Reclaiming Water from Wastewater using Forward Osmosis



Kerusha Lutchmiah

Reclaiming Water from Wastewater using Forward Osmosis

Proefschrift

ter verkrijging van de graad van doctor aan de Technische Universiteit Delft, op gezag van de Rector Magnificus prof. ir. K.C.A.M. Luyben, voorzitter van het College voor Promoties, in het openbaar te verdedigen op woensdag 2 juli 2014 om 10:00 uur

door

Kerusha LUTCHMIAH

Master of Science in Biotechnology Mannheim University of Applied Sciences

geboren te East London, Zuid-Afrika

Dit proefschrift is goedgekeurd door de promotor: Prof. dr. ir. L.C. Rietveld

Samenstelling promotiecommissie:	
Rector Magnificus,	voorzitter
Prof. dr. ir. L.C. Rietveld,	Technische Universiteit Delft, promotor
Prof. dr. ir. J.B. van Lier,	Technische Universiteit Delft
Prof. dr. ir. D.C Nijmeijer,	Universiteit Twente
Prof. dr. ir. W.G.J. van der Meer,	Technische Universiteit Delft
Prof. dr. ir. A.R.D. Verliefde,	Universiteit Gent
Dr. ir. E.R. Cornelissen,	KWR Watercycle Research Institute
Dr. ir. C.Y. Tang,	University of Hong Kong
Prof. dr. ir. M. Kennedy,	Technische Universiteit Delft, reservelid

Dr. E.R. Cornelissen en Dr. K. Roest, KWR Watercycle Research Institute hebben als begeleiders in belangrijke mate aan de totstandkoming van het proefschrift bijgedragen.

This research "Sewer Mining" (IWA10003) was funded by the Dutch Ministry of Economic Affairs, Agriculture and Innovation (AgentschapNL).

ISBN/EAN: 978-94-6186-316-4

Copyright © 2014 by K. Lutchmiah

All rights reserved. No part of the material protected by the copyright may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the copyright owner.

Cover design: Gloria Font (www.atelierfont.com) Printer: Ecodrukkers, ecodrukkers.nl

Acknowledgements

Attaining a PhD was not the initial plan. After my Master's degree I wanted to jump straight in and make an immediate difference to society. Coming from a region where water scarcity (and rolling blackouts) is rife and shockingly real, my goal has always been to give back to these communities. When I read the Sewer Mining project description, I found it an offer too tempting to resist. The concept of water and energy seemed to fit in perfectly with my ambitions.

Many a PhD candidate will tell you that passion can carry you a long way, but when your legs tire, only an amazing support group will carry you across the finish line. The completion of this dissertation would therefore not have been possible without the many, many people supporting me along the way.

Firstly, I would like to thank my promotor, Prof. Luuk Rietveld, for accepting to take on this project, and me as his PhD student. Thank you for giving me this platform to grow, for your advice, understanding, guidance and for keeping me focussed. And for responding to my relentless emails regardless of the hour, I am very grateful. Furthermore, your work in developing countries truly inspires me.

To my daily supervisor, Emile Cornelissen, I could not have been luckier! It was an honour working with you. Thank you for driving me to be the best I could be, for the encouraging and inspirational discussions and for never failing to read and re-read my roughest of drafts. Your expertise and criticism were invaluable to this research and my growth as a researcher. Thank you for all the sandpapering to make this thesis what it is today. I am grateful also, for introducing me to your network, for allowing me to gain confidence in the field and to execute my own ideas. Also, the meals shared with your family were always very special and memorable.

Much appreciation goes to Kees Roest for all the significant and arbitrary conversations, for your genuine concern, invaluable knowledge in wastewater, for all the laughs, ridiculousness and word games. You too worked closely with me at the beginning, at times pushing me beyond my limits; for that I am extremely grateful.

Furthermore to my paranymphs and dear friends Sara, whom I met while carpooling daily from Den Haag to Nieuwegein and Annelies, whom I met during the Wetskills programme to Morocco. Thank you for your friendship throughout these 4 years. Sarita, additionally, thank you for pulling me along with you to the finish line! You were the light at the end of a very long tunnel.

At KWR, I would like to thank Jan P, for his motivational talks and enthusiasm; Danny H and Wolter S for their continuous assistance in the lab; Bas W and Dirk for their sharp modelling skills, Hans H, for his encyclopaedia of knowledge in all things membranes; Erwin B, for filling in as my project manager during the last few months; the IAH team, thank you for your support; Nanda and Anke for their help in lab; Patrick B, for putting up with all my chemistry questions, dankeschön! To Harry and Sidney, from the "The Charlie and the Chocolate Factory" workshop, an immense thanks for all your help over the years, whether it be constructing the set-up, trouble-shooting or helping me with my flat tyres, you guys are great! And to the secretaries Claire and Beryl for all their assistance and smiles. Furthermore, I am indebted to my interns: Laura, Max, Qian, Lionel, Dong and Cynthia for inspiring me to be a better supervisor, allowing me to stimulate their curiosity and enriching me with their French and Chinese cultures.

I would furthermore like to thank my KWR friends: Yuki, Andreas, Bea, Sabrina, Melanie, Diego, Helena, Ana, Claudia, Vicky, Christian E ("life is just one big coffee break"), Roberto, Erik E (and Sandra); Chris B and Andrew – thank you for all the lunches, food supplies, walks, talks and breaks.

At the TUD, Prof. Jules van Lier, for his input in the project; the secretaries, Mieke, Jennifer and Anouk for being omnipresent - I was so very grateful to have you around. To all those who assisted in the lab(s), especially David M for sending me my TOC files so often, Tonny Schuit, Louw Florusse (TNW) for assisting with the contact angle measurements and Michel van den Brink (P&E) for all the ICP measurements. Furthermore, a huge thanks to Jenny, Sam, Jorge (and Paula), Ran, Dara, Sandra, Thabo and Guido for making the times I was present at the TUD really enjoyable.

To the project partners and others who assisted me with this thesis: HTI – Keith (and family), Ed and John for never failing to respond my questions and queries; Triqua - Hans and Joris; Waternet -Ron Weerstand, for kindly assisting me during sampling, Adrien Aze for sending me the data, Marcel and Joost, thank you; Chuyang Tang (HKU), for his assistance and advice; Arie Zwijnenburg (Wetsus) for all his help and willingness, always - it was a tremendous pleasure working with and learning from you – a true master. Ghent University - Arne, thank you so much for all your input and constant enthusiasm, you never cease to amaze me, Arnout, Gaetan and Machawe for all their assistance. Additionally, for all the stimulating discussions via email or phone: Prof. Ian R. Booth (University of Aberdeen) for our many discussions regarding GB and osmometers, Aaron Wilson (Idaho National Laboratory), for his immense help and insight into the units and colligative properties we use in FO thank you!

An enormous amount of gratitude to my international family, the Mannheim crew: Rami, Cem (for the layout ideas and tips - Teşekkürler!), Pablo, Tatyana, Li Ming, Juliana, Maria, Greta, Axel (and the rest of the Moser family) for supporting me throughout these last 12 years; my dear USC friends: Daga, Denisse, Isaac (for reading my chapters!), Angelica and everyone else from ETSE, for all the love; my South African friends, regardless of distance some friendships are just meant to last forever; and my friends much closer: Selma, Gloria (Gracias por la magnífica portada!), Charlie, Fatemeh, Stevia, Jorge, Dina, Jayshree and Diane, I'm glad to have you all in my life.

Last but not least, to the incredible family I have been blessed with, thank you for all the support, no matter what, when or where: Aya, for always being so proud of me and sharing that with anyone who would listen; the Mayers, for being there from day one; my brothers, Lish and Nash, for the love and laughter and Mum, words cannot express how much I appreciate the unconditional love and freedom you have given me to live my life.

Finally, to Michael, because in the history of PhD candidacies, I do not believe anyone has eaten as well, and deliciously, as I have! Thank you for all your patience, understanding and for making my life a little easier.

Kerusha Lutchmiah Utrecht, May 2014

Summary

&

Nederlandse samenvatting



Summary

This thesis is part of the Sewer Mining project aimed at developing a new technological concept to extract water from wastewater by means of forward osmosis (FO), a novel membrane technology. In general, greater than 99.93 % of municipal wastewater is composed of water. If the water can be separated from the solids (suspended and dissolved), it can be reused, alleviating the global water stress that currently exists.

FO is driven by osmosis and therefore differs from other membrane processes which depend on hydraulic pressure. FO, in combination with a reconcentration system, e.g. reverse osmosis (RO) is used to recover high-quality water for use in industrial processes. Furthermore, the subsequent concentrated wastewater (containing an inherent energy content) can be converted into a renewable energy source, i.e. biogas, for further use in the system.

FO, incorporated in sewer mining applications shows great potential, as it could lead to a more economical and sustainable treatment of wastewater, but before it can reach full-scale feasibility, several research questions need to be addressed.

Efforts to address these pending questions culminated into this thesis. The research approach consisted of:

- Inventory of existing knowledge on FO, specifically relating to wastewater, via data collection from scientific literature and other sources;
- Characterisation of wastewater (primary effluent) from wastewater treatment plants, to assess and analyse fouling properties on the FO membrane;
- Experimental investigations on lab-scale (U-tube, cross-flow) and pilot-scale;
- Validation of experimental work via existing and newly developed FO transport models, coupled to a technical economic model.

The major topics in this thesis, which cover limitations experienced by FO processes during wastewater applications, are summarised below.

Solute leakage

The draw solution (osmotic agent) is the driving force in FO processes. Transport of draw solutes through the membrane, i.e. via reverse solute leakage, can pose substantial limitations to the implementation of FO processes, lowering the driving force and therefore the flux performance, while recovery of the draw solution (in closedloops) is also financially limiting.

Several alternative solutes as draw solutions were systematically investigated on lab-scale to enhance the FO performance and minimise the solute loss. The highly soluble zwitterions: glycine, L-proline, glycine betaine and the anthropogenic amino acid, EDTA, demonstrated comparable water fluxes to NaCl (~5 L/m²h), but with significantly lower solute losses, which is advantageous for cost reduction. The physicochemical properties, charge and size of the solutes all played dominant roles in the flux efficiencies. The FO mass transfer model furthermore verified the experimental investigations of the solute transport through the membrane. The use of these draw solutions in FO for wastewater reclamation applications also showed the benefits of the solute leakage, in terms of energy production (biogas) and reduction of the reconcentration costs for the process.

Membrane Fouling

Membrane fouling concerns a process whereby an accumulation of solutes and/or particles exists on a membrane surface, within the membrane pores or within the feed spacer channel. The permeate quality and quantity of the process is subsequently limited. Fouling has been reported to have only a marginal effect on FO membranes, due to the lack of hydraulic pressure. This thesis employed raw wastewater to test the extent of fouling.

The effects of fouling on the surface characteristics and operational conditions of FO membranes were investigated on lab-scale. FO treated wastewater resulted in the formation of a fouling layer on the investigated membrane, causing an 18 % water flux decline compared to the baseline study. Surface properties and rejection behaviours of virgin, fouled and mechanically-cleaned membranes were further compared. In terms of surface charge analyses, fouling was found to increase the negative charge

of the membrane surface, while contact angle measurements established an increase in hydrophilicity compared to the virgin membrane. The surface tensions of the cleaned membrane differed slightly from the virgin membrane, confirming the presence of foulant attachment on the membrane, which may have led to irreversible fouling. ATP measurements determined high concentrations of active bacteria in the fouling layer (70.9 ng ATP/cm^2), while the carbohydrate analyses, Fourier transform infrared spectroscopy (FTIR) and liquid chromatography (LC-OCD) ascertained the existence of polysaccharides (3.3 mg glucose/cm²), the main composition of polymeric extracellular substances (EPS). Biopolymers (more specifically, polysaccharides) were found to be the main cause of fouling on the FO membrane

Flux enhancement

In the FO process, internal concentration polarisation (ICP) within the porous layer is considered a major problem, reducing the water flux and increasing reverse solute transport. Flux optimisation can be carried out by improving membrane properties, i.e. designing thinner, more porous and less tortuous support layers to reduce ICP or varying process-related properties, e.g. temperature and flow conditions. Improved flux performance will allow FO to compete with fluxes achieved by hydraulically driven membrane processes. During this thesis, the concept of pressure assisted osmosis (PAO) was developed.

PAO, an FO process involving the use of hydraulic pressure on the set-up feed side, was proposed to enhance FO performance. An FO mass transport model (active layer to feed side orientation) incorporating pressure was developed to describe the fluxes in PAO. Continuous and discontinuous PAO operations (0.1 - 0.8 bar) on laboratory scale were evaluated using draw solutions equivalent to 24 bar. The fluxes increased with increasing hydraulic feed pressures for all PAO experiments, including activated sludge feeds, owing to the increased driving force and membrane deformation. Discontinuous PAO was found to have an adverse effect on the salt fluxes, due to the occurrence of hydraulic back pressure. This study emphasized the benefits of PAO using diverse feeds, while illustrating the

importance of developing more rigid membranes and better support designs.

Feasibility of a sewer mining concept

Closed-loop FO differs from osmotic dilution/ concentration, in that the draw solution is recycled and reused by the process. The latter process tends to be more economically feasible as no recovery step is required, reducing the energy cost. It is therefore more often applied in practice. If the energy consumption of the recovery step could be reduced, closed-loop FO would become a more feasible technology. Sewer mining allows for energy generation from wastewater which can be applied in the recovery step.

In this thesis, a technical economic model (TEM) was developed to describe the economic aspects of a general FO-RO process and more particularly for sewer mining concepts. The TEM was based on the FO mass transfer model and a mass transfer model for larger FO membrane installations combined with RO. As such, the total cost pertaining to the treatment of wastewater for use in industry was also determined.

The total treatment cost of the process, including capital and operational costs, was determined to be $0.65 \notin m^3$ with the FO membrane cost significantly influencing the price.

Despite some restrictions of the TEM model, the Sewer Mining concept was found to be economically feasible when compared to fullscale water treatment (seawater desalination < 1 ϵ/m^3). Further viability will increase if future FO membranes are optimised to reduce leakage, increase fluxes and become more economical.

Water scarcity is a global problem and waste accumulation is a steadily growing one. By implementing this green, self-sufficient FO technology to extract water and energy from wastewater, this thesis has attempted to contribute to changing the way wastewater is perceived: not as waste, but as a resource. In this way, water which we use today can be reused for generations to come.

Samenvatting

Dit proefschrift is een onderdeel van het Sewer Mining project gericht op het ontwikkelen van een nieuw technologisch concept om water te onttrekken uit afvalwater door middel van directe of forward osmose (FO), een nieuw membraanproces. Over het algemeen bestaat municipaal afvalwater voor meer dan 99% uit water, wat kan worden hergebruikt als het wordt gescheiden van de opgeloste stoffen en deeltjes in het afvalwater. Het Sewer Mining concept kan een bijdrage leveren aan het verlagen van de mondiale waterstress.

FO wordt gedreven door een osmotisch verschil over het membraan, en verschilt daardoor van de meer bekende drukgedreven membraanprocessen, zoals omgekeerde osmose en nanofiltratie. FO in combinatie met een terugwinningsproces voor de osmotische oplossing, zoals omgekeerde osmose, kan worden gebruikt voor het produceren van hoog kwaliteitswater voor industriële processen uit afvalwater. Hiernaast kan het geconcentreerde afvalwater worden omgezet in een hernieuwbare energiebron, zoals biogas, dat vervolgens kan worden gebruikt in het systeem. FO toegepast in Sewer Mining toepassingen heeft een grote potentie, en kan leiden tot een goedkopere en duurzamere behandeling van afvalwater. Echter voordat het concept grootschalig kan worden toegepast, moeten nog een aantal onderzoeksvragen worden beantwoord.

Inspanningen naar het beantwoorden van deze onderzoeksvragen hebben geleid tot dit proefschrift. De onderzoeksaanpak bestaat uit:

- Het verkrijgen van een overzicht van de beschikbare kennis op het gebied van FO, specifiek gericht op afvalwatertoepassingen, door data collectie uit de wetenschappelijke literatuur en andere bronnen;
- Het karakteriseren van primair behandeld afvalwater (primair effluent) afkomstig van afvalwaterzuiveringsinstallaties om de vervuilingseigenschappen van FO membranen te bepalen en analyseren;

- Experimenteel onderzoek op laboratorium en pilot schaal (U-buis en langsstroomcel);
- Validatie van experimenteel werk met bestaande en nieuw ontwikkelde FO transportmodellen gekoppeld aan een technisch economisch model (TEM).

De in dit proefschrift bestudeerde hoofdthema's, inclusief limiteringen van FO in afvalwatertoepassingen, zijn hieronder opgesomd.

Verlies van de osmotische oplossing

De osmotische oplossing is de drijvende kracht van het FO proces. Het transport van deze oplossing door het membraan leidt tot limiteringen in het FO proces, zoals een verlies van de drijvende kracht over het FO membraan resulterend in flux verliezen. Hiernaast is het terugwinnen van de osmotische oplossing in een additioneel proces (bijvoorbeeld RO) in gesloten systemen een bijkomstige financiële limitatie. Verschillende alternatieve osmotische oplossingen zijn systematisch bestudeerd op laboratorium schaal om de FO opbrengst te vergroten en het verlies van de osmotische oplossing te verlagen. De goed oplosbare zwitterion oplossingen, glycine, L-proline, glycine betaïne en het antropogeene aminozuur en EDTA, vertoonden vergelijkbare flux waarden als NaCl (~5 L/m²h), echter met significant lagere verliezen van de osmotische oplossing wat kan resulteren in een kostenbesparing. De fysicochemische eigenschappen, zoals lading en molecuulgewicht van de stoffen, spelen een belangrijke rol in de efficiëntie van de oplossingen in het FO proces. Hiernaast worden de experimentele resultaten gevalideerd met modelberekeningen met een FO stoftransportmodel. Het gebruik van de genoemde alternatieve osmotische oplossingen bij FO in afvalwatertoepassingen resulteerde in voordelen met betrekking tot (i) het beperken van verliezen van de osmotische oplossing, (ii) energieproductie in de vorm van biogas en (iii) een reductie van terugwinningskosten voor het proces.

Membraanvervuiling

Membraanvervuiling betreft de ophoping van stoffen en/of deeltjes op het membraanoppervlak, in de membraanstructuur of in het membraanvoedingskanaal waarin zich (meestal) een voedingsspacer bevindt. Hierdoor wordt de kwaliteit en de kwantiteit van het membraanproces negatief beïnvloed. Uit de literatuur is bekend dat membraanvervuiling een geringe rol speelt bij FO membranen, ten gevolge van het ontbreken van een hydraulische druk. In dit proefschrift is gekeken naar de rol van FO membraanvervuiling met onbehandeld afvalwater als voeding. Zowel de effecten van de membraanoppervlaktekarakteristieken als de bedrijfsvoeringscondities op FO membraanvervuiling zijn bestudeerd op laboratoriumschaal. FO met onbehandeld afvalwater resulteerde in een vervuilingslaag op het bestudeerde membraan, resulterend in een 18% flux afname vergeleken met een referentie experiment met schoon water. De membraanoppervlakte-eigenschappen en het retentiegedrag van nieuwe, vervuilde en hydraulisch gereinigde membranen zijn met elkaar vergeleken. Uit een oppervlaktelading analyse bleek dat de negatieve lading van het membraanoppervlak toenam ten gevolge van vervuiling, en uit contacthoekmetingen bleek dat de membranen hydrofieler werden. De oppervlaktespanning van het gereinigd membraan verschilde van het nieuwe membraan, wat een indicatie kan zijn van de aanwezigheid van een irreversibele vervuilingslaag. ATP metingen wezen op een hoge concentratie van actieve bacteriën in de vervuilingslaag (70.9 ng ATP/cm²), terwijl de koolhydratenbepaling, Fouriertransformatie infrarood spectrometer (FTIR) en vloeistofchromatografie (LC-OCD) analyses de aanwezigheid bevestigden van polysachariden (3.3 mg glucose/cm²), wat het hoofdbestanddeel is van extracellulair polymere substanties (EPS). Uit deze studie blijken biopolymeren, en meer specifiek polysachariden, de belangrijkste oorzaak te zijn van FO membraanvervuiling in afvalwaterbehandeling.

Fluxverbetering

Interne concentratiepolarisatie (ICP) in de poreuze steunlaag van FO membranen is een groot probleem in FO, resulterend in een flux afname en toename van het verlies van de osmotische oplossing door het membraan. Fluxverbetering kan worden bereikt door (i) het verbeteren van de membraaneigenschappen, door dunnere, poreuzere en minder tortueuze steunlagen te ontwerpen die resulteren in minder ICP of (ii) het variëren van procesparameters, zoals de temperatuur en voedingsdebiet. Fluxverbetering van FO membranen brengt de flux waarden dichterbij de flux waarden van druk gedreven membraanprocessen. In dit proefschrift is druk geassisteerde osmose of in het Engels pressure assisted osmose (PAO) ontwikkeld. PAO is FO waarbij de voedingsdruk wordt verhoogd om de flux prestatie van het FO proces te verbeteren. Een FO stoftransportmodel met een additionele drukterm aan de voedingszijde van het FO membraan is ontwikkeld om de PAO flux waarden te kunnen beschrijven (alleen voor de oriëntatie waarbij de actieve membraanzijde grenst aan de voedingszijde). Op laboratoriumschaal is zowel continue en discontinue PAO bedrijfsvoering (0.1 - 0.8 bar)bestudeerd met een osmotische oplossing van 24 bar. Tijdens alle PAO experimenten, inclusief met actief slib als voeding, namen de flux waarden toe met een toename in de hydraulische voedingsdruk, ten gevolge van een toename in de drijvende kracht en door membraanvervorming. Discontinue PAO bleek het verlies van de osmotische oplossing te een negatieve vergroten ten gevolge van

hydraulische druk. Deze studie toont de voordelen aan van PAO met verschillende voedingswaters, terwijl het belang van rigide FO membranen en betere steunlagen wordt onderschreven.

Haalbaarheid van een sewer mining concept

Een gesloten FO systeem verschilt van osmotische verdunning of concentreren, vanwege het recyclen en hergebruiken van de osmotische oplossing. Osmotisch verdunnen of concentreren is doorgaans economisch haalbaar en komt in de praktijk vaker voor omdat er geen energie-intensieve terugwinningsproces nodig is. Indien het energieverbruik van het terugwinningsproces kan worden beperkt, worden gesloten FO toepassingen economisch aantrekkelijker. In het Sewer Mining concept wordt energie gewonnen uit het (geconcentreerde) afvalwater en gebruikt in het terugwinningsproces.

In dit proefschrift is een technische economisch model (TEM) ontwikkeld die de kostenaspecten in kaart brengt van FO-RO processen en meer specifiek van het Sewer Mining concept. Het TEM is gebaseerd op een FO membraanstoftransportmodel gekoppeld aan een massabalans voor het complete FO proces gecombineerd met RO voor terugwinning van de osmotische oplossing. Hiernaast zijn de totale kosten meegenomen voor behandeling van afvalwater tot hoog kwaliteitswater voor het gebruik in de industrie. De totale behandelingskosten van het proces bevatten zowel kapitaal als operationele kosten en worden berekend op 0,65 €/m³ waarin de FO membraankosten een significante bijdrage leveren. Ondanks beperkingen van het TEM, werd het Sewer Mining concept economisch haalbaar opzicht full-scale geacht ten van een waterbehandelingsinstallatie, zoals een zeewaterontziltingsinstallatie (< 1 \notin /m³). De haalbaarheid van het concept verbetert met nieuwe toekomstige goedkope FO membranen die zijn geoptimaliseerd naar verlies van osmotische oplossing en permeaatopbrengst.

Waterschaarste en accumulatie van afval zijn mondiaal groeiende problemen. Door implementatie van de groene en onafhankelijke FO technologie om water en energie te onttrekken uit afvalwater, heeft het in dit proefschrift beschreven onderzoek geprobeerd bij te dragen aan de wijze waarop afvalwater wordt beschouwd; niet als afval, maar als een resource. Op deze manier, wordt het water dat we vandaag gebruiken een blijvende bron voor vele volgende generaties. "There is no passion to be found playing small – in settling for a life that is less than the one you are capable of living" Nelson Mandela

To my Family

Contents

	Acknowledgements	
	Summary & Nederlandse samenvatting	i
Chapter 1	Introduction	1
Chapter 2	Forward Osmosis for Application in Wastewater Treatment	11
Chapter 3	Zwitterions as Alternative Draw Solutions in Forward Osmosis For Application in Wastewater Reclamation	43
Chapter 4	EDTA: A Synthetic Draw Solution for Forward Osmosis	67
Chapter 5	Water Recovery and FO Membrane Fouling	79
Chapter 6	Polysaccharide Dominance in FO Fouling Studies of Raw Wastewater	91
Chapter 7	Continuous And Discontinuous Pressure Assisted Osmosis (PAO)	115
Chapter 8	A Technical Economic Assessment of Sewer Mining using Forward Osmosis	145
Chapter 9	Conclusions	173
	Appendices	179
	Bibliography	183
	Glossary	201
	List of publications	205
	Curriculum Vitae	209



Parts of this chapter are based on:

Lutchmiah K., A.R.D. Verliefde, K. Roest, L.C. Rietveld, E.R. Cornelissen: Forward Osmosis for Application in Wastewater Treatment: A Review, Water Research, 58 (2014) 179-197.

Lutchmiah K., E.R. Cornelissen, D.J.H. Harmsen, J.W. Post, K. Lampi, H. Ramaekers, L.C. Rietveld, K. Roest, Water recovery from sewage using forward osmosis, Water Science & Technology, 64 (2011) 1443-1449.

An Introduction to Forward Osmosis and the Sewer Mining Concept

1.1 Water scarcity, a global problem

Water is a basic necessity. Worldwide, access to safe drinking water is rapidly diminishing and the future outlook remains bleak. To adequately support the world's growing population, the future of water needs to follow a sustainable path, i.e. reduce the environmental impact and promote reuse. For this reason the demand for more efficient, sustainable techniques to recover drinking water is increasing. It is therefore startling to realise that only a small proportion of this available drinking quality water is actually used for sustenance. A large portion is exhausted by agriculture, for example, which accounts for 70% of all water withdrawn by agricultural, municipal and industrial (including energy) sectors [1], several of which could be utilising high quality reclaimed water instead. Reclaimed water is a low cost alternative for industries. It is therefore not surprising that many have turned their interest to this solution: water recovery from impaired waters and/or waste streams.

Several technologies already exist in this regard:

membrane bioreactors (MBR) coupled to reverse osmosis (RO) [2]; effluent polishing combining ultrafiltration (UF) or microfiltration (MF) and RO; sand filtration [3] and advanced oxidation processes (AOP) [4], but these all have their own set of disadvantages, such as energy consumption and concentrate disposal. Forward Osmosis (FO), as an alternative membrane process, also has the potential to treat effluent and produce high quality water, but with additional benefits and drawbacks Furthermore, the high quality effluent can be reused as industrial process water, or when needed, as a source of potable water.

1.2 What is Forward Osmosis?

Forward Osmosis (also known as Engineered Osmosis (EO), Direct Osmosis (DO) or Manipulated Osmosis (MO), is a membrane technology utilising the natural process of osmosis (Figure 1.1). FO requires two solutions: a feed solution and an osmotic (draw) solution, together with a semipermeable membrane. The draw solution requires an osmotic concentration higher than that of the feed, in order to induce a net water flow through the semipermeable membrane towards the draw side. In this way, water can be effectively separated from the rest of the feed water constituents.



Figure 1.1: The process of osmosis: water molecules move through a semi-permeable membrane from a solution of low solute concentration to a solution of higher solute concentration.

The driving force, unlike other state-of-the-art technologies, is the osmotic pressure gradient over the membrane and not hydraulic pressure, i.e. RO requires 10-15 bar and UF 1-10 bar for their processes. FO is therefore expected to operate with a low energy demand; the challenge is more the energy demand of the reconcentration system. FO also offers additional potential advantages for the subsequent reconcentration step, such as a lower risk of scaling [5] and biofouling than for example an RO process. The key to achieving high performance in FO is the composition of important factors influencing the osmotically-driven process; amongst others: temperature; membrane type and orientation; the osmotic solution (type and concentration) and feed water type.

Despite the availability of over 1000 publications on FO since the 18^{th} century [6, 7], research in this field has grown significantly since 2005 (Figure 1.2). The growing interest was sparked by the commercialisation of membranes specifically tailored to the FO process. The recent completion and operation of the first fully commercial FO desalination facility (200 m³/day), situated in Oman, makes FO technology even more tangible [8].



Figure 1.1: Overview of FO publications. The annual number of publications has increased significantly since 2005. Articles determined based on the extraction from main online journal directories [9, 10].

1.3 Pros and Cons of FO

Of the FO literature produced in the last 10 years, approximately 7% employ complex waters. Nonethe-less, growth in wastewater treatment is steadily increasing. Ultimately, the motivation surrounding FO for the treatment of complex feeds is due to its potential advantages over current technologies: • When compared to RO, many advantages exist for an FO system. FO demonstrates similarly high salt rejections, but without the need of high hydraulic pressures. Therefore neither the same energy input nor high strength materials are required [11, 12]. However, whether FO is less energy-consuming than RO depends on the need of a recovery system. In once-through FO systems where recovery is

unnecessary, FO will indeed be more energy-efficient than RO, enabling applicability in areas with limited access to electricity [13].

- FO rejects particles, pathogens and emerging substances [14-16], and unlike normal treatment facilities, efficiently removes total dissolved solids (TDS) from complex solutions [13, 17], due to its mean pore radius of 0.25–0.37 nm [18, 19].
- Extensive pre-treatment systems for FO may be redundant when treating complex feeds, but depends on FO performance and membrane design. In contrast, RO and NF are susceptible to fouling and require pre-treatment to promote longevity and reduce costs [20, 21].
- FO has proven excellent operation in terms of durability, reliability and water quality in highly polluted waters because of the dense membrane structure, e.g. Hydropack Emergency Supply product (HTI) allows ingestion of water after FO treatment, from sources possibly containing pathogens or toxins [22].
- FO has shown flexibility and applicability due to: a) scalability of the membrane system [23]; b) reduced fouling propensity [24, 25] and simple cleaning [26, 27] compared to RO.

- FO can be applied for dewatering feeds [28, 29], useful for effective anaerobic digestion of wastewater, and is simpler, greener and higher in efficacy than traditional dewatering treatments [30].
- Highly saline streams, > 83 bar, are treatable by FO, but not possible by RO [31].

Some of the listed advantages may apply to other (membrane) techniques as well, but it is the combination of all these advantages together that makes FO an interesting technology for wastewater treatment.

Shortcomings of FO include the recovery step in closed-loop systems, low water fluxes compared to RO [32] and reverse solute leakage [33]. The latter increases operational costs and decreases the driving force. The potential need for wastewater pre-treatment, which is module-type and application dependant, is also disadvantageous, but is not exclusive to FO. Furthermore, the incomplete rejection of trace organic contaminants (TrOCs) is still an issue, but depends on the employed recovery system [34]. Additionally, saline solutions on either side of the membrane may aggravate concentration polarisation (CP).

1.4 The Sewer Mining Concept

FO is a process that can be engineered and adapted to various water treatment applications. Applications in the field of wastewater treatment and water reuse have been successfully carried out using different types of wastewater feeds, i.e. industrial wastewater [35, 36] landfill leachate [14], simulated wastewaters [15, 16, 37-39], raw and filtered nutrient-rich liquid streams (concentrate) from dewatered digested biomass [40]; activated sludge [41, 42]; wastewater from textile industries [43] and primary effluent from municipal sources [26]. The Sewer Mining concept is another example of an integrated FO application. This concept innovatively incorporates different technologies to attain one goal: water recovery from wastewater, and subsequent energy production (Figure 1.2). Sewage contains inherent organic material, which can be converted into renewable energy. However, sewage also contains a substantial amount of water, resulting in diluted



Figure 1.2: A schematic overview of the Sewer Mining concept for the recovery of high quality water from wastewater via (1) FO and (2) RO (reconcentration), coupled to (3) anaerobic digestion, resulting in the production of renewable energy. Adapted from [44].

organic content. This makes efficient digestion more demanding. Application of FO allows for the extraction of water from the wastewater, i.e. dewatering, concentrating the remaining wastewater and resulting in an easier conversion to energy in much smaller bioreactors.

The chemically-bound energy in the concentrated wastewater can be converted by anaerobic digestion into energy-rich biogas. Biogas is a renewable source of energy, like solar power and wind energy, and is mainly composed of methane and carbon dioxide. By converting the biogas into electrical (and thermal) energy, and utilising it in the reconcentration unit, much energy could be saved, lowering the energy costs of the entire process. In addition, concentrated nutrients from the digestate can be recovered and used elsewhere, i.e. for fertilisation.

1.5 The focus of this thesis

FO is a relatively new membrane technology, which has grown rapidly in recent years. The focus of FO has mostly been concerned with membrane development, fundamental understanding of concentration polarisation and membrane fouling control (via model foulants), while work on the treatment of raw wastewater has been minimal. FO in a sewer mining concept is a novel technology showing great potential, but before it can reach fullscale feasibility, several research questions need to be addressed.

The research questions have been identified as gaps in this particular research field and have been grouped into the following main themes:

- What are ideal draw solutions for FO-wastewater applications, i.e. specifically pertaining to direct wastewater treatment?
- What is the cause and extent of fouling on FO membranes when applied to raw wastewater?
- Can the FO efficiency, i.e. water flux and solute leakage, be improved via external hydrodynamic conditions?
- Can FO reach full-scale potential in wastewater treatment and water reclamation? Additionally, is FO, in the frame of sewer mining applications economically feasible, when compared to other state-of the-art processes?

These defined gaps form the basis of the main research questions for each chapter of this thesis. A detailed approach per chapter is described below:

Chapter 2: Forward Osmosis for Application in Wastewater Treatment

In Chapter 2 an overview of FO work performed with impaired waters and waste streams is established. This overview attempts to define the steps still required for FO to reach full-scale potential in wastewater treatment and water reclamation by describing and discussing the current developments, bottlenecks and future perspectives of FO technology in the wastewater sector.

Chapter 3: Zwitterions as Alternative Draw Solutions in Forward Osmosis for Application in Wastewater Reclamation

Chapter 3 presents a study on several naturally occurring zwitterions to find the ideal draw solute to enhance FO performance, minimise solute loss and enhance energy production in wastewater applications.

Chapter 4: EDTA: A synthetic Draw Solution for Forward Osmosis

Chapter 4 continues with the experimental work mentioned in Chapter 3, employing larger molecules

as potential draw solutes for FO.

Chapter 5: Water Recovery and FO Membrane Fouling

In Chapter 5 the effectiveness of FO membranes in the recovery of water from sewage is evaluated, focusing on membrane performance and fouling of the FO membrane. Investigations were carried out via short-term lab-scale experiments.

Chapter 6: Polysaccharide Dominance in FO Fouling Studies of Raw Wastewater

Chapter 6 deals with the effects of fouling presented in Chapter 5. Additional long-term studies were performed and the fouling layers were extensively analysed.

Chapter 7: Continuous and Discontinuous Pressure Assisted Osmosis (PAO)

Chapter 7 focuses on improving water flux performances by adding hydraulic pressure to the feed side of the membrane process. An FO transport model was also developed, incorporating the additional hydraulic pressure to describe and validate the experimental fluxes.

Chapter 8: A Technical Economic Assessment of Sewer Mining using Forward Osmosis

In Chapter 8 the FO transport model mentioned in Chapter 7 together with an existing ICP model was used to predict mass transfer in larger scale FO membrane installations and to develop and describe the economic aspects of both a general FO-RO process and more particularly, for the case of the Sewer Mining concept.

Chapter 9: Conclusions

Chapter 9 provides the reader with the main overall conclusions of this thesis. These conclusions view this work from a broader perspective and offer recommendations for future research.

CHAPTER

2

Forward Osmosis for Application in Wastewater Treatment



This chapter is adapted from:

Lutchmiah K., A.R.D. Verliefde, K. Roest, L.C. Rietveld, E.R. Cornelissen: Forward Osmosis for Application in Wastewater Treatment: A Review, Water Research, 58 (2014) 179-197.

2.1 Introduction

Drinking water is produced mainly from safe water sources, i.e. groundwater, but due to population growth and economic development, exploitation of aquifers and declining groundwater levels have diminished fresh water sources. The unsustainable use of drinking water for purposes other than sustenance, i.e. industrial processes, is therefore of great concern. A possible alternative source is wastewater. Via microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO), high quality water can be produced. Important examples of such applications are provided in Table 2.1.

Forward Osmosis (FO), an alternative membrane

Year	Feed type	Application	Project/Company	Location	Membrane Treatment
1968	municipal wastewater	potable use	Old Goreangab Water Reclamation Plant	Windhoek, Namibia	UF
1976	wastewater	groundwater recharge	Water Factory 21	Orange County, California	RO
2002	municipal wastewater effluent	aquifer recharge, potable use	Torreele Wastewater Treatment Plant	Veurne Region, Belgium	UF-RO
2002	wastewater	potable and industrial use	NEWater	Bedok and Kranji, Singapore	MF-RO
2007	municipal wastewater	industrial use	DOW Chemical	Terneuzen, the Netherlands	UF-RO
2010	wastewater	groundwater recharge	The Groundwater Replenishment Trial	Perth, Australia	UF-RO

· · · ·	Table 2.	l Important	examples	of	^c membrane	treated	wastewaters f	or re	use
---------	----------	-------------	----------	----	-----------------------	---------	---------------	-------	-----

process, also has the potential to treat wastewater, producing high quality water. FO is a technical term describing the natural phenomenon of osmosis: the transport of water molecules across a semipermeable membrane. The osmotic pressure difference is the driving force of water transport, as opposed to pressure-driven membrane processes.

This chapter, stimulated by the rapid growth and expansion in water reuse ventures, attempts to define the steps still required for FO to reach fullscale wastewater treatment and water reclamation by summarising the current developments and bottlenecks of FO technology used in the wastewater sector.

2.2 FO Membranes

The first recorded investigations of membrane phenomena date back to the accidental discovery of osmotic pressure in 1748 using pigs' bladders [45]. Thereafter, studies focused on the mechanism of osmosis through natural materials. Membranes and osmotic processes have since evolved. Special attention was given specifically to FO, to avoid the need of energy sources for pressure-driven production [46]. FO was trialled through synthetic materials, which began with the first asymmetric cellulose acetate (CA) RO membranes developed in the 1960's [47]. These were initially intended for FO, however, due to inherent transport limitations were considered ineffective. Other RO membranes too, have not shown convincing results in FO due to hydrophobicity and relatively thick support layers $(\sim 150 \ \mu m)$ [48]. Thick support layers lead to poor performance of osmotically driven membrane processes, which is mainly related to concentration polarisation (CP). Both internal CP (ICP) and external CP (ECP) exist. CP is caused by a balance between flux, rejection and diffusion, and lowers flux and membrane selectivity (intrinsic membrane selectivity remains unaltered). ICP is exclusive to FO and generally occurs within the porous support layer of the membrane, while ECP is present at the surface of the dense active layer (AL). The breakthrough for FO came with the development of thin, FO-tailored CTA membranes (~50 µm) by HTI, allowing higher fluxes through reduced ICP [49, 50]. ICP, however, is still an issue for FO and the main driver for further membrane development.

Several recent reviews have focused on FO membrane developments [6, 12, 51]; this chapter will only focus on findings important for wastewater applications.

For wastewater treatment, the FO membrane fouling propensity needs to be addressed more vigilantly. In addition, the ideal FO membrane must allow fast transport of water towards the draw side, with ideally no migration of solutes between the draw and feed solutions, especially in closed-loop applications. Desired FO membrane characteristics for use in wastewater applications thus entail:

- a dense, ultra-thin, active-separating layer for high solute rejection;
- an open, thin (as possible), hydrophilic SL, with high mechanical stability, sustaining long-term operation and reducing ICP;
- a high affinity for water (hydrophilicity) for enhanced flux and reduced fouling propensity.

Significant advances have been made in these areas, and new, commercial FO membrane modules have hit the market, with more soon to follow [12, 13]. The dimensions of common industrial spiral-wound FO (SWFO) elements can be found in Table 2.2.

Previously, Cath et al. [17] stressed the need for developing high performance FO membranes, as they were found to be limited in terms of quantity (limited produced membrane area) and quality (limited variation in materials). While some of these issues have been improved, FO membranes remain limited with regards to commercial use in wastewater treatment and water reclamation, e.g. spiral wound configurations with spacers (section 2.5.2) may not be ideal for raw waters, due to the higher fouling (biofouling, colloidal fouling etc.) potential.

Module	Diameter		Diameter Length		Effective membrane area*	
	inches	mm	inches	<u>mm</u>	\underline{m}^2	
2521	2.5	63.5	21	533.4	0.38 - 0.53	
4040	4	101.6	40	1016	1.5 - 3.2	
8040	8	203.2	40	1016	7.5 – 17.6	

Table 2.2: The dimensions of common SWFO elements and the corresponding effective membrane area.

* Dependent on the number of membrane leaves

2.2.1 Membrane Materials

FO membranes are currently developed from diverse material formulations. Basically, two strategies exist in FO membrane development: modification of commercial membranes or development of new membranes [12].

The commercially available and widely-used CTA membrane is non-toxic, odourless and less flammable than nitrocellulose (originally used for MF membranes). Furthermore, CTA offers a high degree of resistance to chlorine [52] and is (for the most part) unsusceptible to adsorption of mineral and fatty oils, including petroleum. Cellulose and its derivatives are very sensitive to thermal, chemical and biological degradation [53], hydrolysing very rapidly at alkaline conditions. CTA however shows greater thermal resistance and better shape stability [54] than CA. Still, new TFC membranes are reported to be superior than the CTA membranes [12], due to increased permeability and a broader pH range: 2 - 12 (vs. 3 - 8 CTA), whilst withstanding the rigorous operating conditions of PRO [55].

Susceptibility to membrane fouling is also material dependant. Generally, hydrophilic membranes, like CA/CTA, with lower contact angles (pure water measurements) are less prone to absorptive fouling than more hydrophobic membranes [56], making them more suitable for the treatment of heavy duty wastewaters. The skin layer of TFC-polyamide (PA) membranes (HTI) was intentionally developed with low contact angles to increase biofouling resistance [57]. In addition, hydrophobicity of the support layer is also important in terms of flux; hydrophilic support layers lead to improved water fluxes and reduced ICP by increasing the wetting of small pores within the support layer [48]. The active layer of fabricated PES HF membranes [58] were found to have smaller contact angles ($\sim 20^{\circ}$ less) than CTA flatsheets, suggesting less fouling tendency in real-life applications, however in spiral-wound form, CTA is less susceptible to fouling than hollow fibre (HF) membranes. This could be due to the significant mixing of the solution for each mesh in the spacer of SW membranes, whereas in open channels the CP film grows undisturbed in the channel [56].

Alsvik and Hägg [6] recently outlined new methods and materials used in FO membrane preparation, showing membrane materials to have moved beyond the traditional CTA and TFC
PA/polysulphone (PS) membranes. Novel FO R&D membranes, specific for wastewater treatment, have shown much promise in recent years. Materials now used include hydrophilic CA, with increased fouling resistance [59]. New CA fabrication methods allow addition of pore-forming agents and annealing to improve fluxes and salt rejections [60]. Double-skinned CA membranes with dense outer skins have also evolved [39, 59, 61], showing the potential for wastewater reclamation. Materials like strong and temperature stable thermoplastic polymers have also been used:

- Polybenzimidazole (PBI), due to its molecular properties is able to self-charge in aqueous solutions, resulting in high salt rejections, high surface hydrophilicity and low fouling tendencies [62];
- Polyamide-imides (PAI) can provide double electric (cationic and anionic) repulsions to the salt transfer through the membrane, reducing salt permeation [63], and can produce NF-like selective layers [64];
- Nanoporous polyethersulphone (PES) membranes with loose finger-like structures and nano-sized pores allow less ICP [65];

- Polysulphone (PS) is commonly used for the support layer in many TFC-FO membranes [66-68], despite its hydrophobicity (lowering fluxes);
- Blends of polymers with polyacrylonitrile (PAN) in the support layer of TFC membranes [69-71] show improvements over commercial FO membranes;
- Polydopamine (PDA), a hydrophilic polymer, improves fouling resistance FO [72].

2.2.2 Membrane Development

The techniques used in developing membranes strongly influence membrane behaviour and filtration efficiency. Generally, conventional phase inversion is used to produce FO membranes, focusing on the formation of a dense selective layer on top of an asymmetric membrane (Figure 2.1), but the support layer should also be thin, porous and possess low tortuosity [12].

In Figure 2.1 CTA membranes were hand-cast to simulate the process within a production plant. In theory, the casting can be done via two methods: 1) the woven reinforcement is placed first on the support plate, or 2) the membrane solution is distributed first. From Figure 2.1 it is apparent that casting a membrane with the solution first does not result in an ideal and stable membrane; the casting

solution is brittle and can be easily separated from the fibrous support layer. For this reason, Method 1, is more commonly used for membrane casting. Various papers [6, 12, 59, 73-75] have elaborated on new design techniques and membrane formation mechanisms to optimise specific parameters. These include: 1) tailoring the membrane surface to decrease fouling and improve water fluxes by functionalising

the membrane surface and/or embedding functionalised nanoparticles in the polymer [76];

2) re-engineering the support structure to withstand stress [6];

3) adding electospun nanofibres to increase mechanical strength [27] or

4) employing advanced co-extrusion techniques for mechanical stability and high power density [77].

The many materials and methods tested show the potential for tailoring FO, regardless of the application, to augment membrane performance.



Figure 2.1: Hand-casting CTA Membranes via Method 1: steps 1 – 3; casting steps and final membrane product via Method 2: steps 4 – 6.

2.2.3 Membrane Orientation

Most FO membranes have an asymmetric structure with two different layers; an AL and a SL. The AL is generally the dense selective layer, while the porous SL provides the mechanical support. Due to the asymmetry, these FO membranes can be positioned either with the AL facing i) the feed side (AL-FS or FO-mode) or ii) the draw side (AL-DS, RO-mode or PRO-mode).

The membrane orientation impacts FO performance (flux and fouling) significantly. Extensive research has reported higher water fluxes in PRO-mode, attributed to less severe concentrative ICP (CICP), but this orientation is also more prone to membrane fouling [40, 78, 79], due to the entrapment of the foulants in the SL, which reduce porosity and enhance ICP. Membrane orientation therefore also influences ICP. Fabrication of the ideal FO membrane thus relies on eliminating the ICP problem, mainly caused by salt accumulation in non-ideal feeds [80], by decreasing the SL thickness. If this could be achieved, then ECP would surely become a limiting factor especially in wastewater and seawater applications.

Jin et al. [81] examined the effects of FO membrane orientation on organic fouling and the

rejection of inorganic contaminants, observing more alginate fouling in PRO-mode. In FO-mode, arsenite rejection was enhanced by the alginate fouling, while in the PRO-mode, alginate fouling caused no observable effect on rejection, reportedly due to the counteractive effects of improved sieving and enhanced CICP. Zhao et al. [82] observed a more dramatic water flux decline in PRO-mode during organic fouling, while the FO-mode also provided higher flux recoveries after cleaning.

In many applications, e.g. osmotic membrane bioreactor (OMBR), the PRO-mode is deemed impractical, due to the high fouling environment [79]. To the best of our knowledge, commercial FO membrane modules are currently only manufactured in FO-mode.

18

2.3 Modelling Membrane Transport

FO mass transport models, especially for use in wastewater applications, are limited. Of the existing models the majority neglect fouling, mainly because of the complexity and variability of wastewaters. Generally, FO models incorporate ICP and ECP phenomena [83] and are based on solution-diffusion (SD) and convection-diffusion equations [84]. Flux and rejection characterise membrane performance. Theoretical derivations of the water flux (J_v) have been established for the FO-mode [83, 85]:

$$J_{\nu} = K_m \ln \left(\frac{A\pi_{DS} + B}{A\pi_{FS} + J_{\nu} + B} \right)$$
(2.1)

In which K_m is the mass transfer coefficient, A the pure water permeability constant and B the solute permeability constant. From Equation 2.1 it is clear that no linear relationship exists between the osmotic pressure difference $(\Delta \pi)$ of the feed (π_{FS}) and draw (π_{DS}) and J_{ν} . This is due to ICP. As mentioned, most FO models do not incorporate fouling, or do so based only on model foulants or synthetic waters, e.g. the salt accumulation model [86] or the SD model for TrOCs [87]. A better

understanding of foulant behaviour in wastewater may lead to more representative models, fouling indications, accurate FO performance predictions and can further assist with membrane tailoring [51].

2.3.1 Concentration Polarisation

ICP is considered a major problem in FO, reducing the water flux and increasing (reverse) solute transport. For CICP (PRO-mode), solutes from the feed penetrate the SL by means of convective water flux and direct diffusion [88], while the dense AL is less permeable. This can be aggravated by salt leakage from the draw to the feed. In dilutive ICP (DICP) (FO-mode, preferred for wastewater), the flux becomes limited by dilution of the draw solution (DS) in the SL by water flux. Higher water fluxes result in more dilution, and as such, are a self-regulating mechanism consequently lowering fluxes. In FO-mode, this DICP is aggravated further by CECP, where the solutes in the feed are forced against the membrane [85, 89-91]. In most flux models for FO, ECP is assumed to be negligible because of low fluxes and a high mass transfer, however ECP severely impacts feeds with high total dissolved solids (TDS). Simulations have shown

ECP to be more prominent when mass-transfer promoting spacers are absent and low cross-flow velocities are used [92].

2.3.2 Membrane Structure Parameter

Recent efforts to improve FO membranes have focused their attention on the membrane structure parameter (S) [93], which is inversely related to mass transfer through FO membranes:

$$K_m = \frac{D}{S} \tag{2.2}$$

In which *D* is the solute diffusion coefficient. *S* is given by the product of the SL thickness (*l*) and tortuosity (τ), and is inversely proportional to the porosity (ε).

$$S = \frac{\tau \cdot l}{\varepsilon} \tag{2.3}$$

FO membranes with large *S* values, i.e. thicker and denser membrane supports, result in decreased membrane performance; mainly due to hindered diffusion and an increase in boundary layer thickness. A lower K_m can significantly reduce FO permeate flux due to the exponential dependence of CP on K_m [94]. By substituting Equation 2.2 into Equation 2.1, *S* can be determined:

$$S = \frac{D}{J_{v}} \left(\ln \frac{A\pi_{d,b} + B}{A\pi_{a,w} + J_{v} + B} \right)$$
(2.4)

Essentially, thinner, more porous and less tortuous support layers [95] will have smaller *S* values and produce higher water fluxes [67]. *S* values depend only on membrane structural properties (Table 2.2). A priori estimation of the *S* value is however hard to attain due to τ , which is intrinsically associated with the microstructure of the support layer [96].

Casting conditions during membrane preparation can optimise the support structure [53] and decrease S, thereby improving FO membrane performance. Immersion precipitation processes to synthesize the substructure will yield different structures depending on the casting solution (i.e. composition and concentration) and casting conditions (i.e. temperature, humidity). For example, adding a solvent to the coagulation bath is known to delay solvent/non-solvent mixing which leads to thinner and more compact structures. The morphology of the SL (finger-like, sponge-like or scaffold-like structures) also influences S [66-68, 95]. By changing annealing conditions and adding fillers during membrane preparation, tortuosity can be influenced to obtain more finger-like pores, which produce low S values.

2.3.3 Membrane Permeability Constants

The constants *A* and *B* are necessary parameters for mathematical models of FO. Water passage through dense membranes is generally described and theoretically calculated by Equation 2.5 [17]:

$$J_{\nu} = A. \sigma. \Delta \pi \tag{2.5}$$

Where σ , the reflection coefficient, is 1 when the membrane completely rejects the solute. This is usually assumed in FO studies, due to high rejections (R_{NaCl} : 93–95%) [88, 97] and is therefore commonly neglected in modelling studies. The actual σ depends on the draw solution used; low σ values result in low effective driving forces by reverse solute leakage [98, 99].

B relates to solute transport and solute leakage and is dependent on *D*, its partition coefficient and effective membrane thickness. Despite high rejections, forward and reverse solute diffusion are significant in FO. Forward diffusion occurs when solutes move from the feed (wastewater) into the draw solution, while reverse diffusion (solute leakage) occurs from the draw solution into the feed [33]. *B* is solute-dependent and should be minimised to avoid solute leakage. Solute leakage decreases $\Delta \pi$ because of (i) a decrease in π_{DS} and (ii) an increase in π_{FS} . Solute leakage impacts draw solution costs and may also affect the biology in OMBR and FOwastewater-energy generating systems.

A and B are, in practice, often determined in pressurised cross-flow filtration tests. These tests are well adapted to RO, but poorly reflect FO operation. It is questionable whether these tests yield reliable results for FO. A more standardised methodology to test A and B in FO conditions has been recently proposed and tested [100].

Commercial CTA membranes typically have water permeabilities of $2.54 \pm 1.69 \times 10^{-12}$ m/s.Pa (Table 2.3), but low values between $0.87 - 1.07 \times 10^{-12}$ m/s.Pa and high values of 7.1×10^{-12} m/s.Pa have also been reported. Additionally, Table 2.3 shows average *B* values of $1.27 \pm 0.48 \times 10^{-7}$ m/s for NaCl. The large standard deviations for *A* and *B* can be attributed to temperature differences [41], deviations between small membrane coupons [101] and/or membrane deformation under hydraulic pressure [102, 103]. In addition, it could be possible that the SD model is not ideal for calculating these parameters or that the translation from RO to FO conditions is flawed. In general, the listed membrane materials in Table 2.3 show NaCl rejections > 90%. TFC membranes are typically more water permeable and show large variations in *B* values $(0.02 - 47.20 \times 10^{-7})$

m/s). The future of FO membranes therefore seems to move in the direction of TFC material, as tailoring appears easier and the design versatile.

Me	embrane type	•	Temperature	Α	В	S	K _m	R	Ref
Manufacturer	Material	<u>Type</u>	[°C]	[10 ⁻¹² m/s.Pa]	[10 ⁻⁷ m/s]	[<u>mm]</u>	$\frac{[10]}{6}$ m/s]	[%]	
HTI	CA	flat-sheet	50±1	5.69	-	-	-	> 95	[83]
HTI	CA	-	20±1, 30±1	3.07	-	-	-	95-99	[104]
NTU	СА	Double skinned	22±0.5	2.17	1.73	-	-	-	[105]
Toray	CA-3000 (RO) (modified)	with + without support	-	3.75	2.13	-	-	98	[61]
HTI	CTA	flat-sheet	25	2.71	-	-	-	> 95	[49]
HTI	СТА	flat-sheet	22.5±1.5	3.08	1.27	-	-	-	[89]
HTI	СТА	-	23±1	0.87	-	-	-	-	[40]
HTI	СТА	-	30	3.95	-	-	-	-	[88]
HTI	СТА	flat-sheet	20±2	7.10	-	-	-	> 92	[41]
HTI	СТА	-	25±0.5	0.98	-	0.60	-	94.1±1.1	[67]
HTI	СТА	-	20±1	3.60	-	-	-	-	[106]
HTI	СТА	-	20±0.5	1.23	0.73	0.48	-	89.1 - 96.1	[101]
HTI	СТА	flat-sheet	31±1	2.21	-	-	-	-	[107]

Table 2.3: A summary of various membrane types used in FO applications and their membrane characteristics.

Μ	embrane type		Temperature	Α	В	S	K _m	R	Ref
<u>Manufacturer</u>	Material	<u>Type</u>	[°C]	[*10 ⁻¹² m/s.Pa]	$\frac{[*10^{-7}]}{m/s}$	[<u>mm]</u>	$\frac{[*10^{-6}]}{m/s}$	[%]	
HTI	СТА	Hydrowell Filter	22 - 24	2.20	1.70	0.40	AL-FS: 4.2	90	[79]
HTI	СТА	Hydrowell Filter	23	2.12	1.60	-	AL-FS: 5	-	[86]
HTI	СТА	-	25±1	1.89	1.68	-	-	> 90	[108]
HTI	СТА	-	25±0.5	1.07	-	0.62	-	92±1.5	[95]
HTI	СТА	-	20±0.5	-	0.63	-	AL-FS: 17.2	-	[99]
Osmotek	CTA (RO)	flat-sheet	25±2	3.08	1.27	-	-	-	[109]
TriSep	TFC (NF)	flat-sheet TS80	20±2	20.0	-	-	-	100	[41]
General Electric	TFC (RO)	DS-11-AG (Aromatic PA)	22±1	11.91	-	-	-	99.5	[110]
Dow	TFC (RO) (modified)	SW30XLE 400i	20±1	3.80	-	-	-	-	[106]
Hydranautics	TFC (RO)	flat-sheet SWC1	20±2	5.60	-	-	-	100	[41]
Dow	TFC (RO)	SW30-HR (with PET)	25±0.5	3.55	-	9.58	-	98.9±0. 4	[67]
Dow	TFC (RO)	SW30-HR (No PET)	25±0.5	4.39	-	2.16	-	98.3±0. 4	[67]
Yale	TFC (FO)	-	25±0.5	3.18	-	0.49	-	97.4±0. 5	[67]
NTU	TFC-1	-	23	5.03	0.02	-	AL-FS: 2.5	-	[86]

Table 2.3 (contd.)

Μ	embrane type		Temperature	Α	В	S	K _m	R	Ref
Manufacturer	Material	<u>Type</u>	[°C]	[*10 ⁻¹² m/s.Pa]	$\frac{[*10^{-7}}{\text{m/s}]}$	[<u>mm]</u>	$\frac{[*10^{-6}]}{m/s}$	[%]	
NTU	TFC-2	-	23	5.05	0.25	-	AL-FS: 2.5	-	[86]
NTU	TFC-3	-	23	5.28	2.60	-	AL-FS: 2.5	-	[86]
NTU	TFC-4	-	23	9.58	47.20	-	AL-FS: 2.5	-	[86]
NTU	TFC-5	-	23	3.5	0.17	-	AL-FS: 2.5	-	[86]
NTU	TFC (#C-FO)	HF	23	9.60	0.61	0.55	-	-	[111]
NUS	TFC (#A-FO)	HF	23	2.60	0.81	1.37	1.1	-	[58]
NUS	TFC (#B-FO)	HF	23	6.20	0.56	0.60	2.5	-	[58]
NUS	TFC (PES/SPSf)	-	-	-	-	0.24	1.9	-	[112]
Yale	TFC (PA/PS nanofibre)	flat- sheet	25±0.3	3.14	0.64	0.65	-	>96	[113]
NTU	#1 nanofibre composite NC-FO	-	25±0.5	4.66	-	0.08	-	97±1.0	[95]
NTU	#2 NC-FO	-	25±0.5	4.52	-	0.11	-	97±1.2	[95]

Table 2.3 (contd.)

2.4 Draw solutions

The draw solution and related osmotic pressures in the FO process are important factors influencing mass transport and overall process performance. Several draw solution types (and concentrations) have already been tested in FO. From Figure 2.2, NaCl is seen to be the most employed draw solution (approximately 40% of experiments), due to its high solubility [17], but also low cost [114] and relatively high osmotic potential. NaCl has been used as a draw solution in concentrations between 0.3 - 6 M,



Figure 2.2: Draw solutions used in FO based on approximately 50% of FO publications. Results are expected to increase in similar ratios when considering all published works.

but is often used at 0.5 M simulating the osmotic power of seawater and prompting the use of real seawater or RO brine as a draw solution [115]. Seawater is abundant and has frequently been used as a draw solution [116], but contains numerous particles and microorganisms which may foul the reconcentration system (in closed-loop systems) or cause (bio)fouling/contamination in the FO unit, hindering performance. This increase in fouling potential may be a limitation when using wastewater feeds. In a once-through system for RO desalination though, an FO pre-treatment step can minimise fouling in RO [17].

2.4.1 Effective Draw Solutions for Wastewater Treatment

A higher osmotic potential than the feed is essential to induce a water flux, but the focus in FO-wastewater treatment for a draw solution, is on good performance, with high water fluxes and low reverse leakages [117]. To evaluate performance, the J_s/J_v ratio is often regarded [101]:

$$\frac{J_s}{J_v} = \frac{B}{A\beta R_g T} \tag{2.6}$$

Where β is the van't Hoff coefficient and R_g the gas constant. Equation 2.6 indicates the dependence of the ratio on the membrane transport properties of the AL, but not the SL. Membranes with better selectivities, i.e. higher *A* and lower *B* values are thus essential [12].

Additionally, the draw solution should be nontoxic, easily recoverable in the reconcentration system, and when operated in a bioreactor, should not deteriorate the OMBR, sludge quality or bacterial growth [118]. Low to no degradability of the substance should also be considered, unless degradation of the draw solution (post-FO) is advantageous [119] or irrelevant. The draw solution price is equally important, unless loss through the FO membrane is nominal and recovery is achieved with minimal energy and costs.

Mass transport properties, i.e. diffusivity (*D*) are also significant. Large molecules diffuse more slowly and therefore leak less through the membrane. Lobo and Quaresma [120] found that *D* changed with concentration and salt type. According to the Stokes-Einstein relation, *D* is further influenced by temperature, viscosity of the fluid and particle size. In dilute aqueous solutions, *D* values of most ions are similar ($0.4x10^{-9}$ m²/s to $2x10^{-9}$ m²/s, at 25 °C), however for the sulphates, MgSO₄ and ZnSO₄, *D* is considerably lower, which may explain the lower solute fluxes achieved during FO investigations.

Wastewater contains many molecules with varying diffusivities, which together with the draw solution can influence the extent and severity of DICP. The lower the diffusivity, the higher the degree of DICP in the porous support layer [33, 108, 114, 121]. Monovalent ions display higher water fluxes as a result of a higher diffusivity [41], however this is accompanied by higher solute leakages, which are ascribed to lower size exclusion and lower electrostatic repulsion of monovalent ions. Higher diffusivity and solute fluxes might simultaneously lower ICP, but the exact effect depends on the operating conditions. Bivalent ions display lower solute leakages as a result of higher steric hindrance and electrostatic repulsions, but also lower water fluxes.

PH and temperature should also be considered when choosing a draw solution. A change in one or both can lead to mineral salt scaling on the membrane surface when scale precursor ions like Ba^{2+} , Ca^{2+} , Mg^{2+} , SO_4^{2-} , and CO_3^{2-} are present [114]. Due to the complex ionic matrix of wastewater feeds, Achilli et al. [114] suggested MgCl₂ to be the most ideal draw solution for wastewater processes in view of its high osmotic efficiency, though material costs are higher than for NaCl. Table 2.4 summarises the advantages and drawbacks of some draw solution types considered for wastewater applications.

2.4.2 Recovery Systems

A thermodynamically favourable reconcentration system, in closed-loops, is required to replenish the draw solution and separate it from the product water. Some methods of recovery involve RO, membrane distillation (MD) and thermal recovery. The chosen recovery system depends on the type of application and solute, the recovery rate required and the energy consumption of the unit. For wastewater treatment, the process in choosing a recovery unit is similar to other FO applications, however forward solute diffusion needs to be considered. Solutes e.g. sparingly soluble salts and boron, from complex feeds can pass through the membrane to the draw side due to bi-directional diffusion [33]. This may cause problems for the reconcentration unit, i.e. ions with low solubilities can precipitate and have deleterious effects on the system's performance. The addition of scale inhibitors to the draw side or filtration of the solution before the reconcentration

Draw solution type	Example	Advantages	Disadvantages	Reference
Inorganic substances	Salts	High solubilityLow costHigh osmotic pressure potential	 Salt leakage may inhibit anaerobic digestion Clogging/scaling/fouling ICP Recovery is not often feasible 	[122]
Highly soluble zwitterionic substances	Glycine	 High flux, low leakage Leakage beneficial to biology in subsequent energy-generating units 	• Limited storage time due to biodegradation	[119]
High charged compounds	EDTA	 High water flux Low reverse leakage Reconcentration via less energy consuming processes, i.e. NF 	 More expensive than common salts pH dependency Questionable environmental repercussions 	[123-125]
Nutrient-rich substances	Fertilisers	Direct fertigation,No recovery necessary	Osmotic equilibrium limitsDilution of nutrients	[126, 127]
Readily available sources	Seawater, RO brine	Abundant source	 TEP fouling, Seawater: only cost-efficient if applied near coastal areas 	[37, 116, 128]
Thermolytic solutes	Ammonium bicarbonate	High solubility in water,Recovery by moderate heat	Toxic thermolytic productHigh diffusive loss	[49, 129]
Engineered draw solutions	Magnetic nanoparticles	 High osmotic pressures at low concentrations No leakage Overcomes scaling and crystallisation issues in MD 	 Agglomeration during magnetic separation Ultrasonication weakens magnetic properties Viscosity of solution reduces effective driving force and flux 	[130, 131]

Table 2.4: An overview of draw solutions considered in wastewater applications.

unit is possible, but will increase operating costs. Furthermore, if solutes, e.g. TrOCs move into the draw solution, they must be removed in the reconcentration loop. The energy consumption of all adjacent treatment processes must be considered. Using feeds with high organic content could consequently be advantageous in these situations as energy can be extracted and fed to the reconcentration (or other) unit. In doing so, the energy consumption of recovery systems could be reduced.

Due to minimised membrane fouling and subsequent reduced costs, the commercialisation of the OMBR is expected in the near future [132]. This however also depends on finding a cost-effective draw solution, e.g. seawater. The use of hybrid systems for wastewater treatment integrated with seawater desalination is interesting to enhance FO and make wastewater recovery commercially feasible. However, as much as these systems are technically feasible, they remain economically and industrially unpractical due to the high energy costs of the recovery unit [122]. Furthermore, energy balances for many of these integrated systems are still lacking.

2.5 **Process Conditions**

2.5.1 Temperature and pH

Increasing the temperature in FO processes will increase the water flux, due to the increase in π_{DS} and the decrease in wastewater viscosity [85]. A simultaneous increase in solute permeability also occurs, resulting from an increase in the solute diffusion rate through the membrane [133] and lower ICP. These findings were corroborated for HF NF membranes [62] and CTA-FO membranes [41, 90], additionally showing a 2.4% rise in water flux per °C increment with 0.5 M NaCl [41]. Li et al. [134] and Razmjou et al. [135] have shown how solar energy can be used to influence fluxes in FO systems. The temperature effect on ICP is also less pronounced in PRO-mode, resulting in enhanced water fluxes [85, 89], and additionally, higher salt fluxes.

Furthermore, in FO-wastewater applications an increase in temperature will concentrate the wastewater faster, possibly leading to greater fouling of the membrane. Wastewater effluents contain delicate ecosystems that can be adversely affected with increasing temperatures and increasing salt concentrations, however when energy is generated from the organic content (COD) of wastewater (anaerobic digestion), temperatures as high as 35 °C may be required.

A change in pH might affect certain draw solutions as well e.g. EDTA or zwitterions. Furthermore, compounds like heavy metals or suspended solids precipitate at high pH ranges, or dissolve (usually) at low pHs. Additionally, energy generation from wastewater requires an optimal pH between 6.5 - 8, although some bacteria can survive extreme pHs.

2.5.2 Cross-flow Velocity and Spacer Designs

In FO, lower cross-flow feed velocities may result in higher CECP effects [83, 104]. Hancock and Cath [33] found ECP to be affected by both draw solution and FS flows, resulting in maximum water fluxes at higher and equal flow velocities on both sides of the membrane, however other studies observed no change in the water flux under different flow regimes [107, 136]. Hancock and Cath [33] also suggested operating FO processes at low feed and draw cross-flows to minimise reverse solute leakage, however this may reduce water fluxes by increasing ECP and membrane fouling.

Spacers effect cross-flow conditions too. influencing mass transfer and encourage mixing, which suppresses the membrane boundary layer and CP. Park and Kim [137] studied six FO spacer configurations based on geometric characteristics. Submerged-type spacers were found to perform the best and cavity-type spacers the worst, in terms of permeate flux. In spiral-wound configurations feed spacers provide a feed channel between membrane envelopes for the feed water to flow evenly through the membrane element. Channel profiles are dependent on the spacer type, but normally run in an approximate 45° angle to the feed. To allow fouling mitigation in SWFOs, corrugated feed spacers, chevron design (thickness 98 mil), have been developed, although pumping energy is high for these modules to maintain high cross-flow velocities. Thinner corrugated spacers are being further developed, which should cut the energy requirements by 25 - 50%, but may increase the effect of fouling in spiral-wound modules as well.

2.5.3 Module Configuration

A membrane module configuration implies the packing of a membrane into a module to (i) maximise the surface to volume area and (ii) reduce particle deposition by sufficient cross-flow [138]. Selecting a module depends on economic considerations, CP, fouling propensity, ease of fabrication into the module design and suitability of the design for FO-wastewater applications. Configurations interesting for FO-wastewater can be found in Table 2.5.

Spiral-wound FO (SWFO) membranes have developed considerably from a design impractical

for the membrane industry [17], to becoming a configuration commonly used in FO tests. SWFO elements are preferred if both feed and draw streams are clean. If fouling occurs in SWFOs, cleaning can occur via chemicals, air/water mixing and/or high fluid velocities. Furthermore, improved SWFO membranes should be backwashable to allow more effective fouling removal from the membrane surface and feed channels. For this, Bamaga et al. [139] suggested short SWFO feed channel lengths and wider spacers.

SWFO elements have a lower packing density (typically 20 m^2 for 8-inch modules) than SWRO

Configuration	Advantages	Disadvantages	Reference
Spiral-wound (SW)	 High packing density Easy cleaning of fouling deposits 	 Limited pressures in membrane envelop Clogging of spacers 	[17, 139]
Hollow fibre (HF)	 Self-supported characteristics Appropriate flow patterns Simplicity of fabrication High packing density 	 Limited mixing at membrane surface CP film grows undisturbed in the open channel 	[56, 91, 137, 140-142]
Plate and frame (PNF)	 Well-suited to wastewater applications Less complicated in design Better backwashing Higher cross-flow velocities 	• More expensive per m ² of membrane area	[139, 143]

Table 2.5: Interesting FO module configurations for wastewater treatment.

elements (typically 30 m² for 8-inch). Additionally, SWFO membrane envelopes contain glue lines to create two independent channels inside and outside the envelope, accounting for membrane area loss [94]. Improved SWFO modules could employ heat welding technology or mechanical methods to seal the membrane edges [139]. Furthermore, the maximum pressure currently allowed in the envelop is 70 kPa [139]; higher pressure differences at the draw side, without damaging the glue lines, are desired.

Pilot-scale experience with SWFO modules is still limited, but steadily growing. Hancock et al. [144] used a SWFO in their pilot-scale study to determine the rejection of TrOCs, showing higher rejections than on bench-scale, while Cornelissen et al. [145] found slightly higher fluxes in a 4-inch SWFO module (constant draw solution concentration) compared to lab-scale. Xu et al. [94] suggested that permeate flow in spiral-wound modules may significantly dilute the bulk draw solution concentration (if not kept constant), reducing flux performance compared to small coupon tests. Factors like membrane area, feed volume and concentration should be considered in such tests, illustrating the importance of developing scalability studies accurately from lab-scale to full-scale.

2.6 Membrane Fouling

Membrane fouling concerns the accumulation of solutes and/or particles on a membrane surface, within membrane pores or clogging of feed spacers. This can lead to fouling, scaling or damage of the membrane [146]. FO membranes are generally at a lower risk of membrane fouling due to the lack of hydraulic pressure. Ultimately fouling leads to an additional hydraulic resistance lowering the effective osmotic pressure and water permeability.

2.6.1 Wastewater foulants

Major foulants in natural and impaired waters are microorganisms, organic matter and inorganic matter (scaling). Biofouling can be the most limiting factor when employing wastewater, due to the presence of microorganisms and their secretion of extracellular polymeric substances (EPS) to establish biofilm integrity [147, 148]. Biofouling is influenced by the feed water quality, membrane physicochemical properties and operating conditions. In an FO-MBR study [149], biofouling did not affect the water permeability much, however the mass transfer coefficient was reduced severely, enhancing ICP. In seawater-FO, silica scaling [150] or membrane biofouling via transparent exo-polymer particles (TEP) [151, 152] can occur.

Organic fouling differs according to the feed water employed. Wastewaters are comprised of effluent organic matter (EfOM), which includes both soluble microbial products and natural organic matter (NOM). NOM has been found to be a serious fouling agent in many membrane processes including FO [25, 152], therefore mimicking the behaviour of these complex feeds to include all, or the most significant, foulants is very important. Model foulants, i.e. sodium alginate or alginic acid, bovine serum albumin (BSA), Aldrich Humic Acid (AHA) have been used to test the severity of NOM fouling on FO membranes [50, 79, 153, 154]. Alginate relates to the hydrophilic fraction of EfOM, AHA represents humic acids and BSA the protein portion.

Mi and Elimelech [50] found calcium ions to enhance alginate (humics) fouling, severely declining the flux, compared to alginate fouling in the absence of calcium ions. This humics–calcium deposition on the membrane surface has been observed using RO brine [109], showing that calcium-binding can enhance the intermolecular adhesion between foulants, increasing membrane fouling. Bypassing these interactions completely may be difficult, but adding calcium, i.e. as a draw solution, should be avoided.

Zhao et al. [82] found organic fouling to be more severe and irreversible than inorganic fouling in FO, but scaling may be a greater issue for wastewater, especially at high recoveries. Precipitation can occur with sparingly soluble salts such as calcium carbonate or calcium sulphate (gypsum). Gypsum scaling cannot be controlled by simple pH adjustments, and is also affected by the membrane material, i.e. heterogeneous/surface crystallisation on PA membranes causes severe flux decline [106]. In practice, salt precipitation in the form of BaSO₄, Mg(OH)₂ or silica contribute more to membrane scaling than gypsum.

2.6.2 Causes of FO Fouling

Many studies have attributed the low fouling propensity in FO to the low flux conditions and lack of applied pressure, however FO fouling works similar to the fouling mechanisms in RO because both processes are governed by chemical and hydrodynamic interactions [50]. The occurrence of ICP makes FO fouling even more complicated [79]. An accumulation of solutes (foulants) in the SL is generally caused by reduced porosity and a reduced mass transfer coefficient, enhancing ICP. ICP adversely affects FO flux and fouling at greater draw solution concentrations and/or greater membrane fluxes, due to the exponential dependence of ICP on the flux level [79]. More frequent cleaning, i.e. flushing or backwashing may reduce the foulant accumulation in the SL and so alleviate ICP. This may be detrimental to the membrane longevity over time, but could avoid the decrease of flux performance during operation and perhaps prevent the subsequent use of chemicals.

Operational parameters like cross-flow velocity can affect the rate and extent of membrane fouling [155]. Increasing the cross-flow velocity, prior to cake-forming compaction, can reduce NOM accumulation and hamper growth of the fouling layer in FO membranes. However once the cake layer forms, changes in hydrodynamic conditions barely affect the fouling behaviour [50].

Module design also plays a role in fouling. Labscale studies may not employ spacers [113], but when applied to full-scale, FO membranes require spacers in both the feed and draw solution channels [156]. The selected spacer type, especially in wastewater applications, should promote mixing, decreasing ECP and consequently, the passage of small solutes through the membrane. Additionally, application-specific feed spacer materials, can be fitted to further prevent colloidal and particulate fouling [55]. The use of a diamond-patterned feed spacer on the feed side dramatically enhances initial FO fluxes (~50% at 0.5 M NaCl and ~100% at 2.0 M NaCl) and improves flux stability during fouling [78]. However, particle accumulation and biofouling is still found near spacer filaments, due to local hydrodynamic conditions (low shear region) and physical blockage (large particle size), suggesting room for improvement in FO spacer design.

The membrane orientation has also been suggested to affect fouling. The FO-mode offers flux

stability against both dilution of the bulk draw solution and membrane fouling, while, the PROmode has shown severe flux reduction after fouling, due to the microstructure difference of the SL, where internal clogging or enhanced ICP can occur [79].

Other factors influencing the development of a fouling layer on the membrane surface include membrane surface morphology (foulant-membrane interactions), i.e. charge [157, 158] and roughness [159]; membrane surface hydrophobicity; electrostatic attraction (leading to calcium binding); elevated ionic strengths which can lead to an increase in EPS thickness [160]; permeation drag, and hydrodynamic shear force. Ultimately, membrane fouling is dependent on the foulant. Therefore it is important to consider the combined interactions of feed water foulants, while still regarding the overall effects of ECP and ICP.

2.6.3 Subsequent Effects on FO Performance

Foulant accumulation adversely affects the quantity (permeate flux) and quality (solute concentration) of the product water. This can influence membrane performance, i.e. reduce water productivity and/or "permeate" quality; change the normalised pressure drop (NPD); increase energy expenditure and treatment costs, and if severe, cause membrane failure [161].

2.6.3.1 Flux decline

Flux decline in FO processes is generally due to a reduction in the driving force, via draw solution dilution [37], membrane fouling [40] and enhanced CP in the fouling layer [88]. Reverse salt diffusion too reduces the driving force, but also intensifies cake enhanced osmotic pressure (CEOP) within the fouling layer, elevating osmotic pressures near the membrane surface (feed side) and subsequently reducing $\Delta \pi$ and permeate flux [25].

When affected by fouling, the extent of the flux decline can vary depending on the fouling stage, installation scale and feed type. Membrane fouling/scaling can cause water flux declines of 20% when treating synthetic feeds (COD: 4.5 ± 0.2 g/L) in lab-scale OMBR systems [24] or between 30–50% when treating landfill leachate in a full-scale FO system [14].

2.6.3.2 Enhanced Rejections

Using wastewater effluent, Hancock et al. [144] found > 99% TrOC rejection due to FO membrane

fouling, because of interactions between hydrophobic hormones and organic matter. Valladares Linares et al. [162] found the increase in micropollutant rejection in the presence of the fouling layer due to higher hydrophilicities in fouled FO membranes than clean ones, reducing mass transport capacity, membrane swelling, and the higher negative charge of the membrane surface (related to NOM acids and polysaccharides).

2.6.4 Fouling Detection and Cleaning Methods

Immediate fouling detection can ensure the longevity of a membrane and restore membrane performance. Determining the fouling potential of the feed can help predict fouling, however once fouling occurs on the membrane surface, ex-situ and off-line methods may be necessary to incorporate future preventative measures. Non-invasive and visual on-line methods can detect early signs of fouling in real-time, i.e. flux decline, solute rejection and changes in NPD and operating parameters (temperature, feed TDS, permeate flow, recovery). Figure 2.3 summarises the fouling detection/ monitoring techniques involved with feeds and FO membrane fouling. Only long-term fouling studies can prove whether FO membranes are resilient to fouling. Short-term vs. long-term studies have varied significantly with regards to fouling severity when treating impaired waters [42, 152]. However once fouling has been detected, cleaning via physical, chemical or physicochemical methods can be introduced to restore system performance.

Depending on the fouling severity, physical cleaning via hydrodynamic modifications [25], forward or backward flushing and osmotic backwashing [13] might be enough to remove fouling deposits. Higher fouling propensities and fluxes have already been mentioned for the PRO-mode. This orientation should therefore make flushing and rinsing easier and faster, however using inorganic and organic foulants, Zhao et al. [82] found the FO-mode to provide higher flux recoveries after cleaning than the PRO-mode.

When severe, fouling mitigation may require chemical reagents. Reagent selection depends on the feed water, foulant type [82] and membrane material [163]. Furthermore, these reagents should be able to dissolve and remove most of the deposited materials, without damaging the membrane surface.



Figure 2.3: Methods used in literature to detect the fouling potential of the feed or monitor/analyse fouling on the FO membrane using i) on-line techniques to detect early signs of fouling via changes in operational parameters (flux or rejection) or other non-invasive tools, ii) off-line techniques to determine morphological, chemical and physical properties of the foulant type influencing FO membrane fouling.

Precipitation and scaling can be mitigated with anti-scalants and commercial inhibitors, while periodic cleaning with one or more chemicals (acids, bases, oxidising agents, surfactants or chelating agents) might be necessary to maintain long-term process performance. Chemical cleaning typically removes the cake layer, but not foulants in the membrane pores [40]. Furthermore, it not only impairs membrane selectivity and shortens membrane life, but also consumes additional energy and produces concentrated waste streams [164].

Valladares Linares et al. [165] assessed various chemical and physical procedures to remove FO membrane fouling, during wastewater-seawater integration. Air scouring proved most effective (~90% flux recovery), with the addition of industrial detergents further increasing recovery; osmotic backwashing proved completely ineffective. Qin et al. [107] confirmed the potential advantages of fouling reversibility with air scouring employing a pilot OMBR, while a further study by Valladares Linares et al. [166] suggested the need for multiple backwashings to achieve flux recovery, due to ICP aggravation by (seawater) salts.

Periodic physico-chemical cleaning or pretreatment are other options. However, regardless of the cleaning method, irreversible fouling may still occur when treating wastewater feeds, due to the adsorption of biopolymers on the membrane [152, 165].

2.7 FO and Other Wastewater Considerations

2.7.1 Energy Aspects

Employing effective, inexpensive, low energy pretreatment practices for high TDS solutions may be essential in reducing the potential for membrane fouling, ensuring acceptable performance and protecting the FO membrane [167]. Multiple methods are available for the removal of particles, but these do not prevent organic fouling. Furthermore, single-pass membrane processes produce a concentrate stream. In wastewater, the method of disposing this concentrated brine must be deliberated well, since some streams may be difficult to discard and can become a costly element, i.e. leachate management [14]. One advantage of applying FO (similar to RO), is that the waste stream becomes concentrated, enabling a smaller flow of processed. Additionally, waste to be the concentration of organic wastewater streams could facilitate renewable energy production and nutrient recovery; the goal of the Sewer Mining Concept [26]. This could reduce the energy required by the

system, e.g. energy produced from the organics can drive the reconcentration unit. Wastewater organics (COD) are directly correlated to the energy value: 1 kg COD = $3.86 \text{ kWh}_{\text{theory}}$ [168]. In this way energy can be recovered from wastewater.

The concept of using FO for energy generation is not new [169, 170] and recent environmental awareness has emphasized the need for sustainable, green technologies. The osmotic Microbial Fuel Cell (OsMFC) [171-173] is similar to the microbial desalination cell [174] desalinating synthetic brackish- and seawater. The OsMFC uses an FO membrane as a barrier between cathode and anode units, extracting water (from wastewater) and generating electricity. These designs, however, require aeration of the cathode chamber, counteracting the benefits of the power generation. Air-cathode OsMFCs have evolved to improve energy recovery [175], but reverse salt leakage and fouling still remain challenges.

Furthermore, energy can be achieved from salinity gradients, where the osmotic pairing of fresh water and seawater is possible. In salinity-driven desalination, pre-dilution can be accomplished by pressure retarded osmosis (PRO) [176]. PRO is a process through which osmotic energy can be harnessed and power generated [177]. Wastewater tested in PRO applications [178-180] demonstrated power densities from $4 - 10 \text{ W/m}^2$. PRO is growing fast, but is still a young technology requiring more comprehensive studies on a large scale, especially with regards to its environmental impact [181].

The operation of FO processes at ambient pressures is interesting as high quality water can be produced using potentially less energy (applicationdependant). To produce clean water from wastewater via FO, RO is necessary to recover the monovalent draw solution, requiring at least 30 bar to operate. That is more than for wastewater treatment via UF-RO. Digestion may thus be the only way to recover energy. Even if magnetic nanoparticles are used, these need to be separated. A permanent magnet is not an option; thermodynamically the same high energy would be required to separate the particles from the magnet. Using a temporary electric/magnetic field will likewise cost more energy than UF-RO, because osmotic pressure will be lost in the FO process due to CP. $(NH_4)_2CO_3$ as a draw solution requires waste heat to decompose the ammonium salt, but another source of heating could be more efficient, i.e. natural solar or geothermal energies [182]. Solar power has been used for draw solution regeneration [23] and increasing dewatering rates [134, 135]. When used for desalination, the reconcentration unit for FO does not require external pumping energy. The minimum thermodynamic energy required to achieve 50% recovery of fresh water from a 35 g/L TDS solution by RO is 3 - 5 kWh/m³ [183, 184]. By excluding external pumping energy, the specific power consumption of an FO-solar desalination process can drop to < 1 kWh/m³ [184].

FO is often reported to be a sustainable technology, particularly when applied to continuous flow systems [27], however, no production of "clean" water exists, unless coupled to a recovery technology that uses almost the same amount of energy (thermodynamically) as the original process. The possibilities of FO for energy generation are growing and FO-wastewater treatment does enhance the potential to yield energy, but many hurdles need to be overcome before economic and commercial feasibility are reached.

2.7.2 Micropollutants

Micropollutants add to the increasing contamination of freshwater systems. Generally these compounds are present at low concentrations, however they raise considerable toxicological concerns, especially when present in complex mixtures. Concentrations of TrOCs have been found to prevail in wastewater effluent.

Complete rejection of micropollutants has not been achieved by FO, but high removal efficiencies have been demonstrated for many TrOCs. Hancock et al. [144], investigating 23 non-ionic and ionic TrOCs, found the rejection (*R*) of charged TrOCs >80% and neutral TrOCs between 40 - 90%. The FO membrane showed R > 90% for most TrOCs at pilotscale, while rejection at bench-scale was generally lower. Membrane compaction, the fouling layer and optimised hydrodynamic conditions in the pilotscale system have been suggested as reasons for improved rejections. Valladares Linares et al. [162], spiking secondary wastewater effluent with 13 micropollutants, achieved similar rejections with FO for neutral compounds and > 92% rejection for ionic compounds. In FO, rejection of charged TrOCs was found to be governed by electrostatic interaction and size exclusion, while rejection of neutral compounds was dominated by size exclusion [185].

Rejection also depends largely on fouling. Valladares Linares et al. [162] found higher rejections of micropollutants on a fouled membrane than a clean one, with the exception of hydrophilic neutral compounds. Each group of compounds behaves differently in the presence of a fouling layer, based on size, charge, polarity, adsorption capacity, mass transport capacity, membrane hydrophilicity after fouling and membrane swelling. By changing the surface properties of FO membranes, the interactions with TrOCs can be limited.

Some TrOCs are of more public concern than others. Endocrine disrupting compounds (EDCs) for example, interfere with the endocrine (hormone) system. Cartinella et al. [16] demonstrated similarly high rejections (77 - 99%) for estrone and estradiol in FO, but rejection was affected by the feed composition. Adding surfactants to the feed improved rejections, however these may change membrane surface properties e.g. hydrophobicity and charge, which can influence the flux. Boron and arsenic are other TrOCs adversely affecting human

health, crop production and aquatic life. Jin et al. [87] found boron rejections in FO experiments (30 - 60%) comparable to rejections achieved in RO (40 - 65%), but boron and arsenic rejections were also affected by the FO membrane orientation [81], due to the degree of fouling. D'Haese et al. [34], testing 20 TrOCs, found FO to achieve comparable rejection rates to NF, but lower rejections than RO. Most FO studies have carried out these investigations with CTA membranes. Using TFC membranes, TrOC rejection has been reported to increase [186, 187]; the rejection of neutral TrOCs was attributed to the more favourable AL structure of the TFC.

Not many stand-alone treatment options can remove TrOCs entirely and regardless of improvements in FO, it may still not completely remove TrOCs. However a combination of treatment processes (FO hybrids) should be sufficient, if used in a once-through system [34, 182].

2.8 Concluding Remarks

In this chapter, FO has been discussed as a potential candidate for treating wastewater, due to, among other things, its high rejection capacity and low fouling propensity.

Ineffective membranes and reverse solute leakage remain the main challenges hindering the growth of FO-wastewater applications. The use of hybrid systems, i.e. FO–MD, FO–RO, FO–NF and OMBR-RO and/or integrated with seawater desalination can enhance FO and make it commercially feasible for wastewater recovery. Overall energy balances for integrated systems, in order to compare the economic benefits, are however still lacking. A better understanding of these concepts will further promote the use of this technology in existing and new applications of wastewater treatment.

Moreover, concentrate disposal must be deliberated well, since waste streams containing high concentrations of heavy metals may be difficult to dispose of. Energy-efficient pre-treatment of the feed is an option. Additionally, concentration of organics by FO could be advantageous for energy production and nutrient recovery.

Higher quality water is in demand, due to the imposition of new and ever-changing water quality standards. Therefore interest in FO technology is growing as a potential, cost-competitive and reliable alternative.

CHAPTER

Zwitterions as Alternative Draw Solutions in Forward Osmosis for Application in Wastewater Reclamation



This chapter is adapted from:

Lutchmiah K., L. Lauber, K. Roest, D.J.H. Harmsen, J.W. Post, L.C. Rietveld, J. B. van Lier, E.R. Cornelissen, Journal of Membrane Science, 460 (2014) 82-90.

3.1 Introduction

The application of forward osmosis (FO) has shown promise in recent years [132], however, a major issue still concerns the use of the draw solution; of which, type and concentration influence the efficiency of the osmotic process. The transport of draw solutes through the membrane can pose substantial limitations to the implementation of FO processes, i.e. migration of the draw solutes into the feed solution (reverse solute leakage [99, 101]) and/or into the reconcentration unit (forward solute leakage) can make the process uneconomical owing to costs required to reconcentrate the draw solution [188], which include treatment of the feed solution before entering the reconcentration unit or prior to discharge. The reverse solute leakage essentially influences the efficiency of the FO process as it reduces the effective osmotic pressure difference across the membrane, and thus the overall efficiency [99]. Therefore the balance between the solute performance and solute cost is important.

Many draw solutions, mostly comprised of inorganic compounds, have already been tried and tested [17, 41, 131, 189]. Organic compounds too have been used in FO [17, 39, 118], but with less frequency than inorganic solutes [12]. This is mainly due to the potential biodegradation of organic compounds over time [118]. Stability of the draw solution (in time) is a requirement of the draw solution [1], but degradation of the compound may not be a limitation if leakage to the feed side ultimately assists processes, like an FO-digestion coupled system, with the organics as a carbon source for microorganisms [118].

FO is used in (waste)water treatment and reclamation [24, 40, 41]. In the Sewer Mining concept (Chapter 1), FO is combined with energy generation from wastewater using an anaerobic digester. In this case, the draw solution criteria should not only fulfil the requirements to attain a high osmotic pressure; ensure effective and easy separation from the product water; be inexpensive, non-toxic and not cause damage to the membrane [17, 132], but the effect on the digestion stage and more specifically the biogas production needs to be considered as well.

Anaerobic digestion (AD) is an efficient waste and wastewater treatment technology to biologically mineralise organics and generate energy, offering low sludge production, low energy requirements and energy recovery [190]. FO-concentrated wastewaters, containing high levels of easily biodegradable organic material, are suitable for biogas production, assuming that high concentrations of the organic matter can be achieved.

Since FO concentrates all wastewater constituents, inhibitory compounds may accumulate as well, potentially limiting the AD reactor capacity. anaerobic microorganisms Although, require minimum concentrations of (earth) alkali metals, such as sodium, potassium, magnesium, etc. in the range of 75 - 400 mg/L, inorganic salts are known to negatively impact the anaerobic conversion process [191]. Non-adapted sludge, may become (partly) inhibited at Na⁺, K⁺, Ca²⁺ and Mg²⁺ concentrations exceeding 3.5 g/L, 2.5 g/L, 2.5 g/L, and 1 g/L, respectively. Substrate conversion is noncompetitively inhibited by high salt concentrations [192, 193], whereas high osmotic pressures may cause cell dehydration [191, 194]. After adaptation, saline digesters can operate well, but fluctuating concentrations might still be detrimental for the microbial growth. Methanogens are crucial, serving as the final electron sink in AD processes, therefore

inhibition or disruption can seriously affect the entire digestion process. Studies have shown that the addition of osmolytes, a substance regulating osmotic pressure equal to that of the external surrounding environment [195], may increase the methane yield in processes treating food waste with high sodium content [196] and effectively reduce toxicity symptoms of high sodium concentrations in anaerobic reactor systems [194]. Natural osmolytes such as betaines and amino acids are also zwitterions [197, 198], having a net charge of zero around pH neutral. These solutes as draw solutions may increase the performance of FO, but might also simultaneously overcome the low methane yield in the anaerobic digestion by promoting energy production, even if marginal, rather than constricting it [199].

Glycine betaine (GB) and several amino acids (selected based on their zwitterionic properties) as draw solutions for FO-wastewater applications were tested. This paper introduces zwitterions as possible draw solutions for use in FO processes. Furthermore, the influence of the physico-chemical properties of the draw solutes were related to their FO transport efficiencies.

3.2 Materials & Methods

3.2.1 Membrane Material

A cellulose triacetate (CTA) FO-type membrane was used ('Expedition' type or 'HydroWell', Hydration Technology Innovations, Albany, OR). The FO membrane is highly hydrophilic and has a thickness of $< 50 \ \mu m$ [49]. It is comprised of an active, dense selective layer and a porous support layer consisting of an embedded polyester mesh which provides the mechanical support. The asymmetric membrane was used in only one of the two possible orientations, namely active layer facing the feed side (AL-FS). The water and solute permeability coefficients (A) and (B) of the membrane were experimentally determined in a cross-flow RO set-up as described in the literature [31].

3.2.2. Experimental Set-up

FO experiments were carried out in a lab-scale Utube set-up similar to that mentioned in previous work [26, 41]. The membrane (active area: 124 cm^2) was placed in a membrane holder. A constant mixing rate of 375 L/h was applied to both the feed and draw side to maintain homogeneity by using magnetically-driven centrifugal pumps (Verder, V-MD15). The pump outlet was placed perpendicular to the membrane surface to diminish external concentration polarisation (ECP). The water flux (J_v in L/m²h) was determined by the volume increase within the measuring tube on the draw side. Dilution of the draw solution over time was also taken into account. The reverse solute flux (J_s in g/m²h) towards the feed side was determined either by means of a conductivity meter (in the case of NaCl) or by total organic carbon (TOC), analysis in time, for all organic compounds unless otherwise mentioned. All experiments were performed for 7 h.

3.2.3 Feed and Draw solutions

Deionised (DI) water (Milli-Q, Millipore) was used as the feed solution and solvent in all cases. The following solutes were tested as draw solutions in the FO U-tube system: (1) NaCl (J.T. Baker, the Netherlands); (2) zwitterions [125]: a) GB (Sigma Aldrich, Germany), b) L-proline (Sigma Aldrich, Germany), c) glycine (Sigma Aldrich, Germany), d) L-valine (SAFC Supply Solutions), e) L-glutamine (Sigma Aldrich, Germany). The properties of the investigated compounds can be found in Table 3.1.

Compound	Molecular weight (g/mol)	Solubility at 20°C (g/L)	Diffusion Coefficent (x10 ⁻⁹ m ² /s)	Chemical structure
Sodium Chloride	58.44	359 [200]	1.23 [120]	Na ⁺ Cl⁻
Glycine Betaine	117.15	585 [200]	0.90 [201]	H ₃ C H ₃ C H ₃ C
Glycine	75.07	250 [202]	1.06 [203]	H ₃ N ⁺ O ⁻ O
L-proline	115.13	115 [200]	0.88 [203]	0
L-glutamine	146.14	14.6 [204]	0.76 [203]	
L-valine	117.15	85 [205]	0.77 [203]	H ₃ N + 0

Table 3.1: Characteristics of the compounds used as draw solutions.

For the experiments, the molal concentration $C_{mol/kg}$ was calculated via Equation 3.1 [206]:

$$C_{mol/kg} = \frac{Cmolarity}{\rho - C_{molarity}MW}$$
(3.1)

Where *MW* denotes the molecular weight and ρ the density of the solute. These concentrations relate to an osmotic pressure of 24.3±1.5 bar, except for L-valine and L-glutamine which relate to osmotic

pressures of 6.8 ± 0.2 bar, due to their low solubilities. The osmotic pressure values were determined based on cryoscopic osmometry (Gonotec Osmomat 030) and converted to osmotic pressure via the factor $24.5*\rho*1.013$ bar [206]. The osmotic pressures for NaCl were also determined by the OLI Stream Analyzer Software (Morris Plains, NJ). The exact concentrations and respective osmotic pressures for each compound can be found in Table 3.2. Temperatures during the experiments remained around 21 ± 2 °C.

Compound	Concentration (mol/kg)		Osmotic pressure (bar)		
NaCl	0.13	0.53	5.2	23.0	
GB	0.27	1.40	5.2	23.5	
Glycine	Glycine 1.24		24.2		
L-proline	1.27		26.4		
L-glutamine	0.27		6.6		
L-valine	0.27		6.9		

Table 3.2: The concentrations and respective osmotic pressures of the draw solutions

3.2.4 TOC analysis

The TOC analysis was done by sparging, i.e. Non-Purgeable Organic Carbon (NPOC) using the Total Organic Carbon analyzer TOC- V_{CPH} (Shimadzu). Sample preservation by means of acid addition (2 M HCl) was carried out to maintain sample integrity by reducing the rate of microbiological growth, which may cause contamination or degradation of the organics. Furthermore, the decrease in pH retards the potential biological growth.

3.2.5 Degradation Tests

Biomass Production Potential (BPP) tests were carried out to measure the biological degradation rate of the various draw solutions over time [207]. The growth measurements were carried out with autochthonous bacteria from the river Lek (Nieuwegein, the Netherlands) by determining the maximum Adenosine Triphosphate (ATP) content in time. ATP analysis is based on extraction of the compounds from biomass using a nucleotide-releasing agent, followed by the light-generating luciferine–luciferase reaction [208]. Each bacterial cell contains approximately $5x10^{-15}$ g ATP, giving an indication of the growth potential over time. All draw solutions were tested using the same concentrations as in the U-tube experiments, however L-valine was excluded from this test due to its low solubility.

3.3 Results & Discussion

3.3.1 Performance of the draw solutes

3.3.1.1 Reference Experiments with NaCl

A 0.53 mol/kg NaCl solution was used to characterise each new membrane coupon before and after an experimental series. The water flux (J_v) and the solute leakage (J_s) were determined from these experiments. An average of 4.91±0.31 L/m²h (n=10) was found for the water flux and 3.26±0.53 g/m²h

for the salt flux. The J_s/J_v ratio (0.66±0.08 g/L) was used as the reference (Figure 3.1b). These results are consistent with previous research [41]. The extracted data of the NaCl salt flux in g/m²h relates to an NaCl concentration of approximately 50–70 mg/L in the feed after the 7 h experiment. This leaked concentration should not impact microbial growth [193, 209] in an AD process, when coupled to an FO unit.

3.3.1.2 Performance of the zwitterions

The results of the five tested zwitterions were compared to NaCl and can be found in Figure 3.1. Figure 3.1a shows the average water and salt fluxes of each compound, while Figure 3.1b shows the J_s/J_v ratios. The organic solutes are not electrolytes and are therefore expected to produce lower water fluxes in FO than NaCl, especially for the larger molecules [210]. However it can be seen that the highly soluble zwitterions: GB: 4.83 ± 0.15 L/m²h (n=6); glycine: 4.59 ± 0.38 L/m²h (n=3) and L-proline: 4.31 ± 0.57 L/m²h (n=2) produced comparable water fluxes to NaCl, but with even lower solute losses (2.13\pm0.54 g/m²h; 1.37 ± 0.09 g/m²h and 0.96 ± 0.4 g/m²h respectively). L-proline showed the lowest J_s/J_v ratio (0.22±0.07 g/L) in the group of highly soluble zwitterions with the CTA FO membrane. Studies have shown proline to induce a stronger localisation of the surrounding water than the osmoprotectant GB [211], which might explain the lower leakage of this solute even though these compounds have similar molecular weights.



Figure 3.1: The efficiency of the zwitterions as FO draw solutions at $\pi = 24$ bar (L-valine and L-glutamine at $\pi = 7$ bar): (a) water and solute fluxes, (b) J_s/J_v ratios compared to NaCl ($10 \ge n \ge 1$).

The zwitterions with low solubilities (Figure 3.1) showed less potential as viable draw solutes due to low fluxes: L-valine 1.72 ± 0.22 L/m²h; 0.34 ± 0.13 g/m²h and L-glutamine 1.34 ± 0.18 L/m²h; 0.15 ± 0 g/m²h (n=2). This is due to the lower driving force used since higher concentrations were not possible. However they did maintain low J_s/J_v ratios of 0.19 ± 0.05 g/L and 0.11 ± 0.02 g/L respectively. These values were further compared to NaCl and

GB (Figure 3.2) at similar osmotic pressures ($\pi = 6.0\pm0.9$ bar). The low fluxes of L-valine and L-glutamine resulted in lower solute losses and therefore lower $J_{s'}J_{v}$ ratios than NaCl or GB; 0.59 g/L and 0.35 g/L respectively. Unfortunately, such low water fluxes and low solubilities [17] limit the use of these compounds in FO processes and as a result are not expected to be applied in practice.



Figure 3.2: Efficiencies of NaCl, GB, L-valine and L-glutamine at π =6.0±0.9 bar (a) water and solute fluxes, (b) J_s/J_v ratios ($n \ge 1$).

3.3.2 Influence of the physico-chemical properties

Specific physico-chemical characteristics of the zwitterions were analysed and compared to their FO process efficiencies (J_v and J_s) to explain the differences in behaviour.

3.3.2.1 Osmotic pressure difference

Figure 3.3 shows the water fluxes for the highly soluble draw solutes increasing with an increase in the osmotic pressure difference. Although, the water fluxes are expected to be similar at similar osmotic
pressures and operational conditions, this study, and others [90, 108], shows otherwise. In Figure 3.3 the difference in flux behaviours are also more significant at higher osmotic pressures (> 50 bar). Usually, when the draw solution faces the membrane porous support layer and pure water is used as the feed, only dilutive internal concentration polarisation (DICP) will occur in the support layer without any occurrence of external CP (ECP) [108]; this will also depend on the hydrodynamic conditions on the feed side. The differences in flux therefore relate to the various degrees of DICP experienced by each draw solution.

In Figure 3.3 the DICP for NaCl was found to be less serious than the zwitterions, however glycine caused more severe DICP than GB and proline. Due to the lower solubility of proline the effect on DICP at higher osmotic pressures is not observable in Figure 3.3. The differences in the degree of DICP are said to be affected by the diffusivity and viscosity of the draw solution [33, 121].



Figure 3.3: Water fluxes for NaCl, GB, glycine and proline at varied osmotic pressures (bar).

3.3.2.2 Charge Effects

Most of the draw solutions in this study, except NaCl, are zwitterionic compounds. There is a high dipole moment inside these compounds due to the proximity of both positive and negative charges on the same molecules. These zwitterionic properties and the hydrophilicity of the solutes are further dependent on the pH. For this reason, the protonated and unprotonated species fractions were calculated as a function of the pH using the CurTIpot software (Figure 3.4).

The isoelectric point (pI), which is the exact midpoint between the two pKa values, lies around pH 6 for all the solutes. At this point, the average net charge of all forms present is zero [212]. At pH values between the two pKa values (~pH 2–10), the zwitterionic form predominates, however a co-existence with small amounts of net negative and net positive ions occur. From Figure 3.4, it appears that all the compounds remained in zwitterionic form whilst in solution.

Furthermore, the pI of the CTA membrane, based on zeta-potential measurements (SurPASS, Anton Paar, Graz, Austria), was found to lie at pH 4.1. Below this pH the membrane becomes more positively charged and above, more negatively charged. Hence, the contribution of charge repulsion or attraction between the negatively or positively charged CTA membrane and the neutral compounds is of little importance.

The pH of GB, glycine and proline at their respective concentrations, calculated via the Henderson-Hasselbalch equation (Equation 3.2), were found to be 6, 5 and 4.6 respectively, while valine and glutamine were more acidic at pH 4 (Figure 3.4). Equation 3.2 is derived from the acid dissociation constant (K_a), where [HA] is the molar concentration of the undissociated weak acid, [A 7] is the molar concentration of the acid's conjugate base and pK_a is $-\log K_a$:

$$pH = pKa + \log_{10}\left(\frac{[A^-]}{[AH]}\right) \tag{3.2}$$







Figure 3.4: Species fractions of the unbound zwitterionic compounds at various pH values (a) GB, (b) glycine, (c) proline, (d) valine and (e) glutamine. Calculated via CurTIpot software and based on pKa values of the compounds. Abbreviations: H2B = diacid; HB = monoanion; B = dianion. The relative fraction (f) = fH2B + fHB- + fB = 1.

3.3.2.3 Polarity

The distribution coefficient logD is the tendency of chemicals to partition between two immiscible phases (octanol/water) at equilibrium, which is used as an indication of partitioning of solutes between the water and membrane "phase". In Figure 3.5, the J_s/J_v ratios of the highly soluble zwitterions are plotted as a function of their pH-dependent hydrophobicities (logD) at pH 5.5, based on the average pH values of the draw solutes at the used

concentrations (section 3.3.2.2). From Figure 3.5 the hydrophobicity of the compounds is found to influence the J_s/J_v ratios; a decrease in the ratio with decreasing hydrophobicity was observed. Several studies also relate the polarity of a substance to the extent of their rejection [186, 213, 214]. An increase in rejection with increasing hydrophobicity, i.e. an increasing affinity of the solute for the membrane, has been previously observed for CTA membranes [186, 215].



Figure 3.5: J_s/J_v ratio as a function of solute hydrophobicity (log D) at pH 5.5. LogD data taken from Chemspider [216].

3.3.2.4 Molecular Weight

The *MW* of the draw solutes plays an important role on the water and solute fluxes. As can be observed in Figure 3.6a and b, both $J_{s'}J_{v}$ ratios decreased with an increase in *MW*. In general, this is due to steric hindrance: defined as the sieving effect, where solutes with a *MW* higher than the molecular weight cut-off (MWCO) of the FO membrane are well rejected, while solutes with a *MW* lower than the MWCO can permeate through the membrane. The FO membrane has a pore size of 0.3 - 0.5 nm [217]. The largest solute, glutamine (Figure 3.6b), was therefore well rejected, resulting in lower reverse solute fluxes and lower J_s/J_v ratios.

Other properties related to the *MW* can also have an influence on the experimental results; molecular



Figure 3.6: Correlations of the J_s/J_v ratios with the molecular weight of the solutes at a) $\pi = 24$ bar and b) at $\pi = 7$ bar.

volume, viscosity or diffusivity, which all affect DICP and subsequently the water flux (section 3.3.2.1). The diffusion coefficient (*D*) of a solute, which is a measure of the rate of entry through the membrane, depends on the *MW*, temperature and

concentration. In this case D is considered to be the bulk diffusion coefficient in water. However the effective diffusion coefficient D_{eff_3} which describes diffusion of the solute through the porous membrane support layer and D^4 , the diffusion coefficient of the draw solute in the active layer, are more specific [101, 108]. These were not considered in this study.

Figure 3.7 shows the rate of *D* increasing with a decrease in *MW*. From this group of solutes NaCl has the highest diffusion coefficient ($D = 1.23 \times 10^{-9}$ m²/s) due to its small average ion size, followed by glycine, GB and proline. The solution diffusivity determines a solute's ability to diffuse through the membrane support layer, and in this way varies the degree of DICP in the porous support layer [108]. The lower water fluxes observed for proline (Figure 3.1a) compared to the solutes at π =24 bar are a result of its large size and lower *D* value (0.88x10⁻⁹ m²/s), increasing the severity of DICP. All *D* values can be found in Table 3.1.

Four physico-chemical parameters have been discussed to explain the differences in water flux, solute flux and the $J_{s'}J_{v}$ ratio between the zwitterionic draw solutes: (i) osmotic pressure, (ii) charge, (iii) polarity and (iv) molecular weight. According to these results, the solute-membrane affinity, which is pH dependent, and size, relating to the solute diffusion coefficients, tend to be the dominating factors. The ratios of the solute size to the membrane pore size (MWCO) are also important [218]. The contributions of diffusion and convection to solute mass transfer have been further investigated in an FO mass transfer model, developed to predict and evaluate the solute transport in the membrane support layer.



Figure 3.7: The relationship between the molecular weight and diffusion coefficient of each draw solute.

3.3.3 FO mass transfer model

The water and solute flux in FO processes can be described by the solution-diffusion model, in which the transport within the membrane support layer is described by diffusion and convection [84]. Using this model, theoretical J_v values were established for the AL-FS orientation [83, 85]:

$$J_{\nu} = K_m \ln \left(\frac{A\pi_{DS} + B}{A\pi_{FS} + J_{\nu} + B} \right)$$
(3.3)

Here K_m (m/s) is the mass transfer coefficient, A (m/s.Pa), the water permeability coefficient and B (m/s), the solute permeability coefficient. From Equation 3.3 it is clear that no linear relationship exists between the π difference and J_ν , due to ICP. K_m depends on membrane properties (thickness, porosity and tortuosity of the membrane support

layer) and reflects the ability of a solute to move through the membrane.

$$K_m = \frac{D}{S} \tag{3.4}$$

The membrane structure parameter (*S*) characterises the average distance a solute molecule travels from the support layer towards the active layer [101]. In this study *S* was calculated to be 0.53 mm; similar values were found in the literature: 0.40 - 0.62 mm [67, 79, 95, 101]. *S* also assesses the importance of ICP [219], by considering *A* (membrane specific parameter [17]) and *B* (solute dependant parameter). The experimentally determined *A* value (1.28x10⁻¹² m/s.Pa) was found to be consistent with previous work [101].

In order to determine *B* in the FO model, *D* needs to be accounted for via Equation 3.5, derived from Fick's Law of diffusion. Here ϕ denotes the partition coefficient (measure of a substance's solubility) and Δx (m) the membrane thickness.

$$B = \frac{D \cdot \phi}{\Delta x} \tag{3.5}$$

From Equation 3.5 it can be observed that B increases proportionally with an increase in D. B should therefore also decrease with an increase in

size, as was described for the J_s/J_v ratio and ultimately, solute flux, but ϕ should also be considered due to the change in concentration (Equation 3.6) and therefore solubility.

$$J_s = B.\Delta c \tag{3.6}$$

From the membrane parameters, the nature of the draw solution and the temperature, J_s can be calculated [79], incorporating the van't Hoff coefficient β , which is the dissociation number of a substance in water.

$$\frac{J_s}{J_v} = \frac{B}{A\beta R_g T}$$
(3.7)

A numerical resolution of the non-linear equation is used to solve Equation 3.3-3.7. For this specific membrane A and S values remain the same in all cases, whilst D, B and β differ per component (Table 3.1 and Table 3.3). The modelled vs. experimental results of the fluxes at varying osmotic pressures are shown in Figure 3.8.





Figure 3.8: Experimental and modelled values of J_v (L/m^2h) and J_s (g/m^2h) for a) NaCl, b) glycine and c) GB at various osmotic pressures using determined and optimised B values.

In Figure 3.8a the modelled results of NaCl correspond well with the experimental data. Moreover NaCl shows similar patterns to most of the commonly used electrolytes, i.e. increasing ratios with an increase in osmotic pressure. For glycine and GB (Figure 3.8b - c) there is a tendency to follow this trend as well, with the predictions for the water fluxes fitting with the experimental data. The advantage of glycine is that a higher concentration increases the water flux, but does not affect the solute leakage much.

The experimentally determined *B* values (B_{exp}) of the draw solutes stipulated in Table 3.3 were furthermore compared to optimised *B* values (B_{opt}) from a fit with the FO model (Figure 3.8) using the same *A* and *S* values. The B_{opt} values demonstrated that lower solute permeabilities were necessary to fit *A* and *S* in all cases. The B_{exp} and B_{opt} values for NaCl (4.12x10⁻⁸ m/s and 5.41x10⁻⁸ m/s) were similar to values found in other investigations [90, 99, 101]. The B_{opt} values for glycine and GB differ largely from B_{exp} found in Table 3.3. These determined B_{exp} values are an issue for the organic solutes, which caused the model to overestimate the solute fluxes substantially. On the other hand, the solute flux predictions in the model work well for all the solutes when using the B_{opt} values. The cause for this deviation is unclear.

Further investigations still need to be done in order to better understand the transport of organic solutes through the FO membrane.

Table 3.3: The van't Hoff factor (β) used to define the solute permeability coefficient B of the draw solutions: B values experimentally determined (B_{exp}) and optimised (B_{opt}).

Compounds	β	$B_{\rm exp}$ (x10 ⁻⁸ m/s)	$B_{\rm opt}$ (x10 ⁻⁸ m/s)
NaCl	2	4.1	5.4
Glycine	1	5.8	1.0
GB	1	24.3	1.5

Reclaiming Water from Wastewater using Forward Osmosis

3.3.4 Degradation tests

Table 3.4 shows the BPP results of the tested substrates GB easilv degraded bv was microorganisms (degradation began after approximately two days) and resulted in an increase in ATP-levels. These ATP-levels were highest when river water was added as inoculum (7.27 µg/L). However, even without the addition of river water the ATP-level increased (to 2.6 µg/L). GB was found to be an effective osmoprotectant for increasing methane productivity [196].

Table 3.4 shows the maximum ATP levels of the substrates with the river water inoculum. Proline and glutamine experienced similar ATP levels (7.41 μ g/L and 7.06 μ g/L, respectively) to GB, whereas glycine displayed the highest overall ATP levels (13.67 μ g/L). Some substrates can result in fast growth, after which the active biomass can be reduced relatively swiftly as well. Under such conditions, a fast increase and decrease in ATP can be seen. Glycine is such a substrate, and thus differs from the other tested substrates, where growth is slower and the maximum biomass remains longer at a certain level. High ATP-values show that this

solute might cause problems in the draw solution loop, with regards to membrane (bio)fouling and loss of draw solute (via degradation or leakage). Preventing degradation in the loop, can although be combatted with biostats. This is, however, outside the scope of this work. Rapid degradation, on the other hand, may be an asset in the anaerobic digester, when leakage from the draw solution to feed side occurs. Also, depending on the type of feed used and concentration on the draw side, the degradation rates may differ. This analysis shows the relative potential of the investigated solutes in a digester and also regards the degradation of the draw solution itself. This could influence the stability of the osmotic pressure in the FO unit, but is also necessary when selecting storage methods for the solutions.

Table 3.4: Maximum ATP levels (μ g/L) of tested solutions after the addition of river water inoculum.

Compound	BPP (ATP) [µg/L]
DI water (without addition)	0
GB	7.27
Glycine	13.67
L-glutamine	7.06
L-proline	7.41

3.3.5 Replenishment costs

The replenishment costs of the draw solution needs to be considered when discussing various draw solutions. The draw solution replenishment cost (\in/L), is the product of the J_s/J_v ratio and the draw solution cost, i.e. purchase price in \in/kg as specified by the distributor. The purchase price considers analytical grade solutes only; however bulk purchases will significantly lower this value for all the compounds. Table 3.5 gives an indication of the draw solution replenishment costs for each of the tested compounds. The NaCl cost $(1.0x10^{-2} \notin/L)$ is consistent with that of previous research [114] and attains the lowest values overall. The zwitterions do have a higher purchase price than the common solute, resulting in higher costs, but these appear to be compensated by the lower reverse solute leakage achieved (< $3.1x10^{-2} \notin/L$). GB shows the highest

DS replenishment cost at 5.6×10^{-2} €/L due to its relatively high J_s/J_v ratio. This cost indicates that a good balance between purchase price and solute

leakage is essential when considering draw solution performance.

Draw Solution	J_{s}/J_{v} ratio (g/L)	Purchase Price (€/kg)*	DS replenishment cost (x10 ⁻² €/L)
NaCl	0.67	15.4	1.0
GB	0.43	130.0	5.6
Glycine	0.29	65.6	1.9
L-proline	0.22	115.5	2.5
L-valine	0.11	260.0	3.0
L-glutamine	0.11	270.0	3.1

Table 3.5: The replenishment cost for each tested draw solution.

*all prices taken from distributors specified under section 3.2.3

3.3.6 Reconcentration and Energy Balances

Replenishment of the draw solution is necessary due to solute leakage. Draw solution replenishment can be decreased when a reconcentration unit is present, and simultaneously facilitates harvesting of the high quality product water. This reconcentration step essentially determines the energy consumption of the FO-reconcentration system [220]. Therefore low energy usage of the reconcentration unit is pivotal for the viability of the draw solutes. Existing reconcentration technologies include thermal separation i.e. evaporation, membrane distillation; and mechanical separation, e.g. RO, nanofiltration (NF) or ultrafiltration (UF). In RO, the most popular membrane process for saline water treatment, the minimum thermodynamic energy required to achieve 50% recovery of fresh water from a 35 g/L total dissolved solids (TDS) solution (approximate to a 0.5 M NaCl draw solution, i.e. 23 bar), including all energy demands, is 3 - 5 kWh/m³ [183, 184, 221, 222].

According to the replenishment costs in section 3.3.5, the zwitterions, on average, cost three-fold more than NaCl per litre. In this case NaCl is more economical. However to maintain a constant draw solution concentration for NaCl in the FO unit, a larger dosing system and a higher recovery is required from the reconcentration system than for

the zwitterions, due to the larger salt leakage. Large molecules like sucrose (342 g/mol) have displayed similar flux behaviours to the zwitterions in FO, showing lower reverse fluxes than NaCl, yet with comparable water fluxes [223]. Promising results were achieved for the recovery of sucrose during wastewater reclamation via an FO-NF system [39]. NF is characterised as having a molecular weight cut-off (MWCO) range from about 100 - 1000 Da. The zwitterions, with the exception of glycine, fall within this MWCO range. Therefore, the less energy-intensive NF process, < 1.7 kWh/m³ estimated for seawater [224], can potentially be used instead of RO to reconcentrate the draw solution. By using less pumping energy and requiring less of the draw solute for regeneration, the energy costs for the process will decrease. Additional research is required to reconcentrate the zwitterions with NF.

Furthermore with the incorporation of an anaerobic digester [26], NaCl may have no impact on the microbial community and methane production at the low concentrations determined in this study (50 - 70 mg/L), but at higher concentrations, adverse effects can arise [225, 226]. Zwitterions on the other hand, are easily

biodegradable substances known to increase methane productivity [196]. Yielding more biogas for use in the selected reconcentration system could potentially lower the overall energy costs. For example, wastewater generally contains 400 - 600 g/m³ COD [227]. Assuming that 80% of the COD can be theoretically converted to energy and 1 kg of oxidised COD generates 3.86 kWh [168], thermodynamically this means that 1.24 - 1.85 kWh/m³ organic energy can be retrieved per m³ of wastewater.

The leakage of the studied zwitterions can increase the methane yield, especially in the case of GB, where the solute leakage on average was found to reach 109 ± 9 g COD/m³ (from the 1 M GB draw solution) in this study. This can potentially increase the amount of energy produced by the anaerobic digester from 19 - 26%. This is approximately half of what is required by the RO unit. However, of the total energy only 40% can be converted into electrical energy, which makes up almost a third of the energy consumption of the RO unit. The rest of the energy, as thermal energy, can be used to heat the digester or the FO feed. Other (positive) effects of the organics on the methane production are

beyond the scope of this study. For this reason further research into the influence of zwitterions on an FO-AD system are required.

3.4 Conclusions

In this study, zwitterions were considered as alternative draw solutions for use in FO wastewater reclamation applications. The main findings include:

- The highly soluble zwitterions glycine, L-proline and GB produced similar water fluxes to NaCl in the FO unit (4.3 – 4.9 L/m²h), but were found to be more advantageous due to the lower solute leakage.
- Of the physico-chemical properties investigated, the pH-dependent charge effects and size were found to be dominant parameters affecting the flux performance; J_s/J_v ratios decreased with a decrease in hydrophobicity and an increase in size. Osmotic pressure results also showed glycine to affect DICP most severely.
- Solute transport in the membrane support layer and the contributions of diffusion and convection

were evaluated in an FO mass transfer model. The model verified the experimental investigations.

- Biodegradation of the zwitterions were confirmed with the BPP analyses. High ATP levels were achieved for all the draw solutes (7 14 µg/L), showing relatively fast degradation. This would be even higher when using more densely, microbially-populated feed solutions, i.e. wastewater.
- The DS replenishment cost of the zwitterions was found to be three-fold higher than NaCl. However the potential use of NF in the reconcentration step and the conversion of the zwitterion leakage to energy is advantageous.

Solute leakage in an FO process for water reclamation need not be a limitation if the solute enhances energy production at the anaerobic digestion stage. Reverse solute leakage in sewer mining applications remains an important issue and zwitterionic draw solutions may therefore be advantageous to the system as a whole.

CHAPTER

EDTA: A synthetic draw solution for forward osmosis



This chapter is adapted from:

Lutchmiah K., K. Roest, J.W. Post, L.C. Rietveld and E.R. Cornelissen (2013): Draw Solutions for Forward Osmosis. IWA Water Reuse, Windhoek, Namibia.

4.1 Introduction

Membrane processes have many advantages compared to conventional treatment processes, which include lowering costs and energy consumption, and/or attaining higher qualities of the required product. Forward osmosis (FO) is a relatively new process within the field of membrane technology and is seen as an energy-efficient process. Unlike most membrane processes, FO is not hydraulically driven. It is osmotically driven and therefore depends on the strength of the driving force, i.e. the draw solution.

A draw solution can, in fact, be produced from any solute creating an osmotic pressure higher than the feed solution, yet finding the ideal draw solution for each application is challenging due to the characteristics required: (i) high osmotic pressures; (ii) easy recovery; (iii) membrane compatibility; (iv) zero toxicity and (v) low reverse solute loss [122, 132]. The issue of solute loss is a general problem for most applications and regards the loss of draw solutes through the membrane towards the feed. This is a substantial limitation, both financial and/or operational and also influences the efficiency of the FO process [99]. Many diverse draw solutes have been investigated over the years in an attempt to overcome this limitation. This includes various organic and inorganic-based substances [114, 122, 132]. Organic compounds tend to have larger molecular structures than inorganic salts for example, and therefore leak less through the membrane, but biological degradation of these substances is an issue, adding additional replenishment costs to long-term studies [119].

Ethylenediaminetetraacetic Acid (EDTA) is an anthropogenic polyamino carboxylic acid and chelating agent, which is widely used to dissolve limescale, due to its formation of soluble complexes with cations in solution [228, 229]. EDTA has a molecular weight of 292.24 g/mol and is therefore not expected to leak much through the FO membrane when compared to lower molecular weight compounds. Furthermore, EDTA is not readily biodegradable [230]. For this reason it could be suitable for long-term studies without requiring continuous replenishment.

To the best of the authors' knowledge, EDTA as a draw solution, has only been presented once before

in an FO set-up, however a reverse osmosis membrane was employed [124]. This paper aims to investigate the performance of the synthetic amino acid, Ethylenediaminetetraacetic Acid, as a possible draw solution in forward osmosis applications, using an FO membrane and based on molecular and colligative properties.

4.2 Materials & Methods

4.2.1 Feed and Draw solutions

Deionised (DI) water (Milli-Q, Millipore) was used as the feed solution and solvent in all cases. The following solutes were tested as draw solutions in the FO U-tube system: (1) NaCl (J.T. Baker, the Netherlands): 0.53 mol/kg; (2) EDTA, buffered to pH=10 with NaOH (Sigma Aldrich, Germany): 0.76 mol/kg; 3) Glucose (Sigma Aldrich, Germany): 1.54 mol/kg. The osmolality of the solutions were determined by cryoscopic osmometry (Gonotec Osmomat 030) with each solution achieving values of approximately 1 ± 0.2 osmol/kg. These values were converted to osmotic pressure via the factor 24.5*density of the solute*1.013 bar [206] to achieve osmotic pressures (π) between 23 - 33 bar (Figure 4.1). Solute leakages of all compounds were considered in time. The characteristics of the above-mentioned compounds can be found in Table 4.1.

4.2.2 Membrane Material

A cellulose triacetate (CTA) FO-type membrane was used ('Expedition' type or 'HydroWell', Hydration Technology Innovations, Albany, OR). The FO membrane is highly hydrophilic and has a thickness $< 50 \ \mu m$ [104]. It is comprised of an active, dense selective layer and a porous support layer consisting of an embedded polyester mesh which provides the mechanical support. The asymmetric membrane was used in only one of the two possible orientations, namely the active layer facing the feed side.

4.2.3 Experimental Set-up

FO experiments were carried out in a lab-scale Utube set-up similar to that mentioned in previous work [26, 41]. The membrane (active area: 124 cm^2) was placed in a membrane holder. A constant

Compound	Molecular formula	Molecular weight (g/mol)	Solubility* (g/L) at 20°C	Chemical structure
Sodium Chloride	NaCl	58.44	359	Na ⁺ Cl ⁻
EDTA	$C_{10}H_{16}N_2O_8$	292.24	146	
NaOH	NaOH	39.99	1100	Na ⁺ OH ⁻
Glucose	$C_6H_{12}O_6$	180.15	1330	он но" Он он

Table 4.1: Characteristics of the compounds used as draw solutions.

*Values taken from [200, 231]

mixing rate of 375 L/h was applied to both the feed and draw side to maintain homogeneity by using magnetically-driven centrifugal pumps (Verder, V-MD15). The pump outlet was placed perpendicular to the membrane surface to diminish external concentration polarisation (ECP). The water flux (J_v in L/m²h) was determined by the volume increase on the draw side via a measuring tube. Dilution of the draw solution in time, due to solute migration towards the feed side, was also taken into account. The reverse solute flux (J_s in g/m²h) towards the feed side was determined by means of total organic carbon (TOC), conductivity and chemical oxygen demand (COD) via kits: LCl 500: 0-150±0.8 mg/L O₂ and LCK 514: 100-2000±3.5 mg/L O₂ (HACH LANGE, Germany). All experiments were performed for 7 h.

4.2.4 TOC analysis

The TOC analysis was done by sparging, i.e. Non-Purgeable Organic Carbon (NPOC) using the Total Organic Carbon analyzer TOC-V_{CPH} (Shimadzu). Sample preservation, by means of acid addition (2 M HCl), was carried out to maintain sample integrity by reducing the rate of microbiological growth, which may cause contamination or degradation of the organics. Furthermore, the decrease in pH retards the potential biological growth.

4.2.5 Membrane surface characterisation

The zeta potential of a virgin HTI FO membrane sample was determined in duplicate (10 mm x 20 mm) in a SurPASS Electrokinetic Analyzer (Anton Paar, Graz, Austria) with Adjustable Gap Cell as measuring cell. The membrane pieces were mounted opposite each other in a measuring cell at a distance of 100 μ m. The background electrolyte solution was 0.001 mmol/L KCl solution. pH adjustment was performed within the range 3.5 - 8.5 with 0.05 M HCl and 0.05 NaOH.

4.2.6 The solute permeability coefficient (*B*)

The *B* values of NaCl and EDTA (pH 10) were experimentally determined in a cross-flow RO setup as described by Tang et al. [79]. These values were furthermore compared to optimised values for *B* from a modelled fit using a water permeability coefficient (*A*) value of 1.28×10^{-12} m/s.Pa, which was determined via the same method and was found to be consistent with previous work [101], and a membrane structure parameter (*S*) value of 532 µm.

4.3 Results & Discussion

4.3.1 Reference Experiments

A 0.52 mol/kg NaCl solution was used to characterise each new membrane coupon before and after an experimental series. The water flux (J_v) and the solute leakage (J_s) were determined from these experiments (Figure 4.1). An average of 4.86 ± 0.33 L/m²h (n=10) was found for the water flux and 3.26 ± 0.50 g/m²h for the salt flux. The J_s/J_v ratio (0.67±0.08 g/L) was used as the reference. These results are consistent with previous research [41].



Figure 4.1: The efficiency (water flux, solute flux and J_s/J_v ratios) of NaCl, EDTA and glucose as FO draw solutions at π =23, 29 and 33 bar respectively.

4.3.2 Flux performance

Figure 4.1 shows the flux comparisons between NaCl (π = 23 bar), EDTA (π = 29 bar) and glucose (π = 33 bar). Here EDTA shows the highest water fluxes (5.29 L/m²h) and lowest solute leakage (0.54 g/m²h). It is probable that the higher initial osmotic pressure of EDTA (than NaCl) is the cause for the higher water flux, however glucose, which, at this concentration produces the highest osmotic pressure

of all the compounds studied, ranks the lowest (3.46 L/m^2h). With regards to the respective J_s/J_v ratios (Figure 4.1b), EDTA (0.10 g/L) was also found to be lower than the other compounds, with glucose showing a J_s/J_v ratio of 2.13 g/L. Solute leakage of EDTA was further investigated (Figure 4.2) at various concentrations and compared to NaCl.

From Figure 4.2 it can be seen that the fluxes for both compounds increase with an increase in π ,



Figure 4.2: The influence of NaCl and EDTA fluxes at increased osmotic pressures (π =6–110 bar).

but the solute leakage of EDTA changes only slightly (0.27 – 0.54 g/m²h). The NaCl leakage [26] is approximately 10-fold higher (2.54 – 5.67 g/m²h). The increasing water flux with a consistently low $J_{s'}/J_{v}$ ratio of 0.10±0.01g/L (Figure 4.3) makes the use of EDTA as a draw solution advantageous. Figure 4.3 also shows the trend in the $J_{s'}/J_{v}$ ratio for NaCl with an increase in π . In this case the NaCl ratio decreases slightly from 6 - 46 bar and then increases again slightly thereafter, however the values remain between 0.50 – 0.59 g/L. Higher concentrations should be tested with EDTA too, but the low solubility of the amino acid tends to be an issue.



Figure 4.3: J_s/J_v ratios for NaCl and EDTA at varied osmotic pressures (bar).

According to Equation 4.1, J_s is derived from the *B* value and the concentration difference of the solute (Δc) . This indicates that an increase in J_s will occur due to the increase in Δc . This also explains the behaviour of the solute leakage observed in Figure 4.2.

$$J_s = B.\Delta c \tag{4.1}$$

 J_s is also influenced by the *B* value (Equation 4.1). *B* represents the solute transport through the membrane; a low *B* value results in a lower solute flux.

The determined and optimised *B* values (i.e. values fitting with the respective *A* and *S* values mentioned previously) for NaCl and EDTA can be found in Table 4.2. The values for NaCl are similar to those found in literature [99, 101]. According to both the determined and optimised values, EDTA shows a lower *B* value than NaCl and can therefore explain the lower solute leakage in general. However the optimised *B* value for EDTA shows a much lower value (1.88×10^{-9} m/s) than that determined (3.92×10^{-8} m/s). This difference could be a cause of the set-up itself or due to the interaction with the membrane at higher pressures. Such a vast difference was although not observed for NaCl,

which leads to the conclusion that the variation is more related to the solute than with the operational parameters.

The *B* value is also influenced by the diffusion coefficient (D) of the solute via Equation 4.2 derived from Fick's Law of diffusion:

$$B = \frac{D \cdot \phi}{\Delta t} \tag{4.2}$$

Where ϕ denotes the partition coefficient (amount of substance per unit volume) and Δt the membrane thickness. From Equation 4.2 it can be observed that *B* increases proportionally with an increase in *D*, however the increase in *D* is dependent on ϕ due to the change in concentration. The *B* and *D* values can be found in Table 4.2.

D is furthermore affected by the viscosity of the solution (η) as defined by Wilke and Chang [232] in the framework of the Stokes–Einstein equation:

$$D = 7.4 * 10^{-8} \frac{(xMW)^{1/2T}}{\eta V^{0.6}}$$
(4.3)

Where:

x =association parameter, which defines the effective molecular weight of the solvent with respect to the diffusion process (for water x = 2.6) MW = molecular weight of the solute T = temperature (K) V = molal volume of solute at normal boiling point

Viscosity generally decreases as the concentration of metal-binding ligands increases (i.e. Na₃EDTA is formed after buffering) and according to Equation 4.3 is inversely proportional to D. This decrease in viscosity could also be the reason for the increase in D and therefore the rise in J_s at increasing concentrations (Equation 4.1).

4.3.3 Influence of Molecular and Membrane **Properties**

4.3.3.1 Molecular Weight

Whilst Figure 4.4 lacks in indicating a specific trend between the water flux and the molecular weight, it does show a decrease in solute leakage with the molecular weight increase. This illustrates that the size of the molecule plays a significant role in the leakage of the solute through the membrane. However Equation 4.3 shows that D is inversely proportional to MW. In this case the D value is also influenced by ϕ and η as mentioned previously and could have therefore led to the linear relationship between J_s and MW. Thus the larger the molecular weight, the more slowly it diffuses through the membrane, i.e. lowering the solute loss, as is the case with ETDA.

Table 4.2: The	Table 4.2: The solute permeability coefficient (B) and diffusion coefficient (D) of the draw solutes.				
Compounds	<u><i>B</i> determined (</u> x10 ⁻⁸ m/s)	<u><i>B</i> optimised fit (x10⁻⁹ m/s)</u>	\underline{D} (x10 ⁻⁹ m ² .s ⁻¹)		
NaCl	4.12	54.1	1.23 [120]		
EDTA(pH 10)	3.92	1.88	0.60 [233]		
Glucose	-	-	0.52 [234]		



Figure 4.4: The effect of molecular weight on the water flux and solute leakage.

4.3.3.2 Membrane Surface Characteristics

Zeta potential was used to quantify the magnitude of the electrical charge at the surface of a virgin FO CTA membrane. In Figure 4.5 it can be seen that the zeta potential was found to be negative over a wide pH range (between pH 3 - 9) for all membrane pieces, on both the active (AL1 and AL2) and support layers (SL). The isoelectric point, i.e. the pH value where the zeta potential = 0 mV, lies at pH 4.1 and drops with an increase in pH. When in contact with EDTA (buffered to pH 10) the membrane charge becomes negative, and EDTA, which is already a negatively charged compound, is repulsed according to Coulomb's Law [235]. The negatively charged EDTA molecule should therefore be repulsed by the active layer of the membrane, theoretically lowering the solute flux in comparison to the uncharged solutes, i.e. NaCl and glucose. This behaviour has been confirmed by the abovementioned experiments.



Figure 4.5: Measured zeta potential for the active and support layers of virgin FO CTA membranes.

4.4 Conclusions

In this study, EDTA was tested as a draw solution for use in FO applications. Various factors affecting the water and solute flux performance in FO systems were evaluated. Based on experimental investigations, the main findings of this study are summarised:

- EDTA showed comparable water fluxes to NaCl, but higher fluxes than glucose: 5.29 L/m²h, 4.86 L/m²h and 3.46 L/m²h respectively.
- Increasing concentrations of EDTA showed consistently low J_s/J_v ratios of 0.10 g/L, demonstrating that the size and ultimately the diffusion coefficient (D) of a molecule is important in reducing solute flux.

• Zeta potential measurements confirmed the negative charge of the FO membrane. This allows the negative EDTA molecule to be repulsed by the active layer and may explain the reason for the low solute fluxes.

EDTA is not readily biodegradable, which is advantageous in applications where the draw solution is required for long periods without much replenishment. The FO product water together with EDTA could be beneficial when applied directly to processes requiring the removal of heavy metals, i.e. during the cleaning of membrane installations.

CHAPTER

Water Recovery and FO Membrane Fouling

This chapter is adapted from:

Lutchmiah K., E.R. Cornelissen, D.J.H. Harmsen, J.W. Post, K. Lampi, H. Ramaekers, L.C. Rietveld, K. Roest, Water recovery from sewage using forward osmosis, Water Science & Technology, 64 (2011) 1443-1449.

5.1 Introduction

Membrane fouling concerns a process whereby solutes and/or particles accumulate on a membrane surface and/or within membrane pores. The various fouling types can lead to either reversible or irreversible fouling. FO membranes are generally at a lower risk of irreversible membrane fouling, compared to pressure-driven membrane processes [17, 24, 25]. This may explain why little has been published on irreversible fouling, even though several FO fouling studies have been performed.

Various feed solutions have already been tested with the FO membranes, such as activated sludge [41], where membrane fouling and FO performance were studied. Fouling, neither reversible nor irreversible, was found. Landfill leachate, a highly variable feed solution, was treated as an alternative to irrigation [14]. During these experiments flux decline only became apparent after the second series of leachate was processed and cleaning occurred only once after the pilot trial. FO was also used in the treatment of simulated wastewater streams for reclamation purposes in space applications [37]. It was stated that flux decline due to the semipermeable membrane was inevitable, but fouling was not stipulated. Furthermore, nutrient-rich liquid streams were concentrated for use as fertilisers [40]. Here the fouling rate for FO was evaluated. The flux decline between cycles was said to be caused by membrane fouling, but these deposits were easily removable. Model organic foulants were also used in the form of alginate [236], representing the polysaccharide fraction of soluble microbial products in wastewater effluent. The results showed alginate fouling in FO, but this was almost fully reversible.

The aim of this chapter is to investigate the influence of primary effluent on the FO performance, but also to evaluate the severity of fouling on the FO membrane by modifying the driving force via i) the draw solution (increasing the osmotic power) and ii) operational conditions (adding hydraulic pressure) to induce membrane fouling. The advantage of such an application is that it can be integrated into the Sewer Mining concept as described in Chapter 1.

5.2 Materials & Methods

5.2.1 Membrane Material

An asymmetric, cellulose triacetate (CTA), FO-type membrane was used ('Expedition' type or 'HydroWell', Hydration Technology Innovations, Albany, OR). The FO membrane is highly hydrophilic and has a thickness of less than 50 µm [104]. It is comprised of an active, dense selective layer and a porous support layer consisting of an embedded polyester mesh which provides the mechanical support. The membrane was used primarily in the orientation: active layer facing feed side (AL to FS), unless otherwise stated. This is due to the fact that spiral wound FO membranes are currently only manufactured in this orientation, to keep fouling at a minimum. The orientations have a significant impact on performance due to the asymmetry of the membrane. Internal concentration polarisation therefore plays a big role in FO [89].

5.2.2 Experimental Set-up

FO experiments were carried out in a lab-scale U-tube set-up similar to that mentioned in previous work [41], together with a pressure regulator to adjust pressures and a control box containing the PLC (more information regarding the set-up can be found in Chapter 7). The membrane (active area: 124 cm²) was placed in a membrane holder and additionally supported in the U-tube by iron meshes on either side to prevent movement and mechanical damage. The mesh placed on the draw side was Teflon-coated to prevent oxidation in high salt concentrations. A constant mixing rate of 375 L/h was applied to both feed and draw side to keep the solutions homogenous with the use of pumps. The water flux (J_{ν}) was determined by the volume increase within the measuring tube on the draw side. Dilution of the draw solution over time due to salt migration towards the feed side was also taken into account. The salt flux (J_s) moving towards the feed side was determined either by means of a conductivity meter (Feed: DI water) or by Inductively Coupled Plasma Atomic Emission Spectroscopy "ICP-AES" (Feed: Primary Effluent),

since a mixture of salts is already present in primary effluent. All experiments were carried out for 6 - 7 h and the temperature, unless otherwise stated, was normalised to 20 °C.

5.2.3 Feed and Draw solutions

Either deionised (DI) water (Milli-Q, Millipore) or primary effluent (screened, not treated) were used as the feed solution. The primary effluent was sampled from the municipal wastewater treatment plant Amsterdam West (Waternet, The Netherlands) and was composed of 424 mg/L COD, 1101 mg/L NaCl and 1300 mg/L of total suspended solids (TSS) and contained an osmotic pressure of 0.26 bar (calculated by DuPont method). The effect of different draw solutions was tested in the system using analytical grade NaCl (J.T. Baker, the Netherlands) and MgCl₂.6H₂O (Merck, Germany). All solutions were prepared in DI water. For all experiments, unless otherwise stated, concentrations relating to an osmotic pressure of approximately 24 bar were used.

5.2.4 Fouling Tests

It has been said that FO fouling is governed by the coupled influence of chemical and hydrodynamic interactions [79]. The coupling effects of fouling and concentration polarisation have also been studied. Fouling of the FO membrane surface was forced by (i) increasing concentrations of the draw solution (0.5 - 4.5 M NaCl) in order to increase the osmotic power of the solution and so extract the water more rapidly through the membrane and (ii) applying low amounts of hydraulic pressure (0.2 - 0.8 bar) to the feed side of the U-tube to again increase the water flux through the membrane and induce fouling. Primary effluent and DI water were used as the feed solutions. 0.33 M MgCl₂.6H₂O was used as the draw solution in pressure experiments.

5.2.5 Microscopic Membrane Characterisation

A JEOL Company Ltd scanning electron microscope (SEM) model JSM 6040LV was used to characterise the fouled FO membrane after usage in pressure experiments with primary effluent as feed and 0.33 M MgCl₂.6H₂O draw solution (orientation: AL-DS).

Membrane samples were coated with a thin layer of gold (no freeze drying). All samples were scanned at an accelerating voltage of 6 kV. For the X-Ray microanalysis (EDX) System a Noran System SIX (Thermo Electron Corporation) was used and samples were scanned at an accelerating voltage of 10 kV to measure the atomic composition of the membrane.

5.3 Results & Discussion

5.3.1 Influence of feed type

In Figure 5.1, average water flux values obtained with (i) DI water and (ii) primary effluent as feed can be seen. The measured water flux with primary effluent (average values = $4.3 \text{ L/m}^2\text{h}$) was approximately 20% lower than the water flux with DI water as feed (5.2 L/m²h). In both cases a 0.5 M NaCl draw solution was used. It must be noted that the initial osmotic pressure (π) difference between

the 0.5 M NaCl solution and the DI water is slightly greater (1%) than that between the 0.5 M NaCl and t=0 sample of primary effluent, as the effluent already includes various salts which increase the osmotic pressure. Holloway et al. [40] also found the water flux to decline with an increase in the total dissolved solids (TDS) concentrations. The osmotic pressure on the feed side, for both DI and effluent, increased over time due to the migration of salts from the draw side. A stable water flux was obtained with the primary effluent. Other than the slight difference in osmotic pressures of the feed, increased internal concentration polarisation (ICP) as well as fouling of the membrane could be a possible reason for the difference in flux performance. Concentration polarisation (CP) is a phenomenon which deals with the accumulation of excess particles in a thin layer adjacent to the membrane surface and can be divided into external and internal concentration polarisation. ICP significantly impacts flux performance. Further fouling tests were carried out.



Figure 5.1: Water flux over time with feed solutions (i) DI water and (ii) primary effluent (Draw solution: 0.5 M NaCl; T = 20 °C; membrane orientation: AL-FS).

5.3.2 Fouling Tests

Figure 5.2 and 5.3 represent the results for the increasing concentration and pressure experiments together with their comparisons to DI water.

(i) Increasing draw solution concentrations

From Figure 5.2 it can be observed that the water flux increased as a result of an increase in concentration of the draw solution, regardless of the feed solution. This relates to an increase in osmotic power on the draw side, but this relationship is nonlinear. It has been previously demonstrated that around 20% of the osmotic pressure driving force for NaCl is utilised at lower concentrations (< 3 M), while at higher draw solution concentrations (> 3 M) as little as 5% or less of the osmotic pressure can be realised for experiments [104]. Modelling results [88] also showed the osmotic pressure to be nonlinear with the NaCl concentration. It has been well established [89] that this reduction results from the dilutive internal concentration polarisation (DICP), which is relatively higher at increasing water fluxes.



Figure 5.2: Water flux with feed solutions (i) DI water and (ii) primary effluent – accumulated fouling from low to high NaCl concentrations, (iii) primary effluent – fouling per fresh membrane, 0.5 - 4.5 M NaCl as draw solution (T = 20 °C; membrane orientation: AL-FS).

Besides the non-linearity of the water flux, it is clear that the primary effluent produces stable fluxes, although lower than DI water, especially at higher concentrations. This could also be due to the ICP being stronger when using feeds of higher salinity or due to fouling. Indeed cake-enhanced concentration polarisation is also something to be considered. This describes the hindrance of the back diffusion of accumulated salts near the membrane by a colloidal fouling layer, subsequently reducing salt rejection [237]. This test series was carried out with one membrane coupon and could therefore have led to "accumulated fouling" on the membrane, influencing the flux performance. A repetition was performed with a fresh membrane coupon at 4.5 M NaCl to check this hypothesis. This experiment was preceded and followed by a DI experiment. As expected, a higher water flux was obtained for the primary effluent with a fresh membrane (12.5 $L/m^{2}h$, compared to the previous experiment 11.4 $L/m^{2}h$) and can be found above the trendline in Figure 5.2. A difference in water flux is still evident between the DI and primary effluent as feed. It is not certain whether this is purely due to ICP or a combination of ICP and fouling. The issue of accumulated fouling can be validated. A muddy, loose cake layer was visually observed on the feed side of the membrane after the series of experiments, but it could be easily washed off. Subsequent DI water experiments with the same membrane showed that fluxes and ratios remained constant, ruling out irreversible fouling.

The salt flux to water flux ratio (J_s/J_v) gives an indication of the amount of salt moving through the

membrane per litre of permeate produced. Figure 5.3 shows these ratios.

For the DI water experiments, ratios increased linearly from 1 – 4.5 M NaCl (0.5 – 0.65 g/L) with the increase in NaCl concentration. This shows that the use of salt concentrations from 1 – 3 M NaCl, also for primary effluent, brings about a better J_s/J_v ratio, i.e. higher water fluxes, and less salt leakage. Experiments with primary effluent also showed increasing J_s/J_v ratios, but ratios from 3 M NaCl onwards were higher than when DI water was used.



Figure 5.3: J_s/J_v ratios of (i) DI water and (ii) primary effluent – accumulated fouling from low to high NaCl concentrations, (iii) primary effluent – fouling per membrane (Draw solution: 0.5 - 4.5 M NaCl, T = 20 °C; membrane orientation: AL-FS).

Water Recovery and FO Membrane Fouling

Due to the fact that J_v for the primary effluent remained lower than DI water throughout the series and that the salt fluxes for the primary effluent remained only slightly lower, it is not surprising that the ratios above 3 M were different. Again accumulated fouling can be suggested. Experiments with a fresh membrane and primary effluent as feed showed J_s/J_v ratios almost on par with DI water; 0.69 g/L and (0.65 g/L) respectively, while using 4.5 M NaCl as a draw solution, whereas the series using the same membrane established a much higher ratio (0.83 g/L). Never-the-less, here too the J_s was lower for the primary effluent (during accumulated fouling) than with DI water; 9.37 g/L and 9.82 g/m²h respectively. It seems that the fouling layer hinders salt migration through the membrane, reiterating the presence of possible cake or gel-enhanced CP.

(ii) Additional pressure

Further fouling was evaluated here by applying additional hydraulic pressure (overpressure) to the feed side of the system in order to induce membrane fouling. The results can be seen in Figure 5.4.



Figure 5.4: a) Water flux with feed solutions (i) DI water and (ii) primary effluent, b) J_s/J_v ratio with DI water (Draw solution: 0.33 M MgCl₂ and 0.2 – 0.8 bar additional pressure (T = 20 °C; membrane orientation: AL-FS).
Figure 5.4a shows water fluxes increasing nonlinearly with an increase in pressure. The nonlinearity is comparable to the water flux with different concentrations of the osmotic draw solution (Figure 5.2). The salt flux increased simultaneously. The J_s/J_v ratios for DI water can be seen in Figure 5.4b. The J_s/J_v ratio during DI water experiments, with increasing overpressure, remained linear. Furthermore, the water flux difference between the DI and primary effluent experiments can be explained by both ICP and fouling. The membrane surface, which was fouled, was characterised further.

5.3.3 Microscopic Membrane Characterisation

The morphology and structure of the fouled FO membrane was characterised by SEM analysis and can be seen in Figure 5.5. The analysis confirmed the reinforcement fabric (mesh) inside the cellulose ester polymeric (otherwise known as cellulose triacetate) membrane (Figure 5.5a). This mesh was arranged orthogonally at a spacing of $\approx 100 \ \mu\text{m}$. The membrane is presumably produced in a single

production run where the CTA solution is cast onto the polyester web. The many cracks that can be observed in Figure 5.5a could be due to the drying out of the membrane. This is quite typical for cellulose membranes.

The analysed components of the fouling layer on the CTA membrane were revealed by EDX and showed the active layer to be rather clean, beside C and O peaks (membrane matrix), smaller peaks for Mg and Cl were found because of the draw solution. The support side (dull side) in Figure 5.5b - d was found to have a thin fouling layer that could easily be removed after storage in water. EDX showed peaks for a number of elements on this surface side: Mg and Cl (due to draw solution migration), Ca, Al, Si, Fe and Na (already contained in the feed and confirmed by ICP-AES). Peaks for C and O, were again found, which are due to the presence of the (i) cellulose ester polymer and (ii) polyolefin or polyester reinforcement fabric and perhaps (iii) some organic fouling. Further investigations will need to be carried out in order to confirm the type of fouling that occurred on the membrane.



Figure 5.5: SEM micrographs of the FO membrane surface a) Image of the fabricated mesh within the membrane (magnification x 100, accelerating voltage: 6kV), cracks in the surface, possibly caused by drying out of the membrane; b-d) Images of the fouled, dull layer of the membrane (magnification x 100, x 500 and x 1000; accelerating voltage: 6kV - 10kV).

5

5.4 Conclusions

In this thesis, sewage is not seen as a waste, but as a source for water, energy and nutrients. The effectiveness of the FO membrane in the recovery of water from different feed sources is apparent, but the overall water recovery is hindered by ICP and fouling (as is the case with primary effluent), which is seen here to accumulate during a series of experiments. Stable FO water flux values were never-the-less obtained with primary effluent (screened, not treated), but produced values (> 4.3 L/m^2h) were approximately 20% lower than with DI water as feed (5.2 L/m^2h). Fouling of the FO

membrane was induced by modifying the driving force, either by increasing the osmotic pressure or increasing hydraulic feed pressure. Fluxes for both feed solutions increased non-linearly under these conditions. The fouled membrane was characterised and fouling was found to be reversible after shortterm experiments (6 - 7 h). The fouling layer was found to be thin and loose. As a result, the FO membrane can be easily cleaned by a simple water rinse without the use of chemical cleaning reagents. On full-scale, accumulated fouling could play a greater role in the water flux performance.

CHAPTER

6

Polysaccharide Dominance in FO Fouling Studies of Raw Wastewater

This chapter is based on:

Lutchmiah K., C. Brignoli, A. Zwijnenburg, L.C. Rietveld, E. R. Cornelissen (to be submitted).

6.1 Introduction

Membrane fouling is an intricate issue whereby an accumulation of solutes and/or particles on the membrane surface, within the membrane pores or within the feed spacer channel is concerned. The permeate quality and quantity of the process is subsequently limited by fouling and scaling of the membrane [139]. Fouling in membrane processes is predominantly due to chemical and hydrodynamic interactions [50], however the mechanism of fouling and flux decline for forward osmosis (FO) processes is reported to be more complicated than for pressure-driven membrane processes, due to the coupled effects of internal concentration polarisation (ICP) and reverse solute leakage [79].

Membrane fouling studies for FO have suggested lower fouling propensities compared to the pressuredriven processes [17, 24, 238], however most studies are based on investigations with synthetic feeds, limited foulant types and/or individual foulant tests with, i.e. humic acids, alginate, bovine serum albumin, silica, latex, dextran and gypsum [50, 78, 79, 153, 154, 238, 239]. Studies combining foulants showed a more prominent flux decline than for individual foulant tests [154, 240], elaborating the importance of using real feed waters, as the interactions between foulants vary and may differ in the extent of membrane fouling. To date, only a few investigations have actually conducted fouling studies using real feed waters [26, 40, 41, 109, 152, 162, 241, 242].

Natural organic matter (NOM), present in raw wastewater, has been found to be a serious fouling agent in many membrane processes including FO [152, 238, 243-245]. NOM can be further divided into various groups: biopolymers, i.e. polysaccharides, proteins, amino sugars and transparent exo-polymer particles (TEP), humic substances, i.e. humic and fulvic acids, building blocks, i.e. hydrolysates of humics, low molecular weight (LMW) neutrals, i.e. monoligosaccharides, alcohols, aldehydes, ketones and amino sugars, and LMW acids, i.e. monoprotic acids. In one study, dosing of high molecular weight (HMW) proteins into an activated sludge feed showed good rejections by the FO membrane, while rejection of LMW compounds was poor [242], suggesting permeation to the draw side. Valladares Linares et al. [152], using secondary effluent, found the membrane to be fouled with biopolymers and protein-like substances, adversely affecting the water flux. Another study observed a higher deposition of humic acids on the FO membrane surface when calcium ions were present in the feed [246].

These NOM fractions are expected to be abundant in raw municipal wastewater, which is also a breeding ground for microorganisms and bacterial communities and affects membrane biofouling. Fluorescence microscopy has been previously employed to investigate biofouling on FO membranes showing depositions of soluble microbial products and extracellular biological organic matter, however microbial activity was only found on the active layer of the membrane [152], but this also depends on the type of draw solution used. The biopolymer, TEP, has also been linked to biofouling of membranes [151], however large concentrations of TEP are not found in wastewater effluents [247]. Zhang et al. [149] studied membrane biofouling using synthetic wastewater in an osmosis membrane bioreactor (OMBR). Their findings equate FO fouling to the coupled influences of biofilm formation and inorganic scaling.

Extracellular polymeric substances (EPS), secreted by microorganisms into their environment to establish the functional and structural integrity of biofilm [147, 148], factor in membrane biofouling [149]. EPS constitutes anywhere from 50% to more than 99% of a biofilm's total organic matter [148, 248, 249] and consists of a variety of HMW organic molecules, of which carbohydrates (CH) are the predominant constituent for many pure cultures, followed by proteins, organic acids and DNA [250]. Adenosine triphosphate (ATP) and CH, a measure for active bacterial biomass and biomass concentrations based on EPS, are reported as an analytical tool for fouling analysis of FO membranes in this study.

In this paper a lab-scale study was run with municipal primary effluent using an NaCl draw solution concentration nine times greater than normal seawater in order to induce rapid fouling on the FO membrane. A comprehensive membrane autopsy was performed using direct and indirect membrane techniques to analyse the fouling layer, including elaborations of the microbial activity. This paper aims to deepen the understanding and knowledge of real foulants in FO wastewater processes.

6.2 Materials & Methods

6.2.1 Experimental Set-up

FO experiments were carried out in a transparent, lab-scale, cross-flow set-up (Figure 6.1) for approximately 50 h. The flow channel in the permeation cell is 25x5 cm. The 1 mm height was created by the thickness of a Teflon gasket. The volume flow rate was set to 170 ml/min for both feed and draw solutions, operating in counter-current mode. The temperature remained at approximately 22.1±0.3 °C for the experiments. The 5 L feed volume in a continuously stirred vessel was maintained and fed via Applikon Software (Schiedam, the Netherlands). The feed solution used was either 5 mM NaCl (baseline study) or fresh municipal wastewater (fouling test). The wastewater feed was sampled after the primary settlement tank at the wastewater treatment plant Amsterdam West (operated by Waternet, the Netherlands).



Figure 6.1: The lab-scale cross-flow cell set-up operating in counter-current mode.

The chemical oxygen demand (COD) and total suspended solids (TSS) of the wastewater are logged regularly by Waternet. Values reported from 2010 - 2013 are shown in Figure 6.2.

Both parameters behaved similarly. When correlating these values with the weather data monitored by the Dutch meteorology institute

1000 -COD A TSS 800 Concentration (mg/L) 600 400 200 0 Aug-11 Sep-12 Apr-13 Jan-10 Jul-10 Feb-11 Mar-12

(KNMI, the Netherlands), peaks in COD and TSS, generally represented drier periods, while dips signified periods of higher rainfall. On average, the wastewater was found to have a COD of 382 mg/L O_2 , TSS of 160 mg/L and a COD/TSS ratio of 2.48±0.62.

Elements (mg/L)								
Al	0.39	К	22.87					
В	0.16	Mg	13.64					
Br	0.35	Mn	0.13					
С	783.17	Na	93.73					
Ca	72.17	PO4	18.97					
Cl	167.68	Si	7.11					
Cu	0.02	SO4	51.32					
Fe	0.27	Sr	0.34					

6

Figure 6.2: (left) COD and TSS parameters of the municipal wastewater from 2010 - 2013, (right) the elemental composition of the raw wastewater (average of all samples taken from 2010 - 2013).

The average of other parameters determined from the wastewater include nitrogen = 63 mg/L, phosphorus = 10 mg/L, pH = 7.2, conductivity = 1.4 mS/cm and total organic carbon (TOC) between 60 - 120 mg/L. The elemental composition determined via inductively coupled plasma atomic emission spectroscopy (ICP-AES) is also shown in Figure 6.2. The 4.5 M NaCl draw solution concentration (diluted in time), used in both fouling and baseline experiments, exerts an initial osmotic pressure of 265.8 bar, determined via OLI Analyzer Software (Morris Plains, NJ). High concentrations were used to induce rapid fouling. The solute leakage on the feed side was determined by conductivity, ICP-AES

and TOC measurements (TOC analyser ASI-V, Shimadzu). The water flux was measured by logging the weight of the draw solution using a TR15RS scale (Ohaus Trooper) and read via a HyperTerminal script.

6.2.2 FO Membrane

The membranes employed in this study were cellulose triacetate (CTA), FO membranes (HTI, Albany, OR), with a pore size of 0.3 - 0.5 nm [217]. The effective surface membrane area was 96 cm², with the active layer facing the feed side. One diamond-shaped spacer with a thickness of 0.8 mm, was placed on the draw side of the cell to prevent external concentration polarisation (ECP), which influences the hydrodynamic conditions.

6.2.3 Baseline and Fouling Studies

The performance of the baseline and fouling studies was analysed by comparing the water and solute fluxes. Three fouling experiments were performed under the same operational conditions. After each fouling experiment, the membranes were removed from the set-up and prepared for the membrane autopsy study.

6.2.4 Sample Preparation for Membrane Autopsy From the first fouling run, the entire fouled membrane was cut into pieces of approximately 5x5

cm. Each piece was mechanically-cleaned using a sterile brush and suspended in 40 ml sterile water. In order to increase biomass recovery from the membrane and to solubilise the foulant material, high energy sonication (Digital Sonifier, Branson) was performed on each membrane sample for 5 min; amplitude 45%. The solubilised fouling layer was used for the determination of SUVA, ATP, CH and LC-OCD analyses.

6.2.5 Membrane and Foulant Characterisation

Membrane samples from subsequent fouling runs, together with the virgin and mechanically-cleaned membranes were cut and analysed via direct and indirect methods. An overview of the techniques used can be found in Table 6.1.

Technique	Virgin Membrane	Fouled Membrane/ fouling layer	Mechanically - Cleaned Membrane	Sample size/volume
Zeta-Potential	x	х	-	1x2 cm
SEM/EDX	x	х	x	3x5 cm
AFM/FTIR	x	Х	-	1x1 cm
Contact Angle Measurements	x	x	x	1x1 cm
СН	-	х	-	20 ml
ATP	-	х	-	1 ml
LC-OCD/SUVA	-	х	-	40 ml
TOC	-	х	-	25 ml

Table 6.1: Membrane and foulant characterisation techniques performed on the virgin, fouled and mechanically-cleaned membranes.

6.2.5.1 Zeta-potential

Zeta-potential of membrane samples were determined in duplicate in a 1 mM KCl background solution using a SurPASS Electrokinetic Analyzer with Adjustable Gap Cell (Anton Paar, Graz, Austria). PH adjustment was performed with 0.05 M HCl and 0.05 NaOH.

6.2.5.2 SEM-EDX

Membrane samples were investigated with a JSM 6040LV Scanning Electron Microscope (JEOL

Company Ltd). Samples were coated with a thin layer of gold and scanned at an accelerating voltage of 6 kV. For the X-Ray microanalysis (EDX) System, a Noran System SIX (Thermo Electron Corporation) was used at an accelerating voltage of 10 kV to measure the atomic composition of the membrane. Detection limit of the instrument is 0.1 (atom %).

6.2.5.3. Spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy was obtained using a single reflection attenuated

total reflection (ATR) accessory equipped with a platinum diamond ATR crystal reflection 1 (Bruker Optik GmbH, Ettlingen, Germany) using a spectral resolution of 4 cm⁻¹ and 32 scans.

6.2.5.4. Adhesion force measurements

Membrane samples were dried at 30 °C under vacuum for 14 h (European Membrane Institute, Twente). Adhesion force measurement (AFM) images were obtained under ambient conditions in tapping mode with a NanoScope V Controller atomic force microscope (Veeco/Bruker, Santa Barbara, CA) using silicon cantilevers with resonance frequencies of 200-500 kHz (type PPP-NCH, Nanosensors, Wetzlar, Germany) and a JV Scanner (Bruker Optik GmbH, Ettlingen, Germany).

6.2.5.5 Contact Angle Measurements

The surface tension (γ_i) of liquids, solids and gases is expressed by:

$$\gamma_i = \gamma_i^{LW} + 2\sqrt{\gamma_i^+ \gamma_i^-} \tag{6.1}$$

, where γ_i^{LW} is the apolar (Lifshitzevan der Waals) component and γ_i^+ and γ_i^- are the apolar electron-accepting and electron-donating components of the

surface tension respectively. Contact angle (θ) measurements were employed to quantify the wettability of the membrane samples and to determine the surface energy via the Young-Dupré equation, linking the contact angle of a drop of liquid (L) on a flat solid surface (M) with the surface tension of the liquid (γ_L) according to van Oss [251]:

$$(1 + \cos\theta)\gamma_L = 2\sqrt{\gamma_M^{LW}\gamma_L^{LW}} + \sqrt{\gamma_M^+\gamma_L^-} + \sqrt{\gamma_M^-\gamma_L^+}$$
(6.2)

After solving the above equations, the surface tension components of the membranes were determined by measuring the contact angles between the membrane and three probe liquids of known γ_L^{LW} , γ_L^+ and γ_L^- ; in this case pure water, glycerol and di-iodomethane [252]. θ measurements of the probe liquids were measured on the membranes via Sessile Drop measurements, using an FM40 EasyDrop goniometer (Krüss GmbH, Germany).

6.2.5.6 ATP and CH

ATP and CH were determined to measure active bacterial biomass and the biomass concentrations. The ATP content of the obtained bacterial suspension (section 6.2.4) was quantified according to Magic-Knezev and van der Kooij [208], detection limit of 4 mg ATP/cm². Quantification of CH enables the estimation of the biomass concentration based on EPS, which is composed of polysaccharides. CH was measured using the Dubois method [253].

6.2.5.7 Liquid chromatography and UV

Size exclusion chromatographic separation of NOM (Het Waterlaboratorium, Haarlem, The Netherlands) was performed with a liquid chromatography - organic carbon detector (LC-OCD) system (DOC-LABOR, Germany). In the system, a TSK HW-50S column is connected to a Gräntzel thin-film reactor [254] in which NOM is oxidised to CO_2 by UV before it is measured by infrared detection. The obtained OCD-chromatogram was split into fractions by means of a deconvolution-program.

DOC concentrations, determined using a Shimadzu TOC- V_{CPN} organic carbon analyser, and UV absorbance at 254 nm, determined at ambient pH using a Shimadzu UV-2501PC UV-VIS spectrophotometer were used to calculate the specific UV Absorbance (SUVA).

6.3. Results & Discussion

6.3.1 Performance of Baseline Studies and Fouling Tests

The efficiency of the baseline study was determined to be 13.7±1.4 L/m²h for the water flux (J_v) and 6.5±0.9 g/m²h for the solute leakage (J_s), with a J_s/J_v ratio of 0.5 g/L. Figure 6.2 shows these results compared to the average of the wastewater runs: $J_v =$ 11.1±1.2 L/m²h, $J_s = 6.8\pm0.2$ g/m²h and J_s/J_v ratio = 0.6±0.2 g/L.



Figure 6.3: Membrane flux efficiencies between the baseline and fouling tests.

For the baseline study, J_{ν} began at 20 L/m²h and ended at 12 L/m²h after 50 h (Figure 6.3). Water flux in FO generally experiences a decline over time, due to osmotic dilution of the draw solution. Using wastewater the water flux was, as expected, worse. The flux decline between the baseline and the wastewater experiments became more severe after the first 10 h, where the flux decline increased above 10%. This severity was attributed to an increased fouling layer. A 30% flux decline difference was found at the end of the experiment with an average flux difference of 19%. Similar behaviours were found by Li et al. [159], who established that higher initial permeate fluxes or higher applied pressures, i.e. in pressure-driven membrane processes, led to faster flux declines, and could only be caused by greater deposition rates of the foulants or a more compact fouling layer.

Regarding the salt fluxes, stabilisation of the wastewater experiments occurred after 8 h. Thereafter the salt leakage showed lower values than the baseline with an approximate 12% difference.

Moreover, a fouling distribution was visually observed over the membrane surface whilst in the cross-flow cell (Figure 6.5h). Due to the laminar flow profiles, a higher foulant deposition was observed along the edges of the membrane, while less deposition was seen around the middle area, which is a result of turbulence, according to the boundary layer theory and has been noticed previously [109]. The characteristics of the fouling layer were further analysed by considering the fouling layer in its entirety.

6.3.2 Feed Water and Draw Solution analyses

Table 6.2 summarises the TOC, inorganic colloids and SUVA results that were obtained and used to characterise the feed water (before and after the experiment) and draw solution (before and after). The initial TOC values of the raw wastewater sampled at the start of each fouling experiment were between 81 - 84 mg/L, while the initial concentration of these substances in the draw solution was very low. The TOC values in the draw solution were found to have increased after the experimental run. This suggests leakage of compounds towards to draw side. This has also been observed on bench-scale by Yangali-Quintanilla et al. [241], explaining the increment to be due to LMW neutrals transported from the feed water. This may be later confirmed in our LC-OCD results.

Inorganic colloids were found in the feed, but also within the solubilised fouling layer = 46.3 m^{-1} . The SUVA value (UV_{254nm}/DOC) in the raw feed water of ~2 L/mg.m is an indication of low humic

substances [255]. This value decreased slightly after the experimental run indicating possible removal of specific HMW compounds, due to adsorption onto the membrane surface. This may later be found retained within the fouling layer.

Sample	<u>TOC</u> mg/L	<u>Inorg. Colloids</u> m ⁻¹	<u>SUVA</u> L/(mg.m)
Feed before	81.9	1.8	2.0
Feed after	-	2.2	1.9
Draw solution before	0.1	-	-
Draw solution after	0.4	-	-

Table 6.2: TOC, inorganic colloids and SUVA results of samples collected before and after the fouling studies.

6.3.3 Membrane and Foulant analyses

6.3.3.1. Surface charge

The surface charge of the virgin and fouled membranes was determined. From Figure 6.4, it can be observed that the zeta-potential of the virgin membrane decreased from 0 to -35 mV with the increase in pH (4 - 8), similar to the decrease of the

fouled membrane from 0 to -46 mV (pH 3 - 8.5). During the experimental runs, the membrane was generally exposed to a pH of 6 - 7 where charges of -25 to -30 mV existed for the virgin membrane. This differs from the results of both Boo et al. [157] and Xu et al. [158] who, at this pH range, found values of approximately -5 to -10 mV. However both 6

studies agreed that the presence of a fouling layer increases the negative charge of the CTA membrane.

This was confirmed in our streaming current measurements, which indicated that the surface charge of the fouled membrane around this pH is significantly lower (-37 to -40 mV). At -37 mV these values represent humic substances and/or colloidal matter, while at -45 mV the hydrophilic of effluent organic fraction matter, i.e. polysaccharides is located, according to zetapotential measurements of model foulants: humic acid, silica and sodium alginate [157, 256]. Valladares Linares et al. [162] also attributed the negativity of the fouled membrane to polysaccharide deposition, and additionally NOM acids.

Furthermore, a pronounced shift towards acidic pH was observed for the fouled membrane at the isoelectric point (pI = pH 3), where the average net charge of the membrane is zero; pI = 4.1 for the virgin membrane. The membrane manufacturer recommends an operating window between pH 3 – 8, however cellulose acetate has been reported to degrade over time at exponentially increasing rates when operated outside the pH range of 4 - 6 [257].



Figure 6.4: Measured zeta-potential data for the virgin and fouled membranes.

6.3.3.2. SEM-EDX investigations

In Figure 6.5 SEM micrographs of the virgin, fouled and cleaned membrane surfaces can be seen at various magnifications. The results, when compared to the virgin membrane (Figure 6.5a), confirmed the presence of a fouling layer (Figure 6.5b–e). Furthermore, micrographs from a 7 h fouling experiment (Figure 6.5b-c) and the 48 h fouling experiment (Figure 6.5d-e) were compared. At low magnification (Figure 6.5b) a thick fouling layer can be seen. The cracks are due to shrinkage of the cake layer in the high vacuum of the SEM. After magnification, Figure 6.5c highlights the possible

presence of Cryptosporidium oocysts (size: 4-6 µm) attached to the surface of the biofilm layer [258]. Cryptosporidium is a common protozoan in wastewater linked to gastro-intestinal illness. Its shrunken form suggests cell dehydration, which may also be caused by the SEM vacuum. In Figure 6.5de, a rougher (thicker) fouling layer is observed for the 48 h-fouled membrane, potentially due to a higher accumulation of EPS. According to Parida and Ng [109] once a foulant layer accumulates on the membrane, foulant deposition is facilitated due to foulant-foulant interactions. In this process, the presence of combined structures of bacteria and EPS cover the membrane substrate surface. Figure 6.5d-e show protozoa attached to a biofilm containing EPS and bacteria.

Moreover, a white haze can be seen on the membrane surface in Figure 6.5d - e. This can be

due to differences in contrast and brightness during the photo scan, however it can also be due to the presence of inorganic contaminants i.e. accumulation of salt crystals from the highlyconcentrated draw solution. Organic foulants generally possess irregular and random structures while salts have a well-defined crystalline structure [109]. The salt accumulation was also visible without microscopy (Figure 6.5h). EDX may further indicate the presence of the elements Na and Cl (Table 6.3).

Besides the few bacterial colonies attached to the EPS layer (Figure 6.5g), the mechanically-cleaned membrane seemed relatively unsoiled. The additional analyses could confirm whether the EPS layer played a role in irreversible fouling.



Figure 6.5: SEM micrographs of the surface of the FO membrane (a) Virgin membrane (x250); (b - c) Fouled membrane after 7 h (x500 and x5000); (d - e). Fouled membrane after 48 h (x1000 and x5000); (f - g) mechanically-cleaned membrane after 48 h fouling experiment (x250 and x 5000); h) photo of salt accumulation on the active layer of the fouled membrane.

The EDX data (Table 6.3) revealed similarly high C and O peaks for all the membrane samples, due to the membrane fabric composition and possibly organic fouling [26], as carbon makes up approximately 63% of the total wastewater feed components (Figure 6.2). Foulant deposition also reduces the carbon and oxygen percentages, as can be seen from the lower values on the fouled membranes compared to the virgin membrane.

The presence of N and P on the fouled and mechanically-cleaned membranes relates to (bio)fouling and EPS. A high N composition was visible on the 48 h fouled membrane, with only small traces found on the mechanically-cleaned membrane (approximately 12.5% and 1.5% respectively).

Higher Na and Cl percentages were observed on the 48 h fouled membrane, possibly due to longer exposure to the draw solution. This additionally confirms the salt accumulation in Figure 6.5h. The mechanically-cleaned membrane also shows small amounts of Na and Cl, however these values fall below the detection limit. For the rest, the cleaned membrane looked very similar to the virgin membrane, demonstrating the removal of most of the fouling layer during cleaning.

The presence of Ca^{2+} in feed waters has been reported to result in more severe membrane fouling [109], as it enhances the intermolecular adhesion between polysaccharides [50, 160]. 6% of the raw wastewater feed composition was composed of Ca^{2+} ions. Ca^{2+} is also related to EPS binding. Studies have shown that the presence of calcium and elevated ionic strengths can lead to an increase in EPS layer thickness [160]. This may be later verified in the CH measurements.

Furthermore silica, a common salt causing membrane scaling [259], was found in small amounts on the fouled membranes. Mg^{2+} and S^{2-} ions which originate in wastewater were also detected. This could originate from salt precipitation in the form of BaSO₄ or Mg(OH)₂, also contributing to membrane scaling.

In general, EPS biopolymers form a highly hydrated matrix. The sorption properties of the matrix allow sequestering of dissolved and particulate substances from the environment, providing nutrients for biofilm organisms [260].

Atom	Fouled membrane	Fouled membrane	Mechanically-	Virgin
%	(7 h)	(48 h)	cleaned membrane	Membrane
С	43.23	36.29	48.14	46.02
0	39.41	34.07	48.43	53.91
Na	0.24	6.34	0.07*	0.07*
Cl	-	6.34	0.02*	-
N	10.49	12.47	1.49	-
Р	1.93	0.89	-	-
Ca	1.04	0.96	-	-
Si	0.33	0.23	-	-
Mg	0.12	0.17	-	-
S	0.17	0.21	-	-

Table 6.3: EDX analysis of the fouled, mechanically-cleaned and virgin membranes.

*Values below detection limit

6.3.3.3. Spectroscopy

ATR-FTIR was used to characterise the nature of the deposits of the fouling cake layer and was compared to the virgin membrane (Figure 6.6). In the ATR-FTIR spectra, three peaks at approximately 1040 cm⁻¹, 1200 cm⁻¹ and 1750 cm⁻¹ of the virgin membrane

represent the chemical CTA structure, as revealed by the EDX analyses and reported by Parida and Ng [109]. Compounds containing carbon-hydrogen bonds are related to organic compounds. Table 6.4 shows the association of the bands and peaks in Figure 6.6 with the membrane structure or the fouling layer.



Figure 6.6: FTIR spectra: overlay plots of the virgin membrane (blue) and the fouled membrane (red).

Polysaccharides (a biopolymer) are made up of many CH and OH groups, exhibiting a peak around 2900 cm⁻¹, and broad absorption bands at 3000 cm⁻¹ and 3600 cm⁻¹. The secondary amides (C-N bond) found at adsorption peaks 1635 cm⁻¹ and 1543 cm⁻¹ are EPS-related and strengthen the observations of the EDX analyses. Deductions from Table 6.4, suggest polysaccharide dominance in the fouling layer. Similar peaks using synthetic municipal

wastewater were observed for the fouling cake-layer with an OMBR [149]. By further characterising the distribution in the biofilm, Zhang et al. [149] found bacteria clusters of biofilm, polysaccharides and proteins to co-exist or overlap on the regions of the biofilm.

From our ATR-FTIR analysis, the presence of polysaccharides was confirmed to be a major foulant on the membrane.

6

Bands and peaks (cm ⁻¹)	Assignment*	Association
3000-3600	OH groups	Dalamasharidan
2900	CH stretching	Polysaccharides
1750	C=O stretching	CTA structure
1600-1700	Aromatic and olefinic C=C, C=O in carboxyl	Carboxylates, esters groups, Humic Acids
1540 - 1640	Secondary Amides	Proteins or Amino sugars
1200	Acetate C-C-O stretching	CTA structure or relevenshowider
1040	C-O stretching	CTA structure or porysaccharides
1030 - 1040 -SO, -CO or -SiO bonds		Sulphonic acids, alcohols, ethers and silicates

Table 6.4: The main absorbance bands in the FTIR overlay plot assigned to the virgin and fouled membranes.

*Interpretations based on data of numerous studies [109, 149, 158, 261, 262]

6.3.3.4. AFM

AFM was used to measure the membrane surface roughness of the virgin and the fouled membranes. AFM showed a smooth membrane surface for the virgin membrane and a rough surface for the fouled membrane (Figure 6.7). Rougher surfaces consist of a larger surface area available to evade shear force; particle/foulant attachment occurs quite favourably in valleys. In this way, rough membrane surfaces like UF and MF membranes are prone to pore plugging and eventually form a cake layer.



Figure 6.7: AFM microscopy images of the virgin (left) and fouled (right) FO membranes.

Table 6.5 indicates: i) the arithmetic average (Ra) of the absolute values of the surface height deviations, measured from the mean plane and ii) the peak to value difference in height within the analysed region (Z-range) of the two membrane samples.

Table 6.5: Morphological statistics of the AFM analyses

Membrane Sample	Ra (nm)	Z-range (nm)		
Virgin	76	935		
Fouled	111	1276		

The roughness of the virgin CTA membrane has been previously investigated, however there is no consensus regarding the values. Values in this study were found to be 76 nm for the membrane active layer (Table 6.5). Parida and Ng [109] found similar values for the active layer = 66 nm, which were lower than the porous support layer (105 nm), suggesting a lower fouling potential for the smoother and tighter active layer. In another study, roughness of the CTA membrane was reported to be similar to a typical RO/NF membrane [263], while Tang et al. [79] determined the active layer to be 36 nm, showing the membrane to be smoother than a typical aromatic polyamide RO membrane ~ 100 nm [264], due to the lack of ridge-and-valley structure. Reduced membrane surface roughness has previously been found to greatly improve fouling behaviour [159]. The deviating values found for the CTA membrane could be due to the membrane production process or even attributed to the membrane preparation process for the analysis.

6.3.3.5. Contact Angle Measurements

The contact angle measurements allowed quantification of the hydrophobicity of the FO membrane surface. The average θ for pure water, glycerol and di-iodomethane, as well as the surface tension of the different membranes are displayed in Table 6.6. Similar results for CTA membranes with water were found in the literature: 58.8° - 76.6° [81, 109, 162, 265]. Using di-iodomethane the value determined was slightly lower than reported: 47° [265].

From Table 6.6, the θ values for water were found to decrease with fouling and increase after cleaning.

Similarly, Hancock et al. [242] and Valladares Linares et al. [162] found increasing hydrophilicities with an increase in fouling. The same trend was seen using glycerol, however with di-iodomethane, the fouled membrane showed a higher contact angle than the other membranes. Higher contact angles for di-iodomethane demonstrate a more hydrophobic surface since di-iodomethane is hydrophobic. The increase in hydrophobicity of the cleaned membrane could be due to attached foulants which were not removed during cleaning.

The calculated surface tensions of the cleaned membrane were found to differ only slightly from the values of the virgin membrane, which also confirms that foulants, probably part of the biofilm as seen in the SEM micrographs, were still attached to the membrane surface or within the pores. Lower surface tensions in biofouled membranes has been previously observed [266].

The foulant attachment, present after mechanical cleaning, could be regarded as irreversible fouling. After chemical cleaning, Valladares Linares et al. [152] too observed irreversible fouling on an FO membrane.

		Contact Angle (°	Surface tension (mJ/m ²)				
Membrane	Pure water	Glycerol	erol <u>Di-iodomethane</u>		<u>Apolar</u>	<u>Polar</u>	
	θ	θ	θ		LW	+	-
Virgin	65.0 ± 7.3	68.5 ± 10.7	41.3 ± 5.0	37.8	36.9	0.0	19.7
Fouled	62.4 ± 5.1	62.9 ± 7.2	66.6 ± 7.0	34.8	24.1	1.2	24.3
Cleaned	72.1 ± 5.2	68.6 ± 8.5	48.7 ± 5.5	36.5	34.4	0.1	13.9

Table 6.6: Contact angle measurements and surface tensions of the virgin, fouled and cleaned membranes.

6.3.3.6. ATP and CH

Bacterial colonies (biofilm) produce and excrete EPS. For the fouling layer on the membrane, the average measured active bacterial biomass was 70.9 ng ATP/cm² and CH = 3.3 mg glucose/cm². These values are very high when compared to studies using anaerobic groundwater, where values from 0.5 - 3 ng ATP/cm² and CH values of 2.2 µg glucose/cm² were found on fouled [267] and extensively biofouled NF membranes [266], however FO membranes in the presence of a pre-soaked (in activated sludge) feed spacer produced values of 40 ng ATP/cm² [34]. The CH values represent large amounts of polysaccharides in the fouling layer,

which can be attributed to the polysaccharide fraction which accumulated in the feed (53 mg glucose/L) and/or EPS excretion due to the high concentrations of active biomass measured.

Bacterial adhesion and growth are one of the causes of fouling, scaling and organic fouling, which result in permeability decline [267]. The type of fouling on the membrane surface was further investigated by the LC-OCD analyses.

6.3.3.7 NOM characterisation

NOM was characterised into five fractions via LC: biopolymers, humic substances (HS), building blocks, LMW neutrals and acids, i.e. monoprotic acids.



Figure 6.8: a) Comparison of the OCD chromatographs for the feed (before and after the experiment) and the draw solution (before and after), b) The total solubilised fouling layer: comparisons between the OCD and UV chromatographs.

Figure 6.8 shows the contributions of each fraction in the chromatographs. LMW acids and humic acids were prominent in the raw feed (before and after experimental run), followed by building blocks, humics and biopolymers. Neutrals, a combination of alcohols, aldehydes, ketones and sugars were also found in the wastewater feed. The measurements showed all these compounds to be higher in the feed after the experimental run. This suggests accumulation of the fractions on the feed side and little to no passage through the membrane, as observed from the draw solution "DS" after results. The chromatograms for the draw solution measured before and after the experiment show only transport of LMW neutrals through the membrane from the feed to the DS, again confirming the large rejection of most NOM fractions. From the solubilised fouling laver, OCD and UV chromatographs (Figure 6.8b) showed the deposition of NOM fractions on the feed side. Although LMW acids and HS were dominant in the raw feed sample (FS before), biopolymers

seem to have a higher affinity for the fouling layer than any other fraction, suggesting that this could be the main cause of fouling (Table 6.7).

No humic substances were found during this analysis demonstrating the complete lack of humic and fulvic acids, or perhaps limited adsorption on the membrane. The presence of calcium in the feed, confirmed by the EDX results, may boost deposition of humic acids and EPS on the membrane surface; however this cannot be confirmed in this study. Humic acid deposition was also reported to be higher when NaCl is used as a draw solution [246], due to an increase in ionic strength at the membrane interface. This may be the case, however the humic acid concentration fell below the detection limit and the influence of NaCl on the humic acid deposition could therefore not be verified. A similar depiction of a fouled FO membrane was seen by Valladares Linares et al. [152] using secondary municipal effluent.

<i>Table 6.7:</i>	Concentrations	ot	f the NOM	fractions su	spended	in the	fouling laver.
		/					

Concentration	Biopolymers	Humics	Building Blocks	Neutrals	LMW Acids
mg/cm ²	881.8	*	594.6	265.2	21.4

*Below detection limit

In this FO study, fouling was induced by using a highly concentrated draw solution. A membrane autopsy was then performed on the fouled membrane and compared to virgin and mechanically-cleaned membrane samples. Specific membrane physiological factors were studied to better understand the fouling and biofouling behaviour of FO membranes.

- Water fluxes were found to decline by 18% when wastewater was used, assuming fouling to be the cause.
- SUVA values in the wastewater feed decreased after the experimental run, suggesting high DOC rejections of the FO membrane.
- The zeta-potential of the fouled membrane was found to cause a pronounced shift towards acidic pH and increased the negative charge of the membrane. At the specific charges observed, humic substances, colloidal matter and polysaccharides were represented. The presence of inorganic colloids was also determined within the solubilised fouling layer (46.3 m⁻¹) and via EDX observations.

- Contact angle measurements showed an increase in hydrophilicity with an increase in fouling, and a more hydrophobic nature for the cleaned membrane, suggesting remnants of foulants attached on the membrane surface and within membrane pores.
- ATR-FTIR and LC-OCD analyses established the predominance of biopolymers, i.e. polysaccharides and proteins within the fouling layer, confirming retention of most NOM fractions on the feed side of the membrane. The secondary amides determined were also related to the EPS layer excreted by the high concentration of active bacteria in the biomass. The CH analyses also ascertained the existence of polysaccharides, and more specifically EPS.

Biopolymers, and more specifically, polysaccharides were found to be the main cause of fouling on the FO membrane surface. Furthermore, cleaning methods should be investigated in order to remove all foulants on the membrane surface, while additional studies into irreversible fouling are also necessary.

CHAPTER

Continuous And Discontinuous Pressure Assisted Osmosis (PAO)

This chapter is adapted from:

Lutchmiah K., D.J.H. Harmsen, B.A. Wols, L.C. Rietveld, J.J. Qin, E.R. Cornelissen: Continuous and Discontinuous Pressure Assisted Osmosis (PAO) (submitted), Journal of Membrane Science (2014).

7.1 Introduction

Forward osmosis (FO) is an osmotically driven membrane process, which has gained a considerable amount of interest from the membrane research community in recent years [132]. Advantages of FO are (i) low energy consumption and (ii) lower fouling propensity compared to state-of-the-art, pressure-driven membrane processes, such as reverse osmosis (RO) [11, 17, 24, 25]. Challenges for FO include low fluxes; internal concentration polarisation (ICP); reverse solute transport from the draw to the feed side (solute leakage); and a need for post-treatment (application dependent) to recover the osmotic solution, an energy consuming step [268]. Flux optimisation can be carried out by improving membrane properties, i.e. designing thinner, more porous and less tortuous support layers to reduce ICP; optimising draw solutions and varying process-related properties, e.g. temperature and flow conditions

The osmotic pressure of the draw solution is the driving force in FO processes, causing an osmotic pressure difference between two solutions separated by the semi-permeable FO membrane. Water transport from the feed to the draw side occurs. FO therefore does not specifically require additional hydraulic pressure for water transport on lab-scale, however industrial FO applications do need an extra power input, due to flow resistance in the membrane module [17]. Pressurisation is required on both the feed and draw sides to overcome hydraulic resistance in the flow channels of spiral-wound (SW) and capillary membranes, i.e. for optimum water circulation [269, 270]. This hydraulic transmembrane pressure (TMP) in FO can reach up to 5 bar in the feed channel [270].

The addition of hydraulic pressure on the feed side has recently been proposed to improve FO performance [26, 103, 270-272]. Pressure assisted osmosis (PAO) involves the external use of hydraulic pressure, together with the osmotic gradient, to assist water permeation across the membrane. This differs from pressure retarded osmosis (PRO), a process harvesting salinity gradient energy [177], because the water transport in PRO flows towards a pressurised draw solution [84]. Figure 7.1 illustrates the theoretical relationship between RO, PRO, FO and PAO with regards to the direction and magnitude of the water flux as a function of the applied pressure.



Figure 7.1: The conceptual relationship between reverse osmosis (RO), pressure retarded osmosis (PRO), forward osmosis (FO) and pressure assisted osmosis (PAO), adapted from [84]. In reality, due to non-idealities in the membrane (e.g. ICP), the relationship between flux and pressure in PRO, FO and PAO regions is far from linear.

FO occurs when the hydraulic pressure difference, $\Delta P = 0$; PRO and RO occur at $\Delta P > 0$ and PAO at $\Delta P < 0$. Previous work on PAO, also called overpressure [26], pressure assisted forward osmosis (PAFO) [271], assisted forward osmosis (AFO) [103] and pressurised FO [270], has been summarised in Table 7.1, showing that PAO can be used to improve membrane performance, water circulation, solute rejection and/or to assess fouling in FO. In these studies the constant applied feed pressures ranged from 0 - 9 bar, enhancing water fluxes by more than 50% in some cases. In some of the PAO investigations both active layer to feed side (AL-FS) and active layer to draw side (AL-DS) membrane orientations were tested.

The work presented by Cornelissen et al. [272] showed an increase in fluxes when the latter orientation was employed, while Blandin et al. [103] found no significant differences between the two. Other studies showed substantial increases for lab-scale experiments, while little to no change was observed for bench-scale experiments (membrane area > 124 cm²). Membrane modules for pilot-scale studies were limited to SW modules, however tubular or plate-and frame modules are possible alternatives in PAO. Furthermore, the limited feed types employed highlight the need for more elaborate studies of feed stream contaminants, to better understand concentration polarisation (CP).

General benefits of PAO include enhanced permeation, limited reverse solute diffusion and advantages for the draw solution recovery unit e.g. RO in PAO systems. In FO-RO concepts, the RO step is the energy consuming stage. By using a PAO-RO concept, a pre-pressurisation of the RO unit can be achieved, potentially saving energy for use in the RO system [273]. Some disadvantages of PAO may involve membrane deterioration or rupturing, due to membrane deformation and/or the use of unsuitable membrane support designs.

In this paper the use of PAO in the form of (i) constant external hydraulic pressure based on our preliminary investigations [26] and (ii) pulsating pressure, on the feed side of a lab-scale set-up was applied in an attempt to improve FO membrane performance (water flux and reverse solute flux). To the best of the authors' knowledge the use of pulsation techniques to increase FO performance has not been previously studied and is interesting in terms its energy input compared to constant PAO. The use of activated sludge under pressure is also novel. Furthermore a model was developed to assess membrane transport under PAO conditions. Existing models for PAO show a need for improvement with regards to more accurate predictions of CP under pressure [103, 271].

Name of Additional Pressure	Feed type	Membrane	Туре	Area (cm ²)*	Orientation	Scale	CF velocity (m/s)	Pressure range (bar)	Water Flux (L/m ² h)	Ref
Overn ressure	DI	flat-sheet	CTA	124	AL-FS	lab-scale	varied	0 - 0.8	3.7 - 6.4	26
Overpressure	Wastewater	flat-sheet	СТА	124	AL-FS	lab-scale	varied	0 - 0.8	3.0 - 5.2	20
II. danulia	Tap water	SWFO(4040)	CTA	32000	AL-FS	pilot-scale	varied	0.3 - 1.2	4 - 15	
nressure	NaCl (0.55 M)	SWFO(4040)	CTA	32000	AL-FS	pilot-scale	varied	0.3 - 1.2	4 - 15	269
pressure	NaCl (0.55 M)	SWFO(4040)	CTA	32000	AL-FS	pilot-scale	varied	0.3 - 1.2	4 - 15	
A d dittion of	DI	flat-sheet	СТА	124	AL-FS	lab-scale	varied	0 - 0.8	4 - 7	
Feed	DI	flat-sheet	СТА	124	AL-DS	lab-scale	varied	0 - 0.8	6 - 12	272
Tressure	DI	flat-sheet	СТА	124	AL-DS	lab-scale	varied	0 - 0.8	5 - 8	
PAFO	DI	flat-sheet	СТА	0.003m ³	n/a	lab-scale	0.27	0 - 9	4.0 - 8	271
AFO	MilliQ	flat-sheet	CTA	n/a	AL-FS	bench-scale	0.1	0 - 6	4.4 - 12.6	
AFO	MilliQ	flat-sheet	СТА	n/a	AL-DS	bench-scale	0.1	0 - 6	4.4 - 23.6	103
		flat-sheet	СТА	145	AL-FS	bench-scale	0.25	0 - 3.45	9 - 11	
		flat-sheet	CTA	145	AL-FS	bench-scale	0.25	0 - 1.24	8 - 9	
Hydraulic TMP	Inorganic feed	flat-sheet	TFC1 (Oasys)	145	AL-FS	bench-scale	0.25	0 - 3.45	28 - 30	
		flat-sheet	TFC1	145	AL-FS	bench-scale	0.25	0 - 1.24	24 - 22	270
		flat-sheet	TFC2 (HTI)	145	AL-FS	bench-scale	0.25	0 - 3.45	8 - 13	
		flat-sheet	TFC2	145	AL-FS	bench-scale	0.25	0 - 1.24	10 - 13	
	Organic Feed	flat-sheet	CTA, TFC1, TFC2	145	AL-FS	bench-scale	0.25	1.24	n/a	

Table 7.1: Summary of studies using PAO to improve various parameters of the FO membrane process.

*An employed membrane area ≤ 124 cm² is considered as lab-scale.

7.2. Theory

7.2.1 FO membrane transport

The water flux (J_v) and solute flux (J_s) in FO processes are often described by the solutiondiffusion model [84], however they can also be written as a function of diffusion and convection [12]. The solution-diffusion model assumes that both water and solutes dissolve in the non-porous, homogeneous FO active layer and diffuse through the membrane along the chemical potential gradient [274], which consists of concentration and pressure differences across the membrane.



Figure 7.2: Concentration profiles in FO membranes for a) $\Delta P = 0$, b) PAO: additional hydraulic feed pressure (P_F), decreasing the effective osmotic pressure, by increasing ICP. Scheme adapted from [104, 275].

In the AL-FS orientation (Figure 7.2), the J_v in FO, based on diffusion alone, is given by [79, 85]:

$$\mathbf{J}_{\mathbf{v},\mathrm{FO}} = \mathbf{A}(\boldsymbol{\pi}_{\mathrm{i}} - \boldsymbol{\pi}_{\mathrm{F}}) \tag{7.1}$$

Where *A* is the water permeability coefficient, π_i the osmotic pressure at the interface of the AL and the membrane support layer and π_F the osmotic pressure of the feed solution. Adding ΔP over the FO membrane (Figure 7.2b) by increasing the feed pressure (*P_F*) gives:

$$\mathbf{J}_{\mathbf{v}} = \mathbf{A}(\boldsymbol{\pi}_{\mathbf{i}} - \boldsymbol{\pi}_{\mathbf{F}}) + \mathbf{A}\mathbf{P}_{\mathbf{F}}$$
(7.2)

Differences in diffusivity and solubility (partition coefficients) in the AL influence the transport of each solute differently. J_s is given by [274]:

$$\mathbf{J}_{\mathrm{s}} = -\mathbf{B}(\mathbf{c}_{\mathrm{i}} - \mathbf{c}_{\mathrm{F}}) \tag{7.3}$$

B represents the solute transport coefficient and is a function of c_i , the solute concentration at the interface of the AL and the support layer, and c_F , the solute concentration of the feed. The solute transport in the support layer is determined by convective solute transport (J_vc) , balanced by

reverse solute transport through the AL, and diffusion of solutes within the support layer [83]:

$$\mathbf{J}_{v}c = \mathbf{J}_{s} + D_{eff} \frac{dc}{dx}$$
(7.4)

The effective diffusion coefficient (D_{eff}) of the solute depends on the porosity (ε) of the support, the tortuosity of the pores (τ) and the free solute diffusion coefficient (*D*) by $D_{eff} = \varepsilon D/\tau$. Substituting Equation 7.3 into Equation 7.4 renders an ordinary differential equation (ODE):

$$\mathbf{J}_{v}c = -B(c_{i} - c_{F}) + D_{eff} \frac{dc}{dx}$$
(7.5)

The ODE can be solved using the following boundary conditions:

(i)
$$x = 0$$
 $c = c_i$
(ii) $x = \delta$ $c = c_D$

Where x is the thickness of the FO support layer ranging from 0 - δ (effective thickness), and c_D the solute concentration of the draw solution. Solving the ODE, the following equation can be obtained for the solute concentration at the membrane interface, incorporating an unknown constant (c_1):

$$c(x) = c_1 \exp\left(\frac{J_v}{D}x\right) - \frac{B}{J_v} (c_i - c_F)$$
(7.6)

Using boundary conditions:

(i)
$$c_i = c_1 - \frac{B}{J_v} (c_i - c_F)$$

(ii) $c_D = c_1 \exp\left(\frac{J_v}{D} \delta\right) - \frac{B}{J_v} (c_i - c_F)$

By rearranging (i), c_1 can be substituted into (ii). Once solved, Equation 7.7a remains, and is simplified to Equation 7.7b.

$$\exp\left(\frac{J_{\nu}}{K_m}\right) = \frac{J_{\nu}c_D + B\left(c_i - c_F\right)}{J_{\nu}c_i + B\left(c_i - c_F\right)}$$
(7.7a)

$$\frac{J_{\nu}}{K_m} = \ln \left(\frac{J_{\nu}c_D + B (c_i - c_F)}{J_{\nu}c_i + B (c_i - c_F)} \right)$$
(7.7b)

 K_m is the mass transfer of a solute in the support layer (or the boundary layer), which is in this case equal to the membrane properties of the support layer: thickness x tortuosity. Furthermore, it is assumed that the ratio of the membrane surface concentration of feed solute to the bulk concentration is equal to the corresponding ratio of osmotic pressures [83, 85]. For PAO processes, rearranging Equation 7.2 ($\pi_i - \pi_{f} = \frac{J_v - AP_F}{A}$ and $A\pi_i$

= $J_v - AP_F + A\pi_f$) and substituting it into Equation 7.7, AP_F can be included (Equation 7.8). By solving for $P_F = 0$, Equation 7.8 can be simplified to Equation 7.9, establishing the theoretical value of J_v for FO processes (AL-FS) [58, 79].

$$\frac{J_{v}}{K_{m}} = \ln \left(\frac{A\pi_{D} + B\left(1 - \frac{AP_{F}}{J_{v}}\right)}{(A\pi_{F} + J_{v} - AP_{F}) + B\left(1 - \frac{AP_{F}}{J_{v}}\right)} \right)$$
(7.8)
$$J_{v} = K_{m} \cdot \ln \left(\frac{A\pi_{D} + B}{A\pi_{F} + Jv + B} \right)$$
(7.9)

For the model, Equation 7.7 was rearranged to:

$$c_{i} = \frac{\left(c_{D} + B\frac{c_{F}}{J_{v}}\right) \cdot \left(exp\left(\frac{Jv}{K_{m}}\right) - 1\right)}{\left(1 + \frac{B}{J_{v}}\right) \cdot exp\left(\frac{Jv}{K_{m}}\right) - \frac{B}{J_{v}}}$$
(7.10)

From Equation 7.10, $\pi_i = f(c_i)$ and Equation 7.2 – 7.3 the iteration for J_v was solved using Matlab.

7.3 Materials & Methods

7.3.1 Membrane Material

A cellulose triacetate (CTA) FO membrane (HTI, Albany, OR) was used in this study. The membrane is comprised of a dense, selective active layer and a porous support layer consisting of an embedded polyester mesh. The asymmetric membrane was used only in the AL-FS orientation. Fresh membrane coupons were used for each experimental series. Experiments in the same series were performed on consecutive days allowing the membrane to rest (in DI water) for at least 15 h between runs.

7.3.2 Experimental Set-up

Two U-tube set-ups were used during this study, due to PAO testing at different research periods. Tests during 2006 – 2008 concluded the potential of the technique, however an optimisation was necessary. The set-up was modified to include a more systematic and controlled process of exerting hydraulic pressure (U-tube 1).

7.3.2.1 U-tube 1

FO experiments were carried out in a lab-scale Utube as mentioned in previous work [26] and illustrated in Figure 7.3. The membrane was placed in a membrane holder between two Teflon-coated, stainless steel meshes (thickness: 1.4 mm, opening size: 2 x 3 mm) (Appendix A: Figure 1a). The meshes were incorporated simply to support the membrane during pressurisation and minimise membrane deformation, which may occur via stretching or compaction [12, 103, 276, 277]. The meshes were not intended to assume the function of spacers, i.e. promote mass-transfer and mixing. Plastic rings (thickness = 2 mm) were placed between the membrane and the mesh (Appendix A: Figure 1b) to avoid direct contact.

The membrane holder separated the feed and draw solution compartments (3 L each). A constant mixing rate of 375 L/h was applied to both the feed and draw sides using magnetically-driven centrifugal pumps (Verder, V-MD15) to maintain homogeneity and diminish external CP (ECP). The flow velocity at the membrane surface, due to the perpendicular flow of the outlet tube (diameter = 1 cm) from the pumps directly onto the membrane, varied between 1.33 - 0.01 m/s.


Figure 7.3: U-tube 1 (left): the feed pressure is controlled by the PLC device (right).

Hydraulic pressure was exerted on the feed side by means of an external air supply connected to a pressure regulator. The desired pressure was set and directly adjusted on the pressure regulator (range: 0 -1 bar), instantaneously applying the set pressure on the feed. This pressure was modified (with regards to frequency and length) by a Programmable Logic Controller (PLC), encased in a control box (Bürkert). The applied pressure from the pressure regulator to the feed side was measured via a pressure gauge (Ceraphant T, Endress+Hauser), mounted directly above the feed. The applied pressure was operated via: 1) continuous PAO or 2) discontinuous PAO (pulsation).

Pulsation parameters were set directly on the PLC. The PLC controls the air valve by opening and closing it at imputed intervals. This allowed variation of the pulse frequency (range: 1 pulse/5 min - 1 pulse/3 h) and length, i.e. duration (range: 1 - 30 min pulse, followed by a 30 min break, then

repeated). During frequency experiments, the pulse length remained constant at 1 min.

7.3.2.2 U-tube 2

In U-tube 2, a similar construction as [41] was used. This set-up did not incorporate additional membrane support as these preliminary experiments did not anticipate membrane deformation at the low pressures applied. Hydraulic pressure was exerted using a +4 meter water column (MWC) on the feed water side (1 MWC = 0.1 bar). At 0 MWC, no pressure was exerted and was therefore the baseline experiment. The water column height was increased in steps of 1 MWC. The flux was measured for 1 h at which point the next 1 MWC was added until 4 MWC was reached, i.e. from 0 - 0.4 bar. An overview of the differences between the two U-tubes are summarised in Table 7.2.

<i>Table 7.2:</i>	Comparisons	between th	e U-tubes	employed	in this v	work.
	1					

<u>Parameter</u>	<u>U-tube 1 (2010 – 2013)</u>	<u>U-tube 2 (2006 – 2008)</u>
Membrane area (cm ²)	124	112
Flow rate (L/h)	375	330
Membrane support	Yes	No
Pressure exerted via	Pressure regulator	MWC
Pressure range (bar)	0 - 0.8	0 - 0.4
PAO mode	continuous / discontinuous	continuous
Feed Type	DI water	DI water, activated sludge
Experimental duration	> 6 h	< 5 h

7.3.3 Solutions and Chemicals

7.3.3.1 Feed Solutions

Deionised (DI) water (Milli-Q, Millipore) was used as the feed solution in both set-ups. Additionally, activated sludge (AS) was tested in U-tube 2. The AS feeds were sampled from the following wastewater treatment plants (WWTP):

- Hilversum (HS), the Netherlands (Waternet)
- Ulu Pandan (UP), Singapore (PUB)

Characteristics of the AS types can be found in Table 7.3.

Table 7.3: Average compositions of the AS types sampled from the various WWTPs.

Parameter	HS	UP
Total Suspended Solids (g/L)	5	5
Conductivity (µS/cm)	630	730
Chemical oxygen demand (mg/L)	550	230
Temperature during test (°C)	25.2±2.7	31.6±1

7.3.3.2 Draw solutions

Either 0.5 M NaCl (J.T. Baker, the Netherlands) or 0.33 M MgCl₂ (Merck, Germany), relating to $\pi \approx 24$ bar was used. Fluxes were normalised to 20 °C, as per [42, 145].

7.3.3.3 Water and Salt Flux Determination

In the U-tubes, J_v (L/m²h) was determined by the volume increase in the measuring tube on the draw side of the set-up. Experiments were operated in batch-mode; and the draw solution dilution over time was considered. The reverse solute flux, J_s (g/m²h), i.e. draw solutes from the draw side towards the feed, were measured in the feed by means of a conductivity meter. From these parameters the J_s/J_v ratio could be determined, and can be described as [99, 101]:

$$\frac{J_s}{J_v} = \frac{B}{A\beta R_g T} \tag{7.11}$$

Where β is the van't Hoff coefficient ($\beta_{\text{NaCl}} = 2$), R_g the gas constant (L.bar/K.mol) and *T*, temperature (K). The J_s/J_v ratio indicates the amount of salt (g)

moving to the feed side, per litre of permeate produced.

She et al. [276], operating with hydraulic pressures in PRO found the J_s/J_v ratio to increase with the increase in pressure, essentially underestimating Equation 7.11, which occurs due to the assumption that *A* and *B* remain constant. They incorporated hydraulic pressure on the draw side and modified the equation accordingly. For PAO, hydraulic pressure was incorporated on the feed side. Using Equation 7.2 – 3 and osmotic pressure ($\pi = \beta RgTC$), Equation 7.11 was derived for the J_s/J_v ratio in PAO:

$$\frac{J_s}{J_v} = \frac{B}{A\beta R_g T} \left(1 - \frac{A\Delta P}{J_v} \right) \tag{7.12}$$

7.3.4 Membrane Characterisation

 J_{ν} in FO is governed by membrane transport properties [58, 66, 67, 278]. For this reason *A* and *B* (section 7.2) need to be determined. RO experiments, which are generally used to determine the membrane transport properties and salt rejection (*R*) [67, 79], were conducted in an RO cell using DI water and 10 mM NaCl solution as feed solutions. The membrane in the RO cell will not deform due the use of an appropriate frit [156], however in U-tube 1 *A*, *B*, and *R* values are expected to differ, due to deformation (no frit). Therefore membrane characteristics were also determined in the U-tube. In both set-ups *A* was obtained from pure water flux results over a range of applied pressures (0.2 - 2 bar); *R* from conductivity measurements of the permeate and feed water; *B* via Equation 7.12 for the U-tube, and the fit with *R* (Equation 7.13) in the RO cell:

$$R = \left(1 + \frac{B}{A(\Delta P - \Delta \pi)}\right)^{-1} \tag{7.13}$$

7.4 Results & Discussion

7.4.1 Continuous PAO

7.4.1.1 Flux efficiency

In Figure 7.4, PAO (0.2 - 0.8 bar) demonstrated a positive effect on J_{ν} for both NaCl $(4.61 - 6.87 \text{ L/m}^2\text{h})$ and MgCl₂ $(3.73 - 6.38 \text{ L/m}^2\text{h})$ as draw solutions. An increase in J_s with the increase in applied hydraulic pressure was also displayed (NaCl: $3.26 - 8.97 \text{ g/m}^2\text{h}$, MgCl₂: $1.65 - 5.11 \text{ g/m}^2\text{h}$), showing larger differences between the two salts for J_s than J_{ν} .

For NaCl J_v increased from 6 - 49% and from 33 -71% for MgCl₂ when additional pressure was applied, causing greater percentage increases for MgCl₂ than NaCl. Although this divalent salt achieves lower fluxes than NaCl under normal conditions [114], similar water fluxes were reached for both salts with PAO (~6.6 L/m²h). In Figure 7.4b J_s was observed to increase faster than J_v for both salts (NaCl: 20 - 175% and MgCl₂ 48 - 209%), resulting in an increase of the J_s/J_v ratios for both salts from approximately 12 – 85% (Figure 7.4c). From Figure 7.4c it can be seen that pressures exceeding 0.4 bar (for the NaCl experiments) reach J_s/J_v ratios > 1, signifying a greater loss of salt than water produced. This may prove uneconomical for some applications.

Due to the synergistic effect of the osmotic pressure and the hydraulic pressure, the increase in J_{ν} as per Equation 7.2 seems quite obvious. PAO and PRO studies have investigated membrane parameters under pressure more elaborately and further attributed enhanced permeate fluxes to the increase in A, as a result of unsuitable membrane support, leading to membrane deformation [103, 156]. The meshes used in this study (Appendix A) are a uniform support and should limit physical movement, unlike regular spacers which stretch under pressure and enhance water fluxes [103], however deformation is still possible. During pressurisation, the membrane is pressed against the mesh. Depending on the amount of pressure applied, the extent and type of deformation may differ. Stretching affects the polymer chains of the AL and expands the pores [12], while compaction may more readily occur in the porous support layer.

The increase in the $J_{s'}/J_{v}$ ratios too can be attributed to membrane deformation, due to the change in Continuous and Discontinuous Pressure Assisted Osmosis (PAO)

solute permeability. This has been confirmed in other PAO and PRO studies as well [103, 276], which generally found increased water fluxes and operating pressures to be accompanied by undesired increases in reverse solute flux. For this reason



membranes with better selectivities, i.e. higher A and lower B values are necessary [12]. A similar rate of membrane deformation should affect B equally for both salts, causing an increase in reverse diffusion



Figure 7.4: Impact of PAO: average values of a) water flux, b) salt flux and c) J_s/J_v ratio, using NaCl and MgCl₂ draw solutions (feed: DI water; t = 6 h per pressure increment). with the increase in pressure. However the lower D of MgCl₂ maintained the lower leakages and J_s/J_v ratios in general. The increase in J_s due to the change in B is also in accordance with Equation 7.3. B can be further elaborated using Equation 7.14, which incorporates the partition coefficient ϕ , i.e. the measure of the solubility of a substance:

$$B = \frac{D \cdot \phi}{\Delta \mathbf{x}} \tag{7.14}$$

External pressure, especially at low pressures, is known to have very little effect on the solubility of liquids and solids, and is usually neglected in practice [279]. The membrane thickness (Δx) and D (=Deff in this case) however are expected to change significantly, especially when considering membrane deformation. A decrease in Δx can cause an increase in B according to Equation 7.14. Changes to the support layer thickness, i.e. compaction, will furthermore affect the membrane structure parameter S, influencing K_m ($K_m = D/S$; D in this case is the diffusion coefficient of the solute and will not change) and consequently J_{ν} . This influence is not incorporated in the model.

7.4.1.2. PAO effect on the draw salts

In Figure 7.4a the water fluxes for both salts were observed to increase in parallel. However, slightly higher water fluxes for NaCl (7 - 19%) were shown in all cases, except at 0.2 bar where NaCl was found to be 1% lower than MgCl₂ (Table 7.4). The differences in the water flux between the two salts (averaging 0.5 L/m²h) were ascribed to the difference in diffusivity of electrolytes in the porous substructure of the membrane, which is consistent with previous research [41, 145]. Moreover, this difference can be explained by the degree of dilutive ICP (DICP), which is said to be affected by the diffusivity and viscosity of the draw solution [33, 121].

From section 7.4.1.1, PAO was found to affect the salt leakages and the J_s/J_v ratios of both salts similarly, i.e. showing similar percentage increases with increasing pressures. Absolute differences in J_s between the salts were however evident (Figure 7.4b) and were amplified with each pressure increment $(1.5 - 3.9 \text{ g/m}^2\text{h})$.

Table 7.4 shows the absolute difference of the salt leakage between NaCl and MgCl₂. On average a 42% higher J_s difference was reached by NaCl under

Continuous and Discontinuous Pressure Assisted Osmosis (PAO)

pressure, leading to a J_s/J_v ratio difference of 39%. Lower reverse solute diffusion decreases the severity of CP, another potential contribution to the similar water fluxes seen by the two salts.

The better rejection of divalent salts by this membrane is due to the higher *D* value for NaCl $(1.23 \times 10^{-9} \text{ m}^2/\text{s} [120])$ which enables it to cross the

membrane more easily, resulting in a higher diffusive flux [33, 41] and follows Equation 7.13. MgCl₂ with a lower D (1.04x10⁻⁹ m²/s [120]), will result in a lower B and will therefore leak less through the membrane.

Table 7.4: The absolute difference in performance between NaCl and $MgCl_2$ draw solutions during continuous PAO studies. NaCl is higher in all instances, except for J_v at 0.2 bar.

Pressure (bar)	$\underline{J}_{\underline{\nu}}(\%)$	$\underline{J}_{\underline{s}}(\%)$	$J_{\underline{s}}/J_{\underline{v}}$ ratio (%)
0	19	49	37
0.2	-1	38	38
0.4	9	42	37
0.6	7	45	41
0.8	7	43	39
Average (PAO)	6	43	39

Table 7.4 displays another interesting trend with regards to the fluxes. Once pressure was applied, a lower absolute difference was displayed than without pressure, i.e. for J_v between 0.2 - 0.8 bar the value was reduced to 6% on average and for J_s 43%. This reduction indicates that the higher J_v advantage,

which NaCl generally experiences over MgCl₂, weakens when PAO is involved. This advantage is attributed to ICP which usually affects NaCl less [121, 280], but the addition of pressure, which deforms the membrane, may also lead to a lower impact of electrostatic repulsion dominance of

MgCl₂, lowering the overall percentage differences between the two salts.

Due to the fact that MgCl₂ has shown similar water fluxes, less salt leakage and lower J_s/J_v ratios during PAO, when compared to NaCl, it is considered a more suitable draw solution for these types of studies.

7.4.1.3 Assessing the driving force

Augmenting the driving force in FO can occur via the draw solution (type/concentration). PAO, though, demonstrates better use of the driving force. In our previous work [26], water fluxes between a 0.5 - 1 M NaCl draw solution concentration (Δ driving force = 23 bar) was found to increase by 44%. In comparison, the difference in water fluxes between the 0.5 M NaCl solution and additional pressure of 0.8 bar (Δ driving force = 0.8 bar) in this study was 49%, reaching approximately the same water flux as a 1 M NaCl draw solution (6.9 and 7.6 L/m²h respectively). The lower efficiency using draw solution concentrations can be explained by the fact that only 20% of the osmotic pressure driving force for NaCl concentrations < 3 M (≈ 160 bar) is realised [104], due to the influence of ICP, i.e. higher draw solution concentrations increase the severity of dilutive ICP (DICP), since higher concentrations yield higher water flux rates [89, 104]. Simultaneously, J_s is also found to increase causing more severe ICP at higher concentrations [99, 281]. Studies of increasing draw solution concentrations generally show greater non-linearity of J_v at higher concentrations (> 50 bar for NaCl) [26, 79], indicating the severity of DICP. Because ECP and ICP are functions of the flux, the increase in J_v alone is self-limiting, restricting the use of draw solution concentrations to increase the driving force [12].

In this study the draw solution concentration remained constant, however the increase in J_{ν} , due to additional feed pressure is apparent (Figure 7.4a). This points to several hypotheses: i) although the addition of PAO decreases the effective osmotic pressure of the draw solution by dilution, increasing the severity of ICP and decreasing π_i , an increase in the water flux is observed and ii) the exerted pressure leads to physical membrane deformation increasing A, but increasing B more rapidly, enhancing J_{ν} and J_s above values measured at comparable draw solution concentrations.

7.4.1.4 Model predictions for continuous PAO

Membrane characterisation was performed in the RO and U-tube as mentioned in section 7.3.4. The values $A = 1.3 \times 10^{-12}$ m/s.Pa and $B = 4.1 \times 10^{-8}$ m/s were determined from the experiment runs in RO and are similar to results found in [99, 101]. The U-tube was employed to accurately account for changes in A and B, due to any membrane deformation experienced during experimental runs. A and B were found to increase with the increase in pressure in the U-tube (Table 7.5).

From Table 7.5, pressure in the U-tube caused an almost three-fold increase in water permeabilities compared to RO measurements; assumed to be a consequence of membrane deformation. These high water permeabilities, however, are not uncommon for this particular membrane. Both [136] and [106] found *A* values between $3.6 - 4.0 \times 10^{-12}$ m/s.Pa during membrane characterisation tests at 20 °C and 30 °C respectively. Besides deformation under hydraulic pressure and temperature differences, the variations in *A* and *B* values can also be attributed to deviations between small membrane coupons

(Phillip et al., 2010). Other conditions implemented in those studies, i.e. use/type of support design are, although, unknown. This observation never-the-less illustrates a very important increase in A and confirms the interest of applying the U-tube configuration to enhance water flux. On the downside, B was found to increase substantially as well.

For the model predictions in RO, the baseline values in Table 7.5 were used. For the U-tube predictions, baseline values were used at $\Delta P = 0$ and a linear increase in *A* and *B* with ΔP . The increase rate was determined from the difference at $\Delta P = 1.0$ bar and $\Delta P = 0.2$ bar for *A* and $\Delta P = 0.8$ bar and $\Delta P = 0.2$ bar for *B*.

By solving the ODE using the boundary conditions for the AL-FS as per Equation 7.8, using $K_m = 2.1 \ge 10^{-6}$ m/s [282] and $S = 6 \ge 10^{-4}$ m, and the parameters from Table 7.5, J_v and J_s were calculated. Figure 7.5 compares the experimental data with model predictions. The model results obtained with parameters from the RO cell predict the behaviour of

Pressure (bar)	A (x 10 ⁻¹² m/s.Pa)	<i>B</i> (x 10 ⁻⁷ m/s)	Set-up
baseline	1.3	0.4	RO cell
0.2	3.2	2.3	
0.4	3.6	2.9	II to be
0.6	3.9	4.5	0-tube
0.8	3.9	5.1	

Table 7.5: Membrane permeabilities determined in the RO and U-tube.

 J_v and J_s when no membrane deformation is involved (P_f = 0 bar). During this progression J_v increased slightly, while J_s decreased. This is similar to PAO findings in [271], but contrary to what was observed in U-tube experiments; both fluxes increased. The predicted values using *A* and *B* from the U-tube ($P_f = 0.2 - 0.8$ bar) showed a linear increase in J_v and non-linearity for J_s . For the water flux values in Figure 7.5a, the predictions were not much higher than the experimental values (11 – 23%). Slight discrepancies between experimental and modelled water flux data were also seen by [271] and [103]. The salt flux predictions on the other hand (Figure 7.5b) were overestimated by 118 – 151%. CP may have no effect on the hydraulic pressure efficiency during PAO [103], however it can still severely affect the salt permeability. This CP effect was obviously underestimated by the U-tube model predictions displayed in Figure 7.5b. In Figure 7.5c the effective osmotic pressure in the U-tube is shown to decrease more than the RO predictions, as a consequence of the higher fluxes. Further incongruity between the model and experimental data may also be due to some uncertainty regarding the determined A and B values in the U-tube.

Continuous and Discontinuous Pressure Assisted Osmosis (PAO)



The model results, based on A and B from the Utube, displayed higher predictions than the experimental data, essentially overestimating membrane deformation and underestimating ICP. Membrane deformation has been listed as a performance-limiting phenomena along with ECP, ICP, and reverse salt diffusion [156]. The major



Figure 7.5: The effect of PAO on: a) J_v and b) J_s as a function of continuous PAO between 0 - 2 bar. Experimental and modelled values are shown ($A=1.29x10^{-12}$ m/s.Pa; $B=4.12x10^{-8}$ m/s and $S=6x10^{-4}$ m); c) osmotic pressure at the membrane interface decreasing as a result of the increase in J_v with the increase in PAO.

limitation seems to be the ability of the FO membrane to withstand deformation in this set-up, even at low pressures. Therefore better support designs, as mentioned by [103], are important, but the production of more rigid membranes for PAO needs to ensue as well. Such rigid membranes may not be useful for spiral wound modules, but may be interesting for tubular membranes.

7.4.2 Discontinuous PAO

7.4.2.1 Pulse frequency tests with NaCl

In section 7.4.1 the highest water flux, while still achieving a J_s/J_v ratio < 1, was found at 0.4 bar. Pulsation tests were therefore tested at this pressure. Figure 7.6 illustrates the increase in water and salt fluxes as a function of the frequency of feed pressure pulsation.

The water flux was found to increase marginally with the increase in frequency, from 4.5 ± 0.2 L/m²h at 0 pulses to 5.3 ± 0.3 L/m²h at a frequency of 12 pulses/h, which led to an overall increase of 17% (Table 7.6). The flux increase at these operating conditions may also be dominated by membrane deformation, however the extent is assumed to be dependent on the pulse frequency, e.g. at a frequency < 6 pulses/h deformation (via pressure) is only possible for less than a tenth of an hour. The water flux increase is also due to the increase in temporary hydraulic feed pressure, as mentioned previously. When no membrane deformation ensues stable permeability coefficients are anticipated. J_s should therefore increase according to Equation 7.12. With more frequent pulses (> 6 pulses/h) a greater extent of deformation, i.e. stretching is expected. Stretching of the pores may explain the rapid increase in B compared to A and the higher J_s/J_v ratios. At 12 pulses/h the water flux neared values similar to 0.4 bar continuous PAO (6.1±0.3 $L/m^{2}h$), however the salt fluxes here were higher. In general, salt fluxes were found to increase with the increase in frequency, showing a more rapid increase of 91% at 12 pulses/h, compared to the baseline study (0 pulses). This J_s trend was similar to the continuous PAO experiments using NaCl (Figure 7.4b). In fact, for discontinuous PAO the termination of each pulse produced a hydraulic back pressure. This was visually observed by the sudden drop in the water level, displayed on the measuring tube. Perhaps membrane relaxation simply happened once hydraulic pressure ceased, however in theory, the force of the back pressure could have caused the membrane to deform in the opposite direction. In this way it is possible that more stretching occurred and reverse salt diffusion from the internal FO membrane structure was greatly enhanced, increasing the overall salt leakage during experiments.

Continuous and Discontinuous Pressure Assisted Osmosis (PAO)



Figure 7.6: Pulse frequency tested in the FO set-up using 0.5 M NaCl. Pulsing with a pressure of 0.4 bar for a length of 1 min: water flux and salt flux, shown at number of pulses per hour.

7.4.2.2 Pulse duration tests with NaCl

Variations in the pulse length during the temporary pressure runs were tested on the FO membrane. Figure 7.7 illustrates the increase in water and salt fluxes with the increase in pulse length (Table 7.6). Again, a greater extent of deformation is expected during longer pulses (> 5 min). Water fluxes may have only improved slightly with pressure, but J_s

values were affected as well. The J_s increase in Figure 7.7 may also be a consequence of the hydraulic back pressure, which was observed during these experiments, and could likely be the cause for the high J_s values between 5 – 30 min pulse lengths. Regardless, J_s/J_v ratios were found to be relatively constant for all pulse durations $(1.0\pm0.1 \text{ g/L})$.

7



Figure 7.7: Water flux and salt flux for pulse duration (min). Pressure = 0.4 bar

Figure 7.8 takes a closer look at the water flux behaviour before and after the 30 min pulses. During the pulse, J_{ν} was observed to increase continuously. Clear peaks are displayed at the end of each pulse (Figure 7.8). An immediate decline in the flux was visible once the pulse ceased. Pulsation enabled fluxes to attain similar values as 0.4 bar continuous pressure (top line, Figure 7.8). A decline in J_{ν} compared to baseline values was thereafter noticed during the relaxation period. This indicates that if the increase is due to membrane deformation, it may just be a temporary effect, seeing that the membrane permeability decreased to its initial state after 6 h.



Figure 7.8: J_v in time; frequency = 12 pulses/h.

Reversible membrane deformation without the loss of integrity has been reported using higher pressures (6 bar) and a relaxation period of 24 h [103]. However there is still some doubt with regards to this hypothesis, as the flux increase could also simply be due to the effect of the temporary hydraulic feed pressure.

From Table 7.6 higher increases in both fluxes and the J_s/J_v ratio is seen during more frequent pulsing. Although similar water fluxes were reached at the highest tested parameters for both operations, salt fluxes remained higher during frequency tests. This is attributed to a more frequent hydraulic back pressure.

Pulse Parameter	$\underline{J_{v}}(\%)$	$\underline{J_s}(\%)$	$J_{\underline{\sqrt{J_v}}}$ ratio (%)
Frequency	-4 to 17	14 to 91	17 to 63
Duration	-10 to 4	11 to 58	24 to 53

Table 7.6: The absolute difference between discontinuous PAO operations at 0.4 bar and the baseline study (0 bar). Frequency: 0.3 - 12 pulse/h; duration: 1 - 360 min. A lower percentage for discontinuous PAO is signified by "-".

7.4.2.3 Comparing PAO operational conditions

In Figure 7.9 a comparison between continuous PAO, discontinuous PAO and baseline experiments (0 bar pressure) are depicted. Continuous PAO at 0.4 bar was compared to frequency (12 pulses/h) and duration (30 min) tests, which achieved the highest

water fluxes. For all tests the water flux decreased in time, due to the dilution of the draw solution and J_s leakage, decreasing the driving force on the draw side. However PAO tests experienced faster declines, due to higher fluxes and consequently, a more rapid dilution.



Figure 7.9: A comparison of the fluxes over time for baseline, continuous and discontinuous PAO - frequency of 12 pulses/h (\Box) and duration of 30 min pulses (\Diamond) at 0.4 bar: a) water flux and b) salt leakage.

It is also clear that the discontinuous PAO tests achieved a lower flux on average (14%) than continuous PAO. The enhancement is attributed to the constant hydraulic feed pressure combined with a greater extent of deformation

Pulsation, coupled with membrane deformation, is assumed to have increased fluxes above baseline values. In fact both pulsing tests produced the similar average water fluxes, as seen in Figure 7.9a. In Figure 7.9b, the salt fluxes of all tests, on average, showed increasing J_s values in time, however these were lower during the baseline study (no PAO applied). For pulsing, it is furthermore possible that the hydraulic back pressure influenced the increase in J_s values, while for continuous PAO, membrane deformation remains the prevailing factor. When considering the higher J_v and lower J_s values, continuous PAO appears more beneficial to FO processes than discontinuous PAO, although minimising the hydraulic back pressure may improve J_s tremendously. Still, the temporary beneficial increase in the water fluxes could be advantageous under the right conditions, and is furthermore interesting to limit fouling.

7.4.3 PAO on Activated Sludge

Results for continuous PAO in U-tube 2, using DI water and activated sludge as feeds are shown in Figure 7.10 An increase in the water flux was observed when PAO was applied from 0 - 0.4 bar (Figure 7.10), clearly increasing the water flux with each 0.1 bar increment. For DI water the increase ranged from 6 - 29%, which is similar to the increase achieved in U-tube 1 for DI at the same pressures (6 - 32%), indicating the comparability of the pressure increase in the two set-ups when pure water is employed. This observation is further discussed in section 7.4.4.



Figure 7.10: Water flux at increasing hydraulic pressures (0 - 0.4bar) using feeds: (i) DI and (ii) AS-HS; draw solution: 0.5M NaCl. $T = 20 \,^{\circ}$ C.

The increase for the AS-HS with PAO was found to be 16 - 35%, similar to the pure water studies, however with lower fluxes (6 - 34% lower). Higher TDS feeds are generally expected to produce lower fluxes than pure water due to lower bulk osmotic pressures and concentrative ECP (CECP) (and possible fouling effects), which strongly impact the hydraulic efficiency of the process. The AS-HS flux increases per increment were attributed to the additional driving force and membrane deformation. A percentage overview per increment compared to the baseline study for each feed type can be found in Table 7.7. PAO investigated at 0.4 bar was also determined using activated sludge from the Ulu Pandan (AS-UP) WWTP. Again an increase in water flux was observed as a result of PAO. Water flux values increased by 19%, which was lower than the DI water study at 0.4 bar by 27%. A closer look at these experiments revealed a temporary effect of the hydraulic pressure within the first hour (Figure 7.11). Initial J_{ν} values were higher than the baseline experiment. After 4 hours water fluxes converged towards baseline values. This was similar to the flux trend during continuous PAO tests, where higher water fluxes with faster declines were noticed.



Figure 7.11: Water flux values in time at 0 bar (O) and 0.4 bar (D) (feed: AS-UP; draw solution: 0.5M NaCl).



Figure 7.12: Water flux values at 0 and 0.4 bar using DI, AS-UP and AS-HS; NaCl. $T = 20 \,^{\circ}$ C.

Membrane fouling could also be a factor, occurring faster at increased pressures, however there was no concrete evidence of this within the experimental time frame of 5 h. Long-term studies would be required to further investigate fouling during PAO.

A comparison of all the feeds during PAO are displayed in Figure 7.12. When employing high TDS feeds, CECP on the feed side needs to be considered as solutes can accumulate at the boundary layer. The higher the TDS, the lower the feed as ECP reduces the effective osmotic pressure [17], explaining the lower fluxes attained by the AS feeds compared to the DI water study. Due to the turbulence produced in the U-tube, CECP is assumed to be negligible; high turbulences generally minimise CECP at the membrane surface [53]. Both AS types showed similar fluxes at 0 and 0.4 bar, showing that the slight variations in the conductivity (Table 7.3) did not affect the bulk osmotic pressure much. From this, the addition of PAO seems advantageous regardless of the feed type, however fouling propensity may play a bigger role during long-term studies using feeds of higher salinities.

7.4.4 Comparing the U-tubes

In section 7.4.3 similar percentage increases were found between the DI water feeds for both set-ups at similar pressures.

Table 7.7: Percentage increase per pressure increment compared to the baseline study (0 bar) for DI water and activated sludge.

Pressure (bar)	DI (%)	AS-HS (%)	AS-UP (%)
0.1	6	16	-
0.2	16	35	-
0.3	28	17	-
0.4	29	31	19

Continuous and Discontinuous Pressure Assisted Osmosis (PAO)

This confirms the consistency of membrane deformation with the increase in pressure, however this does not necessarily illustrate the extent of deformation. From Figure 7.13a higher increase in J_{ν} is visible in all instances for set-up 2 (without support), even at 0 bar, where similar fluxes are expected. The discrepancies could relate to differences between the set-up parameters (flows, membrane area) or the membrane coupon. The same FO membrane was employed, but the large flat-sheet membranes tend to be non-uniform [101]. However,

due to the lack of membrane support in U-tube 2, greater membrane deformation (stretching) is more likely to have contributed to the water permeability augmentation at higher pressures. Furthermore, compaction in U-tube 1 could also have played a role during PAO, possibly occurring when the membrane surface compressed against the support. This deformation type decreases porosity in the support layer, reducing K_m and lowering permeate fluxes, due to the exponential dependence of CP on K_m [94].



Figure 7.13: A comparison between the U-tubes (feed: DI-water; draw solution: 0.5 M NaCl, T = 20 °C).

7.5 Conclusions

In this study continuous and discontinuous PAO was used to enhance FO performance by increasing the driving force with the addition of hydraulic feed pressure. Furthermore an FO transport model, incorporating the hydraulic pressure, was developed to understand the flux behaviour during PAO. The main findings of this study include:

• Increasing water and salt fluxes were found with the increase in continuous PAO for both draw solutions (NaCl and MgCl₂) due to the combination of feed pressure and membrane deformation. NaCl fluxes were higher in all cases, however its advantageous increase in J_{ν} over MgCl₂ declined with the addition of PAO. This decline is attributed to the increasing severity in ICP, which results from the additional feed pressure.

• The increase in experimental fluxes (< 50%) with the increase in continuous PAO was found to be overestimated by the model, especially with regards to the salt leakage. The determination of A

and *B* values in the loose set-up may have caused these discrepancies.

• Discontinuous PAO at 0.4 bar increased J_s/J_v ratios with the increase in frequency, but remained constant during the increase in pulse length (~1 g/L). Due to hydraulic back pressure subsequent to pulse termination, salt fluxes were found to increase faster than the water flux, especially at higher frequencies and lengths.

• Using activated sludge as the feed, continuous PAO experiments displayed a positive effect on the water flux, indicating benefits for a broad range of feeds.

The increase in water fluxes during PAO confirms the potential benefits of this technique, however the prevention of membrane deformation, which increases salt fluxes as well, requires further attention. Future PAO techniques will need to: i) develop more rigid FO membranes; ii) explore the potential adverse effects of fouling in FO with diverse feeds; iii) perform more rigorous testing in larger set-ups; and iv) evaluate the additional energy costs involved.

CHAPTER

A Technical Economic Assessment of Sewer Mining using Forward Osmosis



This chapter is based on:

Lutchmiah K., L. Lauber, B.A. Wols, J.W. Post, L.C. Rietveld, E. R. Cornelissen (to be submitted).

8.1 Introduction

Closed-loop forward osmosis (FO) has been used for many purposes since Sidney Loeb's pioneering efforts with osmotic processes three decades ago [177]. FO in a closed loop differs from osmotic dilution/concentration, in that the draw solution is recycled and reused by the process. The latter process tends to be more feasible and is therefore more often applied in practice. One purpose of FO is to gain a high product quality with the consumption of less energy than that used in current state-of-theart pressure-driven membrane processes, i.e. reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF). Optimisation of the FO process however is still necessary. Major drawbacks include: i) internal concentration polarisation (ICP), ii) reverse solute leakage, iii) the recovery step and iv) insufficient availability of FO membranes.

The recovery step essentially determines the energy consumption of the entire FO process [220] as reconcentration of the draw solution and separation from the product water, in a closed loop, is essential. Altaee et al. [283] found the reconcentration step in an FO-RO desalination system to use 96 – 98% of the total power consumption. If this could be reduced, closed loop FO would become a more feasible technology. The Sewer Mining concept (Chapter 1), aimed at extracting water from wastewater by means of FO-RO, includes an anaerobic digestion unit, which enables energy generation from the concentrated wastewater [26]. This can be used in the energyconsuming recovery system, reducing the overall energy cost.

Two main types of anaerobic digestion processes are investigated within the Sewer Mining concept: wet and dry digestion. In wet anaerobic digestion the dry solids content of the reactor input is approximately 10 - 15%, while 25 - 40% is kept for dry digestion [284]. In the concept the largest wastewater particles are removed using fine sieves. This thesis focuses mainly on the wet digestion stage subsequent to the FO process.

The aim of this chapter is to provide a technical economic model (TEM) of the Sewer Mining concept, which is a fundamental part of any feasibility study. An FO model is proposed for pilot and full-scale FO modules, including both the RO and anaerobic digestion processes in the TEM. This TEM is based on and derived from: 1) A mass transfer model, established upon solution and diffusion transport through the FO membrane [86] and 2) Mass transfer in larger FO membrane installations combined with an RO reconcentration step. By using a mass balance, the mass transfer model in (1) is extended to describe/predict the mass flows in larger scale membrane elements (2). These models are also included here. Finally, the TEM is proposed to describe the economic aspects of a general FO-RO process and more particularly, for the Sewer Mining concept.

8.2 Theory and Model Development

8.2.1 Technical Economic Model

The aim of the TEM is to validate the feasibility of the Sewer Mining concept (Figure 8.1).

From Figure 8.1 a mass balance can be established. The water flow from the FO system (Q_{FO}) needs to equal the water flow from the RO system (Q_{RO}) . Also, the salt flow to reconcentrate the draw solution should equal the sum of the salt flows in both the FO and RO systems.



Figure 8.1: The flow diagram assumed for cost calculations of the TEM, which focus on the FO-RO process connected to the wet digestion (WD).

In order to describe the flows and fluxes, a mass transfer model (section 8.2.1.1) is required. This model also incorporates internal concentration polarisation (ICP) which hinders both water and solute transport. To solve these predictions for larger scale installations a technical model for an FO membrane module (section 8.2.1.2) was further derived.

8.2.1.1 FO mass transfer model

The water flux (J_v) and solute flux (J_s) in FO processes are described by the solution-diffusion (SD) model [84], as elaborated in Chapter 6. ICP decreases the solute concentration within the membrane, which is lower than the concentration in the bulk solution (Figure 8.2). In Figure 8.2, two types of ICP are illustrated: i) dilutive ICP (DICP) and ii) concentrative ICP (CICP). When in the active layer to feed side (AL-FS) orientation, DICP occurs (Figure 8.2a). The water flux is transported from the active layer to the support layer, diluting the solution because of convection. Therefore the effective osmotic pressure $(\Delta \pi)$ diminishes [285]. CICP occurs in the active layer to draw side (AL-DS) orientation (Figure 8.2b). The water flux is transported from the support layer to the active layer causing the solutes against the interior surface of the active layer to become more concentrated.

Using the SD model, the theoretical value of J_{ν} can be established for both membrane orientations [83, 85], i.e. AL-FS (Equation 8.1) and AL-DS (Equation 8.2):

$$J_{\nu} = K_m ln \left(\frac{A\pi_{DS} + B}{A\pi_{FS} + J_{\nu} + B} \right)$$
(8.1)

$$J_{\nu} = K_m ln \left(\frac{A\pi_{DS} - J_{\nu} + B}{A\pi_{FS} + B} \right)$$
(8.2)

The water permeability constant (A) represents the transport of pure water through the membrane. For similar conditions, a larger A value results in a higher water flux. The solute permeability constant (B) is solute-dependent and represents the solute transport through the membrane. A low B value signifies a reduced solute flux. The SD model can be used to construct a mass balance.



Figure 8.2: Illustration of the two types of ICP: a) DICP with AL-FS and b) CICP with AL-DS [85, 89, 275].

Equation 8.1-8.2 use a reflection coefficient (σ) of 1, assuming no ECP effect [17], and the van't Hoff equation: $\pi = \beta R_g T C$ (β is the van't Hoff coefficient). From these equations it is clear that there is no linear relationship between $\Delta \pi$ and J_{ν} , as a result of ICP effects. The mass transfer coefficient (K_m) reflects the ability of a solute to cross the membrane and depends on the diffusion coefficient (D) and the membrane structure parameter (S):

$$K_m = \frac{D}{S} \tag{8.3}$$

S is used to assess the importance of ICP which appears in the support layer [93] and depends on the membrane structure (tortuosity, porosity and membrane thickness). *A*, *B* and *S* can be determined experimentally [79] and are specific for each membrane type [17]. Some values for these parameters found in various membranes are summarised in Table 8.1. A more elaborate overview of these parameters from literature can be found in Chapter 2.

Marshuara	A	В	S
Wiembrane	(x10 ¹² m/s.bar)	(x10 ⁸ m/s)	(μm)
HTI-CTA [this thesis]	1.3	4.1	600
Oasys [286]	13	12	350-400
Nitto Denko [287]	7.4	11	310
NTU HF-TFC [288]	9.6	6.2	550
HTI-TFC [289]	6.9	73	612
HTI-target [289]	>11	< 20	< 600

Table 8.1: A, B and S parameters of various FO membranes taken from the literature.

Furthermore, the draw solution related parameters Dand β are also significant. D represents the ability of a compound to diffuse through the membrane. β is a theoretical value of the dissociation of a compound in water and is important for calculating π of both feed and draw solutions. Both factors are assumed to be constant in the model for all concentrations and temperatures. Table 8.2 displays the *D* and β factors of the draw solutes used in this study.

Additionally, it is assumed that the diffusion rate of the anion is equal to the diffusion rate of the cation [290].

Compounds	$D (x10^{-9} \text{ m}^2/\text{s}) [291]$	β
NaCl	1.23	2
MgCl ₂	1.04	3
CaCl ₂	1.12	3

Table 8.2: Diffusion coefficient and van't Hoff factors of three salts, at 20°C

 J_s can be calculated for both membrane orientations by considering the membrane parameters, the nature of the draw solution and the temperature [79], where R_a is the J_s/J_v ratio (g/L).

$$\frac{J_s}{J_v} = \frac{B}{A\beta R_g T} = R_a \tag{8.4}$$

A numerical resolution of the non-linear equation (Newton-Raphson approach) was used to solve Equation 8.1 and 8.2.

8.2.1.2 Technical model for larger FO systems

The aim of this technical model is to predict the fluxes, concentrations and outlet flows along an FO membrane module, in co-current mode, as depicted in Figure 8.3.

In Figure 8.3 X_{in} , X_{out} , C_{in} and C_{out} are the respective concentrations at the inlet and outlet of the FO module, while Q_{in} , Q_{out} , Φ_{in} and Φ_{out} are the respective flows.



Figure 8.3: Scheme of an FO module defining the flows and concentrations

Due to the concentration gradient, the FO module is divided into small sections. A 0.5 M NaCl draw solution is employed. To describe the flows in a (series of) commercial spiral wound FO module(s), a mass balance was established (Equation 8.5 – 8.8) using the known parameters: X_{in} , Q_{in} , C_{in} , Φ_{in} , A, B, K_m , R_g , T. Unknown parameters are: X_{out} , Q_{out} , C_{out} , Φ_{out} , J_v , J_s , S, A_m , where A_m is the specific membrane area (m²).

Mass balances for the flows and concentrations:

$$\boldsymbol{\Phi}_{aut} = \boldsymbol{\Phi}_{in} + \boldsymbol{J}_{v}\boldsymbol{A}_{m} \tag{8.5}$$

$$Q_{out} = Q_{in} - J_{\nu}A_m \tag{8.6}$$

$$C_{out} \boldsymbol{\Phi}_{out} = C_{in} \boldsymbol{\Phi}_{i_n} - J_s \boldsymbol{A}_m \tag{8.7}$$

$$X_{out} Q_{out} = X_{in} Q_{in} + J_v A_m \tag{8.8}$$

In an FO module water and solute fluxes will vary over the length of the membrane module, as a result of changes in the feed and draw solution concentrations and the feed and draw solution flow rates along the FO membrane. This will lead to a lower driving force at the outlet compared to the inlet of the membrane module. Water flows from both sides of the membrane, impacting the evolution of the water flux across the module. The osmotic pressures on the draw and feed sides can be calculated as follows:

 i) <u>Concentration on draw side from Equation 8.4 to</u> 8.5 and 8.7:

$$C_{out} = \frac{C_{in}\Phi_{in} - J_sA_m}{\Phi_{out}} = \frac{C_{in}\Phi_{in} - J_sA_m}{\Phi_{in} + J_vA_m} = \frac{C_{in}\Phi_{in} - R_aJ_vA_m}{\Phi_{in} + J_vA_m}$$
(8.9)

Assuming a small membrane section of:

$$C_{DS} = 0.5(C_{in} + C_{out}) \tag{8.10}$$

ii) <u>Concentration on feed side from Equation 4, 6</u> and 8:

$$X_{out} = \frac{X_{in}Q_{in} + J_sA_m}{Q_{out}} = \frac{X_{in}Q_{in} + J_sA_m}{Q_{in} - J_vA_m} = \frac{X_{in}Q_{in} + R_aJ_vA_m}{Q_{in} - J_vA_m}$$
(8.11)

Assuming a small membrane section of:

$$X_{FS} = 0.5(X_{in} + X_{out})$$
(8.12)

By combining the van't Hoff equation with Equation 8.9 - 8.10 and Equation 8.11 - 8.12, the following osmotic pressures are derived:

$$\Rightarrow \pi_{DS} = \frac{\beta R_g T}{2} \left(\frac{C_{in} \Phi_{in} - R_a J_v A_m}{\Phi_{in} + J_v A_m} + C_{in} \right)$$

$$(8.13)$$

$$=> \pi_{FS} = \frac{\beta R_g T}{2} \left(\frac{X_{in} Q_{in} + R_a J_v A_m}{Q_{in} - J_v A_m} + X_{in} \right)$$
(8.14)

By incorporating the concentration and dilution effects occurring in the FO membrane module (Equation 8.13 to 8.14) together with Equation 8.4 from the FO mass transfer model, Equation 8.15 (using co-current flow) can be derived:

$$J_{v} = K_{m} \ln \left(\frac{\frac{A\beta R_{g}T}{2} \left(\frac{C_{in} \Phi_{in} - \frac{B}{A\beta RgT} J_{v} A_{m}}{\Phi_{in} + J_{v} A_{m}} + C_{in} \right) + B}{\frac{A\beta R_{g}T}{2} \left(\frac{X_{in} Q_{in} + \frac{B}{A\beta RgT} J_{v} A_{m}}{Q_{in} - J_{v} A_{m}} + X_{in} \right) + J_{v} + B} \right)$$

$$(8.15)$$

Equation 8.15 is numerically solved using a Newton-Raphson approach for a small section of the element. This involves the use of a numerical analysis to solve non-linear equations by approximation. The real value is calculated via an

initial estimate of the results and the tangent line of a function. The following equation is applied:

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$$
(8.16)

Several assumptions were made for the model: i) orientation: AL-FS; ii) co-current flow; iii) for a small membrane section the overall concentration is the average of the concentrations at the beginning and the end; iv) σ = 1. Once the water flux of a small membrane area is known, the section of membrane is solved by using a solving routine in Excel to calculate the water flux variation across the FO module:

$$Q_{in}(i+1) = Q_{out}(i) \text{ and } X_{in}(i+1) = X_{out}(i)$$

(8.17)

$$\Phi_{in}(i+1) = \Phi_{out}(i) \text{ and } C_{in}(i+1) = C_{out}(i)$$

Solving Equation 8.15 for a certain membrane section continues until $J_{\nu} = 0$ or if the desired total membrane area is reached. From the iterative procedure using Equation 8.17 it is possible to calculate (i) the water (and salt) flux gradient over the length of a membrane module and (ii) the total water production over a membrane module. To

calculate the total water production, an integration of the water flux for all membrane sections along the FO membrane is done by numerical approximation of the trapezoidal rule [292]:

$$Q_{FO} = \int_{A_m} J_{\nu} dA_m = 0.5 \sum_{i=0}^{Am} \left(A_{m,i+1} - A_{m,i} \right) \left(J_{\nu,i+1} - J_{\nu,i} \right)$$
(8.18)

From this technical model the water flux was found to decrease along the FO membrane module. The water flow reaches a maximum depending on both flows and concentrations at the inlet. In addition, the outlet flows, concentrations and recovery (φ) along the membrane are calculated. The FO recovery for one section of the membrane is defined by the feed type, i.e. wastewater:

$$\varphi(i) = 1 - \frac{Q_{out}(i)}{Q_{in}(0)}$$
(8.19)

All equations were solved using a Visual Basic Application macro in Excel.

A major drawback of this model is that unrealistic conditions can be set with the inlet flows. Furthermore, for accuracy of a larger membrane area e.g. larger FO plants, several calculation steps are required to calculate the overall water flux, which may time-consuming. To avoid this, the membrane area can be considered as one individual membrane module or divided over a combination of multiple modules.

8.2.2 Cost aspects

Different cost aspects are considered, including FO and RO membrane costs, energy costs, and draw solution consumption costs, to estimate the cost of water production using a Sewer Mining concept. In addition, the amount of salt required to reconcentrate the draw solution (to compensate for draw solution losses due to reverse salt leakage) and the potential energy production of the anaerobic digester incorporated in the Sewer Mining concept are included.

Other costs, such as 1) pre-treatment cost, 2) installation cost, 3) recirculation pumping energy cost, 4) membrane cleaning costs and 5) maintenance costs were provided based on indications from RO or NF plants (Table 8.3). Capital cost (capex) estimations for the pre-treatment processes are dependent on the feed composition and temperature, membrane materials,

and recovery ratio. The capex and operational costs (opex) used in this study can be found in Table 8.3. The sum of the opex C_{op} and capex C_{cap} gives the total cost *C* to produce a ton of product water [220], expressed as:

$$C = C_{op} + C_{cap} \tag{8.20}$$

The cost aspects proposed in this section were considered for the TEM. All equations were solved with Excel in a Visual Basic Application macro.

Parameter	Costs (€/m ³)	Additional information	Reference
Capex			
pre-treatment	< 0.01	• 35 mm screens, 15 year depreciation	[293, 294]
installation	0.20	• 0.88 M€, 100 m ³ /h, 5 year depreciation	[295]
C _{cap}	0.21		
<u>Opex</u>			
pumping (recirculation)	0.003	• Pressure drop per element = 0.1 bar; 6 elements	
membrane cleaning	< 0.03	CIP frequency 1x monthMembrane replacement 1x5 years	[296, 297]
maintenance	0.01	• Based on full-scale NF	[298]
Cop	0.043		
Total Cost (C)	0.253		

Table 8.3: The estimated capex and opex costs for FO.

8.2.2.1 FO and RO membrane cost

Reclaiming Water from Wastewater using Forward Osmosis

The investment cost of both FO and RO membranes depends on the total membrane area and the membrane unit cost (\notin/m^2) . The membrane cost is dependent on the specific membrane cost (ℓ/m^2), J_{ν} , and the flow to treatment (L/h). An FO membrane cost of 33 €/m² [299] and an RO membrane cost of $20 \notin m^2$ [300, 301] were used (Table 8.4). The cost of the RO membrane and the RO energy consumption (mainly pumping energy of RO) were considered. In addition the amount of salt necessary to reconcentrate the draw solution and the potential energy production of the anaerobic digester used in the Sewer Mining concept are calculated. Additional capital costs are assumed to be 37% of the major equipment cost and include auxiliary equipment, land costs, construction, management overheads, contingency costs, building interest etc. Amortised annual capital costs, C_A are calculated using the work of Owen et. al [297].

$$C_A = \frac{i.P}{1 - (1+i)^{-n}}$$
(8.21)

Where P is the capital cost in the original year, i the interest rate and n the amortisation years. The amortisation time of the membranes depends on the

membrane replacement. Membrane replacement is assumed to occur every 5 years and the interest rate is set at 7% for both the FO and RO membranes.

8.2.2.2 RO energy consumption

As mentioned previously, the RO unit can be a major limitation in an FO-RO system, due to the energy consumption. However RO treatment has other limitations too. RO is dependent on the feed water quality. RO requires pre-treatment (especially for suspended solids). With a preceding FO step the high quality of diluted draw solution is ensured. Pretreatment, prior to FO, can although be omitted, because of the dense membrane structure of FO. Furthermore RO is limited with regards to pump pressure [302-304]. The pump on the feed side of the RO needs to exceed the osmotic pressure of the draw solution, which may reach 300 bar (equivalent to 5 M NaCl, the highest concentration used in this study). These concentrations are not treatable with RO; maximum limit of 83 bar for seawater membranes [31]. This process is therefore highly dependent on the dilution step in the FO.

The RO permeate flow needs to equal to the FO flow (Figure 8.3). The water flux of the RO system

should be kept constant, around 30 L/m²h, a typical value in seawater desalination [305]. The necessary RO membrane area ($A_{m,RO}$) was therefore recalculated for a fluctuating recovery (Equation 8.22):

$$A_{m,RO} = \frac{Q_{FO}}{J_{\nu,RO}}$$
(8.22)

In order to calculate the energy cost of the RO pressure pump [304], the pressure on the RO feed side ($P_{F, RO}$ in bar, which neglects pressure losses) was calculated via Equation 8.23, for a small membrane section. The recovery (R) and specific power consumption (E) for RO were then determined via Equation 8.24 [306], where Q_p and Q_f are the permeate and feed flows (m³/h). In Equation 8.25 [283], a pump efficiency $\eta = 0.8$ was assumed (Table 8.4).

$$P_{F,RO} = \frac{J_{\nu,RO}}{A_{RO}} + (\beta R_g T C_{in} - \pi_f)$$
(8.23)

$$R_{RO} = \frac{Q_p}{Q_f} = \frac{Q_{FO}}{\Phi_{out}} = \frac{J_v \cdot A_{m,FO}}{\Phi_{out}}$$
(8.24)

$$E_{RO} = \frac{P_f}{36*\eta * R_{RO}}$$
 (8.25)

*Density (ρ) is assumed to be 1 although saline waters have $\rho > 1$.

*Energy price = 0.0789 €/kWh [307].

8.2.2.3 Draw solution cost

Due to reverse solute diffusion through the FO membrane from the draw to the feed side (Chapter 2 – 4), replenishment of the draw solution to maintain a constant concentration in the draw solution loop is required. By assumption, the leakage at the RO membrane is considered negligible compared to the FO leakage. The draw solution cost is defined by Equation 8.26, where Pr_{NaCl} is the price of the salt = 0.08 \in /kg (Table 8.4).

$$DS_{\rm cost} = \frac{Q_{FO,salt}}{Q_{FO}} \Pr_{NaCl}$$
(8.26)

Reconcentration of the draw solution is also required when impaired/waste waters are used as the feed solution. This is due to the various ions comprising these feeds and can be transported through the FO membrane via bi-directional diffusion [33], "contaminating" the draw solution. These ions may concentrate in the draw solution over time and may require removal. They can be rejected by the RO membrane, however there is a lack of data to estimate the replacement time. This is not considered in the model.

157

8.2.2.4 Anaerobic digestion

The anaerobic digestion stage for sewer mining processes should yield enough energy to compensate for the energy consumption in the reconcentration unit. As mentioned previously, the largest wastewater particles in this process are removed using fine sieves (mesh size 0.35 mm). Fine sieves, used as an alternative pre-treatment for wastewater, have been reported to efficiently remove cellulose fibres from raw sewage [308], which are a large component of the chemical oxygen demand (COD) concentration. Approximately 30 - 35% of this COD (based on Dutch wastewater) can efficiently be used for energy generation [293, 308]. The wastewater moving through the fine sieves towards the feed side of the FO module is then concentrated. At this point 50% of the COD, depending on the FO recovery, can be used for energy generation in the wet digestion stage. A recent study investigated the technical and economic feasibility of the wet digestion with regards to the FO recovery [309]. They found that the FO recovery determined the success of this unit; recovery needs to exceed 90%, otherwise the (wet) bioreactor is oversized and too expensive.

Scaling and/or clogging can also occur at high FO recoveries, furthermore limiting the success of the wet digester. The potential energy which can be generated from wastewater, depending on the recovery, can lie between 2 - 3.5 KWh/m^3 (1 kg COD = 3.9 kWh of energy [168]). In this case an ideal situation is supposed, but many factors, such as the salt concentration or low temperatures, can reduce the biogas production. These are neglected in the model.

8.2.2.5 Input parameters

For the full-scale FO set-up design a production capacity of 100 m³/h was set. The process includes commercially available FO membranes (HTI) of membrane area 100 m² and membrane parameters A= 1.3×10^{-12} m/s.Pa, $B = 4.1 \times 10^{-8}$ m/s, $S = 6 \times 10^{-4}$ m and $K_m = 2.05 \times 10^{-6}$ m/s. The 0.5 M NaCl draw solution has a molecular weight (MW) of 58 g/mol and is employed at a constant temperature of 20 °C. The Dow Filmtech RO membrane has an A = 1.90×10^{-11} m/s.Pa and $B = 1.43 \times 10^{-1}$ m/s. All imputed parameters can be found in Table 8.4.

	Parameter	Value	Unit
Water production capacity		100	m ³ /h
Interest rate		7	%
	A	1.30×10^{-12}	m/s.Pa
	В	4.10x10 ⁻⁸	m/s
	S	6.00 x10 ⁻⁴	m
FO Membrane	K_m	2.05x10 ⁻⁶	m/s
	A_m	100	m^2
	Cost	33	€/m ²
	i	2	-
	R_g	8.3145	Pa.m ³ /mol.K
	MW	58	g/mol
	D	1.23E-09	m ² /s
Draw solution (NaCl)	Т	20	С
	C_{in}	0.5	mol/L
	<i>ф</i> in	12000	L/h
	Cost	0.08	€/kg
	J_s/J_v ratio	0.7	g/L
Food solution	X_{in}	0	mol/L
r eeu solution	Q_{in}	130000	L/h
	A	1.90x10 ⁻¹¹	m/s.Pa
DO monteses	В	1.43×10^{-1}	m/s
KU membrane	Rejection	100	%
	Cost	20	€/m ²

Table 8.4: Input parameters for the technical economic model of the Sewer Mining concept.
Table 8.4 (contd.)

	Parameter	Value	Unit
RO pumps	Water flux	30	L/m ² h
	Pump efficiency	0.8	-
	price per KWh	0.065	€/KWh
Wet Anaerobic Digestion	COD	420	mg/L

8.3 Materials & Methods

8.3.1 Membrane Material

A cellulose triacetate (CTA) FO-type membrane was used (HTI, Albany, OR). The asymmetric membrane was used in only one of the two possible orientations, namely AL-FS.

8.3.2 Set-ups

FO experiments were carried out in a lab-scale Utube set-up similar to that mentioned in previous work [26, 41]. Furthermore, some of the theoretical calculations are based on the dimensions of the labscale cross-flow set-up mentioned in Chapter 6 and on an existing FO pilot plant design (Triqua B.V, Wageningen) constructed specifically for this thesis (Appendix B).

8.3.3 Feed and Draw solutions

Deionised (DI) water (Milli-Q, Millipore) from an RO installation (Home Waterbehandeling BV, the Netherlands) was used as the feed solution and solvent in all cases. NaCl (J.T. Baker, the Netherlands), MgCl₂ (Merck, Germany) and CaCl₂ (Boom, the Netherlands) from 0.5 - 4.5 M were tested as a draw solution in the FO U-tube system and corrected to 20 °C as mentioned in [42].

8.4 Results & Discussion

8.4.1 Verification of the FO mass transfer model

In Figure 8.4 the FO mass transfer model was compared to the laboratory scale U-tube results from 0 - 4.5 M obtained for NaCl (Chapter 3), MgCl₂



(Chapter 5) and CaCl₂. Water and salt fluxes for the different draw solutions at increasing concentrations are shown as a function of osmotic pressure. The model and experimental data results are derived from Equation 8.1, using parameters from Table 8.2 and incorporating the membrane parameters as mentioned in Table 8.4.



Figure 8.4: Comparison of both theoretical and experimental water and salt fluxes using (a) NaCl (b) MgCl₂ and (c) CaCl₂ as draw solutions. In Figure 8.4a-c, the model predictions fit well with the water fluxes, increasing with an increase in osmotic pressure. Therefore the assumptions and parameters used at this point seem to be accurate. However, the modelled water fluxes for magnesium chloride (Figure 8.4b) deviated more from the experimental data per increment in osmotic pressure. CaCl₂ was also slightly overestimated by the model. These deviances may be due to the fact that divalent compounds experience more severe ICP than monovalent compounds [114], which is not considered by the model.

The experimentally obtained salt fluxes were also less accurately predicted by the model for the divalent salts, especially for MgCl₂. In the case of CaCl₂, this only began from osmotic pressures of 150 bar. Again this can be attributed to the greater ICP in comparison to monovalent compounds, however the degree of severity differs for each solute. From the experimental results it was found that the J_s/J_v ratios remained relatively constant for NaCl and MgCl₂ with the increase in osmotic pressure, however for CaCl₂ the ratio changed at higher concentrations. Phillip et al. [101] reported the ratio to be independent of the solute concentration and should therefore remain constant. However for $CaCl_2$ the difference may be due to changes in the membrane structure at the higher salt concentrations. It is also hypothesized that the discrepancy between the theoretical and experimental results at high osmotic pressures is related to the diffusion coefficient which changes with the concentration [88].

8.4.2 Comparing the technical and mass transfer models

In Figure 8.5 the results of the technical model for large FO installations based on the dimensions of the existing cross-flow FO cell, as described in Chapter 6, were compared to the results of the FO mass transfer model from 3.1 in terms of water flux and osmotic pressure. The imputed parameters can be found in Table 8.5. The ICP model is the non-linear equation with which water fluxes can be calculated, using known inlet/outlet osmotic pressures. The FO mass transfer model uses the ICP model to calculate the water fluxes along the FO membrane. In this way the membrane area can be modified.



Figure 8.5: A comparison of the water fluxes between the FO mass transfer model and the ICP model using a) NaCl, b) MgCl₂, and c) CaCl₂ as draw solutions. The percentage difference between the models can be seen in (d)

In Figure 8.5a an identical simulation from both models is observed for the calculated water fluxes using NaCl. In Figure 8.5b - d, the water fluxes for both MgCl₂ and CaCl₂ are slightly overestimated by the technical model compared to the FO mass

transfer model. The exact reason for this difference is unclear, but only one common denominator differentiates these two divalent draw solutes from NaCl: $\beta = 3$. 8

Parameter	Name	Imputed value	unit	
FO membrane	A_m section	0.06	m ²	
Feed Solution	X_{in}	0	mol/m ³	
	Q_{in}	2.33x10 ⁻³	m ³ /s	
Draw Solution	C_{in}	500	mol/m ³	
	$arPsi_{in}$	2.17 x10 ⁻⁴	m ³ /s	
	Cost	8 x10 ⁻⁵	€/g	

Table 8.5: Parameters used for the larger scale installation

8.4.3 The technical economic model

The aim of this section is to predict the most efficient design of the Sewer Mining concept to produce 100 m³/h of water using the TEM presented in section 8.8.2.1. In this section the term recovery is defined as the recovery compared to that in the feed solution of the FO step, calculated via Equation 8.24. Therefore, for a specific set-up the recovery will increase with the FO membrane area for as long as $J_{\nu} \neq 0$. The selection of the input parameters is a key step to ensuring realistic results. One of the major problems is setting realistic flow rates at the inlet of the FO membrane for both the feed and draw solution channels. Table 8.6 illustrates different feed and draw flows of 4" and 8" FO elements. The membrane rejection layer is in contact with the feed solution pumped through the side ports. For FO applications, the draw solution is typically fed to/from the end ports.

Accordingly, subsection 8.4.3.1 is dedicated to TEM calculations using input parameters based on the existing FO pilot plant design. The plant uses a fixed flow rate ratio between the feed and draw solutions. Subsection 8.4.3.2 presents the influence of the flow rate ratio on cost estimates as a function of the recovery, while subsection 8.4.3.3 determines cost estimates of a sewer mining installation using different types of draw solutions and draw solution concentrations.

OsMem™ Number	Effective Membrane Area (m ²)	Water flow via side ports (L/min)	Water flow via end ports (L/min)*
8040FO-MS-P	14.4	140	13
8040FO-CS-P	9.0	520	8.8
4040FO-MS	3.2	30	2.9
4040FO-CS	1.5	90	1.5

Table 8.6: FO 4" and 8" elements for pumped housings: water flows for a pressure drop of 35 kPa

* average pressure drop of 140 kPa through side ports

MS – Medium Spacer = 1.14 mm diamond-type polypropylene feed spacer

CS – Corrugated Spacer = 2.5 mm polystyrene chevron design flow path

8.4.3.1 Model calculations based on the FO pilot plant

The three units: FO, RO and anaerobic digestion are described in this section. In Figure 8.6a, the water flux at a 0.4% recovery was 5.30 L/m²h and the salt flux $3.74 \text{ g/m}^2\text{h}$. Due to the fact that the draw solution concentration and the employed membrane remained the same throughout this study, the results were comparable to the FO mass transfer model and the experimental data presented in section 8.4.1. The fluxes decreased as the recovery increased due to the combined effects of the draw solution dilution and dewatering of the feed solution, as well as reverse solute diffusion, which all reduce the bulk osmotic pressure.

Furthermore, the recovery was found to reach only 75% for the selected draw solution, which is not feasible for maintaining the wet digester(s). In Figure 8.6b, both flows increased linearly with the FO recovery. When the required production rate of 100 m³/h was reached, a maximum recovery of 75% was attained from the model. At this high recovery the salt flow was found to be very high ~70 kg/h which implies the necessity of a cheap solute and/or optimisation of the FO membrane to reduce reverse solute transport altogether.



Figure 8.6: (a) Fluxes and (b) flows for larger scale FO units as a function of FO system recovery.



Figure 8.7: Illustration of (a) the osmotic pressure at the RO feed and (b) COD at the outlet of the FO membrane as a function of FO recovery.

In Figure 8.7a, a rapid decline in the feed osmotic pressure of RO as a function of the FO system recovery is displayed. The osmotic pressure at 0.2% recovery is approximately 24 bar, while at 20% recovery the osmotic pressure dropped to approximately 7.3 bar. This was due to the lower draw solution flow compared to the feed flow. At the required production rate, reaching > 60% recovery, the feed entering the RO has an osmotic pressure of approximately 3 bar. The low osmotic pressures are significant because they indicate an increase in RO pumping (energy cost) to achieve the osmotic pressure required for the draw solution in the FO. The low osmotic pressures are significant because they indicate a necessary increase in RO pumping (energy cost) to achieve the osmotic pressure required for the draw solution in FO.

In Figure 8.7b, the COD concentration at the outlet of the FO membrane slowly increased from 0 -50%, followed by a rapid exponential increase. However, the recovery does not reach the required goal of 4 - 5 g/L necessary for the feasibility of the wet digestion. The final COD concentration at 0.5 M NaCl was limited to 1.7 g/L, which at these low concentrations is not feasible.



Figure 8.8: The incurred cost of the Sewer Mining concept as a function of FO system recovery: (a) in ϵ/m^3 and (b) in price percentage.

Figure 8.8 illustrates that the cost of the draw solution and the energy generated by the digester are shown to be independent of the FO recovery. These remain constant at 0.06 and 0.22 €/m^3 respectively. The price per m³ remains constant because the ratio of salt leakage is constant, e.g. for 1 L of water produced 0.7 g of salt is lost to the feed side. Therefore, even if the amount of salt increases with the water production, the same amount of salt is lost for each L (or m³) of water produced.

For the concentrations investigated in this study, E (kWh/m³) of the RO pump decreased with the increase in FO process recovery, which is in agreement with the results reported in previous studies [283]. The cost of the energy consumption of the RO unit becomes negligible quickly, due to the simultaneous increase in water production (m³). After 34% recovery, the cost of the FO membrane makes up between > 70% of the total cost. The cost of the FO membrane increases with the recovery due to the decrease in the water flux; each section of membrane became less efficient as the water flux decreases. With this configuration the lowest cost was found at 6% recovery with 0.16 \notin /m³, but the required production of 100 m³/h was not achieved (Figure 8.6b). Furthermore, at this low recovery anaerobic digestion cannot be efficiently used. The cost, excluding the digestion unit, would be 0.38 ϵ/m^3 . The dominating factor is therefore the price of the FO membrane, which is one of the major costs for the Sewer Mining concept. At a water production capacity of 100 m³/h, the cost 0.9 ϵ/m^3 , excluding capex and opex costs, seems economically viable when compared to full-scale water treatment (seawater desalination < 1 ϵ/m^3).

In this simulation it was observed that the FO membrane and the flows of both the feed and draw solutions were major factors affecting the price of the produced water. In this design the water produced is expensive, mostly due to the cost of the FO membrane. Alternative ways to enhance the setup efficiency can be carried out by either varying i) the draw solution concentration or ii) the flows.

Varying the draw solution concentration would allow for the selection of the most optimal driving force in the FO system, to attain a good water flux, while limiting the energy consumption of the RO recovery system. The cost of the reconcentration will however increase with the increase in the draw solution concentration. The problem with this type of variation is that the goal of 100 m^3 /h was difficult to attain with the model. For this reason a variation of the flows was further explored.

8.4.3.1.1 Variation of the flows

As stated in previous sections the wet anaerobic digester is only feasible at high FO recoveries (> 90%), which reduce the volume. Using the operational conditions stated in section 8.4.3.1 it is

not possible to reach a 90% recovery. Therefore other flow rate conditions were calculated. By changing the ratio of the flows an increase in the FO recovery can be attempted. The change in the flow ratio is possible for the calculated TEM, but might have repercussions on the physical limitations of FO membrane modules (Table 8.6). All operational conditions, except the draw and feed flows, remained the same. The water flow production was maintained at 100 m³/h \pm 2% for comparability.





Figure 8.9: The production cost in a) and b) as a function of the FO system recovery, c) the total cost and water flow as a function of the Q_{in}/Φ_{in} ratio.

In Figure 8.9a, the cost of the produced water was determined to be around 0.4 C/m^3 from 70 - 90% recovery. The cost declined linearly thereafter reaching 0.29 C/m^3 at 95% recovery. Initially in Figure 8.9b, all the costs (%) remained constant up to 90% recovery, thereafter an increase, except for the FO membrane cost, was observed. The cost of the FO membrane is most significant as it remains above 65%, and predominantly around 75%.

In Figure 8.9c, a smaller Q_{in}/Φ_{in} flow ratio (< 2) is seen to lower the cost of the water production. Between a flow ratio of 1 – 2, the cost was found to rise until 0.4 ϵ/m^3 and thereafter stabilised, despite the ratio increase. In Figure 8.9, the water flow maintained the 100 m³/h ± 2% production throughout the ratio increase. From the results it appears that a ratio of 2 is the threshold; above this value the cost is independent of the ratio. In this scenario the operational conditions seem more efficient and more cost-effective. Table 8.7, displays the total treatment cost of the process including the capex and opex costs.

<u>Cost (€/m³)</u>	Parameter	
0.40	Water production	
0.25	Capex+Opex Costs	
0.65	Total Treatment Cost	

Table 8.7: Total treatment cost of the process.

8.5 Conclusion

In this study a technical economic model was developed to describe the economic aspects of a general FO-RO process and more particularly, for sewer mining applications. The TEM was based on the FO mass transfer model (Chapter 3) and a mass transfer model for larger FO membrane installations combined with RO. The following observations were found:

- The flow rates and draw solution concentration severely affected the recovery achievable and the cost of the water production.
- The COD concentration at the outlet of the FO membrane can technically achieve more than 5 g/L, which allows for the use of small anaerobic digesters.

8

- Reclaiming Water from Wastewater using Forward Osmosis
- Using input parameters based on an actual FO pilot plant, the water production was found to be on par or lower than current treatment processes; however the price of the FO membrane is the costly factor.
- Simulations with different feed and draw flows displayed a threshold of 2 for the Q_{in}/Φ_{in} ratio. When compared with the initially determined results, these operational conditions were found to be more efficient and cost-effective.

Research is still required with regards to the FO membrane module design. Moreover, membrane clogging at high recoveries, required frequency of draw solution replenishment, biogas yield (in thermal and electrical energy) and feasibility of the wet digestion need further investigation.

Furthermore each model presented encountered its own set of limitations:

- In the FO mass transfer model the effect of the temperature on the water flux was not realistic and was therefore underestimated by the model; the J_s/J_y ratio as well.
- In the technical model, the results are not comparable with the FO mass transfer model if a draw solution other than NaCl is used and the

biogas production is based on ideal conditions, without considering inhibitory effects.

 Furthermore, potential fouling affects and cleaning costs of the RO membrane were neglected.

Despite the restrictions of the TEM model, the Sewer Mining concept still seems economically feasible, especially if FO membranes are optimised and prices decrease in the future. Additionally, these predictions should be validated by future pilot-scale FO studies.



9.1 Main conclusion

In this concluding chapter, the main issues of this thesis are addressed, as defined in Chapter 1. The combination of forward osmosis (FO) studies using various feeds, draw solutes and scales together with modelling validation and the combination of FO with other treatment processes, has contributed towards filling the knowledge gaps of FO for application in sewer mining concepts. These results have all led to the main conclusion of this thesis:

Forward Osmosis in sewer mining applications is a technically viable solution for the potential treatment of wastewater. The choice of draw solution and reconcentration unit, as well as the membrane and FO design are vital for producing an optimal driving force, costeffective re-concentration and a high biogas yield. Current vulnerability of the process lies in the potential extent of fouling and the cost of FO membranes. This conclusion underlines the prospectiveness of FO in sewer mining applications for full-scale feasibility. Eventually FO membrane costs will decrease, as has been seen with the development of other membranes (e.g. reverse osmosis (RO)), however for now it factors largely in the feasibility of the system.

The following sections reflect upon the findings of each individual chapter from a broader perspective to support the main conclusion of this thesis. Additionally, the future outlook of FO as a wastewater treatment technology is elaborated upon, while recommendations and suggestions for future research are presented.

9.2 Draw solutions for FO-wastewater applications

Being a green, energy-neutral concept, FO in sewer mining is concluded to be a potential treatment for wastewater. Reverse solute leakage in sewer mining applications remains an important issue due to the loss in driving force or increased consumption of added draw solution. For FO-wastewater applications it depends largely on reconcentration of the draw solution. While the ideal draw solution is perhaps still out there, zwitterions (Chapter 3) and EDTA (Chapter 4) come very close to fulfilling the criteria of draw solutes for sewer mining applications (Chapter 2); their initial cost price, pH sensitivity and potential toxicity effects being limiting factors. Better understanding of the mechanisms of these solutes at the methane production stage will further promote the use of this technology in existing and new applications of water and wastewater treatment.

9.3 Membrane Water Permeability

FO membranes are able to recover water from raw wastewater (Chapter 5), but the overall water permeability, which is already low in comparison to pressure-driven membrane processes, is hindered further by internal concentration polarisation (ICP) and fouling. Membrane optimisation therefore remains a key player in FO development and so does selection of the appropriate membrane material, i.e. cellulose triacetate (CTA) vs. thin-film composite (TFC) FO membranes. Essentially, thinner, more porous and less tortuous support layers in FO membranes perform better in FO processes. In this way, smaller membrane structure parameter (S) values will exist, reducing the resistance to mass transfer and producing higher water fluxes, while simultaneously reducing the ICP bottleneck. By achieving greater water permeabilities, FO can become a more cost-competitive technology.

FO permeability can be also be increased by the use of PAO (Chapter 7). However, from the study in Chapter 7 it was concluded that the future of PAO depends heavily on the development of more rigid, optimised membranes and support designs, i.e. ceramic membranes may be a possibility. In the case of wastewater treatment this is an important consideration as fouling is more likely to occur during an increase in the driving force, whether it be via PAO or an increase in the draw solution concentration.

9.4 The Impact of Fouling

Biopolymers, and more specifically, polysaccharides were found to contribute significantly to fouling on

the FO membrane surface when using raw wastewater (Chapter 6). This is similar for RO and other pressure-driven membrane processes, however to a lesser extent, due to the absence of pressure. Polysaccharides directly foul membranes, thus facilitating the development of a fouling layer on the membranes. Pre-treatment methods to remove these polysaccharides prior to the FO stage are available, i.e. coagulation/flocculation. ultrafiltration. flotation etc., and may be considered, though should be avoided unless absolutely necessary. The inclusion of a pre-treatment process would make FO less feasible and perhaps redundant. Cleaning methods should also be further investigated in order to remove any foulant remnants on the membrane surface subsequent to FO treatment. Simultaneously, minimal energy consumption needs to be achieved by both the pre-treatment and cleaning processes.

On full-scale, accumulated fouling/biofouling may play a greater role in the water flux performance, due to the length of operation. Moreover when dealing with wastewater digestate reuse, nutrient recovery and energy harvesting need to be deliberated to make the most out of the wastewater resource.

9.5 Feasibility Studies

When regarding the feasibility of a study, the cost of water production is essentially determined by its capital, operating and maintenance costs. The technical economic model (TEM) (Chapter 8) was developed to assess the technical and economic aspects of a general FO-RO process and more particularly for the Sewer Mining concept (Chapter 1). A full-scale FO installation in wastewater treatment and water reclamation is technically feasible, however it is economically limited; the FO membrane cost is currently a bottleneck. Over the next few years this is expected to decrease in price, as an increase in sale and production of FO membranes is anticipated (comparable to the RO trend). This would make such sewer mining processes become more economically and industrially practical.

Furthermore, energy produced from the organic content in wastewater can be a substantial compensation for the energy consumption of the process. An energy self-sufficient process is attainable, but for now membrane development plays a dominant role in the feasibility factor.

9.6 Future Outlook

This thesis has shown the potential of FO in sewer mining applications to achieve treatment of wastewater by facilitating the extraction of water and energy. However, the future of FO-wastewater applications still has a long way to go before reaching full-scale, commercial potential; both in R&D and with regards to public perception. For direct reuse of wastewater, transparency to transform current public opinion is, first and foremost, essential. Wastewater is a rich source of organic matter and in these water-stressed times, should be seen and employed as a resource, not wasted.

Sewer mining as a cradle to cradle concept is very flexible, displaying potential use not only in centralised water and wastewater management systems, but particularly in small-scale decentralised systems [182], e.g. decentralised sanitation for individual households or existing communities, either independent from or as part of a larger system, which include informal settlements. Decentralised sewer mining can relieve overtaxed wastewater systems, trim water and wastewater infrastructure costs, reduce energy and chemical use, and save drinking water for activities that really need drinking-quality water [310]. To implement the acquisition, treatment and reuse of the wastewater at one location, the FO membranes certainly require rigidness, the water quality must be controlled, the appropriate scale for the application must be identified and an investigation of the most suitable pipe systems must be carried out. This is very significant when dealing with developing countries as well. Besides the appropriateness of the technology, it is also very important that social and cultural circumstances be researched, respected and regarded. The ultimate goal is to close the gap between our growing water demands and the Earth's finite supply.

Appendices

A. Appendix



Figure 1: U-tube 1 showing the membrane holder in more detail: a) the mesh support and b) the plastic ring between the mesh and membrane.

Appendices

B. Appendix



Figure 1: The FO pilot plant.



Figure 2: The four FO membrane modules in the pilot plant.



Figure 4: The flow diagram of the FO pilot plant system.

Bibliography

[1] UN, Managing Water under Uncertainty and Risk, in: The United Nations World Water Development Report 2012.

[2] J.-J. Qin, K.A. Kekre, G. Tao, M.H. Oo, M.N. Wai, T.C. Lee, B. Viswanath, H. Seah, New option of MBR-RO process for production of NEWater from domestic sewage, Journal of Membrane Science, 272 (2006) 70-77.

[3] M.F. Hamoda, I. Al-Ghusain, N.Z. Al-Mutairi, Sand filtration of wastewater for tertiary treatment and water reuse, Desalination, 164 (2004) 203-211.

[4] I. Oller, S. Malato, J.A. Sánchez-Pérez, Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination--A review, Science of The Total Environment, In Press, Corrected Proof (2010).

[5] J. Zukus, The Use of Ion Exchange Resins in a Forward Osmosis Desalination System for the Softening of Feed Water, Journal of the U.S. SJWP: For the Future, From the Future, 3 (2008) 102-115.

[6] I. Alsvik, M.-B. Hägg, Pressure Retarded Osmosis and Forward Osmosis Membranes: Materials and Methods, Polymers, 5 (2013) 303-327.

[7] J.-J. Qin, W.C.L. Lay, K.A. Kekre, Recent developments and future challenges of forward osmosis: A review, Desalination and Water Treatment, 1 (2012).

[8] Modern Water commissions FO plant in Oman, Filtration + Separation, 49 (2012) 7.

[9] ScienceDirect, in, Elsevier B.V.

[10] ACS, in, American Chemical Society.

[11] N.A. Thompson, P.G. Nicoll, Forward Osmosis Desalination: A commercial reality, in: IDA World

Congress, Perth Convention and Exhibition Centre (PCEC), Perth, Western Australia, 2011.

[12] C. Klaysom, T.Y. Cath, T. Depuydt, I.F.J. Vankelecom, Forward and pressure retarded osmosis: potential solutions for global challenges in energy and water supply, Chemical Society Reviews, 42 (2013) 6959-6989.

[13] B.D. Coday, P. Xu, E.G. Beaudry, J. Herron, K. Lampi, N.T. Hancock, T.Y. Cath, The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams, Desalination, 333 (2014) 23-35.

[14] R.J. York, R.S. Thiel, E.G. Beaudry, Full-scale experience of direct osmosis concentration applied to leachate management, in: Sardinia '99 Seventh International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Sardinia, Italy, 1999.

[15] T.Y. Cath, S. Gormly, E.G. Beaudry, M.T. Flynn, V.D. Adams, A.E. Childress, Membrane contactor processes for wastewater reclamation in space: Part I. Direct osmotic concentration as pretreatment for reverse osmosis, Journal of Membrane Science, 257 (2005a) 85-98.

[16] J.L. Cartinella, T.Y. Cath, M.T. Flynn, G.C. Miller, K.W. Hunter, A.E. Childress, Removal of natural steroid hormones from wastewater using membrane contactor processes, Environmental Science and Technology, 40 (2006) 7381-7386.

[17] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: Principles, applications, and recent developments, Journal of Membrane Science, 281 (2006) 70-87.

[18] Y. Fang, L. Bian, Q. Bi, Q. Li, X. Wang, Evaluation of the pore size distribution of a forward osmosis membrane in three different ways, Journal of Membrane Science, 454 (2014) 390-397.

[19] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, Comparison of the removal of hydrophobic trace organic contaminants by forward osmosis and reverse osmosis, Water Research, 46 (2012) 2683-2692.

[20] I. Sutzkover-Gutman, D. Hasson, Feed water pretreatment for desalination plants, Desalination, 264 (2010) 289-296.

[21] E.S. Kim, Y. Liu, M.G. El-Din, The effects of pretreatment on nanofiltration and reverse osmosis membrane filtration for desalination of oil sands process-affected water, Separation and Purification Technology, 81 (2011) 418-428.

[22] S. Atkinson, HTI delivers life-saving water filters to aid flood victims in Kenya, Membrane Technology, 2012 (2012) 2.

[23] J. Schrier, Ethanol concentration by forward osmosis with solar-regenerated draw solution, Solar Energy, 86 (2012) 1351-1358.

[24] A. Achilli, T.Y. Cath, E.A. Marchand, A.E. Childress, The forward osmosis membrane bioreactor: A low fouling alternative to MBR processes, Desalination, 238 (2009) 10-21.

[25] S. Lee, C. Boo, M. Elimelech, S. Hong, Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO), Journal of Membrane Science, 365 (2010) 34-39.

[26] K. Lutchmiah, E.R. Cornelissen, D.J.H. Harmsen, J.W. Post, K. Lampi, H. Ramaekers, L.C. Rietveld, K. Roest, Water recovery from sewage using forward

osmosis, Water Science & Technology, 64 (2011) 1443-1449.

[27] L.A. Hoover, W.A. Phillip, A. Tiraferri, N.Y. Yip, M. Elimelech, Forward with Osmosis: Emerging Applications for Greater Sustainability, Environmental Science & Technology, 45 (2011) 9824-9830.

[28] K.B. Petrotos, H.N. Lazarides, Osmotic concentration of liquid foods, Journal of Food Engineering, 49 (2001) 201-206.

[29] H. Zhu, L. Zhang, X. Wen, X. Huang, Feasibility of applying forward osmosis to the simultaneous thickening, digestion, and direct dewatering of waste activated sludge, Bioresource Technology, 113 (2012) 207-213.

[30] T.-S. Chung, S. Zhang, K.Y. Wang, J. Su, M.M. Ling, Forward osmosis processes: Yesterday, today and tomorrow, Desalination, 287 (2012) 78-81.

[31] Hydranautics, Element Spec Sheets, in, 2014.

[32] A. Seppälä, M.J. Lampinen, On the non-linearity of osmotic flow, Experimental Thermal and Fluid Science, 28 (2004) 283-296.

[33] N.T. Hancock, T.Y. Cath, Solute coupled diffusion in osmotically driven membrane processes, Environmental Science and Technology, 43 (2009) 6769-6775.

[34] A. D'Haese, P. Le-Clech, S. Van Nevel, K. Verbeken, E.R. Cornelissen, S.J. Khan, A.R.D. Verliefde, Trace organic solutes in closed-loop forward osmosis applications: Influence of membrane fouling and modeling of solute build-up, Water Research, 47 (2013) 5232-5244.

[35] F. Votta, S.M. Barnett, D.K. Anderson, Concentration of industrial waste by direct osmosis: completion report, in, Providence, RI, 1974.

[36] D.K. Anderson, Concentration of Dilute Industrial Wastes by Direct Osmosis, in, University of Rhode Island, Providence, 1977.

[37] T.Y. Cath, D. Adams, A.E. Childress, Membrane contactor processes for wastewater reclamation in space: II. Combined direct osmosis, osmotic distillation, and membrane distillation for treatment of metabolic wastewater, Journal of Membrane Science, 257 (2005b) 111-119.

[38] E.G. Beaudry, J.R. Herron, Direct osmosis for concentrating wastewater, in: 27th International Conference on Environmental Systems, Lake Tahoe, NV, 1997.

[39] J. Su, T.-S. Chung, B.J. Helmer, J.S. de Wit, Enhanced double-skinned FO membranes with inner dense layer for wastewater treatment and macromolecule recycle using Sucrose as draw solute, Journal of Membrane Science, 396 (2012) 92-100.

[40] R.W. Holloway, A.E. Childress, K.E. Dennett, T.Y. Cath, Forward osmosis for concentration of anaerobic digester centrate, Water Research, 41 (2007) 4005-4014.

[41] E.R. Cornelissen, D. Harmsen, K.F. de Korte, C.J. Ruiken, J.J. Qin, H. Oo, L.P. Wessels, Membrane fouling and process performance of forward osmosis membranes on activated sludge, Journal of Membrane Science, 319 (2008) 158-168.

[42] E.R. Cornelissen, D. Harmsen, E.F. Beerendonk, J.J. Qin, H. Oo, K.F.d. Korte, J.W.M.N. Kappelhof, The innovative Osmotic Membrane Bioreactor (OMBR) for reuse of wastewater, Water Science & Technology, 63 (2011) 1557-1565.

[43] R.R. Said, Forward Osmosis Process for the Treatment of Wastewater from Textile Industries, in:

Chemical Engineering, The College Of Engineering – University Of Baghdad, Baghdad, 2011.

[44] F. Biesboer, Rioleringoogst, in: De Ingenieur, The Netherlands, 2011, pp. 1.

[45] T.C. Zhang, R.Y. Surampalli, S. Vigneswaran, R.D. Tyagi, S.L. Ong, C.M. Kao, Membrane Technology and Environmental Application, ASCE Publications, 2012.

[46] R.E. Kravath, J.A. Davis, Desalination of sea water by direct osmosis, Desalination, 16 (1975) 151-155.

[47] S. Loeb, The Loeb-Sourirajan Membrane: How It Came About, in: Synthetic Membranes, American Chemical Society, 1981, pp. 1-9.

[48] J.R. McCutcheon, M. Elimelech, Influence of membrane support layer hydrophobicity on water flux in osmotically driven membrane processes, Journal of Membrane Science, 318 (2008) 458-466.

[49] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, A novel ammonia-carbon dioxide forward (direct) osmosis desalination process, Desalination, 174 (2005) 1-11.

[50] B. Mi, M. Elimelech, Chemical and physical aspects of organic fouling of forward osmosis membranes, Journal of Membrane Science, 320 (2008) 292-302.

[51] J. Wang, D.S. Dlamini, A.K. Mishra, M.T.M. Pendergast, M.C.Y. Wong, B.B. Mamba, V. Freger, A.R.D. Verliefde, E.M.V. Hoek, A critical review of transport through osmotic membranes, Journal of Membrane Science, 454 (2014) 516-537.

[52] N. Lior, G. Amy, A.Z. Barak, A. Chakraborty, A.E. Nashar, Y. El-Sayed, M.D. Kennedy, A. Kumano, S. Lattemann, Advances in Water Desalination, Volume 1, John Wiley & Sons Inc., Hoboken, New Jersey, 2013.

[53] M. Mulder, Basic Principles of Membrane Technology, 2nd ed, 2 ed., Kluwer Academic Publishers, 1996.

[54] Whatman, Cellulose Acetate Membranes, in, 2007.

[55] HTI starts producing thin-film composite FO membrane, Membrane Technology, 2012 (2012) 5-6.

[56] T. Thorsen, Concentration polarisation by natural organic matter (NOM) in NF and UF, Journal of Membrane Science, 233 (2004) 79-91.

[57] Water Desalination Report: EDS Barcelona Special, in: T. Pankratz (Ed.), 2012.

[58] C.-Y. Chen, K.-L. Yeh, Y.-C. Lo, H.-M. Wang, J.-S. Chang, Engineering strategies for the enhanced photo-H2 production using effluents of dark fermentation processes as substrate, International Journal of Hydrogen Energy, 35 (2010) 13356-13364.

[59] S. Zhang, K.Y. Wang, T.S. Chung, H. Chen, Y.C. Jean, G. Amy, Well-constructed cellulose acetate membranes for forward osmosis: Minimized internal concentration polarization with an ultra-thin selective layer, Journal of Membrane Science, 360 (2010) 522-535.

[60] M. Sairam, E. Sereewatthanawut, K. Li, A. Bismarck, A.G. Livingston, Method for the preparation of cellulose acetate flat sheet composite membranes for forward osmosis—Desalination using MgSO4 draw solution, Desalination, 273 (2011) 299-307.

[61] K.Y. Wang, R.C. Ong, T.S. Chung, Double-skinned forward osmosis membranes for reducing internal concentration polarization within the porous sublayer, Industrial and Engineering Chemistry Research, 49 (2010) 4824-4831.

[62] K.Y. Wang, Q. Yang, T.S. Chung, R. Rajagopalan, Enhanced forward osmosis from chemically modified polybenzimidazole (PBI) nanofiltration hollow fiber membranes with a thin wall, Chemical Engineering Science, 64 (2009) 1577-1584.

[63] L. Setiawan, R. Wang, K. Li, A.G. Fane, Fabrication of novel poly(amide-imide) forward osmosis hollow fiber membranes with a positively charged nanofiltration-like selective layer, Journal of Membrane Science, 369 (2011) 196-205.

[64] C. Qiu, L. Setiawan, R. Wang, C.Y. Tang, A.G. Fane, High performance flat sheet forward osmosis membrane with an NF-like selective layer on a woven fabric embedded substrate, Desalination, 287 (2012) 266-270.

[65] Y. Yu, S. Seo, I.-C. Kim, S. Lee, Nanoporous polyethersulfone (PES) membrane with enhanced flux applied in forward osmosis process, Journal of Membrane Science, 375 (2011) 63-68.

[66] A. Tiraferri, N.Y. Yip, W.A. Phillip, J.D. Schiffman, M. Elimelech, Relating performance of thin-film composite forward osmosis membranes to support layer formation and structure, Journal of Membrane Science, 367 (2011) 340-352.

[67] N. Yin Yip, A. Tiraferri, W.A. Phillip, J.D. Schiffman, M. Elimelech, High performance thin-film composite forward osmosis membrane, Environmental Science and Technology, 44 (2010) 3812-3818.

[68] J. Wei, C. Qiu, C.Y. Tang, R. Wang, A.G. Fane, Synthesis and characterization of flat-sheet thin film composite forward osmosis membranes, Journal of Membrane Science, 372 (2011) 292-302.

[69] N.-N. Bui, M.L. Lind, E.M.V. Hoek, J.R. McCutcheon, Electrospun nanofiber supported thin film composite membranes for engineered osmosis, Journal of Membrane Science, 385–386 (2011) 10-19.

[70] N.N. Bui, J.R. McCutcheon, Hydrophilic nanofibers as new supports for thin film composite membranes for

engineered osmosis, Environmental Science and Technology, 47 (2013) 1761-1769.

[71] C. Qiu, S. Qi, C.Y. Tang, Synthesis of high flux forward osmosis membranes by chemically crosslinked layer-by-layer polyelectrolytes, Journal of Membrane Science, 381 (2011) 74-80.

[72] J.T. Arena, B. McCloskey, B.D. Freeman, J.R. McCutcheon, Surface modification of thin film composite membrane support layers with polydopamine: Enabling use of reverse osmosis membranes in pressure retarded osmosis, Journal of Membrane Science, 375 (2011) 55-62.

[73] S. Zhang, F. Fu, T.-S. Chung, Substrate modifications and alcohol treatment on thin film composite membranes for osmotic power, Chemical Engineering Science, 87 (2013) 40-50.

[74] S. Zhang, R. Zhang, Y.C. Jean, D.R. Paul, T.-S. Chung, Cellulose esters for forward osmosis: Characterization of water and salt transport properties and free volume, Polymer, 53 (2012) 2664-2672.

[75] S. Zhang, K.Y. Wang, T.-S. Chung, Y.C. Jean, H. Chen, Molecular design of the cellulose ester-based forward osmosis membranes for desalination, Chemical Engineering Science, 66 (2011) 2008-2018.

[76] A. Tiraferri, Y. Kang, E.P. Giannelis, M. Elimelech, Highly Hydrophilic Thin-Film Composite Forward Osmosis Membranes Functionalized with Surface-Tailored Nanoparticles, ACS Applied Materials & Interfaces, 4 (2012) 5044-5053.

[77] S. Zhang, P. Sukitpaneenit, T.-S. Chung, Design of robust hollow fiber membranes with high power density for osmotic energy production, Chemical Engineering Journal, 241 (2014) 457-465.

[78] Y. Wang, F. Wicaksana, C.Y. Tang, A.G. Fane, Direct Microscopic Observation of Forward Osmosis Membrane Fouling, Environmental Science & Technology, 44 (2010) 7102-7109.

[79] C.Y. Tang, Q. She, W.C.L. Lay, R. Wang, A.G. Fane, Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration, Journal of Membrane Science, 354 (2010) 123-133.

[80] G.Z. Ramon, B.J. Feinberg, E.M.V. Hoek, Membrane-based production of salinity-gradient power, Energy & Environmental Science, 4 (2011) 4423-4434.

[81] X. Jin, Q. She, X. Ang, C.Y. Tang, Removal of boron and arsenic by forward osmosis membrane: Influence of membrane orientation and organic fouling, Journal of Membrane Science, 389 (2012) 182-187.

[82] S. Zhao, L. Zou, D. Mulcahy, Effects of membrane orientation on process performance in forward osmosis applications, Journal of Membrane Science, 382 (2011) 308-315.

[83] S. Loeb, L. Titelman, E. Korngold, J. Freiman, Effect of porous support fabric on osmosis through a Loeb-Sourirajan type asymmetric membrane, Journal of Membrane Science, 129 (1997) 243-249.

[84] K.L. Lee, R.W. Baker, H.K. Lonsdale, Membranes for power generation by pressure-retarded osmosis, Journal of Membrane Science, 8 (1981) 141-171.

[85] J.R. McCutcheon, M. Elimelech, Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis, Journal of Membrane Science, 284 (2006) 237-247.

[86] D. Xiao, C.Y. Tang, J. Zhang, W.C.L. Lay, R. Wang, A.G. Fane, Modeling salt accumulation in osmotic membrane bioreactors: Implications for FO membrane selection and system operation, Journal of Membrane Science, 366 (2011) 314-324.

[87] X. Jin, C.Y. Tang, Y. Gu, Q. She, S. Qi, Boric Acid Permeation in Forward Osmosis Membrane Processes: Modeling, Experiments, and Implications, Environmental Science & Technology, 45 (2011) 2323-2330.

[88] C.H. Tan, H.Y. Ng, Modified models to predict flux behavior in forward osmosis in consideration of external and internal concentration polarizations, Journal of Membrane Science, 324 (2008) 209-219.

[89] G.T. Gray, J.R. McCutcheon, M. Elimelech, Internal concentration polarization in forward osmosis: role of membrane orientation, Desalination, 197 (2006) 1-8.

[90] H.Y. Ng, W. Tang, W.S. Wong, Performance of forward (direct) osmosis process: Membrane structure and transport phenomenon, Environmental Science and Technology, 40 (2006) 2408-2413.

[91] K.Y. Wang, T.S. Chung, J.J. Qin, Polybenzimidazole (PBI) nanofiltration hollow fiber membranes applied in forward osmosis process, Journal of Membrane Science, 300 (2007) 6-12.

[92] M.F. Gruber, C.J. Johnson, C.Y. Tang, M.H. Jensen, L. Yde, C. Hélix-Nielsen, Computational fluid dynamics simulations of flow and concentration polarization in forward osmosis membrane systems, Journal of Membrane Science, 379 (2011) 488-495.

[93] M. Park, J.J. Lee, S. Lee, J.H. Kim, Determination of a constant membrane structure parameter in forward osmosis processes, Journal of Membrane Science, 375 (2011) 241-248.

[94] Y. Xu, X. Peng, C.Y. Tang, Q.S. Fu, S. Nie, Effect of draw solution concentration and operating conditions on forward osmosis and pressure retarded osmosis

performance in a spiral wound module, Journal of Membrane Science, 348 (2010) 298-309.

[95] X. Song, Z. Liu, D.D. Sun, Nano Gives the Answer: Breaking the Bottleneck of Internal Concentration Polarization with a Nanofiber Composite Forward Osmosis Membrane for a High Water Production Rate, Advanced Materials, 23 (2011) 3256-3260.

[96] W. Li, Y. Gao, C.Y. Tang, Network modeling for studying the effect of support structure on internal concentration polarization during forward osmosis: Model development and theoretical analysis with FEM, Journal of Membrane Science, 379 (2011) 307-321.

[97] J.R. McCutcheon, M. Elimelech, Modeling water flux in forward osmosis: Implications for improved membrane design, AIChE Journal, 53 (2007) 1736-1744.

[98] J. Su, T.-S. Chung, Sublayer structure and reflection coefficient and their effects on concentration polarization and membrane performance in FO processes, Journal of Membrane Science, 376 (2011) 214-224.

[99] J.S. Yong, W.A. Phillip, M. Elimelech, Coupled reverse draw solute permeation and water flux in forward osmosis with neutral draw solutes, Journal of Membrane Science, 392–393 (2012) 9-17.

[100] T.Y. Cath, M. Elimelech, J.R. McCutcheon, R.L. McGinnis, A. Achilli, D. Anastasio, A.R. Brady, A.E. Childress, I.V. Farr, N.T. Hancock, J. Lampi, L.D. Nghiem, M. Xie, N.Y. Yip, Standard Methodology for Evaluating Membrane Performance in Osmotically Driven Membrane Processes, Desalination, 312 (2013) 31-38.

[101] W.A. Phillip, J.S. Yong, M. Elimelech, Reverse draw solute permeation in forward osmosis: Modeling and experiments, Environmental Science and Technology, 44 (2010) 5170-5176.

[102] Y.C. Kim, M. Elimelech, Potential of osmotic power generation by pressure retarded osmosis using seawater as feed solution: Analysis and experiments, Journal of Membrane Science, 429 (2013) 330-337.

[103] G. Blandin, A.R.D. Verliefde, C.Y. Tang, A.E. Childress, P. Le-Clech, Validation of assisted forward osmosis (AFO) process: Impact of hydraulic pressure, Journal of Membrane Science, 447 (2013) 1-11.

[104] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, Desalination by ammonia-carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance, Journal of Membrane Science, 278 (2006) 114-123.

[105] E.M. Garcia-Castello, J.R. McCutcheon, M. Elimelech, Performance evaluation of sucrose concentration using forward osmosis, Journal of Membrane Science, 338 (2009) 61-66.

[106] B. Mi, M. Elimelech, Gypsum scaling and cleaning in forward osmosis: Measurements and mechanisms, Environmental Science and Technology, 44 (2010) 2022-2028.

[107] J.J. Qin, S. Chen, M.H. Oo, K.A. Kekre, E.R. Cornelissen, C.J. Ruiken, Experimental studies and modeling on concentration polarization in forward osmosis, Water Science and Technology, 61 (2010) 2897-2904.

[108] S. Zhao, L. Zou, Relating solution physicochemical properties to internal concentration polarization in forward osmosis, Journal of Membrane Science, 379 (2011) 459-467.

[109] V. Parida, H.Y. Ng, Forward osmosis organic fouling: Effects of organic loading, calcium and membrane orientation, Desalination, 312 (2013) 88-98.

[110] M.I. Dova, K.B. Petrotos, H.N. Lazarides, On the direct osmotic concentration of liquid foods. Part I: Impact of process parameters on process performance, Journal of Food Engineering, 78 (2007) 422-430.

[111] S. Chou, L. Shi, R. Wang, C.Y. Tang, C. Qiu, A.G. Fane, Characteristics and potential applications of a novel forward osmosis hollow fiber membrane, Desalination, 261 (2010) 365-372.

[112] K.Y. Wang, T.-S. Chung, G. Amy, Developing thinfilm-composite forward osmosis membranes on the PES/SPSf substrate through interfacial polymerization, AIChE Journal, 58 (2012) 770-781.

[113] L.A. Hoover, J.D. Schiffman, M. Elimelech, Nanofibers in thin-film composite membrane support layers: Enabling expanded application of forward and pressure retarded osmosis, Desalination, 308 (2013) 73-81.

[114] A. Achilli, T.Y. Cath, A.E. Childress, Selection of inorganic-based draw solutions for forward osmosis applications, Journal of Membrane Science, 364 (2010) 233-241.

[115] L. Chekli, S. Phuntsho, H.K. Shon, S. Vigneswaran, J. Kandasamy, A. Chanan, A review of draw solutes in forward osmosis process and their use in modern applications, Desalination and Water Treatment, 43 (2012) 167-184.

[116] T.Y. Cath, N.T. Hancock, C.D. Lundin, C. Hoppe-Jones, J.E. Drewes, A multi-barrier osmotic dilution process for simultaneous desalination and purification of impaired water, Journal of Membrane Science, 362 (2010) 417-426.

[117] Q. Ge, M. Ling, T.-S. Chung, Draw solutions for forward osmosis processes: Developments, challenges,

and prospects for the future, Journal of Membrane Science, 442 (2013) 225-237.

[118] K.S. Bowden, A. Achilli, A.E. Childress, Organic ionic salt draw solutions for osmotic membrane bioreactors, Bioresource Technology, 122 (2012) 207-216.

[119] K. Lutchmiah, L. Lauber, K. Roest, D.J.H. Harmsen, J.W. Post, L.C. Rietveld, J.B. van Lier, E.R. Cornelissen, Zwitterions as alternative draw solutions in forward osmosis for application in wastewater reclamation, Journal of Membrane Science, 460 (2014) 82-90.

[120] V.M.M. Lobo, J.L. Quaresma, Handbook of Electrolyte Solutions, Part A, Elsevier, 1989.

[121] C.H. Tan, H.Y. Ng, Revised external and internal concentration polarization models to improve flux prediction in forward osmosis process, Desalination, 309 (2013) 125-140.

[122] T.-S. Chung, X. Li, R.C. Ong, Q. Ge, H. Wang, G. Han, Emerging forward osmosis (FO) technologies and challenges ahead for clean water and clean energy applications, Current Opinion in Chemical Engineering, 1 (2012) 246-257.

[123] N.T. Hau, S.-S. Chen, N.C. Nguyen, K.Z. Huang, H.H. Ngo, W. Guo, Exploration of EDTA sodium salt as novel draw solution in forward osmosis process for dewatering of high nutrient sludge, Journal of Membrane Science, 455 (2014) 305-311.

[124] M. Yuchun, Liu Ankang, Chen Dengxing, Li Gang, He Tao, L. Xuemei, Draw agent in forward osmosis based on EDTA, Journal of Nanjing University of Technology (Natural Science Edition), 34 (2012) 79-83.

[125] E.R. Cornelissen, J.B. van Lier, K. Lutchmiah, C. Roest, Solution comprising an osmotic agent and method of extracting water using said solution, in: Google Patents, The Netherlands, 2013.

[126] S. Phuntsho, H.K. Shon, T. Majeed, I. El Saliby, S. Vigneswaran, J. Kandasamy, S. Hong, S. Lee, Blended Fertilizers as Draw Solutions for Fertilizer-Drawn Forward Osmosis Desalination, Environmental Science & Technology, 46 (2012) 4567-4575.

[127] S. Phuntsho, H.K. Shon, S. Hong, S. Lee, S. Vigneswaran, A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: Evaluating the performance of fertilizer draw solutions, Journal of Membrane Science, 375 (2011) 172-181.

[128] B.E. Logan, M. Elimelech, Membrane-based processes for sustainable power generation using water, Nature, 488 (2012) 313-319.

[129] J.-J. Qin, G. Danasamy, W.C.L. Lay, K.A. Kekre, Challenges in Forward Osmosis of Seawater Using Ammonium Bicarbonate as Osmotic Agent, American Journal of Water Resources, 1 (2013) 51-55.

[130] Q. Ge, J. Su, T.-S. Chung, G. Amy, Hydrophilic Superparamagnetic Nanoparticles: Synthesis, Characterization, and Performance in Forward Osmosis Processes, Industrial & Engineering Chemistry Research, 50 (2011) 382-388.

[131] M.M. Ling, K.Y. Wang, T.S. Chung, Highly watersoluble magnetic nanoparticles as novel draw solutes in forward osmosis for water reuse, Industrial and Engineering Chemistry Research, 49 (2010) 5869-5876.

[132] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: Opportunities and challenges, Journal of Membrane Science, 396 (2012) 1-21.

[133] S.M.S. Ghiu, R.P. Carnahan, M. Barger, Permeability of electrolytes through a flat RO membrane in a direct osmosis study, Desalination, 144 (2002) 387-392. [134] D. Li, X. Zhang, J. Yao, Y. Zeng, G.P. Simon, H. Wang, Composite polymer hydrogels as draw agents in forward osmosis and solar dewatering, Soft Matter, 7 (2011) 10048-10056.

[135] A. Razmjou, Q. Liu, G.P. Simon, H. Wang, Bifunctional Polymer Hydrogel Layers As Forward Osmosis Draw Agents for Continuous Production of Fresh Water Using Solar Energy, Environmental Science & Technology, 47 (2013) 13160-13166.

[136] C.H. Tan, H.Y. Ng, Modeling of external and internal concentration polarization effect on flux behaviour of forward osmosis, in: Water Science and Technology: Water Supply, 2008, pp. 533-539.

[137] M. Park, J.H. Kim, Numerical analysis of spacer impacts on forward osmosis membrane process using concentration polarization index, Journal of Membrane Science, 427 (2013) 10-20.

[138] Degremont, Urban Wastewater, in: Degremont Water Treatment Handbook Factsheets, 2011.

[139] O.A. Bamaga, A. Yokochi, B. Zabara, A.S. Babaqi, Hybrid FO/RO desalination system: Preliminary assessment of osmotic energy recovery and designs of new FO membrane module configurations, Desalination, 268 (2011) 163-169.

[140] C. Liu, W. Fang, S. Chou, L. Shi, A.G. Fane, R. Wang, Fabrication of layer-by-layer assembled FO hollow fiber membranes and their performances using low concentration draw solutions, Desalination, 308 (2013) 147-153.

[141] L. Setiawan, R. Wang, K. Li, A.G. Fane, Fabrication and characterization of forward osmosis hollow fiber membranes with antifouling NF-like selective layer, Journal of Membrane Science, 394–395 (2012) 80-88. [142] L. Setiawan, R. Wang, K. Li, A.G. Fane, Fabrication of novel poly(amide–imide) forward osmosis hollow fiber membranes with a positively charged nanofiltration-like selective layer, Journal of Membrane Science, 369 (2011) 196-205.

[143] B. Gu, D.Y. Kim, J.H. Kim, D.R. Yang, Mathematical model of flat sheet membrane modules for FO process: Plate-and-frame module and spiral-wound module, Journal of Membrane Science, 379 (2011) 403-415.

[144] N.T. Hancock, P. Xu, D.M. Heil, C. Bellona, T.Y. Cath, Comprehensive Bench- and Pilot-Scale Investigation of Trace Organic Compounds Rejection by Forward Osmosis, Environmental Science & Technology, 45 (2011) 8483-8490.

[145] E.R. Cornelissen, D. J. H. Harmsen, E. F. Beerendonk, J.J. Qin, J.W.M.N. Kappelhof, Effect of draw solution type and operational mode of forward osmosis with laboratory-scale membranes and a spiral wound membrane module., Journal of Water Reuse and Desalination 1 (2011) 133–140.

[146] Metcalf, Eddy, Wastewater Engineering: Treatment and Reuse, McGraw-Hill Education, 2003.

[147] C. Staudt, H. Horn, D.C. Hempel, T.R. Neu, Volumetric measurements of bacterial cells and extracellular polymeric substance glycoconjugates in biofilms, Biotechnology and Bioengineering, 88 (2004) 585-592.

[148] H.-C. Flemming, J. Wingender, T. Griebe, C. Mayer, Physico-Chemical Properties of Biofilms in: L.V. Evans (Ed.) Biofilms: Recent Advances in their Study and Control, CRC Press, 2000.

[149] J. Zhang, W.L.C. Loong, S. Chou, C. Tang, R. Wang, A.G. Fane, Membrane biofouling and scaling in

forward osmosis membrane bioreactor, Journal of Membrane Science, 403–404 (2012) 8-14.

[150] Z.-Y. Li, V. Yangali-Quintanilla, R. Valladares-Linares, Q. Li, T. Zhan, G. Amy, Flux patterns and membrane fouling propensity during desalination of seawater by forward osmosis, Water Research, 46 (2012) 195-204.

[151] E. Bar-Zeev, I. Berman-Frank, B. Liberman, E. Rahav, U. Passow, T. Berman, Transparent exopolymer particles: potential agents for organic fouling and biofilm formation in desalination and water treatment plants, Desalin. Water Treat., 3 (2009) 7.

[152] R. Valladares Linares, V. Yangali-Quintanilla, Z. Li, G. Amy, NOM and TEP fouling of a forward osmosis (FO) membrane: Foulant identification and cleaning, Journal of Membrane Science, 421–422 (2012) 217-224.

[153] S. Qi, C.Q. Qiu, Y. Zhao, C.Y. Tang, Doubleskinned forward osmosis membranes based on layer-bylayer assembly—FO performance and fouling behavior, Journal of Membrane Science, 405–406 (2012) 20-29.

[154] Y. Liu, B. Mi, Combined fouling of forward osmosis membranes: Synergistic foulant interaction and direct observation of fouling layer formation, Journal of Membrane Science, 407–408 (2012) 136-144.

[155] H. Choi, K. Zhang, D.D. Dionysiou, D.B. Oerther, G.A. Sorial, Influence of cross-flow velocity on membrane performance during filtration of biological suspension, Journal of Membrane Science, 248 (2005) 189-199.

[156] Y.C. Kim, M. Elimelech, Adverse Impact of Feed Channel Spacers on the Performance of Pressure Retarded Osmosis, Environmental Science & Technology, 46 (2012) 4673-4681.

[157] C. Boo, S. Lee, M. Elimelech, Z. Meng, S. Hong, Colloidal fouling in forward osmosis: Role of reverse salt diffusion, Journal of Membrane Science, 390–391 (2012) 277-284.

[158] P. Xu, J.E. Drewes, T.-U. Kim, C. Bellona, G. Amy, Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications, Journal of Membrane Science, 279 (2006) 165-175.

[159] Q. Li, Z. Xu, I. Pinnau, Fouling of reverse osmosis membranes by biopolymers in wastewater secondary effluent: Role of membrane surface properties and initial permeate flux, Journal of Membrane Science, 290 (2007) 173-181.

[160] O. Orgad, Y. Oren, S.L. Walker, M. Herzberg, The role of alginate in Pseudomonas aeruginosa EPS adherence, viscoelastic properties and cell attachment., Biofouling, 27 (2011) 787-798.

[161] M.F.A. Goosen, S.S. Sablani, H. Al-Hinai, S. Al-Obeidani, R. Al-Belushi, D. Jackson, Fouling of Reverse Osmosis and Ultrafiltration Membranes: A Critical Review, Separation Science and Technology, 39 (2005) 2261-2297.

[162] R. Valladares Linares, V. Yangali-Quintanilla, Z. Li, G. Amy, Rejection of micropollutants by clean and fouled forward osmosis membrane, Water Research, 45 (2011) 6737-6744.

[163] W.C.L. Lay, J. Zhang, C. Tang, R. Wang, Y. Liu, A.G. Fane, Factors affecting flux performance of forward osmosis systems, Journal of Membrane Science, 394–395 (2012) 151-168.

[164] W.S. Ang, S. Lee, M. Elimelech, Chemical and physical aspects of cleaning of organic-fouled reverse osmosis membranes, Journal of Membrane Science, 272 (2006) 198-210.

[165] R. Valladares Linares, Z. Li, V. Yangali-Quintanilla, Q. Li, G. Amy, Cleaning protocol for a FO membrane fouled in wastewater reuse, Desalination and Water Treatment, 51 (2013) 4821-4824.

[166] R. Valladares Linares, Z. Li, M. Abu-Ghdaib, C.-H. Wei, G. Amy, J.S. Vrouwenvelder, Water harvesting from municipal wastewater via osmotic gradient: An evaluation of process performance, Journal of Membrane Science, 447 (2013) 50-56.

[167] N.T. Hancock, N.D. Black, T.Y. Cath, A comparative life cycle assessment of hybrid osmotic dilution desalination and established seawater desalination and wastewater reclamation processes, Water Research, 46 (2012) 1145-1154.

[168] I. Shizas, D. Bagley, Experimental Determination of Energy Content of Unknown Organics in Municipal Wastewater Streams., J. Energy Eng, 130 (2004) 45-53.

[169] I.W. Devoe, Osmosis process for producing energy, in: Google Patents, 2005.

[170] K. Lampi, E. Beaudry, J. Herron, Forward osmosis pressurized device and process for generating potable water, in, Google Patents, US, 2007.

[171] F. Zhang, K.S. Brastad, Z. He, Integrating Forward Osmosis into Microbial Fuel Cells for Wastewater Treatment, Water Extraction and Bioelectricity Generation, Environmental Science & Technology, 45 (2011) 6690-6696.

[172] Z. Ge, Z. He, Effects of draw solutions and membrane conditions on electricity generation and water flux in osmotic microbial fuel cells, Bioresource Technology, 109 (2012) 70-76.

[173] Z. Ge, Q. Ping, L. Xiao, Z. He, Reducing effluent discharge and recovering bioenergy in an osmotic microbial fuel cell treating domestic wastewater, Desalination, 312 (2013) 52-59.

[174] X. Cao, X. Huang, P. Liang, K. Xiao, Y. Zhou, X. Zhang, B.E. Logan, A New Method for Water Desalination Using Microbial Desalination Cells, Environmental Science & Technology, 43 (2009) 7148-7152.

[175] C.M. Werner, B.E. Logan, P.E. Saikaly, G.L. Amy, Wastewater treatment, energy recovery and desalination using a forward osmosis membrane in an air-cathode microbial osmotic fuel cell, Journal of Membrane Science, 428 (2013) 116-122.

[176] J.W. Post, J. Veerman, H.V.M. Hamelers, G.J.W. Euverink, S.J. Metz, K. Nymeijer, C.J.N. Buisman, Salinity-gradient power: Evaluation of pressure-retarded osmosis and reverse electrodialysis, Journal of Membrane Science, 288 (2007) 218-230.

[177] S. Loeb, Osmotic power plants, Science, 189 (1975) 654-655.

[178] R. Wang, C.Tang, A.G.Fane, Development of pressure retarded osmosis (PRO) membranes with high power density for osmotic power harvesting., in: Osmosis Membrane Summit, Statkraft, Barcelona, 2012.

[179] S. Chou, R. Wang, L. Shi, Q. She, C. Tang, A.G. Fane, Thin-film composite hollow fiber membranes for pressure retarded osmosis (PRO) process with high power density, Journal of Membrane Science, 389 (2012) 25-33.

[180] K. Saito, M. Irie, S. Zaitsu, H. Sakai, H. Hayashi, A. Tanioka, Power generation with salinity gradient by pressure retarded osmosis using concentrated brine from SWRO system and treated sewage as pure water, Desalination and Water Treatment, 41 (2012) 114-121.

[181] F. Helfer, C. Lemckert, Y.G. Anissimov, Osmotic power with Pressure Retarded Osmosis: Theory, performance and trends – A review, Journal of Membrane Science, 453 (2014) 337-358.

[182] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, A Forward Osmosis–Membrane Distillation Hybrid Process for Direct Sewer Mining: System Performance and Limitations, Environmental Science & Technology, 47 (2013) 13486-13493.

[183] M. Elimelech, W.A. Phillip, The Future of Seawater Desalination: Energy, Technology, and the Environment, Science, 333 (2011) 712-717.

[184] R.A. Khaydarov, R.R. Khaydarov, Solar powered direct osmosis desalination, Desalination, 217 (2007) 225-232.

[185] A.A. Alturki, J.A. McDonald, S.J. Khan, W.E. Price, L.D. Nghiem, M. Elimelech, Removal of trace organic contaminants by the forward osmosis process, Separation and Purification Technology, 103 (2013) 258-266.

[186] X. Jin, J. Shan, C. Wang, J. Wei, C.Y. Tang, Rejection of pharmaceuticals by forward osmosis membranes, Journal of Hazardous Materials, 227–228 (2012) 55-61.

[187] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, Relating rejection of trace organic contaminants to membrane properties in forward osmosis: measurement, modelling and implications, Water Research, 49 (2013) 265–274.

[188] Q. Ge, J. Su, G.L. Amy, T.-S. Chung, Exploration of polyelectrolytes as draw solutes in forward osmosis processes, Water Research, 46 (2012) 1318-1326.

[189] D. Li, X. Zhang, J. Yao, G.P. Simon, H. Wang, Stimuli-responsive polymer hydrogels as a new class of draw agent for forward osmosis desalination, Chemical Communications, 47 (2011) 1710-1712.

[190] S. Ghosh, F.G. Pohland, Kinetics of Substrate Assimilation and Product Formation in Anaerobic Digestion, Journal (Water Pollution Control Federation), 46 (1974) 748-759.

[191] L.A. de Baere, M. Devocht, P. Van Assche, W. Verstraete, Influence of high NaCl and NH4Cl salt levels on methanogenic associations, Water Research, 18 (1984) 543-548.

[192] S.G. Pavlostathis, E. Giraldo-Gomez, Kinetics of anaerobic treatment: A critical review, Critical Reviews in Environmental Control, 21 (1991) 411-490.

[193] O. Lefebvre, R. Moletta, Treatment of organic pollution in industrial saline wastewater: A literature review, Water Research, 40 (2006) 3671-3682.

[194] D.W. Yerkes, S. Boonyakitsombut, R.E. Speece, Antagonism of sodium toxicity by the compatible solute betaine in anaerobic methanogenic systems, Water Science and Technology, 36 (1997) 15-24.

[195] P.H. Yancey, Organic osmolytes as compatible, metabolic and counteracting cytoprotectants in high osmolarity and other stresses, The Journal of Experimental Biology 208 (2005) 2819-2830 2819.

[196] G. Oh, L. Zhang, D. Jahng, Osmoprotectants enhance methane production from the anaerobic digestion of food wastes containing a high content of salt, Journal of Chemical Technology & Biotechnology, 83 (2008) 1204-1210.

[197] S. Kol, M.E. Merlo, R.A. Scheltema, M.d. Vries, R.J. Vonk, N.A. Kikkert, L. Dijkhuizen, R. Breitling, E. Takano, Metabolomic Characterization of the Salt Stress Response in Streptomyces coelicolor, Applied and Environmental Microbiology, 76 (2010) 2574-2581.

[198] J. Kopyra, H. Abdoul-Carime, Dissociation of gaseous zwitterion glycine-betaine by slow electrons, Journal of Chemical Physics, 132 (2010) 204302.
[199] W.C.L. Lay, Q. Zhang, J. Zhang, D. McDougald, C. Tang, R. Wang, Y. Liu, A.G. Fane, Study of integration of forward osmosis and biological process: Membrane performance under elevated salt environment, Desalination, 283 (2011) 123-130.

[200] Sigma-aldrich, MSDS database, in: http://www.sigmaaldrich.com/, 2012.

[201] M. Civera, A. Fornili, M. Sironi, S.L. Fornili, Molecular dynamics simulation of aqueous solutions of glycine betaine, Chemical Physics Letters, 367 (2003) 238-244.

[202] ScienceLab.com, Glycine in: www.sciencelab.com, MSDS, Houston, Texas, 2011.

[203] L.G. Longsworth, Diffusion Measurements, at 25°, of Aqueous Solutions of Amino Acids, Peptides and Sugars, Journal of the American Chemical Society, 75 (1953) 5705-5709.

[204] Sigma-Aldrich, L-glutamine in: www.aminoscience.fr, MSDS, France, 2011.

[205] ChemicalBook, ChemicalBook in, 2008

[206] A.D. Wilson, F.F. Stewart, Deriving osmotic pressures of draw solutes used in osmotically driven membrane processes, Journal of Membrane Science, 431 (2013) 205-211.

[207] D.v.d. Kooij, H.R. Veenendaal, Biomass production potential of materials in contact with drinking water: method and practical importance, Water Science and Technology: Water Supply, 1 (2001) 39-45.

[208] A. Magic-Knezev, D. van der Kooij, Optimisation and significance of ATP analysis for measuring active biomass in granular activated carbon filters used in water treatment., Water Research, 38 (2004) 3971-3979. [209] M.S. Nawaz, G. Gadelha, S.J. Khan, N. Hankins, Microbial toxicity effects of reverse transported draw solute in the forward osmosis membrane bioreactor (FO-MBR), Journal of Membrane Science, 429 (2013) 323-329.

[210] S. Adham, J. Oppenheimer, L. Liu, M. Kumar, Dewatering Reverse Osmosis Concentrate from Water Reuse Applications using Forward Osmosis, in: WateReuse Foundation Research Report, WateReuse Foundation Research, U.S, 2007.

[211] M. Civera, M. Sironi, S.L. Fornili, Unusual properties of aqueous solutions of l-proline: A molecular dynamics study, Chemical Physics Letters, 415 (2005) 274-278.

[212] O.R. Fennema, Food Chemistry, 3rd ed., Marcel Dekker, 1996.

[213] E.S. Tarleton, J.P. Robinson, C.R. Millington, A. Nijmeijer, M.L. Taylor, The influence of polarity on flux and rejection behaviour in solvent resistant nanofiltration—Experimental observations, Journal of Membrane Science, 278 (2006) 318-327.

[214] A.R.D. Verliefde, S.G.J. Heijman, E.R. Cornelissen, G. Amy, B. Van der Bruggen, J.C. van Dijk, Influence of electrostatic interactions on the rejection with NF and assessment of the removal efficiency during NF/GAC treatment of pharmaceutically active compounds in surface water, Water Research, 41 (2007) 3227-3240.

[215] Y. Kiso, Factors affecting adsorption of organic solutes on cellulose acetate in an aqueous solution system, Chromatographia, 22 (1986) 55-58.

[216] C. Royal Society of Chemistry, ChemSpider, in, Cambridge.

[217] D. Quick, HTI's revolutionary forward osmosis filtration system, in: Gizmag, 2007.

[218] T.-U. Kim, J.E. Drewes, R. Scott Summers, G.L. Amy, Solute transport model for trace organic neutral and charged compounds through nanofiltration and reverse osmosis membranes., Water Research, 41 (2007) 3977-3988.

[219] M. Park, J.J. Lee, S. Lee, J.H. Kim, Determination of a constant membrane structure parameter in forward osmosis processes, Journal of Membrane Science, In Press, Accepted Manuscript (2011).

[220] T.-w. Kim, S. Park, K. Yeh, Cost-effective design of a draw solution recovery process for forward osmosis desalination, Desalination, 327 (2013) 46-51.

[221] R. Semiat, Energy Issues in Desalination Processes, Environmental Science & Technology, 42 (2008) 8193-8201.

[222] R. Semiat, J. Sapoznik, D. Hasson, Energy aspects in osmotic processes, Desalination and Water Treatment, 15 (2010) 228-235.

[223] J.R.Herron, E.G.Beaudry, C.E.Jochums, L.E.Medina, Osmotic Concentration Apparatus and Method for Direct Osmotic Concentration of Fruit Juices., in, US, 1994.

[224] A.M. Hassan, M.A.K. Al-Sofi, A.S. Al-Amoudi, A.T.M. Jamaluddin, A.M. Farooque, A. Rowaili, A.G.I. Dalvi, N.M. Kither, G.M. Mustafa, I.A.R. Al-Tisan, A new approach to membrane and thermal seawater desalination processes using nanofiltration membranes (Part 1), Desalination, 118 (1998) 35-51.

[225] G. Feijoo, M. Soto, R. Méndez, J.M. Lema, Sodium inhibition in the anaerobic digestion process: Antagonism and adaptation phenomena, Enzyme and Microbial Technology, 17 (1995) 180-188.

[226] S. Mahajan, N. Tuteja, Cold, salinity and drought stresses: An overview, Archives of Biochemistry and Biophysics, 444 (2005) 139-158.

[227] C.M. López-Vázquez, C.M. Hooijmans, D. Brdjanovic, H.J. Gijzen, M.C.M. van Loosdrecht, Factors affecting the microbial populations at full-scale enhanced biological phosphorus removal (EBPR) wastewater treatment plants in The Netherlands, Water Research, 42 (2008) 2349-2360.

[228] H.-b. Zhen, Q. Xu, Y.-y. Hu, J.-h. Cheng, Characteristics of heavy metals capturing agent dithiocarbamate (DTC) for treatment of ethylene diamine tetraacetic acid–Cu (EDTA–Cu) contaminated wastewater, Chemical Engineering Journal, 209 (2012) 547-557.

[229] C.A. Campos, A.M. Rojas, L.N. Gerschenson, Studies of the effect of ethylene diamine tetraacetic acid (EDTA) on sorbic acid degradation, Food Research International, 29 (1996) 259-264.

[230] Dow, Product Safety Assessment (PSA): Salts of Ethylenediaminetetraacetic Acid (EDTA), in, 2006.

[231] N.Bonnard, M.T. Brondeau, D. Jargot, S. Malard, S. Miraval, O. Schneider, EDTA et sel tétrasodique, in: INRS, FT-276 (Eds.), 2009.

[232] C.R. Wilke, P. Chang, Correlation Of Diffusion Coefficients In Dilute Solutions, AIChE Journal, 1 (1995) 264-270.

[233] C.N. Fredd, H.S. Fogler, Alternative Stimulation Fluids and Their Impact on Carbonate Acidizing, Society of Petroleum Engineers Journal, 3 (1998).

[234] E.W. Washburn, International Critical Tables, 1 ed., McGraw-Hdl, New York, 1929.

[235] B.B. Laud, Electromagnetics in, New Age International, 1987, pp. 25.

[236] B. Mi, M. Elimelech, Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents, Journal of Membrane Science, 348 (2010) 337-345.

[237] E.M.V. Hoek, M. Elimelech, Cake-Enhanced Concentration Polarization: A New Fouling Mechanism for Salt-Rejecting Membranes, Environmental Science & Technology, 37 (2003) 5581-5588.

[238] S. Lee, C. Boo, M. Elimelech, S. Hong, Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO), Journal of Membrane Science, In Press, Corrected Proof (2010).

[239] W.C.L. Lay, T.H. Chong, C.Y. Tang, A.G. Fane, J. Zhang, Y. Liu, Fouling propensity of forward osmosis: Investigation of the slower flux decline phenomenon, Water Science and Technology, 61 (2010) 927-936.

[240] Q. Li, M. Elimelech, Synergistic effects in combined fouling of a loose nanofiltration membrane by colloidal materials and natural organic matter, Journal of Membrane Science, 278 (2006) 72-82.

[241] V. Yangali-Quintanilla, Z. Li, R. Valladares, Q. Li, G. Amy, Indirect desalination of Red Sea water with forward osmosis and low pressure reverse osmosis for water reuse, Desalination, In Press, Corrected Proof (2011).

[242] N.T. Hancock, P. Xu, M.J. Roby, J.D. Gomez, T.Y. Cath, Towards direct potable reuse with forward osmosis: Technical assessment of long-term process performance at the pilot scale, Journal of Membrane Science, 445 (2013) 34-46.

[243] N. Lee, G. Amy, J.-P. Croué, H. Buisson, Identification and understanding of fouling in lowpressure membrane (MF/UF) filtration by natural organic matter (NOM), Water Research, 38 (2004) 4511-4523. [244] J. Cho, G. Amy, J. Pellegrino, Membrane filtration of natural organic matter: factors and mechanisms affecting rejection and flux decline with charged ultrafiltration (UF) membrane, Journal of Membrane Science, 164 (2000) 89-110.

[245] S. Hong, M. Elimelech, Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes, Journal of Membrane Science, 132 (1997) 159-181.

[246] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, Impact of humic acid fouling on membrane performance and transport of pharmaceutically active compounds in forward osmosis, Water Research, 47 (2013) 4567-4575.

[247] L.O. Villacorte, M.D. Kennedy, G.L. Amy, J.C. Schippers, The fate of Transparent Exopolymer Particles (TEP) in integrated membrane systems: Removal through pre-treatment processes and deposition on reverse osmosis membranes, Water Research, 43 (2009) 5039-5052.

[248] R.M. Donlan, J.W. Costerton, Biofilms: Survival Mechanisms of Clinically Relevant Microorganisms, Clin. Microbiol. Rev., 15 (2002) 167-193.

[249] C. Dreszer, J.S. Vrouwenvelder, A.H. Paulitsch-Fuchs, A. Zwijnenburg, J.C. Kruithof, H.C. Flemming, Hydraulic resistance of biofilms, Journal of Membrane Science, 429 (2013) 436-447.

[250] H. Liu, H.H.P. Fang, Extraction of extracellular polymeric substances (EPS) of sludges, Journal of Biotechnology, 95 (2002) 249-256.

[251] C.J. van Oss, Development and applications of the interfacial tension between water and organic or biological surfaces, Colloids and Surfaces B: Biointerfaces, 54 (2007) 2-9.

[252] C.J. van Oss, Interfacial Forces in Aqueous Media, 2 ed., Taylor-Francis Group LLC, New York, 2006.

[253] M. Dubois, K.A. Gilles, J.K. Hamilton, P.A. Rebers, F. Smith, Colorimetric method for determination of sugars and related substances., Analytical Chemistry 28 (1956) 350-356.

[254] S.A. Huber, F.H. Frimmel, A new method for the characterization of organic carbon in aquatic systems., Int. J. Environ. Anal. Chem., 49 (1992) 49-57.

[255] R.D. Letterman, AWWA, Water quality and treatment: A Handbook of Community WaterSupplies, 5 ed., McGraw-Hill, NewYork, 1999.

[256] A.E. Harris, A Mechanistic Study on the Coupled Organic and Colloidal Fouling of Nanofiltration Membranes, in: Civil and Environmental Engineering, RICE University, Houston, Texas, 2008.

[257] K.D. Vos, F.O. Burris, R.L. Riley, Kinetic study of hydrolysis of cellulose acetate in pH range of 2-10., J. Appl. Polym. Sci., 10 (1966) 825-832.

[258] Z. Ran, Shaofeng Li, Junli Huang, Yixing Yuan, Chongwei Cui, C.D. Williams, Inactivation of Cryptosporidium by ozone and cell ultrastructures, Journal of Environmental Sciences, 22 (2010) 1954-1959.

[259] B. Mi, M. Elimelech, Silica scaling and scaling reversibility in forward osmosis, Desalination, (2012).

[260] H.-C. Flemming, T.R. Neu, D.J. Wozniak, The EPS Matrix: The "House of Biofilm Cells", J. Bacteriol., 189 (2007) 7945-7947

[261] S. Amir, A. Jouraiphy, A. Meddich, M. El Gharous, P. Winterton, M. Hafidi, Structural study of humic acids during composting of activated sludge-green waste: Elemental analysis, FTIR and 13C NMR, Journal of Hazardous Materials, 177 (2010) 524-529.

[262] H.-D. Youn, Y.C. Hah, S.-O. Kang, Role of laccase in lignin degradation by white-rot fungi, FEMS Microbiology Letters, 132 (1995) 183-188. [263] B. Mi, M. Elimelech, Chemical and physical aspects of organic fouling of forward osmosis membranes, Journal of Membrane Science, 320 (2008) 292-302.

[264] C.Y. Tang, Y.-N. Kwon, J.O. Leckie, Probing the nano- and micro-scales of reverse osmosis membranes—a comprehensive characterization of physiochemical properties of uncoated and coated membranes by XPS, TEM, ATR-FTIR, and streaming potential measurements., Journal of Membrane Science, 287 (2007) 146–156.

[265] J.J. Bikerman, Physical surfaces, in, Academic Press, 2012, pp. 488

[266] S. Botton, A.R.D. Verliefde, N.T. Quach, E.R. Cornelissen, Influence of biofouling on pharmaceuticals rejection in NF membrane filtration, Water Research, 46 (2012) 5848-5860.

[267] E.R. Cornelissen, D. Chasseriaud, W.G. Siegers, E.F. Beerendonk, D. van der Kooij, Effect of anionic fluidized ion exchange (FIX) pre-treatment on nanofiltration (NF) membrane fouling., Water Research, 44 (2010) 3283-3293.

[268] K. Lutchmiah, A.R.D. Verliefde, K. Roest, L.C. Rietveld, E.R. Cornelissen, Forward osmosis for application in wastewater treatment: A review, Water Research, 58 (2014) 179-197.

[269] Y.C. Kim, S.-J. Park, Experimental Study of a 4040 Spiral-Wound Forward-Osmosis Membrane Module, Environmental Science & Technology, 45 (2011) 7737-7745.

[270] B.D. Coday, D.M. Heil, P. Xu, T.Y. Cath, Effects of Transmembrane Hydraulic Pressure on Performance of Forward Osmosis Membranes, Environmental Science & Technology, 47 (2013) 2386-2393.

[271] T. Yun, Y.-J. Kim, S. Lee, S. Hong, G.I. Kim, Flux behavior and membrane fouling in pressure-assisted

forward osmosis, Desalination and Water Treatment, (2013) 1-6.

[272] E.R. Cornelissen, K. Lutchmiah, D. Harmsen, J. Qin, J. Kappelhof, Additional Feed Pressure (Pulsation) to Increase Forward Osmosis Membrane Performance, in: International Congress on Membranes (ICOM), Amsterdam, 2011.

[273] P. Le-Clech, Assisted forward osmosis for energy savings in RO desalination, in: Research Project Portfolio, The National Centre of Excellence in Desalination Australia, 2012.

[274] H.K. Lonsdale, U. Merten, R.L. Riley, Transport properties of cellulose acetate osmotic membranes, J. Appl. Polym. Sci., 9 (1965) 1341.

[275] H.Y. Ng, W. Tang, W.S. Wong, Performance of Forward (Direct) Osmosis Process: Membrane Structure and Transport Phenomenon, Environmental Science & Technology, 40 (2006) 2408-2413.

[276] Q. She, X. Jin, C.Y. Tang, Osmotic power production from salinity gradient resource by pressure retarded osmosis: Effects of operating conditions and reverse solute diffusion, Journal of Membrane Science, 401–402 (2012) 262-273.

[277] G. Yu, Rock Mechanics: Pore pressure prediction sees improvements, in: Exploration & Production, Hart Energy Publishings Houston, Texas, 2008.

[278] Q. Yang, K.Y. Wang, T.S. Chung, Dual-layer hollow fibers with enhanced flux as novel forward osmosis membranes for water production, Environmental Science and Technology, 43 (2009) 2800-2805.

[279] N.D. Jespersen, Barron's AP Chemistry, 7 ed., 2014

[280] C.H. Tan, H.Y. Ng, A novel hybrid forward osmosis - nanofiltration (FO-NF) process for seawater desalination: Draw solution selection and system configuration, Desalination and Water Treatment, 13 (2010) 356-361.

[281] Q. She, X. Jin, Q. Li, C.Y. Tang, Relating reverse and forward solute diffusion to membrane fouling in osmotically driven membrane processes, Water Research, 46 (2012) 2478-2486.

[282] A. Simon, L. Penpenic, N. Gondrexon, S. Taha, G. Dorange, A comparative study between classical stirred and ultrasonically-assisted dead-end ultrafiltration, Ultrasonics Sonochemistry, 7 (2000) 183-186.

[283] A. Altaee, G. Zaragoza, H.R. van Tonningen, Comparison between Forward Osmosis-Reverse Osmosis and Reverse Osmosis processes for seawater desalination, Desalination, 336 (2014) 50-57.

[284] L. Luning, E.H.M.v. Zundert, A.J.F. Brinkmann, Comparison of dry and wet digestion for solid waste., Water Science & Technology, 48 (2003) 15-20.

[285] G.T. Gray, J.R. McCutcheon, M. Elimelech, Internal concentration polarization in FO: role of membrane orientation, Desalination, 197 (2006) 1-8.

[286] R. McGinnes, The development of applications and markets for FO, in: FO Summit, Barcelona, 2012.

[287] M. Hirose, Development of membranes and membrane elements for osmotic power, in: Osmosis membrane summit, Barcelona, 2012.

[288] R. Wang, Development of pressure retarded osmosis (PRO) membranes with high power density for osmotic power harvesting, in: Osmosis membrane summit Barcelona, 2012.

[289] U. Bharwada, High Performance TFC Polyamide Forward Osmosis Membrane Systems- Commercial Reality, in: Osmosis membrane summit Barcelona, 2012. [290] Calcium Chloride Handbook A Guide to Properties, Forms, Storage and Handling, in: Calcium Chloride Handbook, The Dow Chemical Company, http://www.glchloride.com/brochure/Brochure%20-%20Calcium%20chloride%20handbook.pdf, 2003.

[291] N.T. Hancock, T.Y. Cath, Solute coupled diffusion in osmotically driven membrane processes, Environmental science & technology, 43 (2009) 6769-6775.

[292] The Trapezoidal Rule for Numerical Integration, in: http://math.fullerton.edu/mathews/n2003/TrapezoidalRule Mod.html, 2003.

[293] C. Ruiken, Influent fijnzeven in rwzi's, in, STOWA, Amersfoort, 2010.

[294] J. Post, A. Hogendoorn, Sewer Mining: high quality water from sewerage on an energy neutral basis, in: Design of Drinking Water & Waste Water Treatment Plants, TUDelft, 2012.

[295] J. van der Ven, Sewer Mining Workshop, in, Wageningen, 2012.

[296] S.H. Ebrahim, M.M. Abdel-Jawad, M. Safar, Conventional pretreatment system for the Doha Reverse Osmosis Plant: Technical and economic assessment, Desalination, 102 (1995) 179-187.

[297] G. Owen, M. Bandi, J.A. Howell, S.J. Churchouse, Economic assessment of membrane processes for water and waste water treatment, Journal of Membrane Science, 102 (1995) 77-91.

[298] A.R. Costa, M.N. de Pinho, Performance and cost estimation of nanofiltration for surface water treatment in drinking water production, Desalination, 196 (2006) 55-65.

[299] J.E.D. T.Y. Cath, Carl D. Lundin, A novel hybrid forward osmosis process for drinking water augmentation

using impaired water and saline water sources, in, Denver, 2009.

[300] M.M. Nederlof, J.C. Kruithof, J.S. Taylor, D. van der Kooij, J.C. Schippers, Comparison of NF/RO membrane performance in integrated membrane systems, Desalination, 131 (2000) 257-269.

[301] R.J. Ray, Cost estimates, Chapman Hall, New York, 1992.

[302] A. Zhu, P.D. Christofides, Y. Cohen, On RO membrane and energy costs and associated incentives for future enhancements of membrane permeability, Journal of Membrane Science, 344 (2009) 1-5.

[303] J. MacHarg, Affordable Desalination Profiles State of the Art SWRO, Watermark, 36 (2008).

[304] L. Song, J.Y. Hu, S.L. Ong, W.J. Ng, M. Elimelech, M. Wilf, Emergence of thermodynamic restriction and its implications for full-scale reverse osmosis processes, Desalination, 155 (2003) 213-228.

[305] Dow, FILMTEC Reverse Osmosis Membrane, in: www.dow.com.

[306] A.G. Fane, C.Y. Tang, R. Wang, 4.11 - Membrane Technology for Water: Microfiltration, Ultrafiltration, Nanofiltration, and Reverse Osmosis, in: P. Wilderer (Ed.) Treatise on Water Science, Elsevier, Oxford, 2011, pp. 301-335.

[307] Eurostat, Electricity prices for industrial consumers, in, 2013.

[308] C.J. Ruiken, G. Breuer, E. Klaversma, T. Santiago, M.C.M. van Loosdrecht, Sieving wastewater – Cellulose recovery, economic and energy evaluation, Water Research, 47 (2013) 43-48.

[309] J. Post, in: 12 July 2012, 2012.

[310] S. Postel, "Sewer Mining" – Efficient Water Recycling Coming to a Community Near You, in: Water Currents, National Geographic Society, 2012.

Glossary

Symbol	Definition	Unit
Α	water permeability constant	m/s.Pa
A_m	membrane area	m ²
$A_{m,RO}$	membrane area of the RO system	m ²
В	solute permeability coefficient	m/s
С	concentration	mol/L or mol/kg
C_{in}	inlet draw solution concentration	mol/m ³
Cout	outlet draw solution concentration	mol/m
CECP	concentrative external concentration polarisation	-
COD	Chemical Oxygen Demand	mg COD/L
СР	concentration polarisation	-
D	solute diffusion coefficient	m ² /s
DICP	dilutive internal concentration polarisation	-
Е	potential energy	kWh/m ³
ECP	external concentration polarisation	-
i	interest rate	-
ICP	internal concentration polarisation	-
J_s	salt flux	g/m ² .h
J_{v}	water flux	L/m ² .h
K_m	mass transfer coefficient	m/s
MW	molecular weight	g/mol
OMBR	osmotic membrane bioreactor	-
P_F	applied feed pressure in FO	bar

$P_{F,RO}$	feed pressure in RO	bar
PAO	Pressure Assisted Osmosis	-
Pr	price of membrane per square meter	€/m ²
Q_{FO}	water flow across the FO membrane	m ³ /s
$Q_{FO, salt}$	salt flow across the FO membrane	kg/s
Q_{in}	inlet feed flow	m ³ /s
$Q_{in}(0)$	inlet water flow at the beginning of the FO module	m ³ /s
Q_{out}	outlet feed flow	m ³ /s
$Q_{out}(i)$	outlet water flow of the membrane section "i"	m ³ /s
R	Rejection of solute	%
Rg	universal gas constant	L.atm/K.mol or J/mol.K
S	membrane structure parameter	mm
Т	Temperature	K
X _{in}	inlet feed concentration	mol/m ³
X _{in} X _{out}	inlet feed concentration outlet feed concentration	mol/m ³ mol/m ³
$\begin{array}{c} X_{in} \\ X_{out} \\ \end{array}$	inlet feed concentration outlet feed concentration van't Hoff coefficient	mol/m ³ mol/m ³
$\begin{array}{c} X_{\rm in} \\ X_{\rm out} \\ \beta \\ \Delta m_{\rm solute} \end{array}$	inlet feed concentrationoutlet feed concentrationvan't Hoff coefficientvariation of the solute weight	mol/m ³ mol/m ³ - g
$ \begin{array}{c} X_{in} \\ X_{out} \\ \beta \\ \Delta m_{solute} \\ \Delta \pi \end{array} $	inlet feed concentrationoutlet feed concentrationvan't Hoff coefficientvariation of the solute weightosmotic pressure differential (π_{DS} - π_{FS})	mol/m ³ mol/m ³ - g bar
$\begin{array}{c} X_{in} \\ X_{out} \\ \beta \\ \Delta m_{solute} \\ \Delta \pi \\ \varepsilon \end{array}$	inlet feed concentrationoutlet feed concentrationvan't Hoff coefficientvariation of the solute weightosmotic pressure differential (π_{DS} - π_{FS})porosity of the support layer	mol/m ³ mol/m ³ - g bar -
$\begin{array}{c} X_{in} \\ X_{out} \\ \hline \\ \beta \\ \Delta m_{solute} \\ \hline \\ \Delta \pi \\ \hline \\ \varepsilon \\ \hline \\ \eta \end{array}$	inlet feed concentrationoutlet feed concentrationvan't Hoff coefficientvariation of the solute weightosmotic pressure differential (π_{DS} - π_{FS})porosity of the support layerpump efficiency	mol/m ³ mol/m ³ - g bar - -
$\begin{array}{c} X_{in} \\ X_{out} \\ \hline \\ \beta \\ \Delta m_{solute} \\ \hline \\ \Delta \pi \\ \hline \\ \varepsilon \\ \hline \\ \eta \\ \hline \\ \phi(i) \end{array}$	inlet feed concentrationoutlet feed concentrationvan't Hoff coefficientvariation of the solute weightosmotic pressure differential (π_{DS} - π_{FS})porosity of the support layerpump efficiencyrecovery at one section of membrane	mol/m³ mol/m³ - g bar - %
$\begin{array}{c} X_{in} \\ X_{out} \\ \hline \\ \beta \\ \Delta m_{solute} \\ \hline \\ \Delta \pi \\ \hline \\ \varepsilon \\ \hline \\ \eta \\ \hline \\ \phi(i) \\ \hline \\ \Phi_{in} \end{array}$	inlet feed concentrationoutlet feed concentrationvan't Hoff coefficientvariation of the solute weightosmotic pressure differential (π_{DS} - π_{FS})porosity of the support layerpump efficiencyrecovery at one section of membraneinlet draw solution flow	mol/m³ mol/m³ - g bar - % m³/s
$\begin{array}{c} X_{in} \\ X_{out} \\ \hline \\ \beta \\ \Delta m_{solute} \\ \hline \\ \Delta \pi \\ \hline \\ \varepsilon \\ \hline \\ \eta \\ \hline \\ \phi(i) \\ \hline \\ \phi_{in} \\ \hline \\ \phi_{out} \end{array}$	inlet feed concentrationoutlet feed concentrationvan't Hoff coefficientvariation of the solute weightosmotic pressure differential (π_{DS} - π_{FS})porosity of the support layerpump efficiencyrecovery at one section of membraneinlet draw solution flowoutlet draw solution flow	mol/m³ mol/m³ - g bar - % m³/s m³/s
$\begin{array}{c} X_{in} \\ X_{out} \\ \hline \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ &$	inlet feed concentrationoutlet feed concentrationvan't Hoff coefficientvariation of the solute weightosmotic pressure differential (π_{DS} - π_{FS})porosity of the support layerpump efficiencyrecovery at one section of membraneinlet draw solution flowoutlet draw solution flowosmotic pressure	mol/m³ mol/m³ - g bar - % m³/s m³/s bar
$\begin{array}{c} X_{in} \\ X_{out} \\ \hline \\ & X_{out} \\ \hline \\ & \beta \\ \hline \\ & \Delta m_{solute} \\ \hline \\ & \Delta \pi \\ \hline \\ & \varepsilon \\ & \eta \\ \hline \\ & \varepsilon \\ & \eta \\ \hline \\ & \varphi \\ & \phi(i) \\ \hline \\ & \phi_{in} \\ \hline \\ & \phi_{out} \\ \hline \\ & \pi \\ \hline \\ & \sigma \end{array}$	inlet feed concentrationoutlet feed concentrationvan't Hoff coefficientvariation of the solute weightosmotic pressure differential (π_{DS} - π_{FS})porosity of the support layerpump efficiencyrecovery at one section of membraneinlet draw solution flowoutlet draw solution flowosmotic pressurereflection coefficient	mol/m³ mol/m³ - g bar - % m³/s m³/s bar -

List of Publications

- Lutchmiah K., A.R.D. Verliefde, K. Roest, L.C. Rietveld, E.R. Cornelissen, Forward osmosis for application in wastewater treatment: A review, Water Research, 58 (2014) 179-197.
- Lutchmiah K., L. Lauber, K. Roest, D.J.H. Harmsen, J.W. Post, L.C. Rietveld, J.B. van Lier, E.R. Cornelissen, Zwitterions as alternative draw solutions in forward osmosis for application in wastewater reclamation, Journal of Membrane Science, 460 (2014) 82-90.
- Lutchmiah K., E.R. Cornelissen, D.J.H. Harmsen, J.W. Post, K. Lampi, H. Ramaekers, L.C. Rietveld, K. Roest: Water recovery from sewage using forward osmosis, Water Science & Technology, 64 (2011) 1443-1449.
- Lutchmiah K., D.J.H. Harmsen, B.A. Wols, L.C. Rietveld, J.J. Qin, E.R. Cornelissen: Continuous and Discontinuous Pressure Assisted Osmosis (PAO) (submitted), Journal of Membrane Science (2014).
- Lutchmiah K., J.W. Post, L.C. Rietveld, E.R. Cornelissen: EDTA: A Synthetic Draw Solution for Forward Osmosis (submitted) Water Science & Technology (2013).
- Lutchmiah K., C. Brignoli, A. Zwijnenburg, L.C. Rietveld, E. R. Cornelissen (to be submitted): Polysaccharide Dominance in FO Fouling Studies of Raw Wastewater

Lutchmiah K., L. Lauber, B.A. Wols, J.W. Post, L.C. Rietveld, E. R. Cornelissen (to be submitted): A Technical Economic Assessment of Sewer Mining using Forward Osmosis

Book Section

Lutchmiah K., Editor: Morris A. Pierce (2012); Encyclopaedia of Energy; Salem Press, Inc., Ipswich MA 01938; 4 vol.

<u>Patent</u>

Cornelissen, E.R., J.B van Lier, K. Lutchmiah and C. Roest (2013): Solution comprising an osmotic agent and method of extracting water using said solution, Google Patents, The Netherlands.

Conference Proceedings

- Lutchmiah K., K. Roest, J.W. Post, L.C. Rietveld and E.R. Cornelissen (2013): Draw Solutions for Forward Osmosis. IWA Water Reuse, Windhoek, Namibia.
- Lutchmiah K., K. Roest, D.J.H. Harmsen, J.W. Post, L.C. Rietveld, J.B van Lier, E.R. Cornelissen (2013): Alternative Draw Solutions in Forward Osmosis for Application in Wastewater Reclamation. IWA Membrane Technology Conference, Toronto, Canada
- Lutchmiah K., D.J.H. Harmsen, B. Wols, A.R.D. Verliefde, J.W. Post and E.R. Cornelissen

(2012): Pressure Assisted Osmosis (PAO) to enhance Forward Osmosis (FO) Performance; NMG/BMG Membrane Symposium and 13th Poster day; Amsterdam, The Netherlands.

- Lutchmiah K, D.J.H. Harmsen, B. Wols, A.R.D Verliefde, J.W. Post and E.R. Cornelissen (2012): Pressure Assisted Osmosis (PAO) to enhance Forward Osmosis (FO) Performance. 3rd Osmosis Membrane Summit; Barcelona, Spain2012.
- Roest K, K. Lutchmiah, D.J.H. Harmsen, L.C. Rietveld and E.R. Cornelissen (2012): Safe and sustainable water extraction from sewage. IWA Disinfection of Water, Wastewater and Biosolids Conference; Mexico City, Mexico.
- Lutchmiah K., K. Roest, D.J.H. Harmsen, J.W. Post, K. Lampi, H. Ramaekers, L.C. Rietveld and E.R. Cornelissen (2012): Application of Forward Osmosis in Sewer Mining; 64ste Vakantiecursus Drinkwater en Afvalwater; Delft, The Netherlands
- Lutchmiah K., E.R. Cornelissen D.J.H. Harmsen , J.W. Post, K. Lampi, H. Ramaekers, L.C. Rietveld and Roest K. (2011): Innovative Water and Energy Recovery from Sewage using Forward Osmosis (Sewer Mining); 6th IWA Specialist Conference on Membrane Technology for Water & Wastewater Treatment, Aachen, Germany
- Lutchmiah K., E.R. Cornelissen D.J.H. Harmsen , J.W. Post, K. Lampi, H. Ramaekers, L.C.

Rietveld and Roest K. (2011): FO application enabling water and energy recovery from sewage; 8th IWA International Conference on Water Reclamation & Reuse, Barcelona, Spain

- Lutchmiah K., E.R. Cornelissen D.J.H. Harmsen, J.W. Post, K. Lampi, H. Ramaekers, L.C. Rietveld and Roest K. (2011); Forward osmosis membranes for water recovery from sewage, Young Water Professionals BeNeLux, Leuven, Belgium.
- Lutchmiah K., E.R. Cornelissen D.J.H. Harmsen , J.W. Post, K. Lampi, H. Ramaekers, L.C. Rietveld and Roest K. (2011): Water Recovery from Sewage using Forward Osmosis Membranes, International Congress on Membranes and Membrane Processes (ICOM), Amsterdam, The Netherlands
- Cornelissen E.R, D.J.H. Harmsen, K. Lutchmiah., B. Wols, J.J. Qin, J.W.M.N. Kappelhof (2011): Additional Feed Pressure (Pulsation) to Increase Forward Osmosis Membrane Performance; International Congress on Membranes and Membrane Processes (ICOM), Amsterdam, The Netherlands
- Lutchmiah K., E.R. Cornelissen D.J.H. Harmsen , J.W. Post, K. Lampi, H. Ramaekers, L.C. Rietveld and Roest K. (2011): Water Recovery from Sewage Using Forward Osmosis; 8th IWA Leading-Edge Conference on Water and Wastewater Technologies; Amsterdam, The Netherlands

- Roest K, K. Lutchmiah, D.J.H. Harmsen , M. Zandvoort, L.C. Rietveld, H. Ramaekers, K. Lampi, J.W. Post and E.R. Cornelissen (2011): Performance of forward osmosis membranes in sewage treatment; International Water Week, Amsterdam, The Netherlands
- Roest K, K. Lutchmiah, D.J.H. Harmsen, J.W. Post, K. Lampi, H. Ramaekers, J.W.M.N. Kappelhof, J.B. van Lier, L.C. Rietveld and E.R. Cornelissen (2010): Innovative water and energy recovery from sewage, IWA Water and Energy, Amsterdam, the Netherlands
- Cornelissen E.R., K. Lutchmiah, D.J.H. Harmsen, J.W. Post and K. Roest (2010): Sewer Mining for Reuse of Sewage, 3rd Oxford Water & Membranes Research Event; Oxford, UK
- Cornelissen E.R., K. Lutchmiah, D.J.H. Harmsen, J.W. Post and K. Roest (2010): Sewer Mining for Reuse of Sewage, 7th IMSTEC; Sydney, Australia

Curriculum Vitae

Kerusha Lutchmiah was born on 3 June 1984 in East London, South Africa. In 2001 she matriculated from Stirling High School, East London. From 2002 – 2009 Kerusha completed her tertiary education at the Mannheim University of Applied Sciences in Germany, where she obtained both her BSc and MSc degrees in Biotechnology. Her Bachelor Thesis involved the determination of oil biodegradation rates employing biosurfactants from thermophilic microorganisms, as an



ecological and economical substitute for conventional emulsifying agents. In 2007, Kerusha interned at the Forschungszentrum Karlsruhe, Germany, investigating the influence of genotoxic substances on DNA defining agents in hospital wastewaters. In 2008 - 2009, Kerusha completed her Master Thesis at the University of Santiago de Compostela, Spain, where she studied the removal of PPCPs in Hybrid Activated Sludge Reactors. Since 2010 Kerusha has worked together with KWR Watercycle Research Institute and the Delft University of Technology, in the Netherlands, on her PhD research, part of the "Sewer Mining" project, which attained the AVG Water Innovation Award in 2010. In 2013, Kerusha was selected for the Wings for Water Youth Programme to participate in multi-stakeholder dialogues in preparation for the Thematic Consultation on Water in the Post-2015 Development Agenda. After 12 years abroad, Kerusha is still fascinated by different cultures, and is continuously expanding her passion for the culinary arts, dance, music and languages - Dutch is her 7th language.

Water scarcity is a global issue and waste accumulation is a steadily growing one. The innovative Sewer Mining concept is an example of an integrated forward osmosis application which incorporates different technologies to attain one goal: water recovery from wastewater, and subsequent energy production. Forward osmosis membrane technology shows great potential as a sustainable treatment of wastewater. The high quality reclaimed water is a suitable and low cost alternative for many industrial processes that currently exhaust much of the available drinking water supply. By extracting water and energy from wastewater, this thesis aims to alleviate water stress while simultaneously changing the way wastewater is perceived: not as waste, but as a useful resource.