (1 mil = 0.025 mm) thickness (Dow-Filmtec, Midland, MI) used in commercial spiral wound RO modules, and one modified FO spacer produced by HTI with a thickness of 46 mil (HTI, Scottsdale, AZ), used in commercially available modified FO spiral wound modules. Table 6.1 lists details concerning feed flow and characteristics for each spacer, used on both the feed and draw solution side of the membrane.
Different spacer thicknesses (28, 31 and 46 mil; 1 mil = 0.025 mm) on forward osmosis (FO) membrane. The small grid shown inside the FO membrane is the embedded polyester mesh support. All figures have the same scale.

Table 6.1 | Feed spacers and flow conditions used in the FO cross-flow channel.

<table>
<thead>
<tr>
<th>Spacer type (both sides*)</th>
<th>Spacer thickness (mm)</th>
<th>Flow rate (L·h⁻¹)</th>
<th>Linear flow velocity (m·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28 mil Dow</td>
<td>0.711</td>
<td>7.2</td>
<td>0.141</td>
</tr>
<tr>
<td>31 mil Dow</td>
<td>0.787</td>
<td>7.2</td>
<td>0.120</td>
</tr>
<tr>
<td>46 mil HTI</td>
<td>1.168</td>
<td>7.2</td>
<td>0.086</td>
</tr>
</tbody>
</table>

* the same feed spacer was used on both sides of the FO membrane. The study focus was on the fouling at the membrane feed side.

All experiments were performed with a similar nutrient load for biomass growth, which implies the use of the same feed flow and processing the same amount of water for all of the studied spacer geometries, resulting in the use of different cross-flow velocities. When biofilm grows at the same nutrient load, the effect of spacer thickness can be assessed and results compared.

6.2.2 Water sources

Two water types were used directly, one after each other. Firstly, a municipal secondary wastewater effluent was used for 20 hours to condition the FO system with bacteria. Subsequently, the system was fed with synthetic municipal water (not containing bacteria) for 5 filtration cycles.
A municipal secondary wastewater effluent was collected from Al-Ruwais wastewater treatment plant in the city of Jeddah, Saudi Arabia. The chemical oxygen demand (COD) was 25 mg·L⁻¹, the total organic carbon (TOC) concentration was 4.84 mg·L⁻¹, the pH was 7.1, the conductivity was 2.33 mS·cm⁻¹ and the osmotic pressure was 0.38 bar. The total suspended solids (TSS) and volatile suspended solids (VSS) of the effluent were 2.25 and 2.15 mg·L⁻¹, respectively. The ATP concentration of the effluent was 215 pg·mL⁻¹, which corresponds to a bacterial cell concentration of approximately 10⁷ cells·mL⁻¹.

For the subsequent 5 FO filtration cycles, the feed solution was a synthetic municipal wastewater already used in previous FO experiments (Valladares Linares et al. 2013a), described in Table 6.2. All the chemicals were purchased from Sigma Aldrich (Munich, Germany) and had a purity grade higher than 99.5%. The COD of the synthetic wastewater was 360 mg·L⁻¹ before the FO process, with a TOC of 115 mg·L⁻¹ and a pH of 5.66. For the draw solution, 4% sodium chloride (NaCl) was used to simulate Red Sea water, with a conductivity of 55 mS·cm⁻¹ and pH of 5.74. All solutions were prepared with deionized (DI) ultra-pure water.

Table 6.2 | Synthetic municipal wastewater constituents.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (mg·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>91.74</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>12.75</td>
</tr>
<tr>
<td>Sodium acetate</td>
<td>79.37</td>
</tr>
<tr>
<td>Peptone</td>
<td>17.41</td>
</tr>
<tr>
<td>MgHPO₄.3H₂O</td>
<td>29.02</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>23.40</td>
</tr>
<tr>
<td>FeSO₄.7H₂O</td>
<td>5.80</td>
</tr>
<tr>
<td>Starch</td>
<td>122.00</td>
</tr>
<tr>
<td>Skimmed milk power</td>
<td>116.19</td>
</tr>
<tr>
<td>Yeast extract</td>
<td>52.24</td>
</tr>
<tr>
<td>Cr(NO₃)₃.9H₂O</td>
<td>0.77</td>
</tr>
<tr>
<td>CuCl₂.2H₂O</td>
<td>0.54</td>
</tr>
<tr>
<td>MnSO₄. H₂O</td>
<td>0.11</td>
</tr>
<tr>
<td>NiSO₄.6H₂O</td>
<td>0.34</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>0.10</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>0.21</td>
</tr>
</tbody>
</table>

6.2.3 Biofilm formation

The following procedure was used to grow a biofilm on the membrane feed side surface: i) inoculation for 20 h with municipal secondary wastewater effluent, and ii) 5-cycle experiment with recirculation of synthetic wastewater effluent as FS and clean 4% NaCl as
DS; each cycle recovered 30% of the initial FS volume (300 mL) from the feed water, after which both FS and DS were replaced with fresh solutions.

Based on results from (Li et al. 2012a) on the minor effect (difference of less than 2%) of cross-flow velocity on reverse solute flux by CTA FO membranes for velocities in the range of 0.04 to 0.16 m s$^{-1}$ (this study uses cross-flow velocities that range from 0.08 to 0.14 m s$^{-1}$), biomass growth was achieved under similar reverse draw solute flux conditions, and thus, results can be compared in terms of the effect of feed spacer thickness.

After the 5 cycles the FO cell was opened and the membrane along with the stacked spacer of the feed side were conserved for an autopsy. For TOC analysis, DI ultra-pure water was used to dilute the samples. Before using the imaging and elemental characterization techniques, membrane samples were kept hydrated and sealed at 4°C.

To remove organic matter and disinfect the system, the following cleaning procedure, adapted from Herzberg and Elimelech (2007), was used before starting a new experiment: i) recirculation of 0.5% sodium hypochlorite for 2 h, ii) recirculation of 5 mM EDTA at pH 11 for 30 min, iii) recirculation of 2 mM SDS at pH 11 for 30 min, and iv) sterilizing the unit by recirculation of 95% ethanol for 10 min. In-between each cleaning agent and at the end, the system was rinsed with DI ultra-pure water for 10 min.

6.2.4 Analytical methods

A Shimadzu TOC-V CPH total organic carbon analyzer (Japan) was used to determine the organic carbon present on the membrane and feed spacer surface. The membrane and spacer were taken from the system, placed in a tube containing 20 mL of DI ultra-pure water and subsequently treated in an ultrasonic bath 3 times for 2 minutes. The obtained homogeneous solution was analyzed for TOC.

A Celsis Advance Luminometer (Belgium) was used to measure the amount of Adenine 5’ Triphosphate (ATP) on membrane (and spacer) samples. The tubes with the samples of the fouling material from the membrane sections with a total area of approximately 4 cm$^2$, diluted in 50 mL sterile water, were placed in an ultrasonic cleaning bath (Bransonic Model 5510, 40 KHz, USA) for 2 minutes, and then mixed on a vortex mixer (Fisher Scientific, 230 V, USA) for 10 seconds at speed 7. This operation was repeated three times. Active biomass was determined in duplicate by measuring the ATP concentration from 50 µL samples, and then related to the area of membrane and spacer.

A stereomicroscope (Leica M205 FA, Leica Microsystems, Wetzlar, Germany) was used to obtain optical images from the FO membrane and spacer before and directly after the fouling experiments.

Confocal Laser Scanning Microscopy (CLSM) (LSM710 upright confocal microscope, Zeiss, Germany) was used to identify and characterize biofouling on the membrane surface after the experiments. The samples were stained with the following dyes based on methods
described in the literature (Chen et al. 2006, Lee et al. 2010b): i) 4',6-Diamidino-2-Phenylindole (DAPI) dye (emission wavelength of 358 nm; excitation wavelength of 461 nm) was used to stain DNA to identify total bacterial cells (incubation in dark room for 20 min), ii) Fluorescein Isothiocyanate (FITC) (emission wavelength of 480 nm; excitation wavelength of 520 nm) was applied to stain the amine-reactive compound-like proteins and amino sugars (incubation time of 60 min); a 0.1 M sodium bicarbonate buffer was used to retain the amine groups so the dying was effective, and iii) Calcofluor White (emission wavelength of 433 nm; excitation wavelength of 355 nm) was used to stain β-D-glucopyranose polysaccharides (incubation time of 1 min). After each of these three staining stages, the sample was washed twice by phosphate-buffered saline (PBS) pH 7 to remove excess stain and a wipe was used to remove excess dye or buffer remaining.

The fouling on the membrane surface was analyzed by Scanning Electron Microscopy Energy Dispersive X-ray Apparatus (SEM-EDX, Magellan, FEI). The samples were freeze dried for environmental SEM.

An overview of the experimental studies and conditions is shown in Table 6.3.

Table 6.3 | Overview of the forward osmosis studies performed with different spacer thicknesses.

<table>
<thead>
<tr>
<th>Study</th>
<th>Feed spacer thickness (mil)*</th>
<th>Parameter evaluated / equipment used</th>
<th>Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect of spacer thickness</td>
<td></td>
<td></td>
<td>3.2</td>
</tr>
<tr>
<td>on performance</td>
<td>28, 31, 46</td>
<td>flux</td>
<td>3.2</td>
</tr>
<tr>
<td>on biomass accumulation</td>
<td>28, 31, 46</td>
<td>ATP and TOC</td>
<td>3.3</td>
</tr>
<tr>
<td>on fouling localization</td>
<td>28, 31, 46</td>
<td>stereomicroscope</td>
<td>3.4</td>
</tr>
<tr>
<td>on fouling composition</td>
<td>28, 31, 46</td>
<td>CLSM and SEM-EDX</td>
<td>3.5</td>
</tr>
</tbody>
</table>

*1 mil = 0.025 mm.

6.3 Results

The development of performance (flux) and fouling amount, spatial localization and composition were investigated in cross flow FO cells with three feed spacers differing in thickness (28, 31 and 46 mil). To relate the flux decline with accumulated fouling material, autopsies were performed on the feed side membrane and spacer sheets.

6.3.1 Reproducibility

To show the reproducibility of results obtained with the proposed system, a parallel study was performed in two FO cells with the same conditions (i.e. spacer thickness, cross flow velocity, nutrient load) to grow biofilm, and flux decline was recorded. Results are shown on Figure 6.2.
Impact of spacer thickness on biofouling in FO

6.3.2 Effect of spacer thickness on performance

The FO flux patterns using the 28, 31 and 46 mil spacers are shown in Figure 6.3A, 6.3B and 6.3C, respectively for 5 filtration cycles. The reduction of water flux through the membrane is due to two processes: i) loss of osmotic pressure difference resulting from the simultaneous process of concentration of the FS and the dilution of DS, ii) fouling and biofilm formation on the membrane and spacer surface. However, when a new cycle is started, and the FS and DS are replaced, restoring the osmotic pressure difference, and thus the driving force for the FO process, the effect on the reduction of the flux compared to the previous cycle is only due to the effect of the biofilm layer.

Results show that the 46 mil feed spacer has the best performance. With the 28 mil spacer, flux is rapidly reduced by the biofilm growth. Figure 6.3D compares the fluxes for the three different spacer thicknesses. The thickest spacer (46 mil) clearly outperforms the thinner spacers.

Figure 6.2 | Flux (L·m⁻²·h⁻¹) patterns over time for FO process ran in parallel cells with the same conditions for biofilm growth: spacer thickness (31 mil), cross flow velocity (0.12 m·s⁻¹), feed water TOC of 115 mg·L⁻¹.

Based on Figure 2, the results presented in the following sections can be considered representative for biofilm growth using the FO cells.
Figure 6.3 | Flux (L·m^{-2}·h^{-1}) patterns over time for FO process with different spacer thicknesses (A) 28 mil, (B) 31 mil, (C) 46 mil and (D) combined graph. Each FO filtration cycle recovers 30% from feed solution to draw solution, after which both feed and draw solutions are replaced.

Flux decline calculations show that a lower flux decline can be obtained by the 46 mil thick spacer (Figure 6.4). The 28 mil spacer has the lowest performance of all spacer thicknesses throughout the experiment. The exponential curves denote the attachment and growth of a biofilm layer.

When comparing flux decline curves of the 31 mil and 46 mil feed spacers in Figure 6.4, a shadow effect (the membrane area pressed under the spacer shape has limited water permeability (Kim and Elimelech 2012)) can be observed. With the thickest spacer the lowest (∼15%) flux decline was achieved. In terms of initial flux decline (cycle 1), the shadow effect may be lower for the 28 mil spacer compared to the 31 mil spacer, but the water mixing effect is reduced when the spacer thickness decreases, increasing concentration polarization. Consequently, a lower initial flux is expected. In the case of 46 mil spacer, the shadow effect is more significant than the mixing effect. Thus, the 46 mil spacer shows a lower initial flux compared to the 31 mil spacer.
Figure 6.4 | Flux decline (%) development for each filtration cycle for different spacer thicknesses (28, 31 and 46 mil); dashed lines show the exponential fit for the flux decline due to membrane surface fouling.

Figure 6.5 | Flux decline (%) after the fifth filtration cycle for three different spacer thicknesses. The thickest spacer has the lowest flux decline, and thus, gives the best performance.

Figure 6.5 compares the flux decline for the last filtration cycle for the 3 different spacer thicknesses. Running the system with the 28 mil spacer for 5 cycles translates into a flux decline of more than 30%; if the system is run at a lower cross-flow velocity (keeping the
same flow rate) using a 46 mil spacer, flux decline is significantly reduced. A thicker spacer performs better for biofouling control.

6.3.3 Effect of spacer thickness on biomass accumulation

After running 5 filtration cycles, recovering 30% of the water in each cycle from the feed solution to the draw solution, for each spacer thickness, the biomass concentration on a measured area of the membrane surface (including the spacer section) in contact with the FS (active layer) was calculated.

ATP values (Figure 6.6A) were found to be between $10^8$ and $10^9$ pg·cm$^{-2}$. Figure 6.6B shows the results for TOC concentration, which range from 0.15 to 0.18 mg·cm$^{-2}$. Spacer thickness had no significant impact on the amount of accumulated bacteria and organic matter including extracellular polymeric substances (EPS) on the membrane surface and the corresponding feed spacer for the same FO operation time.

![Biomass concentrations ATP (in pg ATP·cm$^{-2}$, A) and TOC (in mg·cm$^{-2}$, B) on the membrane and spacer in the flow cell operated at the same feed flow (7.2 L·h$^{-1}$) after 5 filtration cycles for different spacer thicknesses.](image)

6.3.4 Effect of spacer thickness on fouling localization

Optical stereomicroscopy images of a fouled section of membrane and spacer show the difference in spatial distribution of biofouling for the three spacer thicknesses (Figure 6.7). Although the biomass concentration showed no significant difference between the 3 feed spacers, the location of the biofilm changes varied with the thickness of the spacer used. For the 28 mil spacer, both membrane and spacer filaments are covered by a thick biofilm (Figure 6.7A). For the 31 mil and 46 mil feed spacers, some membrane areas and spacer filaments are not covered by the biofilm (Figure 6.7B and 6.7C). The consequence of using
Impact of spacer thickness on biofouling in FO

different feed spacer thicknesses with the same feed flow is that the cross-flow velocity varies in the FO flow channel (Table 1). Apparently, growth of biofilm occurs in a less compact structure when a low cross-flow velocity is used (46 mil spacer) compared to a higher flow velocity (28 mil spacer). Spacer thickness and cross-flow velocity have an impact on the localization of the biofilm on the membrane surface and feed spacer filaments.

Figure 6.7 | Varying localization patterns of fouling material (indicated within yellow marked areas) for different spacer thicknesses (A) 28 mil, (B) 31 mil and (C) 46 mil after 5 filtration cycles at constant flow rate (7.2 L·h⁻¹). Images were taken directly after the membrane and the spacer were removed from the FO cell and placed under a stereomicroscope. The white lines are light reflections.

6.3.5 Effect of spacer thickness on fouling composition

Results from CLSM imaging of the biofilm after the FO process are shown in Figure 6.8. Presence of bacteria on the membrane surface was confirmed for all spacer thicknesses. As example the 28 mil spacer data is shown in Figure 6.8A and 6.8B, where the blue spots represent stained bacterial cells with a DNA target dye (DAPI). Figure 6.8B shows the EPS (matrix of polysaccharides (purple) and proteins (green)), and bacteria (blue) on the fouling layer. Bacterial cells shown in Figure 6.8, together with operational performance decline demonstrated in section 6.3.2, confirm biofouling occurrence.
Figure 6.8 | CLSM images indicating presence of (A) bacterial cells (blue) and (B) accumulation of polysaccharides (purple), proteins (green) and bacterial cells (blue) attached to the membrane surface (feed side) (425 μm²) after 5 FO filtration cycles. The presented 28 mil spacer data is representative for all spacer thicknesses.

SEM images obtained from the fouled membrane surface for all spacer thicknesses do show similar structures resembling bacteria, EPS and some salt crystals. Figure 6.9 illustrates SEM images of a fouled membrane (using a 28 mil feed spacer) at different magnifications after 5 filtration cycles. Bacterial cells can be identified in combination with organic deposits and sodium chloride crystals, most probably coming from the DS side due to reverse draw solute flow.

An EDX analysis on the membrane surface (after the filtration experiment) for the different spacer thicknesses is shown in Table 6.4. The surface of the fouled membrane has a different composition than the virgin membrane due to the presence of EPS and some inorganic deposits, shown as an increase in the amount of sodium and chloride ions (Table 6.4). Deposited material composition showed no significant difference among the three spacer thicknesses used. Apparently, based on the few elements detected (Table 6.4) only biofouling and limited sodium chloride scaling occurred.
Impact of spacer thickness on biofouling in FO

Figure 6.9 | SEM images of the accumulated material (at magnification 18,000× (A) and 52,000× (B)) on the FO membrane feed side showing structures resembling bacteria, EPS material and salt crystals. The presented 28 mil spacer data is representative for all spacer thicknesses.

Table 6.4 | Elemental composition (energy dispersive x-ray analysis) of the fouled surface of an FO membrane (feed side) using the 28, 31 and 46 mil thick feed spacers.

<table>
<thead>
<tr>
<th>Element</th>
<th>Virgin membrane</th>
<th>28 mil</th>
<th>31 mil</th>
<th>46 mil</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>71.31</td>
<td>52.90</td>
<td>44.09</td>
<td>50.41</td>
</tr>
<tr>
<td>O</td>
<td>15.50</td>
<td>19.68</td>
<td>16.89</td>
<td>13.84</td>
</tr>
<tr>
<td>Na</td>
<td>3.58</td>
<td>3.47</td>
<td>5.63</td>
<td>4.50</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>2.71</td>
<td>5.83</td>
<td>6.80</td>
</tr>
</tbody>
</table>

6.4 Discussion

The objective of the study was to determine the influence of feed spacer thickness on FO performance and biofouling development and their potential for biofouling control. For all spacer thicknesses (28, 31 and 46 mil), operated at the same feed flow and the same run time, the same amount of biomass was found (Figure 6.6), while the flux reduction decreased with thicker spacers (Figures 6.4 and 6.5). The thicker spacer reduced the impact of biofilm on FO membrane performance.

A previous study showed that there is limited impact on biofilm formation with and without permeate production in RO modules (Vrouwenvelder et al. 2009a). Inventories of full scale installations performance have shown that the feed channel pressure drop increase is the major problem in practice (Vrouwenvelder et al. 2008). Lab-scale studies to investigate biofilm formation in RO most often are performed without flux permeation; therefore, the
parameter used to determine the impact of accumulated biomass is feed channel pressure drop. FO studies in any condition have to be performed with permeate flux. The most sensitive parameter to fouling in FO systems is permeate flux. Considering the relation for ATP/TOC shown in previous RO experiments (biofouling) compared to the relation obtained in this study (further discussed in section 6.4.2), a meaningful comparison between the two systems (RO and FO) can be made when relating the most sensitive parameter on each process: feed channel pressure drop for RO and permeate flux decline for FO.

### 6.4.1 Thickest spacer provides the best performance

The use of a thick spacer (46 mil) translates into a better performance of the FO filtration process due to the reduced effect of biofouling. A lower flux decline is achieved when the system is run at a low linear flow velocity (use of a thick spacer). Spacer thickness influences the spatial localization of biofilm in FO. Flux patterns change and due to the less compact biofilm formed, a slower flux decline was obtained when the 46 mil spacer was used. Araújo et al. (2012a, 2012b) obtained similar results for RO experiments, reporting that similar amounts of biomass accumulated during the experiment for different spacer thicknesses, but a lower feed channel pressure increase was observed when the thickest spacer was used. Bucs et al. (2013) found the same trend (lower impact biomass at thicker spacer) using numerical modeling. Thick spacers were demonstrated to be a feasible control strategy for biofouling.

The shadow effect (limited water permeability under spacer area) for thick spacers shows a smaller influence in FO than in other osmotic membrane processes that require hydraulic pressure (i.e. pressure retarded osmosis) (Kim and Elimelech 2012). Loose biofouling structures obtained with a thick spacer (46 mil) showed a higher positive impact (improved performance) on reducing flux decline than the negative effect (reduced performance) of the shadow effect. Results show that biofouling in FO is better controlled with thick spacers, limiting the shadow effect due to the lack of hydraulic pressure.

When no spacer is used with different types of fouling in FO membrane systems, an opposite effect for a low cross-flow velocity was reported. Lee et al. (2010a) established that when three different initial cross-flow velocities (0.171, 0.256, and 0.342 m·s⁻¹) were employed in FO fouling filtration, the flux curve for the lowest cross-flow velocity showed the highest flux decline, whilst at the highest cross-flow velocity, almost no flux decline was observed. FO feed spacers play an important role in biofouling control.

The consequence of using different feed spacer thicknesses in the FO flow channel with the same feed flow is that the cross-flow velocity varies (Table 6.1). Spacer thickness and cross-flow velocity both impacted the (i) localization of the biofilm on the membrane surface and feed spacer filaments and the (ii) effect of accumulated biomass on membrane performance. For FO, at low linear velocity the impact of biomass on flux decline is reduced, which is in agreement with results of studies on spiral wound nanofiltration and reverse osmosis systems (Vrouwenvelder et al. 2009b, Vrouwenvelder et al. 2010, Ying et al. 2013).
6.4.2 FO and RO show similar biofouling patterns

FO and RO systems differ from each other in several aspects: i) membrane water flux (up to 10 times higher for RO compared to FO), ii) driving force (applied hydraulic pressure versus osmotic pressure difference), iii) biofouling potential in both sides of the membrane for FO systems, and iv) existence of a reverse draw solute flux in FO processes.

The effect of biofouling on the FO system performance in relation with different feed spacer thicknesses (different cross-flow velocities) is similar to reported data for RO processes. Vrouwenvelder et al. (2009b) stated that the impact of biomass on the pressure drop increase will be lower when a low cross-flow velocity is used in the membrane system, inferring that the thickest spacer shows the best performance, and even suggesting modified spacer use as an approach to control biofouling. The 46 mil spacer used in FO filtration (lowest cross-flow velocity) controls biofouling and reduces the impact on flux decline.

This study on FO is in good agreement with results of earlier studies on RO systems concerning the impact of spacer thickness on biomass accumulation and impact of biomass on performance. Previous studies by Vrouwenvelder et al. (2010) reported that the same biomass concentrations showed different effects on pressure drop for RO. The same trend is observed in FO filtration, where similar amounts of biomass (ATP and TOC) do not determine performance decline.

The ATP concentrations found for the RO experiments ($10^4 - 10^5$ pg cm$^{-2}$) (Vrouwenvelder et al. 2009b) are significantly lower compared to the results obtained in FO study ($10^9 - 10^5$ pg cm$^{-2}$) (this manuscript), which indicates a higher bacterial concentration of the fouling layer for the FO process (biofouling). Although the FO experiment was performed with a high TOC feed solution (115 mg L$^{-1}$), the TOC values for the FO experiments (0.15 - 0.18 mg cm$^{-2}$) are only one order of magnitude larger than the results reported for RO membranes (0.01 mg cm$^{-2}$). The relation ATP/TOC is higher for the FO tests ($6.6 \times 10^2 - 5.5 \times 10^3$) than for the RO tests ($1.0 \times 10^5$), suggesting that a higher bacterial presence/growth on the membrane occurred during the FO tests. Moreover, a previous study on biofouling in FO processes (Yoon et al. 2013) found that the dominant factor when accounting the effect of biofouling on flux decline is the resistance of bacterial cells and not the resistance due to exopolymeric substances (EPS), mainly composed of biopolymers and protein-like substances, which are common substances found in organic fouling. Therefore, organic fouling induced by the feed solution composition cannot be considered as a critical factor in terms of its effect on flux decline; biofouling is clearly the predominant form of fouling in FO experiments performed in this study. As far as the authors’ knowledge, similarities on biofouling patterns for FO and RO have not been reported before.

6.4.3 Effect of biofilm on flux decline

Water flux through the FO membrane was affected adversely by biofilm growth. The effects of biofilm formation on membrane flux decline in the FO process can be explained by two
mechanisms: (i) cake-layer formation, which includes both the resistance of bacterial cells and the resistance of the EPS (the latter being significantly lower than the former), and (ii) concentration polarization, which is expected due to the use of different spacer thicknesses and cross flow. Both cake-layer formation and concentration polarization are influenced by the spacer geometry.

The lowest flux decline after 5 days was achieved with the thickest spacer, which shows the most significant concentration polarization due to the lowest cross flow velocity (negative impact on flux). However, due to the structure of biofouling layer on the thickest spacer, a considerable lower impact on flux decline is observed compared to thinner spacers.

6.4.4 Future studies

This study focused on biofouling on the feed side of the FO membrane when a wastewater effluent is used as feed water. Nevertheless, the seawater biofouling potential on the draw solution side may present new insights into FO indirect desalination. Special attention should be given to the transport of small molecular weight carbon and nitrogen compounds from the FS to the DS, which may act as substrate for bacteria to grow and represent a problem for long-term operation of this type of system.

Modeling can be a useful tool to predict and prevent biofouling in FO membranes. Along with this, future studies should focus on the use of modified spacers and novel cleaning strategies, which may be in agreement with cleaning protocols already developed for FO membranes (Valladares Linares et al. 2013b), to mitigate biofouling in FO indirect desalination systems.

6.5 Conclusions

Evaluation of the study on the influence of feed spacer thickness (28, 31 and 46 mil) on performance and biofouling development on the feed side of forward osmosis membranes led to the following conclusions:

- The biomass amount alone does not determine the flux decline: The same amount of biomass was found for all spacer thicknesses after the same run time at the same feed flow, while the flux reduction decreased with thicker spacer.
- The flux decline caused by biomass accumulation can be reduced by using a thicker spacer.
- Spatial distribution of the biofilm differs with feed spacer thickness.

Our findings are in agreement with reported data for reverse osmosis cross-flow systems: thicker spacers reduce impact of biofouling on performance. This result clearly contradicts observations obtained with particulate and colloidal fouling in forward osmosis.
References


Adham, S., J. Oppenheimer, L. Liu, and M. Kumar. 2007. WateReuse Dewatering Reverse Osmosis Concentrate from Water Reuse Applications using Forward Osmosis. WateReuse Foundation.


Chapter 7

Forward osmosis niches in seawater desalination and wastewater reuse

Abstract

This review focuses on the present status of forward osmosis (FO) niches in two main areas: seawater desalination and wastewater reuse. Specific applications for desalination and impaired-quality water treatment and reuse are described, as well as the benefits, advantages, challenges, costs and knowledge gaps on FO hybrid systems are discussed. FO can play a role as a bridge to integrate upstream and downstream processes, to reduce the energy consumption of the entire desalination or water recovery and reuse processes, thus achieving a sustainable solution for the water-energy nexus. FO hybrid membrane systems have been shown to have advantages over traditional membrane processes like high pressure reverse osmosis and nanofiltration for desalination and wastewater treatment: (i) chemical storage and feed systems may be reduced for capital, operational and maintenance cost, (ii) water quality is improved, (iii) reduced process piping costs, (iv) more flexible treatment units, and (v) higher overall sustainability of the desalination and wastewater treatment process. Nevertheless, major challenges make FO systems not yet a commercially viable technology, the most critical being development of a high flux membrane, capable of maintaining an elevated salt rejection and a reduced internal concentration polarization effect, and the availability of appropriate draw solutions (cost effective and non-toxic), which can be recirculated via an efficient recovery process. This review article highlights the features of hybrid FO systems and specifically provides the state-of-the-art applications in the water industry.

Submitted to: Water Research
7.1 Introduction

7.1.1 Increasing need for fresh water along coasts

Due to the development of coastal regions in many countries, two-fifths of cities with populations of 1 million to 10 million people are located near coastlines (Tibbetts 2002). Moreover, 14 of the largest 17 cities in the world are situated along coasts (Figure 7.1) (Creel 2003b). More than 3 billion people will live under water-scarce or water-stressed conditions by year 2025 (The Barila Group et al. 2009). Since more than 97% of the water in the world is seawater, desalination technologies have the potential to solve the fresh water crisis, particularly in coastal areas. Present conventional desalination technologies such as high pressure reverse osmosis (RO) involve expensive and energy intensive processes. A similar situation is faced when a wastewater effluent is treated with advanced technologies to produce high quality water. Therefore, there is an urgent need for a better technology that can recover water from impaired sources, providing an economic supply of fresh water to the increasing global human population.

Figure 7.1 | Fourteen of the world’s largest cities are located along the coast (indicated in orange), which translates into an opportunity to economically integrate drinking water and wastewater management, especially in water-stressed areas (Creel, 2003) (Image adapted from: NASA (2000)).

7.1.2 Current membrane systems in the water industry: reverse osmosis

Desalination is a general term for the process of removing salt from water to produce fresh water. Fresh water is defined as containing less than 1000 mg·L⁻¹ of salts or total dissolved solids (TDS) (Miller and Evans 2006). The most common membrane desalination process in
the world is reverse osmosis (RO) (Fritzmann et al. 2007). It is based on a property of certain polymers called semi-permeability, in which the polymer membrane has high permeability to water, but not for dissolved solids (i.e. salts). By applying a pressure difference across the membrane higher than the osmotic pressure of the feed water (i.e., seawater), fresh water is forced to permeate through the membrane. Common operating pressures for seawater desalination systems range between 55 to 68 bar (Liberman 2003). For water reuse, where the feed water is a treated wastewater effluent or a brackish groundwater, lower pressures are used to produce fresh water, but the pretreatment steps are usually similar to those used in seawater desalination installations.

The three major drawbacks of using RO filtration systems to produce fresh water are: i) energy intensive operation due to high hydraulic pressure used to drive the process (≈60 bar), ii) extensive pretreatment needed to maintain long-term operation of membrane modules, and iii) membrane fouling, resulting in decreasing membrane permeability and in feed channel pressure drop increase. To compensate for the loss in water production, systems require an increase in hydraulic pressure applied and more frequent chemical cleanings, all of which translate into higher operational costs.

7.1.3 Forward osmosis hybrid systems: an opportunity

Forward osmosis (FO) is an emerging membrane technology with a range of possible water treatment applications. In FO, water is extracted from a lower osmotic pressure feed solution (FS) into a higher osmotic pressure draw solution (DS); the process is driven by the osmotic pressure difference over the membrane and results in concentration of the FS and dilution of the DS. Almost no external hydraulic pressure is required to run the process. Potential FO applications are a function of the respective feed and draw solutions selected, and the water quality objectives.

For FO membranes, water flux decline due to fouling is lower when compared to RO systems, especially when wastewater with high fouling propensity is used as feed solution, because the FO process itself does not induce suspended solids and other organic contaminants into the membrane (Holloway et al. 2007), reducing as well the need for an extensive pretreatment. Experiments by (Lee et al. 2010a) comparing fouling behavior under identical hydrodynamic operating conditions (i.e., initial permeate flux and cross-flow velocity) and feed water chemistries (i.e., pH, ionic strength, and calcium concentration) of FO and RO systems showed that the thickness and compactness of the fouling layers of FO and RO are significantly different. Permeate flux during organic fouling in FO was after hydraulic cleaning almost completely recovered, while no noticeable change was observed for the RO system. In another study, data showed that FO fouling is governed by the coupled influence of chemical and hydrodynamic interactions. Calcium binding, permeation drag, and hydrodynamic shear force are the major factors governing the development of a fouling layer on the FO membrane surface (Mi and Elimelech 2008).

Consequently, research has identified the potential for hybrid forward osmosis/low pressure reverse osmosis (FO/LPRO) systems for several applications, including seawater desalination
Forward osmosis niches in seawater desalination and wastewater reuse (Choi et al. 2009), to reduce the cost and fouling propensity of producing fresh water from impaired-quality water sources (Chang et al. 2002, Achilli et al. 2009, Boo et al. 2013). Recently, studies have shown the potential of FO/LPRO systems to produce low cost high quality fresh water using low pressure desalination, while simultaneously recovering impaired water from a recycled feed water (Cath et al. 2009, Yangali-Quintanilla et al. 2011).

There are mainly two clusters of applications concerning FO in the water production and water treatment industry (Zhao et al. 2012b) (Figure 7.2): (i) desalination and (ii) water reuse. Specific applications and present status for both application types are described. Additionally, an evaluation of the energy and economics of forward osmosis, major challenges, and the future direction of research in the field are presented.

Figure 7.2 | Forward osmosis applications in the water industry clustered in two main areas: water desalination (left) and water reuse (right).

### 7.2 Desalination applications

There are two FO desalination approaches: i) direct FO desalination and ii) indirect FO desalination. Figure 7.3 describes the general layout of the processes.
Figure 7.3 | Layout of the two forward osmosis processes for water desalination: (a) direct and (b) indirect. Adapted from (Li et al. 2013b).

7.2.1 Direct desalination

The direct FO desalination concept is similar to other conventional membrane based desalination processes (e.g. reverse osmosis, nanofiltration) in which fresh water is directly extracted from a saline water (seawater or brackish water). Direct FO desalination uses saline water as the feed solution (FS) and an osmotic reagent such as a non-volatile salt like NaCl, or a volatile salt such as ammonium bicarbonate, among others (Chekli et al. 2012, Ge et al. 2013), as the draw solution (DS). In this process, an additional step, a draw solution recovery process, is needed to separate the DS from the solution in the diluted DS to recover fresh water (McCutcheon et al. 2005, Li et al. 2012a, Li et al. 2013a).

Various work efforts have been done from patents (McGinnis 2009), lab tests (Choi et al. 2009), process modeling (Shaffer et al. 2012) and pilot scale demonstrations (Hancock et al. 2011a). Table 7.1 presents the most recent studies/patents on direct FO desalination.

One of the most studied processes for direct desalination involves the use of ammonium bicarbonate (NH₄HCO₃) as a draw solution, and a thermal process to recover fresh water and regenerate the osmotic agent (McCutcheon et al. 2005, Cath et al. 2006, Gray et al. 2006, McCutcheon et al. 2006, Chanukya et al. 2013). (McCutcheon and Elimelech 2006) demonstrated that a water flux of 36 L·m⁻²·h⁻¹ could be obtained when using a 6 M ammonium bicarbonate draw solution and a 0.05 M NaCl feed solution. Another study showed that the total equivalent work requirements of this process are significantly lower than the work required in conventional desalination technologies (i.e. RO), translated to energy savings ranging from 72% to 85% (McGinnis and Elimelech 2007). (Chanukya et al. 2013) studied the concentration polarization effect using ammonium bicarbonate as draw solution in direct desalination experiments, concluding that forward osmosis is a feasible technique for the recovery of water from saline water.
**Direct** FO desalination has also been conducted using different novel draw solutions in order to achieve an easier and more sustainable draw solution regeneration process. (Li et al. 2011) used special hydrogels with carbon filler particles incorporated as DS to enhance the water flux through the FO membrane, achieving fluxes of approximately 1.2 L·m⁻²·h⁻¹ for the highest DS concentration. Another study on hydrogels used as DS for the FO process showed lower fluxes (≈ 0.2 L·m⁻²·h⁻¹), thermally regenerating the absorption capacity of the hydrogels (Cai et al. 2013). Hydrophilic nanoparticles have been shown to produce a water flux slightly higher than 6 L·m⁻²·h⁻¹ using synthetic seawater as a feed solution; the DS regeneration process (ultrafiltration) achieved a recovery of 92.7% (Ling and Chung 2011). Recently, divalent salts such as Na₂SO₄ showed to achieve fluxes between 8 to 10 L·m⁻²·h⁻¹ when desalinating brackish water; the DS recovery process (nanofiltration) had a rejection of 98% (Zhao et al. 2012a). Most of the draw solutes investigated for direct FO desalination are still not commercially feasible due to their cost, maximum water fluxes that they can produce, or the relatively low efficiency of the regeneration step (further discussed in section 7.6).

(Carmignani et al. 2012) developed a patent used by Trevi Systems Inc. to commercialize a technology that can desalinate seawater using 87.5% less electrical energy than current RO membrane systems, using a retrograde soluble solute as osmotic agent and a two-stage recovery process: in the first stage a coalescer (used to separate emulsions into their components) is used to heat, agglomerate and cool down the draw solution to produce a cooled single-phase water rich stream, which is purified in the second stage by a nanofiltration system, producing pure water. The concentrated single-phase draw solute stream is recirculated back to the coalescer.

Modern Water has deployed FO as a platform technology to produce desalinated water via direct FO desalination. It is the only company in the world with a commercial FO plant for direct seawater desalination (located in Al Najdah, Oman). Construction of the plant was completed in September 2012 and it is currently under operation. The process has shown to deliver significant operating and capital expenditure savings, reduced chemical consumption, robust fouling resistant membranes and a lower carbon footprint than competing technologies such as conventional high pressure RO membrane systems (Modern Water 2013). These benefits are mainly associated to the reduction in RO membrane fouling due to the use of FO as a pretreatment step.
### Table 7.1 | Overview of direct FO desalination investigations reported in the last two decades.

<table>
<thead>
<tr>
<th>Year</th>
<th>Feed solution</th>
<th>Draw solution</th>
<th>Post-treatment</th>
<th>Status</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>Seawater</td>
<td>KNO$_3$, SO$_2$, and NH$_4$NO$_3$</td>
<td>Precipitation (cooling) and separation through thermal waste heat</td>
<td>Patent</td>
<td>(McGinnis 2002)</td>
</tr>
<tr>
<td>2006</td>
<td>N.D.</td>
<td>Magnetoferritin particles</td>
<td>Magnetic field</td>
<td>Patent</td>
<td>(Oriard and Haggerty 2006)</td>
</tr>
<tr>
<td>2010</td>
<td>Contaminated water</td>
<td>Crosslinked superabsorbent polymer</td>
<td>Microfiltration</td>
<td>Patent</td>
<td>(Jones et al. 2010)</td>
</tr>
<tr>
<td>2011</td>
<td>NaCl (0.034 M)</td>
<td>Ionic polymer hydrogels</td>
<td>Dewatering hydrogels via external pressure</td>
<td>Bench</td>
<td>(Li et al. 2011, Li et al. 2013a)</td>
</tr>
<tr>
<td>2011</td>
<td>Synthetic seawater</td>
<td>Hydrophilic nanoparticles</td>
<td>Ultrafiltration</td>
<td>Bench</td>
<td>(Ling and Chung 2011)</td>
</tr>
<tr>
<td>2012</td>
<td>Brackish water</td>
<td>Divalent salts (i.e. Na$_2$SO$_4$ or MgSO$_4$)</td>
<td>Nanofiltration</td>
<td>Bench</td>
<td>(Zhao et al. 2012a)</td>
</tr>
<tr>
<td>2012</td>
<td>Seawater and brackish water</td>
<td>Cloud point solutes (i.e. polyethylene glycols)</td>
<td>Cloud point extraction (thermal process)</td>
<td>Patent</td>
<td>(Iyer 2012)</td>
</tr>
<tr>
<td>2012</td>
<td>Seawater, brackish water and</td>
<td>Retrograde soluble solutes (i.e. polyoxy random copolymer)</td>
<td>Coalescer (thermal process) and nanofiltration</td>
<td>Pilot and patent</td>
<td>(CARMIGNANI et al. 2012) Trevi Systems Inc.</td>
</tr>
<tr>
<td>2013</td>
<td>NaCl (0.034 M)</td>
<td>Thermally responsive hydrogels with a semi-interpenetrating network</td>
<td>Dewatering hydrogels via thermal process</td>
<td>Bench</td>
<td>(Cai et al. 2013)</td>
</tr>
<tr>
<td>2013</td>
<td>NaCl (0.086 M)</td>
<td>CuSO$_4$</td>
<td>Metathesis precipitation</td>
<td>Bench</td>
<td>(Alnaizy et al. 2013)</td>
</tr>
<tr>
<td>2013</td>
<td>Saline water and synthetic seawater</td>
<td>Thermo-responsive magnetic nanoparticles</td>
<td>Magnetic field</td>
<td>Bench</td>
<td>(Zhao et al. 2013)</td>
</tr>
<tr>
<td>2013</td>
<td>Synthetic water and brackish water</td>
<td>NaCl 0.2 - 1 M</td>
<td>Solar-powered electrodialysis</td>
<td>Bench</td>
<td>(Zhang et al. 2013)</td>
</tr>
</tbody>
</table>
7.2.2 *Indirect* desalination

*Indirect* desalination uses a high salinity water as the draw solution and an impaired-quality water source such as wastewater effluent (Valladares Linares et al. 2013a) or urban stormwater runoff (Li et al. 2014) is used as feed solution. Seawater and brackish water are potential DS for indirect desalination. In addition to the free-of-charge draw solution (seawater/brackish water), the attractiveness of this process is to extract clean water from the feed using free osmotic energy, leading to partially desalinated water (diluted DS) which can be further desalinated by a subsequent low-pressure reverse osmosis (LPRO) step as part of an FO-LPRO hybrid process (Cath et al. 2010, Yangali-Quintanilla et al. 2011), and thus reduce the cost of the entire desalination process (Table 7.2).

Table 7.2 | Relation between osmotic pressure and specific energy consumption for desalination in seawater reverse osmosis (SWRO) systems. Adapted from (Li et al. 2014).

<table>
<thead>
<tr>
<th></th>
<th>Natural seawater</th>
<th>Osmotically diluted seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS (ppm)(^a)</td>
<td>35,627</td>
<td>11,876</td>
</tr>
<tr>
<td>Osmotic pressure (bar)(^b)</td>
<td>26.14</td>
<td>8.71</td>
</tr>
<tr>
<td>Specific energy consumption for SWRO (kWh∙m(^-3))(^c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of elements: 1</td>
<td>12.23</td>
<td>5.49</td>
</tr>
<tr>
<td>Number of elements: 7</td>
<td>7.74</td>
<td>2.80</td>
</tr>
</tbody>
</table>

\(^a\) The calculations were made using a recovery rate of 90% and rejection rate of 100% in the osmotic detention pond, and a dilution factor of 3 for seawater in each batch.
\(^b\) The osmotic pressure was evaluated by Lenntech Osmotic Pressure Calculator (www.lenntech.com/calculators/osmotic/osmotic-pressure.htm).
\(^c\) The calculations were made by DOW Reverse Osmosis System Analysis (ROSA) using membrane SW 30-4040 from DOW Filmtec with a water production of 4.50 m\(^3\)∙day\(^-1\), 1 stage and 1 vessel operation.

In addition, the promising role of the FO process to integrate wastewater treatment and seawater desalination has been shown, aiming for a sustainable solution of the water-energy nexus for coastal cities (Valladares Linares et al. 2013a, Li et al. 2014). These studies, particularly the use of primary effluent as feed for the FO process, have provided insight into the concept of using FO to avoid costly treatment of wastewater effluents in conventional treatment processes. The concentrated primary wastewater effluent can provide an opportunity for subsequent, more cost-effective wastewater treatment, including the recovery of bio-energy (bio-gas) when an anaerobic process is used to treat the concentrated FS (McCarty et al. 2011).

*Indirect* desalination experiments showed the ability of FO membranes to reject nutrients from wastewater, particularly chemical oxygen demand (COD) and phosphate. Rejection of nitrogen compounds was moderate (Cath et al. 2009, Valladares Linares et al. 2013a). Additionally, Valladares Linares et al. (2013a) studied partial desalination of seawater with the use of a submerged membrane module which makes it possible to adapt the process to
a primary clarifier tank. This work also showed that FO membranes have high rejection of heavy metals present in the wastewater (>98%). An analysis of fractional organic carbon composition in the fouling layer on the FO membrane showed it is mainly formed by biopolymers and protein-like substances.

When the FO system was coupled with a low pressure RO system it was found that the hybrid process worked as a double barrier against selected micropollutants, including pharmaceutically active compounds, hormones and other organic micropollutants (Cath et al. 2009). In practice conditions, using municipal secondary effluent as feed solution and seawater as draw solution, FO membranes were able to reject most of the micropollutants; rejections were moderate for hydrophilic neutral compounds (44 – 95%), moderate for hydrophobic neutral contaminants (48 – 92%), and high for the hydrophilic ionic micropollutants (96 – 99%). FO coupled with low pressure RO was effective in rejecting low molecular weight hydrophilic neutral micropollutants, with rejections that went beyond 89.1%. For the rest of the compounds, rejections were greater than 99% (Valladares Linares et al. 2011).

A cleaning protocol was studied and the cleaning efficiency of several methods to remove NOM-fouling on the active layer (AL) and transparent exopolymeric particles (TEP) from the support layer (SL) of a FO membrane immersed in a municipal secondary wastewater effluent was reported, using seawater as draw solution (Figure 7.4). Osmotic backwash did not help to recover flux of the FO membrane. Nevertheless, NOM-fouling showed high hydraulic reversibility (89.5% flux recovery) when air scouring for 15 minutes within the concentrated wastewater effluent was used as a cleaning technique. Chemical cleaning of the AL with Alconox (and industrial cleaning agent based on phosphate compounds) and sodium ethylenediaminetetraacetic acid (EDTA) proved to slightly increase the fouling reversibility (93.6%). Chemical cleaning of the SL removed the reversible fouling up to 94.5%. The irreversible fouling in this set of experiments was 5.5%, which may be attributed to biopolymers that cannot be removed from the membrane surface, along with the trace TEP left on the membrane surface (Valladares Linares et al. 2013b). (Cath et al. 2009) suggested that the nature of the FO membrane, in conjunction with the minimal compaction of the fouling layer, is responsible for the negligible irreversible fouling observed after chemical membrane cleaning.
Figure 7.4 | Flux recovery compared to initial flux achieved after consecutive cleaning steps to the active layer (AL) and support layer (SL) of an FO membrane used for indirect desalination using a secondary wastewater effluent as feed solution and seawater as draw solution.

The influence of feed spacer thickness (28, 31 and 46 mil) on biofouling development and membrane performance in a FO system was assessed (Valladares Linares et al. 2014). For all spacer thicknesses, operated at the same feed flow and the same run time, the same amount of biomass was found, while the flux reduction decreased with thicker spacers. These observations are in good agreement with biofouling studies for RO systems, considering the key differences between FO and RO. These findings contradict previous FO cross-flow studies on particulate/colloidal fouling, where higher cross-flow velocities improved system performance. At the end of the study it could be determined that the biomass amount alone does not determine the flux decline.

In either case, direct or indirect FO desalination, the baseline for energy comparison is seawater reverse osmosis (SWRO) with a specific energy of 2.5 – 4 kWh·m⁻³ (Fritzmann et al. 2007). Recent work (Yangali-Quintanilla et al. 2011) has suggested that the FO-LPRO hybrid can approach a specific energy threshold of 2 kWh·m⁻³ and possible pass this threshold with a new higher flux FO membrane of about 10 L·m⁻²·h⁻¹ (further discussed in section 7.4).

7.3 Impaired-quality water treatment and reuse applications

Most FO approaches for impaired-quality water treatment and reuse are similar to the direct seawater desalination method described in section 7.2.1, where impaired-quality water is used as feed, while a draw solution is used to reduce the volume of feed; the DS is further
Chapter 7 treated by the other post-treatment process for the recovery of clean water and recirculation of DS. The applications of FO process for impaired-quality water treatment and reuse are highlighted in Table 7.3. Examples of water harvesting from wastewater have been described in the indirect desalination section because seawater/brackish water was used as draw solution. Section 7.3 describes processes that do not necessarily involve seawater or brackish water as draw solutions.

7.3.1 Water harvesting from municipal wastewater

In the municipal wastewater treatment processes, FO integrated with membrane distillation (MD) process was applied for sewer mining. A stable water flux was attained in a continuous operation at the recovery rate up to 80% (Xie et al., 2013). The FO showed a moderate to high rejection of most organic contaminants while MD rejected the residue contaminants to achieve a near complete rejection in this hybrid process. To recover clean water from secondary wastewater effluent, a photovoltaic powered forward osmosis – electrodialysis (FO-ED) process was tested as well. The process showed a good efficiency for removal of total organic carbon from feed wastewater and production of fresh water (Zhang et al. 2013). By using the natural energy (osmotic pressure and solar energy), this hybrid system is favorable to supply the potable water in isolated areas, remote areas and islands.

Membrane bioreactor (MBR), which involves both biological–activated sludge process and membrane filtration, has become one of the most commonly applied technologies in the treatment of many wastewater types. The integration of FO and MBR could reduce the energy consumption in the conventional MBR. The study of novel FO-MBR or osmotic MBR (OsMBR) has been initiated in the last five years (Cornelissen et al. 2008, Achilli et al. 2009, Qin et al. 2010, Lay et al. 2011, Yangali-Quintanilla et al. 2011, Li et al. 2012b, Yap et al. 2012, Zhang et al. 2012). The OsMBR process can not only reduce the energy cost in the pressure driven membrane process (e.g. microfiltration or ultrafiltration) as well as fouling control by air scouring in the conventional MBR, but also provides a more sustainable flux and reliable removal of contaminants. This is guaranteed by the lower fouling propensity without applied hydraulic pressure and separation capacity of FO membranes in OsMBR.
Table 7.3 | Overview of most recent approaches of forward osmosis used for reclamation and treatment of impaired-quality water.

<table>
<thead>
<tr>
<th>Feed water</th>
<th>Draw solution</th>
<th>Process configuration</th>
<th>FO membrane material</th>
<th>Membrane module and testing status</th>
<th>Process purpose</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw sewage</td>
<td>NaCl solution</td>
<td>FO-MD</td>
<td>CTA</td>
<td>Flat-sheet, lab scale</td>
<td>Direct sewer mining</td>
<td>(Xie et al. 2013)</td>
</tr>
<tr>
<td>Secondary wastewater effluent</td>
<td>NaCl solution</td>
<td>FO-ED</td>
<td>CTA</td>
<td>Flat-sheet, parallel plate-and-frame module, lab scale</td>
<td>Potable water production, utilization of natural energy for water treatment and reuse</td>
<td>(Zhang et al. 2013)</td>
</tr>
<tr>
<td>Activated sludge solution</td>
<td>MgSO₄, NaSO₄, ZnSO₄, NaCl solutions</td>
<td>OsMBR</td>
<td>TFC NF, TFC RO and CTA FO membranes,</td>
<td>Flat-sheet, lab scale</td>
<td>Water reclamation from activated sludge</td>
<td>(Cornelissen et al. 2008)</td>
</tr>
<tr>
<td>Domestic sewage</td>
<td>NaCl/MgSO₄ solution</td>
<td>OsMBR</td>
<td>CTA</td>
<td>Flat-sheet, pilot scale</td>
<td>Pilot system composing the anoxic/aerobic and FO processes for domestic sewage treatment</td>
<td>(Qin et al. 2010)</td>
</tr>
<tr>
<td>Synthetic wastewater with seed sludge from WWTPs</td>
<td>NaCl solution</td>
<td>Submerged OMBR</td>
<td>CTA</td>
<td>Flat-sheet, lab scale</td>
<td>Long-term OMBR testing for water reclamation from wastewater</td>
<td>(Lay et al. 2011)</td>
</tr>
<tr>
<td>Activated sludge</td>
<td>NaCl solution</td>
<td>Submerged OsMBR</td>
<td>TFC</td>
<td>Hollow fiber, lab scale, submerged module</td>
<td>Reclamation of water from activated sludge</td>
<td>(Zhang et al. 2012)</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>NaCl solution</td>
<td>OsMBR-RO</td>
<td>CTA</td>
<td>Flat-sheet, lab scale, immersed plate-and-frame module</td>
<td>Water reclamation from wastewater, potable water production</td>
<td>(Achilli et al. 2009)</td>
</tr>
<tr>
<td>Synthetic wastewater with seed sludge from WWTPs</td>
<td>Natural seawater</td>
<td>FO-SBR-LPRO</td>
<td>CTA</td>
<td>Flat-sheet, lab scale, submerged plat-and-frame module</td>
<td>Water reclamation from wastewater and potable water production</td>
<td>(Yangali-Quintanilla et al. 2011)</td>
</tr>
<tr>
<td>Process Type</td>
<td>Feedstock</td>
<td>Membrane Type</td>
<td>Module Type</td>
<td>Process Type</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td>----------------------------------</td>
<td>---------------</td>
<td>---------------------</td>
<td>------------------------------------------</td>
<td>----------------------------</td>
<td></td>
</tr>
<tr>
<td>Activated sludge</td>
<td>Synthetic RO brine</td>
<td>Single FO</td>
<td>CTA</td>
<td>Sludge thickening, digestion and dewatering</td>
<td>(Zhu et al. 2012)</td>
<td></td>
</tr>
<tr>
<td>High nutrient sludge</td>
<td>EDTA sodium salt</td>
<td>FO-NF</td>
<td>CTA</td>
<td>Dewatering of sludge, fresh water recovery</td>
<td>(Hau et al. 2014)</td>
<td></td>
</tr>
<tr>
<td>Synthetic dye wastewater</td>
<td>Poly(acrylic acid) sodium salt</td>
<td>FO-MD</td>
<td>CA</td>
<td>Dye wastewater treatment and fresh water recovery</td>
<td>(Ge et al. 2012)</td>
<td></td>
</tr>
<tr>
<td>Synthetic industrial wastewater containing heavy metals</td>
<td>NaCl solution</td>
<td>FO-RO</td>
<td>CTA</td>
<td>Heavy metal removal from industrial wastewater</td>
<td>(Rassoul et al. 2012)</td>
<td></td>
</tr>
<tr>
<td>Synthetic oil-water emulsion</td>
<td>NaCl solution</td>
<td>Single FO</td>
<td>TFC</td>
<td>Water reclamation and treatment of oily wastewater</td>
<td>(Duong and Chung 2014)</td>
<td></td>
</tr>
<tr>
<td>Drilling wastewater</td>
<td>NaCl solution</td>
<td>FO/RO closed loop system</td>
<td>CTA</td>
<td>Oilfield wastewater reclamation</td>
<td>(HTI 2011)</td>
<td></td>
</tr>
<tr>
<td>Produced water from oil/natural gas processing</td>
<td>NH₄HCO₃ solution</td>
<td>FO-Thermal distillation</td>
<td>CTA</td>
<td>Treatment of produced water from oil and/or natural gas operations</td>
<td>(Nelson and Ghosh 2011)</td>
<td></td>
</tr>
<tr>
<td>Drilling wastewater from shale gas field</td>
<td>NaCl solution</td>
<td>Single FO</td>
<td>CTA</td>
<td>Treatment of drilling mud and fracturing wastewater from oil and gas operations</td>
<td>(Hickenbottom et al. 2013)</td>
<td></td>
</tr>
<tr>
<td>Produced water from shale gas field</td>
<td>NH₃/CO₂ solution</td>
<td>FO-Thermal distillation-RO</td>
<td>TFC</td>
<td>Water reclamation of frac flowback and produced waters from natural gas extraction operations</td>
<td>(McGinnis et al. 2013)</td>
<td></td>
</tr>
<tr>
<td>Concentrated RO brine</td>
<td>NaCl solution</td>
<td>FO-RO</td>
<td>CTA</td>
<td>Flat sheet, lab scale</td>
<td>Post-treatment of RO brine for ZLD</td>
<td>(Martinetti et al. 2009)</td>
</tr>
<tr>
<td>-----------------------</td>
<td>---------------</td>
<td>-------</td>
<td>-----</td>
<td>-----------------------</td>
<td>----------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>Saline water or other impaired quality water</td>
<td>Fertilizer solution</td>
<td>FO-Irrigation</td>
<td>CTA</td>
<td>Flat-sheet, lab scale</td>
<td>Water reclamation and reuse for irrigation</td>
<td>(Phuntsho et al. 2011)</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>NaCl solution</td>
<td>OsMFC</td>
<td>CTA</td>
<td>Flat-sheet, lab scale</td>
<td>Wastewater Treatment, Water Extraction and Bioelectricity Generation</td>
<td>(Zhang et al. 2011, Werner et al. 2013)</td>
</tr>
<tr>
<td>Sewage</td>
<td>Seawater</td>
<td>Floatable FO enclosure</td>
<td>CTA</td>
<td>Flat-sheet, transparent plastic bag with inserts of FO membrane, pilot scale</td>
<td>Wastewater treatment, bio-energy production</td>
<td>(NASA 2012)</td>
</tr>
</tbody>
</table>
FO has been tested for dewatering of nutrient-rich anaerobic digester centrate (Holloway et al., 2007). A RO process could be used to recover the fresh water from the clean and diluted DS (i.e. NaCl solution) while organic compounds were rejected in the FO step. The FO process was also used to dewater activated sludge (Zhu et al. 2012, Hau et al. 2014). EDTA sodium salt was tested as a possible DS for dewatering of high nutrient sludge. The nutrients in the sludge were successfully removed by the FO process. The macromolecular DS (i.e. EDTA based salt) can be post-treated by a NF process for fresh water recovery. Alternatively, RO brine was used as the DS in Zhu’s research. A good thickening efficiency of sludge was reached. In addition to reduction of sludge volume for lower cost of further transportation and handling, the concentrated RO brine was also osmotically diluted and could be safely disposed to limit the negative impact to the environment which is a problem in the conventional RO process.

7.3.2 Industrial wastewater reclamation and reuse

Another major part of impaired-quality water treatment and reclamation is industrial wastewater. A company in the US has successfully piloted a system, based on forward osmosis, that recycles wastewater generated by textile and carpet mills using dyeing processes (Catalyx 2009a, b). Another FO application is to remove heavy metals from industrial wastewater or other impaired-quality water (Rassoul et al. 2012, Li et al. 2014). The effects of hydrodynamic conditions, organic fouling, temperature, feed and draw solution properties have been studied. FO membrane shows a nearly complete rejection to the metals tested (e.g. Pb, Zn, Cu, Cd), indicating its potential to be a convenient and economic method for industrial wastewater treatment.

Nowadays, most efforts of FO applications for industrial wastewater treatment have been dedicated to the treatment and reclamation of produced water from oil and gas (O&G) industry. Bench scale testing indicates the capacity of FO process for the separation of emulsified oil-water (Duong and Chung 2014). Fresh water can be recovered from high concentration (up to 200,000 ppm) synthetic oily solution by a customized TFC FO membrane, at a reasonable flux of about 11.8 L·m⁻²·h⁻¹. Some tests from bench to commercial scale have been conducted directly to the real produced water from O&G processing. FO combined with RO in a closed loop has been used to reclaim drilling wastewater from gas exploration operations (HTI 2011), and it is capable of recycling 242,000 gallons drilling wastewater per day, consequently reducing the need for additional fresh water and truck traffic. Similar studies and applications have been conducted by individual research teams and companies using different membrane materials, membrane modules, draw solutions and process configurations (Nelson and Ghosh 2011, Abousnina 2012, Hickenbottom et al. 2013). Major benefits were achieved by the use of FO: the volume of the waste stream and the need for a fresh water source were greatly reduced in all cases, for feed solutions having a dissolved contaminant concentration greater than 10,000 ppm, a well-designed FO process can economically outperform an RO process, and a high rejection of organic and inorganic contaminants was obtained. However, due to the complexity of both organic and inorganic compounds in the produced water, a relatively complicated pre-treatment process may be required (McGinnis et al. 2013)
7.3.3 Other applications for impaired-quality water treatment

In contrast to the osmotic dilution of desalination brine for safe dispose mentioned in section 7.3.1, FO can be used to minimize the volume and increase the concentration of brine by directly extracting water from the brine. Easier post-treatment (such as crystallization) of the FO concentrated brine can help to attain a zero liquid discharge (ZLD) or near-ZLD system. Bench scale testing shows that FO can reach water recovery up to 90% from RO brine from brackish water desalination, and the total water recovery can be enhanced to 98% by a hybrid RO-FO process (Martinetti et al. 2009). Other studies have shown the potential of FO to concentrate and recover water from brines (Tang and Ng 2008, Saito et al. 2012).

Furthermore, fertilizer driven FO is a novel application of FO in water reclamation and reuse. A blend of fertilizers was used as the DS (i.e., fertigation). The preliminary tests show that 1 Kg of commercial fertilizer can extract 11-29 L of fresh water from seawater. The technology shows its potential for the irrigation in coastal areas with water scarcity (Phuntsho et al. 2011). In addition to seawater, other impaired-quality water could also be utilized as the feed water to osmotically dilute the fertilizer DS, while FO membranes provide a reliable barrier to reject the feed water contaminants.

Integrating FO into microbial fuel cells (MFC) has gained interest in recent years. A new concept of osmotic microbial fuel cell (OsMFC) has been introduced by several researchers has shown its promising future even though the testing has been conducted under a small bench scale (Zhang et al. 2011, Werner et al. 2013). Compared to indirect FO desalination, in which wastewater is concentrated and seawater is diluted for future post-treatment, OsMFC can achieve water extraction, biological wastewater treatment, and bio-energy production, simultaneously. OsMFC also provides a high power density than conventional MFC.

Different from OsMFC, NASA has been creating another novel route involving FO, namely Offshore Membrane Enclosure for Growing Algae (OMEGA), for clean bio-energy production (NASA 2012). In this process, the freshwater algae and sewage is contained by the transparent plastic bags with inserts of FO membrane. The algae absorb carbon dioxide from atmosphere and nutrients from sewage to produce biofuel and oxygen. The FO membrane allows the exchange of carbon dioxide and oxygen between the atmosphere and enclosures, and fresh water from sewage into the surrounding seawater, while nutrients remain in the enclosed bags.

7.4 Energy and economics of FO systems

The driving factor for considering implementing a FO system versus a RO system (for desalination purposes) or versus a ultrafiltration/nanofiltration (UF/NF) - advance oxidation process (AOP) (for secondary wastewater recovery) or a MBR - RO - AOP hybrid process (for primary wastewater recovery) should be the energy savings related to the capital expenses. FO has been depicted as a near horizon low-energy desalination technology (see Figure 7.5, (Amy et al. 2013)).
Figure 7.5 | Technology roadmap for low-energy desalination. Adapted from (Amy et al. 2013).

The energy consumption for desalinating water with RO membranes lies between 2.5 and 4 kWh·m$^{-3}$ (Fritzmann et al. 2007), as a result of the development of new efficient membranes and the use of energy recovery devices over the last decade.

According to Shaffer et al. (2012) (Table 7.4), the specific energy consumption (SEC) of a direct desalination FO system coupled with a RO process is lower when compared to a two-pass RO process for a total system recovery higher than 25% (total production capacity of 100,000 m$^3$·d$^{-1}$).

Table 7.4 | Modelled specific energy consumption (SEC) for an integrated direct desalination FO-RO and a RO system. Adapted from (Shaffer et al. 2012).

<table>
<thead>
<tr>
<th>Total system recovery (%)</th>
<th>SEC (kWh·m$^{-3}$)</th>
<th>SEC (kWh·m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.03</td>
<td>3.39</td>
</tr>
<tr>
<td>25</td>
<td>2.40</td>
<td>2.88</td>
</tr>
<tr>
<td>50</td>
<td>2.93</td>
<td>3.79</td>
</tr>
<tr>
<td>70</td>
<td>4.49</td>
<td>6.43</td>
</tr>
</tbody>
</table>

For an indirect desalination system, the SEC associated to the FO-RO process, after an energy consumption analysis based on a conservative estimate, ranged between 1.3 to 1.5 kWh·m$^{-3}$ using a secondary wastewater effluent as feed and seawater as draw solution (total production capacity of 2400 m$^3$·d$^{-1}$) (Yangali-Quintanilla et al. 2011).

Energy savings associated with the integrated FO-RO system compared to a two-pass RO system are mainly related to the reduction in the osmotic pressure of the partially desalinated water and the hydraulic operational pressure required by the recovery process (i.e. low pressure RO system) to produce fresh water, compared to a traditional RO system.
(Table 7.5). It is clear that lower energy consumption is possible as the dilution rate increases. This, however, represents a higher capital cost for the membrane area required. With current commercial technology, hybrid FO systems for both desalination and water recovery applications have proven to have higher capital cost compared to conventional technologies (Yangali-Quintanilla et al. 2011, Aydiner et al. 2013). Nevertheless, due to the demonstrated lower operational costs of hybrid FO systems, the payback time for the construction and the unit cost for each m$^3$ of fresh water produced with the FO system is shorter than conventional desalination/water recovery technologies (i.e. ultrafiltration/RO systems). Minimum water flux considerations are made for these evaluations, where the average FO water flux should be $10.5\, \text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ when competing against water reuse technologies (UF-LPRO), and a water flux of $5.5\, \text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ is needed to recover and desalinate water at a lower cost compared to RO systems (Yangali-Quintanilla et al. 2011).

Table 7.5 | Osmotic pressure and operational system pressure calculations for different seawater dilution scenarios in a RO system.

<table>
<thead>
<tr>
<th>Dilution (%)</th>
<th>TDS (mg·L$^{-1}$)</th>
<th>Osmotic pressure* (bar)</th>
<th>Operational system pressure* (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40,625</td>
<td>27.6</td>
<td>68.9</td>
</tr>
<tr>
<td>25</td>
<td>30,471</td>
<td>20.7</td>
<td>56.9</td>
</tr>
<tr>
<td>40</td>
<td>24,378</td>
<td>16.5</td>
<td>45.5</td>
</tr>
<tr>
<td>50</td>
<td>20,313</td>
<td>13.8</td>
<td>46.5</td>
</tr>
<tr>
<td>60</td>
<td>16,250</td>
<td>11.0</td>
<td>37.2</td>
</tr>
</tbody>
</table>

*Osmotic pressure was calculated by Lenntech Osmotic Pressure Calculator, considering 1 membrane with a production of 0.2 m$^3$·h$^{-1}$. The membrane used for seawater is SW 30-4040 from Dow/Filmtec; for brackish water the BW 30-4040 membrane for Dow/Filmtec is considered.

Recently, a company in the US, Trevi Systems Inc., developed a patent (Carmignani et al. 2012) which can desalinate seawater using 87.5% less electrical energy than current RO systems. Furthermore, the low pressure system can use waste heat or low grade thermal heat at 75°C to drive the FO desalination process. The operating cost for each m$^3$·d$^{-1}$ of fresh water using natural gas as heat source can be 30% lower than cost of conventional RO technologies; savings increase to more than 50% if a co-generation heat source is used. For this case, both the capital and operational expenses are lower for the FO hybrid system.

Besides the costs associated with the system, there are key benefits of using FO hybrid systems compared to RO: (i) chemical storage and feed systems may be reduced for capital, operational and maintenance cost, (ii) water quality is improved, (iii) reduced process piping costs, (iv) more flexible treatment units, and (v) higher overall sustainability of the desalination process.
7.5 Pressure retarded osmosis: special FO application for energy recovery in water industry

Pressure retarded osmosis (PRO) is a special type of FO application, where the primary and end product is energy instead of water. Potential energy of a natural or engineered salinity gradient system can be utilized by a PRO process in the form of electricity or hydraulic pressure. Even though the idea of using salinity gradient for energy production was suggested in the early 50’s (Pattle 1954, Norman 1974), some of the first known applications of PRO were suggested and tested by Sydney Loeb in the 70’s (Loeb 1975, 1976, Loeb et al. 1976, Mehta and Loeb 1979). The main difference between a modern PRO and an FO process is the applied pressure on the high salinity draw solution. The pressure of the high salinity draw solution can be kept relatively constant during the PRO process, even though the volumetric flow rate is to be increased. Therefore, the draw side of the PRO process can be assumed to be isobaric, in most cases. The near-isobaric behavior of the draw side of the PRO process can be explained by the harvested Gibbs free energy of mixing and volumetric expansion. Thus, PRO can be used to increase the internal energy of the draw solution with respect to the ratio of the permeated water flux (Thorsen and Holt 2009, Achilli and Childress 2010, La Mantia et al. 2011, Ramon et al. 2011, Yip and Elimelech 2012).

7.5.1 Water flux in PRO

The driving force of an osmotic process is the osmotic pressure difference between the two aqueous solutions on the opposite sides of the semi-permeable membrane. Osmotic pressure of an aqueous solution can be calculated by using the Van’t Hoff relation:

\[ \pi = R T \sum M \]  

(Eq. 7.1)

where \( i \) is the dimensionless van’t Hoff factor for the specific ion, \( M \) is the molarity of the specific ion, \( R \) is the gas constant (0.08206 L·atm·mol\(^{-1}·K\)^{-1}), and \( T \) is the temperature in Kelvin. The water flux through a semi-permeable membrane by the osmotic pressure difference is given as (McCutcheon and Elimelech 2007):

\[ J_w = A(\pi_D - \pi_F) \]  

(Eq. 7.2)

where, \( J_w \) is the water flux through the semi-permeable membrane, \( A \) is the pure water permeability coefficient of the semi-permeable membrane, \( \pi_D \) and \( \pi_F \) are the bulk osmotic pressures of the draw and feed solutions, respectively. However, in the PRO process, the equation should be modified in order to include the effect of applied pressure on the water flux:

\[ J_w = A[(\pi_D + P_D) - (\pi_F + P_F)] = A(\Delta \pi - \Delta P) \]  

(Eq. 7.3)

where, \( P_D \) and \( P_F \) are the bulk hydraulic pressures of the draw and feed solutions, respectively. “\( \Delta \pi \)” and “\( \Delta P \)” are the effective osmotic and hydraulic pressures, respectively.
7.5.2 Generating power with PRO

PRO can be used to generate (electricity) or recover energy (hydraulic pressure) by utilizing the Gibbs free energy of mixing with respect to the salinity difference of two aqueous solutions (Sandler 1999).

\[
\Delta G_{mix} = RT\left\{\sum x_i \ln y_i \right\}_M - \phi_A \left(\sum x_i \ln y_i \right)_A - \phi_B \left(\sum x_i \ln y_i \right)_B \tag{Eq. 7.4}
\]

where, \(x_i\) is the mole fraction of species \(i\) in solution, \(R\) is the gas constant, \(T\) is temperature, \(\phi_A\) and \(\phi_B\) are the molar ratios of solutions A and B in the system, and \(y\) is the activity coefficient of the species. Since, in such conditions, the system can be assumed as strong electrolyte and ideal solutions system, the above equation can be further simplified to:

\[
-\frac{\Delta G_{mix} y^\phi}{vRT} \approx \frac{c_M}{\phi} \ln c_M - c_{LC} \ln c_{LC} - \frac{1-\phi}{\phi} c_{HC} \ln c_{HC} \tag{Eq. 7.5}
\]

where, \(c\) is the molar concentration, \(\phi\) is the volume fraction of the low concentration stream, \(v\) is the number of electrolyte ions, \(M\) is the mixture, \(LC\) is the low concentration stream, and \(HC\) is the high concentration stream. Adaptation of the negative convention was chosen to reflect that energy is released from the system (Yip and Elimelech 2012).

In a continuous PRO system, a constant hydraulic pressure is applied on a high salinity aqueous solution and permeation of water from low salinity aqueous solution continues while the osmotic pressure difference of two solutions is higher than the applied hydraulic pressure. It was theorized that, when seawater and river water were used for draw and feed solutions, respectively, the highest extractable work in a constant-pressure PRO process is 0.75 kWh m\(^{-3}\) (Yip and Elimelech 2012). Power density (\(W\), which can be extracted from a PRO system per membrane area (m\(^2\)), can be defined as a function of water flux and hydraulic pressure difference across the membrane (Achilli and Childress 2010):

\[
W = J_w \Delta P = A(\Delta \pi - \Delta P)\Delta P \tag{Eq. 7.6}
\]

If differentiating \(W\) is plotted (Figure 7.6) with respect to \(\Delta P\), it can be seen that \(W\) reaches a maximum when:

\[
\Delta P = \frac{\Delta \pi}{2} \tag{Eq. 7.7}
\]

substituting this value for \(\Delta P\) in equation, yields:

\[
W_{max} = A \left(\frac{\Delta \pi}{2}\right)^2 \tag{Eq. 7.8}
\]
In the case of energy production from PRO systems; a hydraulic turbine can be used to generate electricity by utilizing the pressure and volumetric flux of the aqueous solution. The power generated by a hydraulic turbine can be calculated by:

\[
\text{Power} = \eta \cdot \rho \cdot Q \cdot g \cdot P
\]  

(Eq. 7.9)

where, \( \eta \) is the efficiency of the turbine, \( Q \) is the flow, \( g \) is the acceleration due to gravity, and \( P \) is the pressure of the aqueous solution. Modern Pelton turbines can reach up to 92% efficiency; however the average efficiency is generally below 90% even though high pressures are applied. In PRO systems, where the applied pressures are in the range from 10 to 30 bars, this efficiency value further drops to between 60 to 80%. Therefore, when seawater is selected as the draw solution, the net produced power per m\(^3\) of draw solution could be around 0.2 – 0.37 kWh (Achilli and Childress 2010).

7.5.3 Large-scale applications of PRO

Until recently, the Norwegian electric company, Statkraft, had been the pioneer of large scale PRO applications by constructing and operating the first prototype PRO facility in the world (Statkraft 2014). Statkraft adopted a system where seawater was used as the draw solution in their system (see Figure 7.7) (Skilhagen et al. 2008). Spiral wound membrane modules, which were supplied by Hydranautics, were used with a projected power density of 5 W·m\(^{-2}\) at around a 12.5 bar hydraulic pressure difference across the membrane. However, low extractable work values of the selected system configuration and parameters (seawater as the draw solution), inefficiencies in the hydraulic power generation systems and high capital investment requirements, forced the company to cease their osmotic power operations in December 2013.
The Japanese Mega-ton Water System project, however, adopted a PRO system which uses seawater reverse osmosis (SWRO) brine as the draw solution (see Figure 7.8) (Kurihara and Hanakawa 2013), in which the highest theoretical extractable work was calculated as 2.75 kWh per m$^3$ of draw solution used as opposed to 0.75 kWh per m$^3$ in seawater systems. The Megaton project selected hollow fiber PRO membrane modules, which were supplied by the Toyobo company, with a predicted power density of more than 12 W-m$^{-2}$ at around a 30 bar hydraulic pressure difference across the membrane. The achievement of 13.3 W-m$^{-2}$ for a 10 inch diameter module was announced during the “Mega-ton Water System” International Symposium (November 21-22, 2013) (Mega-ton Water System 2014). The Mega-ton project, as Statkraft did, used hydraulic turbines to convert the salinity gradient potential of SWRO brine to electricity in its 460 m$^3$-day$^{-1}$ brine flow rate capacity pilot plant, in Fukuoka, Japan (Kurihara and Hanakawa 2013).
So far, there have not been many PRO applications where the salinity gradient is harvested and converted to the hydraulic pressure in order to be used in different pressure dependent systems. A recently initiated Korean national research project, Global MVP (Membrane Distillation, Valuable Source Recovery, PRO), is one of the first multimillion dollar projects, where PRO is used to utilize hydraulic pressure without converting it to electricity. Global MVP adopts an SWRO-PRO hybrid system, where diluted draw solution from PRO is used to pre-pressurize the seawater prior to the SWRO process. Seawater pre-pressurizing is established by deploying isobaric pressure exchangers, which can reach up to 97% efficiency in terms of energy recovery. Woongjin Chemical (CSM membranes) is the membrane producer partner in the project and supplies spiral wound PRO membrane modules with a predicted power density of 7.5 W·m⁻². Energy Recovery Inc. (USA) is another key partner in the project in order to optimize and supply high efficiency isobaric pressure exchangers which are customized for the specified purpose.

7.5.4 PRO membranes

There have been several companies and research groups working intensively on the PRO membrane development in order to increase the power density of these membranes at relatively high pressures (Arena et al. 2011, Bui et al. 2011, Tiraferri et al. 2011, Alsvik and Hägg 2013). During the recent evolution of high performance PRO membranes, thin-film composite membranes emerged as a better choice for relatively higher mechanical durability and salt rejection. Furthermore, macrovoid-free support layers were accepted as a solution to membrane deformation during high pressure PRO operations (Sukitpaneenit and Chung 2012, Chou et al. 2013).

Flat sheet PRO membranes can be produced with a very thin support layer, which enables higher permeate fluxes at a given osmotic and hydraulic pressure difference. However, flat sheet membranes, even with the macrovoid free structure, can be subject to deformation under high hydraulic pressures. Moreover, spiral wound membrane modules are the most common application of flat sheet membranes, which can cause a serious shadow effect during osmotic processes, with respect to its mechanical structure. HTI, Hydranautics and Woongjin Chemical (CSM) are three global companies working on the development of the efficient and high power density PRO membranes. Hollow fiber PRO membranes, on the other hand, have distinct advantages over flat sheet membranes as being distinguished to have a self-supported mechanical structure, high packing density, and outstanding flow patterns. However, Toyobo is the sole globally recognized membrane producer, which has the proven capability, background, and experience to develop high efficiency hollow fiber PRO membranes.

7.6 Major challenges for commercialization

FO is not yet a mature technology, but it is expected to help reduce the cost of producing fresh water from impaired-quality sources in the next decade. According to the 25th Desal Data IDA Worldwide Desalting Plant Inventory, the installed SWRO capacity of desalination plants around the world as of June 30, 2012 was 74.8 million m³·d⁻¹. The cumulative
contracted capacity, which includes plants that are contracted or under construction, reached 80.5 million m$^3\cdot$d$^{-1}$. It is expected that the installed capacity will reach 120 million m$^3\cdot$d$^{-1}$ by 2020 (Bennett 2013). Clearly there is a need for fresh water; therefore, new generation FO systems will play a significant role in the desalination and water treatment industries. The main advantages, disadvantages and challenges of FO technology compared to present RO standards are depicted in Table 7.6.

<table>
<thead>
<tr>
<th>Process</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Challenges</th>
</tr>
</thead>
<tbody>
<tr>
<td>FO</td>
<td>Less energy intensive for water transport across the membrane; reversible fouling; lower operational costs</td>
<td>Permeate water requires a second separation step; higher capital costs; ICP* in FO membranes</td>
<td>Low water flux membranes; lack of cost-effective draw solutes; limited studies on fouling and biofouling; reduction of ICP</td>
</tr>
<tr>
<td>RO</td>
<td>Permeate water is high quality product; lower capital costs</td>
<td>High energy consumption; irreversible fouling; higher operational costs</td>
<td>How to improve energy recovery efficiency; How to mitigate membrane fouling</td>
</tr>
</tbody>
</table>

*ICP – internal concentration polarization

The major challenges of FO to be a commercially viable technology are: (i) developing a high flux membrane, capable of maintaining an elevated salt rejection and a reduced internal concentration polarization (ICP) effect, (ii) for PRO applications, the membrane has to additionally give adequate mechanical support to withstand hydraulic pressure, (iii) in some applications, the availability of appropriate draw solutions, which can be recirculated via an efficient recovery process, (iv) better understanding of fouling and biofouling occurrence in osmotically driven processes, (v) assuring the high quality of the water produced, (vi) hybridization with other technologies that can increase the benefits of FO use (i.e. water recovery, energy production, etc.). (Chung et al. 2012) suggested the use of RO concentrate instead of seawater as the draw solute for water reuse to lower the operational cost and bring FO closer to commercialization. (Choi et al. 2009) found that the integration of FO and RO may result in a high flux of fresh water and a stable performance under some operating conditions; however, the internal concentration polarization in FO is an important factor affecting the overall performance, since it reduces the effective osmotic pressure that drives the filtration process. These are just examples of listed technologies that integrate FO with other processes (Table 7.3).

From the listed challenges above, research has largely focused on producing a better FO membrane (Wang et al. 2007, Chou et al. 2010, Wang et al. 2010a, Wang et al. 2010b, Zhang et al. 2010, Setiawan et al. 2011, Fu et al. 2013, You et al. 2013, Zhong et al. 2013, Romero-Vargas Castrillón et al. 2014). Biofouling is, on the contrary, one of the least
understood and investigated topics in forward osmosis systems (Valladares Linares et al. 2014). Valladares Linares et al. (2012) studied the fouling layer on the FO membrane operated in an indirect desalination system. The natural organic matter (NOM) fouling layer was found to be composed of biopolymers and protein-like substances, which adversely affect the flux of water through the FO membrane. On the support layer of the membrane, in contact with seawater, transparent exopolymeric particles (TEP) formed clusters clearly identifiable with an optical microscope and a TEP-specific dye.

7.7 Knowledge gaps and future research

The shortage of favorable and commercially available FO membranes is still the major constrain limiting application of this FO process. More studies should be conducted to improve the process efficiency by developing novel FO membranes, investigating the stability and sustainability of the process under long-term operation and improving the module design to tailor them for the different niches in the water industry.

Special attention should be given to the transport of small molecular weight carbon and nitrogen compounds from the feed solution to the draw solution, which may act as substrate for bacteria to grow and represent a problem for long-term operation and biofouling control of an FO indirect desalination system.

Numerical modeling can be a useful tool to predict and prevent biofouling in FO membranes. Along with this, future studies should focus on the use of modified spacers and novel cleaning strategies, which may be in agreement with cleaning protocols already developed for FO and RO membranes, to mitigate biofouling in FO systems.

Finally, it is strongly suggested to upscale the process into a pilot scale facility in which a comprehensive evaluation of water quality and energy parameters can be done, facilitating a life cycle assessment and a cost cycle assessment of a hybrid process (i.e., FO-LPRO), which will give important information on the direction that should be taken to develop robust low cost water treatment hybrid systems to produce high quality water.

There is no distinct boundary between desalination and water reuse in this review. Unless a very successful draw solution is invented, a single FO process cannot compete against an entire desalination and/or water treatment/reuse process. However, FO can play a role as a bridge to integrate upstream and downstream processes, to reduce the energy consumption of the entire process, thus achieving a sustainable solution for the water-energy nexus.

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Nomenclature

This section provides a list of the most commonly used symbols in this thesis.

### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-D FEEM</td>
<td>3-dimensional fluorescence excitation emission matrix</td>
<td>(-)</td>
</tr>
<tr>
<td>AL</td>
<td>active layer</td>
<td>(-)</td>
</tr>
<tr>
<td>AL-DS</td>
<td>active layer facing draw solution</td>
<td>(-)</td>
</tr>
<tr>
<td>AL-FS</td>
<td>active layer facing feed solution</td>
<td>(-)</td>
</tr>
<tr>
<td>ATP</td>
<td>adenosine 5’triphosphate</td>
<td>(pg∙cm²)</td>
</tr>
<tr>
<td>BOD₅</td>
<td>biochemical oxygen demand at 5 days</td>
<td>(mg∙L⁻¹)</td>
</tr>
<tr>
<td>BSA</td>
<td>bovine serum albumin</td>
<td>(-)</td>
</tr>
<tr>
<td>CDOC</td>
<td>chromatographic dissolved organic carbon</td>
<td>(-)</td>
</tr>
<tr>
<td>CFW</td>
<td>concentrated feed water</td>
<td>(-)</td>
</tr>
<tr>
<td>CLSM</td>
<td>confocal laser scanning microscopy</td>
<td>(-)</td>
</tr>
<tr>
<td>COD</td>
<td>chemical oxygen demand</td>
<td>(mg∙L⁻¹)</td>
</tr>
<tr>
<td>CP</td>
<td>concentration polarization</td>
<td>(-)</td>
</tr>
<tr>
<td>CTA</td>
<td>cellulose triacetate</td>
<td>(-)</td>
</tr>
<tr>
<td>CWWE</td>
<td>concentrated wastewater effluent</td>
<td>(-)</td>
</tr>
<tr>
<td>DAPI</td>
<td>4′,6-diamidino-2-phenylindole</td>
<td>(-)</td>
</tr>
<tr>
<td>DDS</td>
<td>diluted draw solution</td>
<td>(-)</td>
</tr>
<tr>
<td>DI</td>
<td>deionized</td>
<td>(-)</td>
</tr>
<tr>
<td>DO</td>
<td>direct osmosis</td>
<td>(-)</td>
</tr>
<tr>
<td>DOC</td>
<td>dissolved organic carbon</td>
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</tr>
<tr>
<td>DS</td>
<td>draw solution</td>
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</tr>
<tr>
<td>ECP</td>
<td>external concentration polarization</td>
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</tr>
<tr>
<td>EDCs</td>
<td>endocrine disruptive compounds</td>
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</tr>
<tr>
<td>EDTA</td>
<td>ethylenediaminetetraacetic acid</td>
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<tr>
<td>EDX</td>
<td>energy dispersive x-ray</td>
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<tr>
<td>EWWE</td>
<td>evaporated waste water effluent</td>
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</tr>
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<td>FC</td>
<td>flow controller</td>
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</tr>
<tr>
<td>FITC</td>
<td>fluorescein isothiocyanate</td>
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</tr>
<tr>
<td>FO</td>
<td>forward osmosis</td>
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<td>FM</td>
<td>flow monitor</td>
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<td>FS</td>
<td>feed solution</td>
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<td>FSW</td>
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</tr>
<tr>
<td>FW</td>
<td>feed water</td>
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</tr>
<tr>
<td>GP</td>
<td>gear pump</td>
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</tr>
<tr>
<td>ICP</td>
<td>internal concentration polarization</td>
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</tr>
<tr>
<td>ICP-MS</td>
<td>inductively coupled plasma/mass spectrometry</td>
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</tr>
<tr>
<td>LC-OCD</td>
<td>liquid chromatography coupled with organic carbon detector</td>
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<tr>
<td>LMW</td>
<td>low molecular weight</td>
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</tr>
<tr>
<td>LPRO</td>
<td>low pressure reverse osmosis</td>
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<tr>
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<td>Description</td>
<td>Unit</td>
</tr>
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<td>---------</td>
<td>--------------------------------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>MBR</td>
<td>membrane biological reactor</td>
<td>(-)</td>
</tr>
<tr>
<td>MF</td>
<td>microfiltration</td>
<td>(-)</td>
</tr>
<tr>
<td>MP</td>
<td>micropollutants</td>
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<tr>
<td>MW</td>
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<td>MWCO</td>
<td>molecular weight cutoff</td>
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<td>NOM</td>
<td>natural organic matter</td>
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<td>NTU</td>
<td>nephelometric turbidity units</td>
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</tr>
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<td>OND</td>
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<td>OsMBR</td>
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<tr>
<td>PBS</td>
<td>phosphate-buffered saline</td>
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<td>positive displacement pump</td>
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<tr>
<td>POC</td>
<td>particulate organic carbon</td>
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<td>PRO</td>
<td>pressure retarded osmosis</td>
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<td>RLU</td>
<td>relative light units</td>
<td>(RLU)</td>
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<td>reverse osmosis</td>
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<td>synthetic diluted draw solution</td>
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<tr>
<td>SEC</td>
<td>specific energy consumption</td>
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<td>SEM</td>
<td>scanning electron microscopy</td>
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<td>TDS</td>
<td>total dissolved solids</td>
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<tr>
<td>TEP</td>
<td>transparent exopolymer particles</td>
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<td>TFC</td>
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<td>total suspended solids</td>
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<td>ZP</td>
<td>zeta potential</td>
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**Symbols**

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>water permeability coefficient</td>
<td>(m·atm⁻¹·d⁻¹)</td>
</tr>
<tr>
<td>B</td>
<td>solute permeability coefficient</td>
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<td>ΔG</td>
<td>Gibbs free energy</td>
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<td>γ</td>
<td>activity coefficient of any given species</td>
<td>(-)</td>
</tr>
<tr>
<td>i</td>
<td>dimensionless van’t Hoff factor</td>
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</tr>
<tr>
<td>Jₐve</td>
<td>average water flux</td>
<td>(L·m⁻²·h⁻¹)</td>
</tr>
<tr>
<td>Jᵢₙᵢ</td>
<td>initial water flux</td>
<td>(L·m⁻²·h⁻¹)</td>
</tr>
<tr>
<td>Jₖᵢ</td>
<td>water flux</td>
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</tr>
<tr>
<td>K</td>
<td>solute resistivity of the membrane</td>
<td>(s·m⁻¹)</td>
</tr>
<tr>
<td>M</td>
<td>molarity</td>
<td>(mol·m⁻³)</td>
</tr>
<tr>
<td>P</td>
<td>hydraulic pressure</td>
<td>(bar)</td>
</tr>
<tr>
<td>ΔP</td>
<td>applied hydraulic pressure</td>
<td>(bar)</td>
</tr>
<tr>
<td>π</td>
<td>osmotic pressure</td>
<td>(bar)</td>
</tr>
<tr>
<td>Δπ</td>
<td>osmotic pressure difference</td>
<td>(bar)</td>
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<tr>
<td>Q</td>
<td>flow</td>
<td>(m³·s⁻¹)</td>
</tr>
<tr>
<td>R</td>
<td>gas constant</td>
<td>(m³·bar·K⁻¹·mol⁻¹)</td>
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<tr>
<td>ρ</td>
<td>density</td>
<td>(Kg·m⁻³)</td>
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<tr>
<td>S</td>
<td>structural parameter</td>
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<tr>
<td>σ</td>
<td>reflection coefficient</td>
<td>(-)</td>
</tr>
<tr>
<td>τ</td>
<td>membrane tortuosity</td>
<td>(-)</td>
</tr>
<tr>
<td>tₛ</td>
<td>support layer thickness</td>
<td>(μm)</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
<td>(°K or °C)</td>
</tr>
<tr>
<td>W</td>
<td>power density</td>
<td>(Watt)</td>
</tr>
<tr>
<td>Φ</td>
<td>molar ratio</td>
<td>(-)</td>
</tr>
<tr>
<td>χᵢ</td>
<td>mole fraction of species i in solution</td>
<td>(-)</td>
</tr>
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List of author publications


Valladares Linares, R., Sz. S. Bucs, Z. Li, M. AbuGhdeeb, G. Amy, and J.S. Vrouwenvelder. Impact of spacer thickness on biofouling in forward osmosis. Accepted for publication in Water Research. (Chapter 6)


Under review/preparation

Valladares Linares, R., Z. Li, S. Sarp, G. Amy, and J.S. Vrouwenvelder. Forward osmosis niches in seawater desalination and wastewater reuse. (Chapter 7)


# Curriculum Vitae

<table>
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<tr>
<th>Period</th>
<th>Position and Details</th>
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<tr>
<td>Aug. 2011 – Present</td>
<td>Engineering Specialist at Water Desalination and Reuse Center – King Abdullah University of Science and Technology (KAUST), Saudi Arabia</td>
</tr>
<tr>
<td>Aug. 2011 – Oct. 2014</td>
<td>PhD at Delft University of Technology, Netherlands</td>
</tr>
<tr>
<td>Jun. 2010 – Aug. 2010</td>
<td>Research Intern at University of California Berkeley, USA</td>
</tr>
<tr>
<td>Sep. 2009 – Jul. 2011</td>
<td>Master in Environmental Science and Engineering at King Abdullah University of Science and Technology (KAUST), Saudi Arabia</td>
</tr>
<tr>
<td>Jan. 2005 – Jun. 2009</td>
<td>Bachelor of Science in Civil Engineering at Universidad Iberoamericana, Mexico</td>
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