FERTILIZER DRAWN HOLLOW FIBER FORWARD OSMOSIS FOR DESALINATION

Submitted by

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A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

University of Technology Sydney
FACULTY OF ENGINEERING

AUGUST 2014

Certificate of Authorship

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

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DEDICATED TO ALL THOSE WHO SPENT THEIR LIFE FOR THE WELFARE OF THE HUMANITY

Acknowledgement

I would like to express my deepest gratitude to my parents Prof. Dr. Abdul Majeed (Abbu) and Hameedah Majeed (Ammi) who have been such an inspiration to me in every sense over the course of my tertiary studies. Although I was away from them, their continuous love, support, and guidance gave me the strength and confidence to complete my PhD thesis within the allotted time frame. My dear parents, you mean so much to me because you have unfailingly nurtured my learning and supported my dreams!

I would like to take this opportunity to express my sincere gratitude to my supervisor Dr. Ho Kyong Shon for giving me the opportunity to work with him. I will always remember his unswerving encouragement, great mentorship, and support throughout my doctoral candidature. Without his consistent guidance and help, this work would not have been possible.

I wish to extend my thanks to my co-supervisor Dr. Sherub Phuntsho who fully supported me in my studies from the beginning to the end and guided me as a true friend.

I would also like to express my appreciation to the other SCEE faculty members Prof. Saravanamuth Vigneswaran, Dr. Hu Hao Ngo, Dr. Christian Kazner, A/Prof. Jaya Khandaswamy and Dr. Robert McLaughlan for their continuous encouragement during my PhD studies.

Further, I acknowledge Mohammad Johir, David Hopper and Rami Hadad for their support in terms of the project’s laboratory work and equipment set up. I also acknowledge the excellent administrative support received from Phyllis Agius, Craig Knowles, Tim Kevin, and Van Lee during this period.

I would like to express my sincere thanks to Samsung Samsung Cheil Industries Inc., Korea for providing me with the hollow fiber forward osmosis membranes for my studies. I would like to thank the National Centre for Excellence in Desalination Australia funded by the Australian Government through the Water for the Future Initiative for providing me with the funding to make this project and thesis possible. This work would also not have been possible without the institutional, experimental and scholarship support from the University of Technology, Sydney.

Special thanks to my FO group mates Soleyman Sahebi, Fouzy Lotfi, Jung Eun Kim who continuously supported me in all phases of my lab research work.

I am also grateful to all of the university research fellows such as Dr. Ibrahim El Salibiy, Dr. Ghausul Hussain, Dr. Tien Thanh, Mohammad Shahzad, Muhammad Shahid, Laura Chakli and Aaron Katz for their valuable support and guidance over my PhD candidature.

It is a pleasure to thank everybody who supported me directly or indirectly over the period of my doctoral studies.

Last but not the least; I would like to thank my loving and devoted wife Tehsin. My work would not have been possible without her patience and commitment. She gave me tremendous support over the entire duration of my PhD studies and really deserves the utmost thanks for all of the sacrifices that she made in relation to supporting my research. Additionally, I would like to thank my extraordinarily gifted and loving children Hasan and Ahsan who not simply shared my routine activities and responsibilities over this important period of my life but also helped in every way they could to ease the burden of my studies.

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Abstract

Continuous increase in fresh water demand has underscored the importance of developing a low cost water desalination process. Fertilizer drawn forward osmosis (FDFO) presents a promising step forward for low cost desalination using the natural osmotic pressure of the fertilizer draw solution (DS) as a driving force. FDFO carries a distinct advantage over other FO processes because the final diluted draw solution requires minimal to no treatment processes and it can be easily used for any useful fertigation application. This helps to eliminate the energy intensive permeate recovery step for the FO process and represents an economical desalination option. However, the performance ratio outcome for the earlier FO studies has highlighted a number of areas that can be improved in relation to FO performance.

This study evaluated FDFO using eight commercial fertilizers as DS for the flat sheet FO membrane using sea water (SW) quality feed (35 g/L NaCl) and targeting the NPK fertilizer and water requirements for tomato crops. Diverse results were achieved as some of the fertilizers showed significant flux while others showed negative or very low flux outcomes. This indicated that all commercial fertilizers may not be effectively used as DS for the SW quality feed. The results with various quality feed solutions (FS) and DS concentrations indicated that the flux performance does not vary in a linear sense with the changes in $\Delta\pi$. Varying flux outcome for various individual or mixed fertilizer DS's carrying similar $\Delta\pi$ values reflects the involvement of some unknown interactions between the DS and membrane surfaces, both at the active layer (AL) and the support layer (SL), for these specific results. These results further highlighted the fact that the osmotic pressure of the DS alone may not be used as the main criteria for the DS selection but rather the association between the DS solutes and the active and support layers of the membrane are also vital in terms of understanding the FO flux performances.

In addition, these outcomes revealed a number of limitations in relation to the FDFO e.g. reverse solute flux issues, higher nutrients concentration in the final DS and low recovery for osmotic equilibrium issues.

These fertilizer DS's were further assessed and their performance was compared for cellulose triacetate (CTA) flatsheet and polyamide (PA) hollow fiber FO (HFFO) membranes to understand the association between the DS properties and the membrane characteristics for the FO outcome. It was observed that at similar operating parameters, the PA hollow fiber showed a comparatively better outcome in terms of flux and reverse solute flux (RSF). HFFO was also evaluated for the effects of various operating conditions and markedly enhanced performances were found. It was observed that for 2 M NaCl as DS and DI water as FS, the HFFO successfully delivered water flux of 62.9 LMH at DS/FS Reynolds number (Re) of 3750/1500 whereas the same membrane in AL-FS orientation showed a flux of 9.67 LMH at DS/FS Re of 200/500. This indicated a flux increase of about 511% for a set of two operating conditions for the same FO membrane which further suggested that the changes in the operating conditions induce some indistinct changes in the membrane structure that can affect the water transport phenomenon through the membrane. It is therefore recommended that further studies be undertaken to investigate the real mechanism for the water transport through the membrane as this could contribute to the development of a higher performing membrane for the FO process. Results also indicate that cationic and anionic parts of the DS seriously affect the RSF outcomes. Further evaluation in this regard may contribute towards the creation of a better DS for the FO process with reduced RSF consequences.

The HFFO membrane was further evaluated for inorganic scaling and organic fouling issues using brackish ground water quality FS loaded with various model organic foulants such as humic acid, alginate and bovine serum albumine (BSA). During these FO fouling studies, it was noted that the commonly used FO fouling protocol which is similar to the RO fouling protocol may not be successfully used to evaluate FO fouling. The RO fouling was evaluated against a fixed driving force (hydraulic pressure) and any changes in the flux performance were referred to the fouling impact. However, in FO, as the driving force (net osmotic pressure difference between the FS and DS) kept changing constantly, it was really difficult to predict any flux change which was particularly associated with the scaling or fouling. For any two tests, at any particular time, the FO did not show the same driving force and hence for the evaluation of the fouling, the flux comparison for two different curves was not always useful. Accordingly, a new protocol is suggested for the FO fouling studies.

The fouling results indicated that FO, like the RO membrane, also posed potential operational risks in terms of scaling and fouling. The HFFO membrane indicated varying degrees of fouling potential for the membrane used in the AL-FS and AL-DS orientation and these were not related to membrane properties. Instead the hydrodynamic conditions employed for the process affected the fouling potential of the membranes used. Results indicated that the higher crossflow rate helped to keep the membrane clean from inorganic scale and the turbulence shear force did not allow scale build-up at the high Re.

It was also observed that the inorganic scaling was not fully reversed for the HFFO membrane used in the AL-FS and AL-DS orientations which employed hydraulic cleaning practices because the cleaning totally depended on how the flow shear forces using various cross flowrates were applied on the membrane surface. For the organic foulants, the turbulence shear force could not overcome the membrane–foulant interactions and foulants

layer deposited on the membrane surfaces and reduce the FO performance which was not recovered by hydraulic flushing. The chemical cleaning which used HCl, NaOH and EDTA was evaluated and it was found that the EDTA (pH 11) showed a better outcome for FO membrane cleaning.

Keywords: Fertilizer drawn forward osmosis, draw solute, desalination, sea water, hollow fiber FO membrane, EDTA cleaning.

Journal Articles Published

1) **T. Majeed**, S. Sahebi, F. Lotfi, J.E. Kim, S. Phuntsho, L.D. Tijing and H.K. Shon, (2014) *Fertilizer-drawn forward osmosis for irrigation of tomatoes*, Desalination and Water Treatment*,* 1-14.

2) **T. Majeed**, F. Lotfi, S. Phuntsho, J.K Yoon, K. Kim,& H.K. Shon, (2013). *Performances of PA hollow fiber membrane with the CTA flat sheet membrane for forward osmosis process*. Desalination and Water Treatment**,** 1-11.

3) **T. Majeed**, S. Phuntsho, S. Sahebi, J.E. Kim, J.K. Yoon, K. Kim,& H.K. Shon,. (2014). *Influence of the process parameters on hollow fiber-forward osmosis membrane performances*. Desalination and Water Treatment**,** 1-12.

4) S. Phuntsho,, S. Sahebi, **T. Majeed**, F. Lotfi, J.E. Kim, & H.K. Shon, (2013). *Assessing the major factors affecting the performances of forward osmosis and its implications on the desalination process*. Chemical Engineering Journal, 231**,** 484-496.

5) S. Phuntsho, H.K. Shon, **T. Majeed**, I. El Saliby, S. Vigneswaran, J. Kandasamy, S. Hong, & S. Lee, (2012). *Blended fertilizers as draw solutions for fertilizer-drawn forward osmosis desalination*. Environmental Science & Technology, 46, 4567-4575.

6) **T. Majeed**, A. Rafiq, M. Yaseen, M. Y. Malik, M. Q. Shahbaz and M. S. A. Taj, (2011). *Some comments on HE's homotopy- perturbation method for solving higher-order boundary value problems*. Nonlinear Analysis Forum *16*, 137–146.

Conference papers and presentations

1. **Tahir Majeed** , Sherub Phuntsho, Ho Kyong Shon; *Evaluation of the scaling and fouling potential with appropriate cleaning strategies for hollow fiber forward osmosis membrane*, Civil and Environmental Engineering Research Seminar (CEERS) April 4, 2014, UTS, Sydney.

2. **Tahir Majeed**, Sherub Phuntsho, Ho Kyong Shon; *Hollow fiber forward osmosis desalination using fertilizers as draw solutes*, 8th International Membrane Science and Technology Conference (IMSTEC 2013), 25-29 November 2013, Melbourne, Australia

3. **Fezeh Lotfi**, Tahir Majeed, Sherub Phuntsho, Ho Kyong Shon; *Membrane fouling during fertilizer drawn forward osmosis desalination*, 8th International Membrane Science and Technology Conference (IMSTEC 2013), 25-29 November 2013, Melbourne, Australia

4. **Tahir Majeed**, Sherub Phuntsho, HoKyong Shon, *Performances of the CTA flat sheet and PA hollow fiber forward osmosis forward osmosis membranes: using fertilizers as draw solutes*, Civil and Environmental Engineering Research Seminar (CEERS), August 16, 2013, UTS, Sydney.

5. **Tahir Majeed**, Sherub Phuntsho and Ho Kyong Shon, Innovative Hollow Fiber Forward Osmosis Desalination for Fertigation, FEIT Showcase 2013, June 12, 2013, Faculty of Engineering & Information Technology, University of Technology Sydney (UTS), Sydney, Australia.

6. **Tahir Majeed**, Sherub Phuntsho, Ho Kyong Shon, Fertilizer draw forward osmosis (FDFO) desalination for fertigation: Application to Tomato, The 5th annual conference on the challenges in environmental science and engineering (CESE) Conference, 9 - 13 September 2012, Melbourne, Australia

7. **Tahir Majeed**, Sherub Phuntsho, HoKyong Shon, A low-energy fertiliser drawn forward osmosis desalination- Possible application for Tomato, Civil and Environmental Engineering Research Seminar (CEERS), August 24, 2012, UTS, Sydney.

8. **Tahir Majeed**, Sherub Phuntsho and HoKyong Shon; Novel Fertilizer draw forward osmosis (FDFO) desalination for fertigation: Application to Tomato, FEIT Showcase 2012, 13 June 2012, School of Civil & Environmental Engineering, Faculty of Engineering & Information Technology University of Technology Sydney (UTS), Sydney, Australia.

9. **Tahir Majeed**, Sherub Phuntsho, Ibrahim El Saliby, Ganesh Sharma, HoKyong Shon, *Mixed ferilizers as draw solutes for the fertilizer drawn forward osmosis desalination*, Civil and Environmental Engineering Research Seminar (CEERS), 28 October 2011, UTS, Sydney.

10. **Tahir Majeed**, Sherub Phuntsho, HoKyong Shon, Ibrahim El Saliby; *Blended Ferilizers as Draw Solution for the Fertilizer Drawn Forward Osmosis Desalination*, 6th IWA Specialist Conference on Membrane Technology for Water and Wastewater Treatment, 4-7 October, 2011, Aachen, Germany

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13. Sherub Phuntsho, Hokyong Shon and **Tahir Majeed**, (2011). *Performance of Commercial bulk Fertilizer as Draw Solution for forward Osmosis Desalination. Paper presented at The Fourth Annual Conference on the Chanllenges in Environmental Science & Engineering*, Tainan City, Taiwan

Nomenclature

TDS : Total dissolved solids
MF : Microfiltration
UF : Ultrafiltration
NF : Nanofiltration
RO : Reverse osmosis
FO : Forward osmosis
FS : Feed solution
DS : Draw solution
AL : Active layer
SL : Support layer
MBR : Membrane biological reactor
FDFO : Fertilizer drawn forward osmosis
CP : Concentration polarization
ECP : External concentration polarization
ICP : Internal concentration polarization
PR : Performance ratio
RSF : Reverse solute flux
AL-DS : Active layer – draw solution
AL-FS : Active layer - feed solution
DI : Deionized
MED : Multi-effect distillation
MSF : Multi-stage flash distillation
VCD : Vapor compression distillation
MD : Membrane distillation
CDI : Capacitive deionization
BWRO : Brackish water reverse osmosis
ED : Electrodialysis
EDR : Electro dialysis reversal
PRO : Pressure-retarded osmosis
PBI : Polybenzimidazole
PSf : Polysulfone
PES : Polyethersulfone
PA : Polyamide
CA : Cellulose acetate
CTA : Cellulose triacetate
TFC : Thin flim composite
IP : Interfacial polymerization
CPSFs : Carboxylated polysulfones
PSF : Polysulphone
TFN : Thin film nanocomposite
PAI : Poly (amide-imide)

OMBR : Osmotic membrane bioreactor
HF : Hollow fiber
FSFO : Flat sheet forward osmosis
HFFO : Hollow fiber forward osmosis
PAO : Pressure assisted osmosis
EPS : Extracellular polymeric substances
BW : Brackish water
SW : Sea water
BGW : Brackish ground water
SIS : Salt interception scheme
MDB : Murray Darling Basin
MFDS : Mixed fertilizer draw solutions
NPK : Nitrogen; phosphorous; potassium
MAP : Mono ammonium phosphate
DAP : Di ammonium phosphate
SOA : Sulphate of Ammonia
CAN : Calcium nitrate
AN : Ammonium nitrate
AC : Ammonium chloride
BSA : Bovine serum albumin
HA : Humic acid
NOC : Natural organic carbon
EDTA : Ethylene di amine tetra acetic acid
SEM : Scanning electron microscope
FDDS : Final diluted draw solutions
LMH : L/m^2/h
AN : Ammonium nitrate
AC : Ammonium chloride
PWP : Pure water permeability
SRSF : Specific reverse solute flux
Re : Reynolds number
HTI : Hydration Technology Innovations

List of Symbols

A : Water permeability coefficient (L .m^{-2} .h^{-1}.bar^{-1})
B : Salt permeability coefficient (m.s^{-1})
C : Solute number density (L^{-1})
c : Solute concentration
D/Ds : Diffusion coefficient (m^{2} s^{-1})
Dh : Hydraulic diameter (m)
I : Intrinsic membrane structural properties
J_s : Solute flux (g.m^{-2}.h^{-1})
J_w : Water flux (L m^{-2} h^{-1})
J_w, sp : Specific water flux (L m^{-2} h^{-1} bar^{-1})
k : Mass transfer coefficient
K : Solute diffusion resistance (s.m^{-1})
K : Boltzmann's constant (1.38x10^{-3} J.K^{-1})
M : Solute molar concentration (mol. L^{-1})
M : Molar concentration of the solution
Mw : Molecular weight (mol.g^{-1})
N : Moles of solute (mol)
N_A : Avogadro's number
n : Van't Hoff factor
P : Applied hydraulic pressure (bar)
R/R_g : Gas constant (0.08314 L bar mol^{-1} K^{-1})
Re : Reynolds number
Sc : Schmidt number
Sh : Sherwood number
T : Absolute temperature (in K)
t : Thickness of the membrane (m)
Δt : Time interval (h)
ΔV : Volume change (L)
ΔP : Pressure change (bar)

Superscripts/subscripts

w : Water
s : Solute
F : Feed
D : Draw
m : Membrane
i : Interface
D, b : Draw, bulk
F, b : Feed, bulk
F, m : Feed, membrane
D, m : Draw, membrane
W, sp : Water, specific

Greek letters

π : Osmotic pressure (bar)
φ : Osmotic pressure coefficient
σ : Reflection coefficient,
ε : Porosity
β : van’t Hoff coefficient
τ : Tortuosity

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Chapter 1

INTRODUCTION

1.1 Background

Water and air are the most important elements to maintain biosphere and life on our planet. There is no equal substitute available on the earth for these valuable elements of life. However, while both of these resources are available on our earth in abundant quantities, their inferior quality is causing serious concern for the global community. Although water is not scarce at all usable water sources are limited. Further, water carries various impurities which can make it unfit for consumption and restrict its usage for various useful applications.

A few centuries back, residential and agricultural sectors were the only two primary users of water. After the eighteenth century, however, the commercial, industrial and power generation sectors stared to grow rapidly and they gained a significant share of the available water resources. In addition, as the world population has increased, the global consumption and demand for water has increased exponentially. Per capita water consumption is increasing not only with rises in the population but with the rising family income. Middle and high income classes across the world consume more water. In addition to the increasing direct water requirements for domestic use, to meet the growing need for food, goods and services, the industrial and agricultural sectors have shown a continuous rise in their water requirements which poses an additional threat to available and useful water resources.

Water is used in different types of residential, commercial, industrial and agricultural applications and each application requires a specific water quality for suitable functioning. To bring about changes to the existing water quality parameters, the available water is subjected to various processes and these activities are collectively known as water treatment. Water treatment involves the use of different techniques to treat water for issues such as suspended solids, dissolved solids, taste, colour, small, odour and microbial (bacteria and viruses). Each of these treatments carries an additional cost which results in a rise to the cost.

About 97% of the world's water resources are carried by sea which is high in total dissolved solids (TDS). Desalination is a process used to remove the dissolved salt and mineral concentration from any sea or brackish water source and it is always regarded as the most important treatment technique in terms of converting the huge volume of inappropriate quality water reservoirs to useful water. There is a similar issue with brackish ground water which carries high dissolved solids. For this, the available sea and brackish water resources present endless opportunities for desalination systems installation and this could help to solve all of the water shortage issues which our globe is facing.

Most of the modern interests in desalination are focused on developing cost-effective ways of providing fresh water for various uses in regions where the availability of fresh water is, or is becoming, limited. To meet the continuously growing demand for water, various desalination technologies have been developed in the past and continued efforts are being made to improve the performance of the existing systems and to develop new techniques.

Membrane based desalination is gaining popularity over thermal processes. Membrane based technologies now claim a major share of the installed desalination capacity in the world (Baker, 2012). Membrane based processes utilise semi permeable selective membranes which allow water molecules to pass through while leaving dissolved salts and other impurities. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are some of the most common technologies used by the water industry. The separation processes work differently for various types of membranes and the impurities removed from the water are usually classified for their separation mechanism, applied pressure, driving force and membrane rejection properties.

Membrane based systems are now successfully used not only for seawater desalination but for brackish water and water re-use and reclamation applications as well. RO is the most dominant technology used by the desalination industry today. This involves forcing water through semi-permeable membranes to remove salts and other impurities under a pressurised environment. The pressurising step represents the major energy requirement for the RO process and most of the energy requirements for the RO process originate from the feed pressurisation step and vary with the feed water TDS. The required operating pressure for the RO process depends on the feed water TDS level and increases with the feed water TDS. Higher dissolved solids feed desalination requires high operating pressure for water permeation and it is thus more energy intensive. The existing desalination processes often face two distinct challenges 1) Economical (high initial and operational cost and higher energy consumption) and 2) environmental (concentrate disposal and management). Beside continuous efforts in process improvements, the higher energy requirement for these desalination processes is still considered to be the most serious concern which restricts the use of these desalination processes for all common applications. This applies to both the thermal and membrane based desalination processes.

Continued research activities for the low cost water desalination process have recently resulted in a remarkable low pressure forward osmosis (FO) water desalination process. FO is a newly introduced membrane based desalination technique harnessing the naturally available power i.e., osmotic pressure of draw solution. Accordingly, it does not require any additional external energy source to drive the diffusion of water through a semipermeable membrane. The driving force for water transport is the difference in the osmotic pressure between the feed solution (FS) and a draw solution (DS); water diffuses from the FS of lower osmotic pressure to a DS of higher osmotic pressure.

Energy requirements for FO are limited to the pumps consumption used for the crossflow arrangement of the FS and DS on both sides of the membranes. This is because the FO utilises the natural osmotic pressure difference between the available draw solution and the brackish/saline feed water. This movement of water molecules in the FO is different from the RO process where water permeates through the membrane under high hydraulic pressure. As the FO does not require the kind of additional energy to pressurise feed water streams as the RO required it can be considered as an environmentally friendly desalination technology having a low carbon footprint.

Owing to these advantages, the FO technology has in a very short period of time been evaluated for a wide range of applications ranging from sea / brackish water desalination (McCutcheon et al., 2005, Kessler and Moody, 1976b, McGinnis et al., 2013, Cath et al., 2006, Kessler and Moody, 1976a, McCutcheon et al., 2006, McGinnis and Elimelech, 2008) to power generation (Garcia-Castello et al., 2009), wastewater treatment (Cath et al., 2005), to osmotic membrane biological reactor processes (MBR) (Achilli et al., 2009b, Cath et al., 2005, Holloway et al., 2007, Warczok et al., 2007), to food processing, and to the concentration & recovery of active organic components (Achilli et al., 2009a). Super magnetic nano-particles (Ling and Chung, 2011a) have been suggested as DS for application in drinking water, yet they are still required to be tested commercially for processing economy.

As water diffuses through the membrane, the feed solution becomes concentrated and the draw solution is diluted. This dilution reduces the available driving force (net osmotic pressure difference) across the semipermeable membrane which results in continuous flux decreases. Thus, the DS is reconcentrated either to maintain the osmotic pressure driving force or to extract a portion of water permeated from the feed side. In all of the above FO techniques, water recovery and draw solute separation are energy consuming steps that diminish the true advantages of low energy FO operation. In some of the cases, the diluted DS is also used as such for their particular application.

Fertilizer drawn forward osmosis (FDFO) is a similar unique concept which uses commercially available fertilizers as draw solution to desalinate brackish/sea water for agricultural use (Phuntsho et al., 2011). Unlike many other FO processes, in FDFO, the resultant low concentration fertilizer DS does not require any necessary regeneration and thus can easily be used with some concentration adjustments to irrigate any suitable agricultural crops (Phuntsho et al., 2011, Phuntsho et al., 2012d). In this FO process, as the final step of draw solute recovery is eliminated, it helps the fertilizer drawn FO process to take real advantages from the low cost forward osmosis desalination. FDFO is among some of the most promising FO technologies and it is gaining the increasing attention of industry and end user groups.

1.2 Research Motivation

Progressive research on the FO process was started about a decade ago and several reports have been published in this field. The main focus of these research activities was to achieve enhanced FO performances using a better quality membrane and a suitable DS.

Different types of FO membranes have been developed over this period and the physical appearance can broadly be divided into two main types 1) Flat sheet and 2) Hollow fiber. Due to the various system design and operational requirements issues, most of these membranes are of an asymmetric (active rejection layer embedded on a porous support layer) nature. The asymmetric nature of the membrane helps the build-up of the concentration polarization (CP) phenomena. The asymmetric structure of the FO membrane enhances the CP on both sides of the membrane which consequently results in a reduction of the actual water flux through the membrane. Four types of CP i.e., concentrative and dilutive external concentration polarization (ECP), and concentrative and dilutive internal concentration polarization (ICP) have been identified which significantly affect the FO process output while using asymmetric membranes (McCutcheon and Elimelech, 2006). ECP is usually linked with DS and FS concentration whereas ICP is mainly associated with the thick support layer structure (Cath et al., 2006).

In FO, this CP drastically reduces the available osmotic pressure gradient at the membrane surface resulting in a sharp decline in the actual flux. Since FO mainly relies on the available osmotic pressure across the membrane surface (e.g contacting DS and FS to drive osmosis), its flux is more seriously affected by the CP effects (Lay et al., 2010, Zhang et al., 2010) and it usually results in poor FO operational performance. For these reasons, most of the FO studies show an extremely low performance ratio (PR) of 8-16% (Phuntsho et al., 2013b) which is not a very good indication to judge any system's performance. PR is defined as the ratio of the experimental flux to the theoretical flux (and this is determined based on the net bulk osmotic pressure). The lower PR for these FO processes highlights some serious issues in terms of membrane characteristics, DS properties and different operating conditions.

FO studies have utilised a wide range of DS to evaluate FO performance. Different DS have shown unusual performance behaviours for these evaluated process and raised serious issues as to how these DS properties affect the flux outcome for different membranes.

Reverse solute flux (RSF) is another serious operational issue observed for FO which represents diffusion of a part of the draw solute towards the FS during FO operations. RSF is also linked with the performance of the FO asymmetric membrane and the DS properties. This loss contributes to the operational cost of the FO process and thus reduces the cost effectiveness of the process.

Along with CP, PR and DS performance, membrane fouling is also considered to be another serious operational issue for FO systems (Cornelissen et al., 2008, Tang et al., 2010b) but this has not yet been explored seriously. Like other membrane processes, new studies have shown that fouling also affects the FO performance which highlights serious operational consequences for FO progress. Chemical cleaning of the fouled FO membrane has not yet even been attempted.

All of the above issues indicate that a clear understanding of the FO operational issues linked to the membrane performance for low flux and high RSF may improve the performance of FO which will in turn help the commercialization of FDFO and other FO based desalination techniques. FO flux is directly linked to the initial capital cost and operating cost of the FO system and a high flux FO operation means a reduced FO plant footprint. Further, a reduced RSF will mean a reduction of the DS leakage to the FO waste streams.

This study is focused on these issues as they exhibit huge room for improvement in the FO performance. Changes in this respect may lead to a revolution in the commercialization of this low cost desalination process. This becomes a primary motive for this current research work. The lower PR and other FO issues as outlined above in this section offer opportunities to enhance the performance of the existing FO system.

1.3 Objectives and Scope of the Study

Earlier FO studies revealed that the FO performance is not affected by net osmotic pressure but rather, it provides complex mechanisms for various factors such as membrane characteristics (e.g. membrane structure, active layer and support layer properties), draw solute and feed solute properties, operational process parameters as co-current or counter-current cross-flow, cross-flow rates, membrane orientations, and operating temperature etc. .

The insignificant outcomes from the earlier studies indicate the complexity of the above concerns as these issues have not been well understood.

Looking into the above research insufficiencies, the main objectives of this study are to:

- Further investigate and explore the low pressure prospect FO process in detail.
- Evaluate the FDFO process for a practical crop application to identify operational issues.
- Understand the issues and associations for various types of membranes and different DS for any particular performance of FO processes and to select a better performing membrane for the fertilizer DS.
- Study the effects of various process parameters on the hollow fiber FO performance.
- Evaluate fouling issues for hollow fiber FO membranes using FS which carries various concentrations of inorganic and organic foulants.
- Investigate the performance of various cleaning chemicals for restoring the fouled hollow fiber FO membrane outcome.

To achieve these objectives, various FO studies were conducted using different configurations of laboratory-scale FO setups. Like, FDFO, this study has been completed using different fertilizer DS, however these useful outcomes can also be equally used for any other FO process applications.

1.4 Structure outline of the thesis

The study looks into six main aspects: FO fundamental characteristics, FDFO evaluation, comparison of the different membrane performances, effects of operating conditions, fouling potential and membrane cleaning techniques.

The structure of the thesis is as follows:

Chapter 2 provides background literature information about various desalination techniques, FO process, its scope and limitations, FO applications, the evaluation of the role of process conditions on performance parameters, the types of FO membranes, operational issues and the fouling and scaling effects on FO performance.

Chapter 3 introduces all materials and methods used in this study.

Chapter 4 investigates FDFO targeting a real application scenario for a tomato crop using single commercial grade fertilizers as DS and seawater quality FS.

Chapter 5 evaluates FDFO for tomato application using mixed fertilizer DS against seawater quality feed. The effects of various combinations of fertilizer mixture DS on FO performance are also evaluated.

Chapter 6 compares the FO performance of various fertilizer DS's using two different types of FO membranes i.e., flat sheet and hollow fiber. The study is designed to evaluate how the various DS properties and membrane characteristics manipulate FO performance.

Chapter 7 studies the role of various operating parameters such as membrane orientation, draw solution properties, cross-flow directions and cross-flow rates on hollow fiber FO flux and RSF outcome.

Chapter 8 explores the role of inorganic scaling and organic fouling on the hollow fiber FO membrane using a brackish ground water feed and three model foulants as alginate, humic acid and bovine serum albumin. FO is evaluated for the active layer – draw solution (AL-DS) and active layer - feed solution (AL-FS) orientation and it is used to study the scaling and fouling issues.

Chapter 9 presents the outcome of various membrane cleaning techniques including hydraulic flushing and chemical cleaning for both the AL-DS and AL-FS orientation. Commonly available chemicals such as HCl, NaOH and EDTA are evaluated for their membrane cleaning efficiencies.

Chapter 10 summarises the main findings and provides general conclusions and recommendations for future work.

University of Technology Sydney
FACULTY OF ENGINEERING

Chapter 2

LITERATURE REVIEW

2.1 Introduction

2.1.1 Water and our world

Water is available everywhere on the earth, in sea, underground, on surface and most importantly in the air. Further, it is available in all of its three forms as water, ice and vapours. On the whole, about two-thirds of our globe is covered with water which represents huge volumes of available water (Panchal and Knudsen, 1998). It is estimated that all water on, in, and above the Earth, is approximately 1.386 x 10^9 cubic kilometres (km^3). This is a huge volume but for various reasons, most of this quantity may not be used in all applications.

Our natural hydrological system helps meet most of the world's fresh water requirements. There are five main processes at work in the hydrologic cycle: evaporation/transpiration, condensation, precipitation, surface runoff/subsurface runoff, and accumulation (Baker, 2012). The hydrologic cycle begins with the evaporation of water from the ocean's surface. Except for precipitation, all these processes occur simultaneously and continuously. This hydrological cycle helps us to continuously replenish our ground and surface water reservoirs. The available water carries characteristics of various quality and some of these quality parameters make this water unsuitable for various applications. To bring about some change in the existing water quality parameters, the available water is subjected to various processes. The processes which bring some changes in the quality of water are collectively known as water treatment. Water treatment involves using different techniques to treat water for issues such as suspended solids, dissolved solids, taste, colour, small, odour and microbial (bacteria and viruses). Each of these treatments carries an additional cost which results in rising water costs.

2.1.2 Water use

In our daily life, water is used for a wide range of applications such as domestic (drinking and cooking, washing, cleaning, leisure and outdoor), commercial, industrial, mining, power generation, marine and agricultura.. Water usage and its demand patterns are changing due to technological advances and the world's rising population. Rising water demand linked to a continuously growing population has raised serious concerns for the available usable water resources. Apart from direct water consumption, the increasing population means more demand for industrial goods and food which require huge volumes of water for their production processes. Fig. 2.1 indicates the effects of rising world population on water usage and agriculture and industry use more water as the population increases.

Growth forecasts further indicate that the world's water demand will increase by 32% for 2020-2025 will only increase the pressure on the limited fresh water resources and treatment options available. Using these statistics, Worldwatch Institute predicted that more than two-thirds of the world's population may experience water shortages by 2025, thus affecting practically every country in the world, including the developed, unless they create new water sources (Tijing et al., 2007). This reflects a need for serious efforts to fulfil rising water demands especially in the agriculture sector.

2.1.3 Water salinity - the biggest challenge

Water is a universal solvent and it dissolves a wide range of impurities during its passage through these infiltration and run-off processes of the hydrological cycle and from sea bed rocks as well. These impurities increase the total dissolved solids (TDS) of water and make it unsuitable for various applications such as residential, commercial, industrial, power generation, mining and agricultural application. This is because each application requires varying qualities of water for suitable functioning.

According to its TDS value, water by quality is categorized into four types (Panchal and Knudsen, 1998):

- Fresh water - Less than 1,000 ppm
- Slightly saline water - From 1,000 ppm to 3,000 ppm
- Moderately saline water - From 3,000 ppm to 10,000 ppm
- Highly saline water - From 10,000 ppm to 35,000 ppm

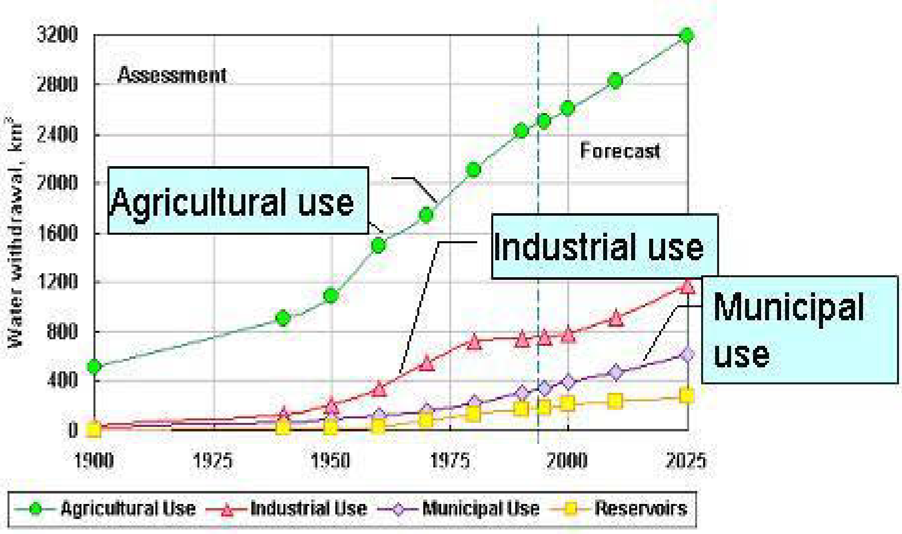

Fig. 2.1 World water usage trends (Shiklomenov, 1999)

Since, about 97% of the world's water is carried by the oceans which have a high percentage of TDS, dissolved salts reduction practices are increasingly regarded as the most important treatment techniques for converting this huge volume of poor quality seawater reservoirs into a suitable quality product.

2.2 Desalination- an outline

According to the World Health Organization, fresh water should have a total dissolved salts level of less than 500 ppm to be safe for human consumption (Bartels et al., 2008). As the available direct sources of clean water such as rivers, lakes, and underground water matching the WHO water quality criteria are not enough to meet the daily consumption needs, alternative water purification technologies have been developed to desalt saline water from sources. These include seawater, underground water, and industrial wastewater to a desired water quality level. To make use of these high TDS waters, some processes that are commonly termed desalination are being used to convert these large bodies of water into some useful applications. With water shortages emerging worldwide, communities are turning to desalination as a solution to create a reliable water supply. Desalination is a means of producing fresh water from saline or brackish water by removing dissolved salts to make it suitable for human direct use, and commercial, agricultural or manufacturing purposes (Tijing et al., 2007).

Desalination is not a new concept and it has in fact been used since ancient times in various ways. Desalination is one of mankind's earliest forms of water treatment, and it is still one of the most popular water treatment solutions used today. Many civilizations used simple distillation processes on their ships to convert sea water into drinking water. To meet the continuous growing demand for the fresh water, the desalination installed capacity is also increasing at a rapid rate as shown in Fig. 2.2 below, indicating the expected trend up to the year 2025.

For continuously emerging water shortages across the world, communities are turning to desalination as a reliable solution for scarce fresh water supply. Looking into the availability of huge sea/brackish water reservoirs, desalination seems to be the only viable solution to world’s water scarcity problems.

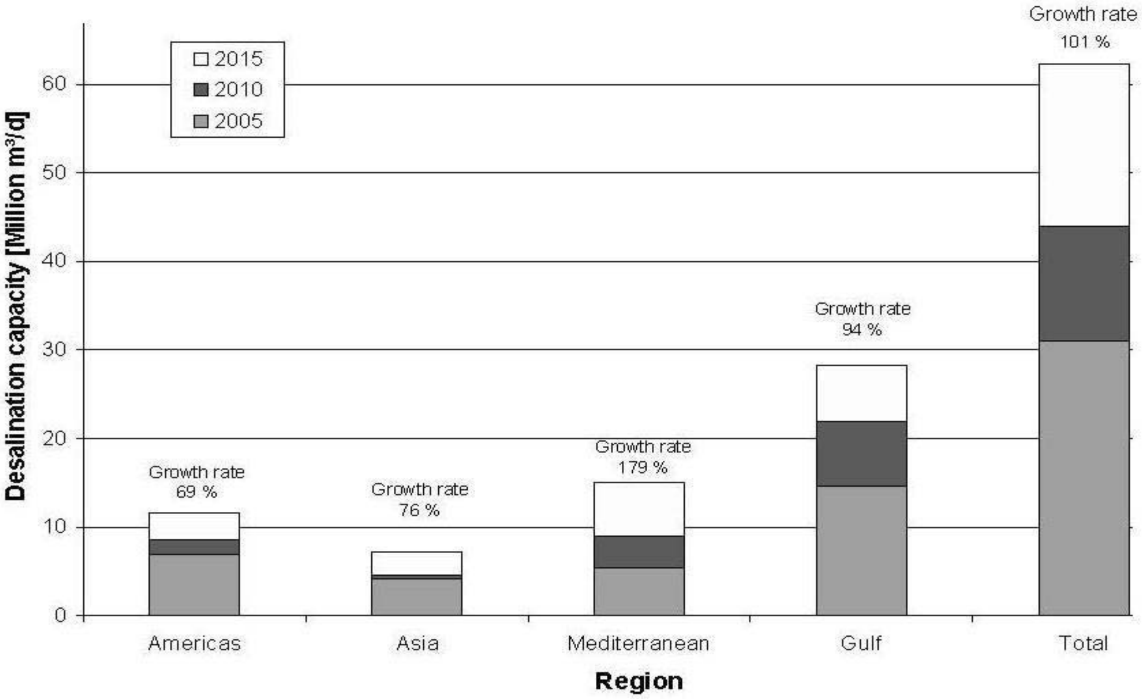

Fig. 2.2. Expected growth of desalination capacities around the world (GWI, 2005a)

2.3 Classification of desalination technologies

Different classification methods are being used for developing desalination technologies. Desalination processes can be classified under two broad headings: (a) Phase change processes (thermal); and (b) single phase diffusion (membrane). These desalination techniques may also be classified by other ways as described in Table 2.1.

Table 2.1. Broad classification of desalination technologies

Classification by	Thermal	Membrane
Separation Mechanism	Phase change	Diffusion
Main type of energy requirements	Thermal	Electricity
Separation driving force	Heat	Pressure

Thermal and membrane-based desalination processes are being used to fill the current gap between water supply and demand but rising energy prices make it difficult to economically produce good quality water (Mulder, 1996). Although thermal desalination was initiated many decades ago, their simple process and comparatively low energy systems have, in the last 30 years, made membrane-based desalination processes more popular and able to compete with long established distillation-based technologies (Baker, 2012).

2.3.1 Thermal desalination processes

The available desalination technologies have separation mechanisms that classify them into thermal, membrane-based and hybrid desalination types. Thermal desalination separates salts from water by evaporation and condensation. In membrane desalination, using hydraulic pressure force, water diffuses through a semi-permeable membrane while salts are almost completely retained. Membrane distillation utilises principles of both thermal and membrane technologies. An overview of available desalination technologies is given in Table 2.2.

Table 2.2 outlines some of the most commonly used desalination processes which include thermal, membrane and hybrid technologies. Distillation is the simplest thermal desalination process. Thermal processes involve changes in the water phase as it is first evaporated to vapours and then condensed back into liquid water leaving dissolved salts and other impurities in the water. Thermal processes are able to reduce the salt contents of saline water (TDS ranging from 60,000-70,000 mg/L) up to 10 ppm or less (Karagiannis and Soldatos, 2008).

Thermal desalination is more energy intensive than membrane-based desalination, but can better deal with more saline water and delivers even higher permeate quality (GWI, 2005a). Solar stills, simple distillation, freezing, etc. also constitute some of the prominent thermal technologies used throughout the world.

Thermal desalination technologies are more popular in the Gulf countries of the Middle East as cheap heat energy sources are abundantly available in that region. As thermal units utilize excess thermal energy, it is thus possible to combine the production of large amounts of power and water in one station, thereby satisfying the demand for both of them. Further, compared to the membrane-based systems, thermal desalination units are also receiving more attention for their great durability under various conditions in treating seawater.

2.3.2 Membrane-based desalination processes

Membrane-based processes utilise semi-permeable selective membranes allowing water molecules to pass through while leaving dissolved salts and other impurities back there. These selective membranes act as physical barriers that separate various impurities existing in the water. Reverse osmosis (RO), nanofiltration and electrodialysis are some of the most commonly used desalination technologies that the water industry embraces. RO is also a leading technique among all membrane-based desalination processes. A few other membrane-based technologies such as microfiltration and ultrafiltrtation are also available and they are used for water treatment. However, their use is not directly meant for desalination (salt rejection) but rather are applied in supporting pre-treatment for the above mentioned desalination technologies.

Table 2.2 Overview of main desalination technologies

Thermal desalination technologies	Membrane desalination technologies	Hybrid desalination technologies
Multi-stage flash distillation (MSF)	Reverse osmosis	Membrane distillation
Multi-effect distillation (MED)	Nanofiltration	
Vapor compression distillation (VCD)	Electrodialysis	

2.3.3 Hybrid desalination processes/ Hybrid systems using distillation and membrane technology

The best scenario which is applied to get the optimized performance is using various desalination systems in hybrid configurations. Usually two approaches such as a combination of distillation and membranes, or integrated membrane systems are employed. Combined distillation/membrane processes, usually MSF/RO, are used in ‘dual-purpose’ plants for the cogeneration of water and electricity. The RO facilities have a greater flexibility and can help to overcome variations in demands (Van der Bruggen, 2003b). They can be operated with maximum permeability because of the preheating that utilises the reject heat from thermal plants.

The advantages of this configuration, in addition to the greater flexibility, are the higher RO product water recovery, less power consumption for RO because of the feed pre-treatment, reduced chemical consumption and membrane replacement rates, and prolonged membrane service. Distillation and membrane technology coexist in this configuration and may have a synergetic effect on each other. Thermal units also help increase the recovery by using waste streams from reverse osmosis and electrodialysis processes.

Membrane operations are also integrated in various ways for sea water desalination such as combining nanofiltration for the pre-treatment step and reverse osmosis. Ultrafiltration can be used before nanofiltration to remove large organic foulants. A gas–liquid membrane contactor can serve to control the concentration of gaseous components. Furthermore membrane crystallization can be used as to dispose of the brine, with solid salts being a useful by-product.

2.4 Choice of desalination technologies

The selection of a suitable desalination technology for any particular project is not so simple and various parameters are considered for the selection process. Cost and energy reductions for desalination are therefore important in minimising the environmental impact of a desalinated fresh water supply. The cost is always the most critical issue in the whole decision-making process. This cost reflects the economy of any desalination process and indicates the limitations of desalinated water use for various applications. Apart from cost and energy requirements issues for a particular desalination technology, available feed water and the desired treated water quality limit the selection process (see Table 2.3).

Table 2.3. Selection criteria of the major desalination technologies for feed water. Also indicates the treated water quality outcome (Laborde et al., 2001, GWI, 2005a).

	MSF	RO	Electrodialysis
Thermal energy consumption	Yes	Nil	Nil
Electrical energy	Yes	Yes	Yes
Typical salt contents of feed water (ppm)	30,000-100,000	1000-45000	1000-3000
Product water quality TDS (ppm)	<10	<500	<500

2.4.1 Total cost of the desalination process

The total desalinated water cost comprises capital and operating costs and they are specific to location, feed water components and composition, energy cost, other cost parameters and the method selected for costing (Reddy and Ghaffour, 2007b). The cost of water treatment by desalination depends upon many factors, unique in each case, such as the desalination method, the level of feed water salinity, the energy source, the capacity of the desalting plant, and other site-related factors (Karagiannis and Soldatos, 2008, Reddy and Ghaffour, 2007b).

For this reason, there is no specific data which may be used for cost estimation of any new water desalination plants.

Various parameters such as the capital cost, energy requirements, maintenance costs, availability of the energy sources, feed water quality, concentrate disposal and management, environmental considerations, technology, adaptability to other energy resources, possibility for coupling with the other hybrid systems and energy recovery are evaluated for a specific site to decide on selecting a particular desalination technology (Lee et al., 2006, Busscher and Weerkamp, 1987). Desalination costs also vary strongly with the capacity and type of plants, the quality of product water required, the period and assumptions about capital and labour costs (Zhou and Tol, 2004).

2.4.2 Operating cost of desalination

Desalination operating cost for any process varies for different types of desalination technologies (Fig. 2.3). Desalination technologies require energy for either phase change or diffusion process against the feed osmotic pressure. The energy cost portion dominates the total cost for all desalination technologies and these also vary for thermal and membrane-based systems. Thermal systems utilise both thermal and electrical energy whereas RO mainly uses electrical energy for water desalination. Membrane replacement cost takes the second largest share in the total operating cost for the membrane-based systems. Other costs include supervision and labour, chemicals, consumables and maintenance costs.

2.4.3 Water desalination cost and its relevance to type of feed water

Table 2.4 indicates a significant difference in the RO desalination cost for seawater and brackish water feed sources and it declines as the feed water TDS decreases. These low energy RO process requirements become the main selection criteria for RO leading to its rapid expansion for economic desalination. Having low energy requirements, the RO process is regarded as the most suitable low cost technology for brackish water desalination. The gap in energy requirements for thermal and RO technology further widens for brackish water feed. Similarly, RO is a favourable choice in used water reclamation apart from its low energy process costs. It carries many other advantages such as simple operation, high rejection, durability, leaving a small footprint as used water usually also carries lower TDS.

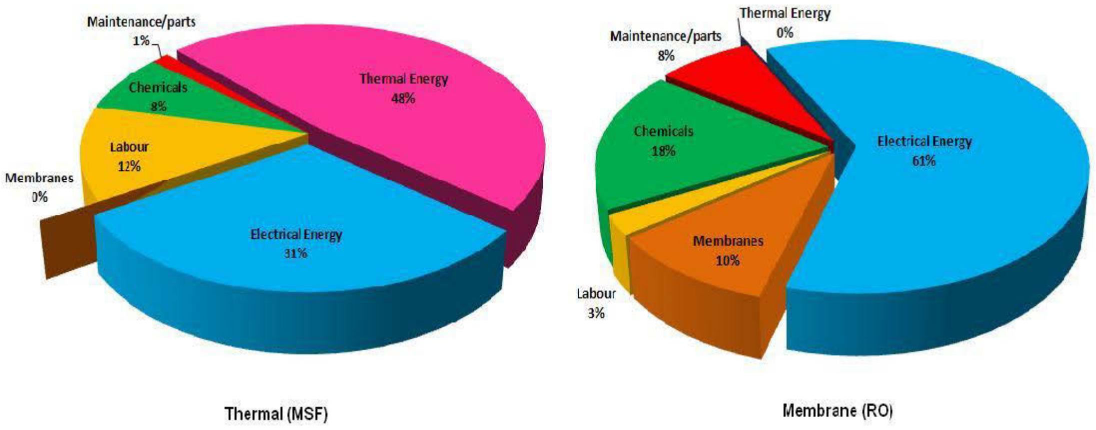

Fig. 2.3 Comparison of the operating cost components for thermal (MSF) and membrane (RO) technologies (GWI, 2013)

Table 2.3, Table 2.4 and Fig. 2.3 further indicate that regarding variation in the energy type and adaptability to a wide range of feed water TDS, RO has the advantage of being the dominant desalination technology for sea water, brackish water feed and/or water reuse.

Regardless of the feed water TDS, energy requirements and consequential costs usually remain the same for all thermal process but they differ for membrane-based systems (Fig. 2.4). Brackish water desalination cost ranges between 0.38-0.6 $\$/m^3$ and seawater varies between 0.75$- 2.80$\$/m^3$ (AMTA, (2013). As the feed water TDS increases, more energy is required to overcome feed osmotic pressure which raises the cost of membrane desalination processes for high TDS feed. It is noted that the cost of desalination (shown in value) in different published data provides a misleading picture. These desalination costs have varied in value because the cost basis of energy continuously changes according to location and time and they are not comparable (Laborde et al., 2001, Bennett, 2011, AMTA, 2013). Only the energy consumption presents meaningful results.

Table 2.4. Effect of feed water source on energy (electrical/thermal) used by various desalination technologies (Sheikholeslami, 2003)

Energy (electrical/thermal) used by various desalination technologies	Electrical energy kWh/m^3	Thermal energy kWh/m^3	Total energy kWh/m^3
MSF	2.5-4	7.5-12	10-16
MED	1.5-2	4-7	5.5-9
RO (seawater)*	3-4*	None	3-4
RO (brackish water)	0.5-2.5	None	0.5-2.5

* Including energy recovery system

Membrane installations are increasing at a rapid rate and global membrane desalination capacity is expected to grow from 30.6 million m^3/day in 2005 to 61.7 million m^3/day in 2015; this represents a 102% increase in one decade (GWI, 2005b). Moreover, global water reuse capacity will rise from 19.4 million m^3/day in 2005 to 33.7 million m^3/day in 2010 and 54.5 million m^3/day in 2015; a 181% increase (GWI, 2005b). These rapid increases are to a large extent due to the maturity of membrane technology in water and wastewater treatment applications, which have reduced costs and broadened the scope of desalination and water reuse market.

Fig. 2.5 below represents usage of the membrane-based system for various water treatment applications. This indicates that in most parts of the world, membrane-based systems are successfully being used for treating sea water feed source.

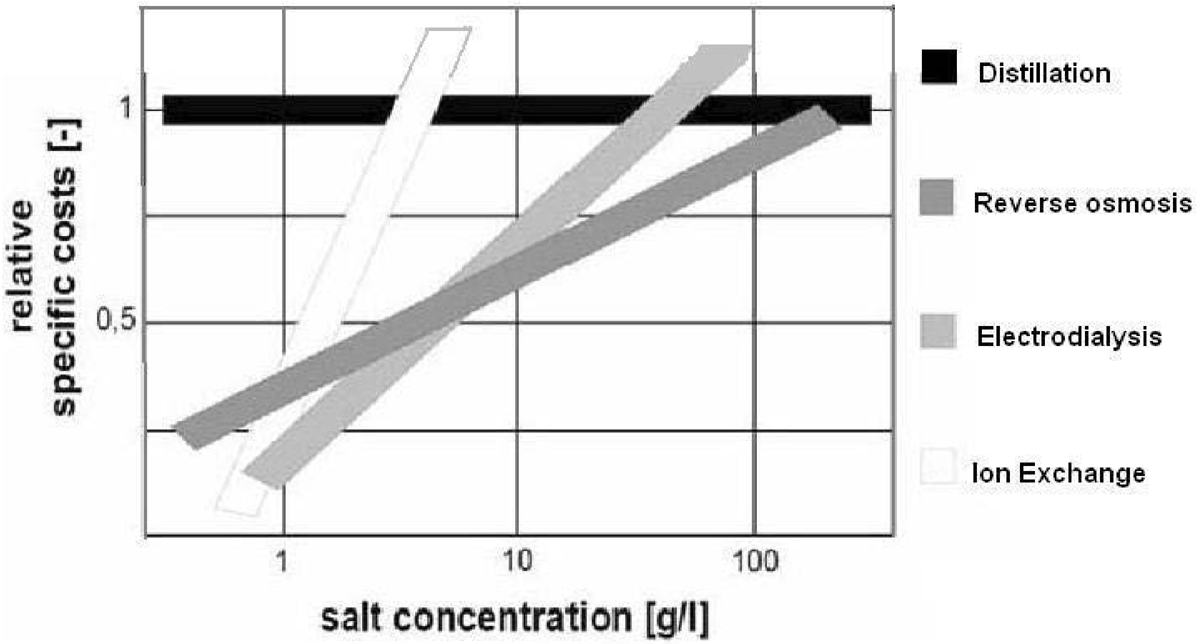

Fig. 2.4 Relative water production cost of various competing technologies for different feed water TDS quality (Fritzmann et al., 2007).

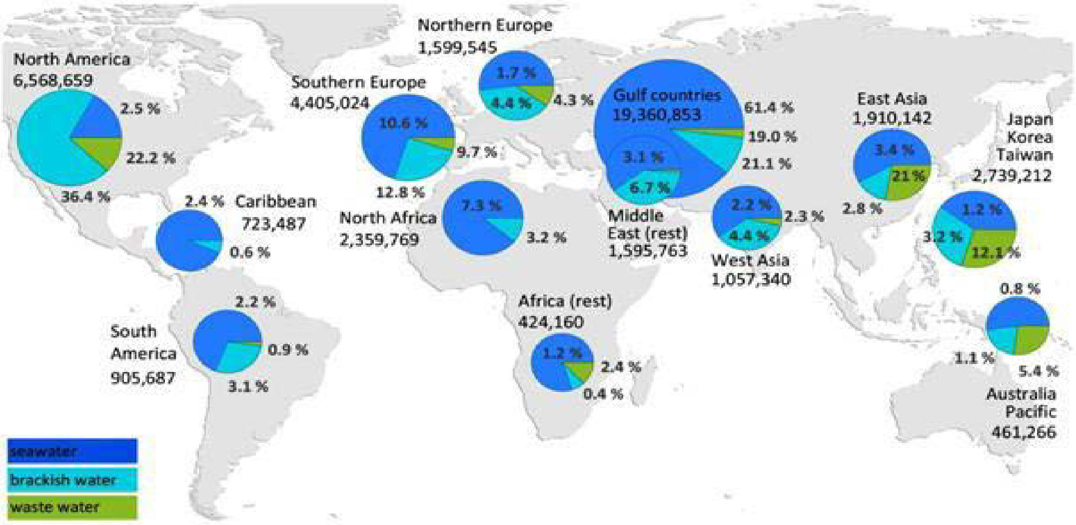

Fig. 2.5 Installed desalination capacities for various feed water sources (Escobar and Schäfer, 2009)

2.4.4 Desalination Economics

The energy requirements for any desalination process are the most important parameter used when selecting a suitable desalination process for a particular feed water source. Table 2.4 compares and presents energy consumption requirements of major desalination technologies, and the differences in total energy requirements between the thermal (MSF, MED) and membrane (RO)-based desalination techniques are highlighted. Apart from many technical advances and design improvements, these commonly used desalination processes are still energy intensive and leave a large carbon footprint. For these reasons, the major emphases in development work on desalination processes seek to improve their energy efficiency.

2.4.5 Hybrid desalination systems

Desalination units use hybrid systems to increase the productivity and/or reduce the cost. A desalination unit can be hybridised not only with regard to the energy source, but also the desalination method. The best option for optimized performance of a desalination system is the application of hybrid systems. Two approaches can be used, and these are a combination of distillation and membranes, or integrated membrane systems. Combined distillation/ membrane processes, usually MSF/ reverse osmosis, are used in 'dual-purpose' plants for the cogeneration of water and electricity. Ample research is available regarding the combination of RO and thermal desalination technologies (Phuntsho et al., 2012d, Mitchell et al., 1991, Li and Elimelech, 2004). RO can be operated at maximum permeability with feed water preheated from the MSF plant (Van der Bruggen, 2003a). In addition to thermal technologies RO can be combined with other desalination technologies, for example electrodialysis, ultrafiltration, and capacitive deionisation (Chen et al., 2014, Ghosh and Hoek, 2009a).

The obvious benefits of integrated/hybrid membrane systems are: firstly, the enhanced quality of the water produced, which cannot be successfully produced by a standalone process; secondly, energy savings due to lower energy consumption; thirdly environmental friendliness due to reduced waste disposal; and fourthly, reduced capital and operating costs due to the higher efficiency and productivity of the plants (Li and Elimelech, 2004). It is imperative to explore new hybrid desalination technologies, and to develop a rigorous methodology representing such systems.

2.4.6 Renewable energy source powered desalination

Reductions in the desalination operating costs and energy requirements are considered important for minimising the environmental impact of desalinated fresh water supply (Busscher and Weerkamp, 1987). The research focus for reducing energy costs is linked to the energy requirements which are in turn connected to greenhouse gas emissions produced by power plants using different fossil fuels. CO_2 is generated during the combustion process for generating energy and discarded into the atmosphere. It signals rapid weather changes that are due to global warming.

To overcome these issues, unlike desalination using conventional energy resources, renewable energy sources-based desalination is considered to be an attractive solution in terms of reduced environmental impact due to less onventional energy consumption and less gas emissions. The majority of desalination systems that use a renewable energy source can be divided into three categories: (a) wind, (b) solar (photovoltaic or solar collectors) and (c) those which use geothermal energy (Van der Bruggen, 2003b). A very common example is the use of solar ponds for treating concentrate from reverse osmosis, MSF or membrane distillation (MD) processes (Al-Obaidani et al., 2008). Likewise, MD has been extensively used in various zero discharge applications for RO, MSF, capacitive deionization (CDI), Vapor compression distillation (VCD) (Blanco Gálvez et al., 2009). MD has been further evaluated for solar energy sources. In a few cases these systems are further connected with additional sources of conventional energy (e.g. local electricity grid) in order to minimise the effect of changes in the level of energy production and consequently water production.

Similarly, thermal processes can utilise waste heat or solar thermal energy more conveniently (Busscher and Weerkamp, 1987). When renewable energy sources are employed the cost is much higher due to more expensive energy supply systems. However, this cost is counterbalanced by the environmental benefits using renewable power generation systems. Thus development of a sustainable desalination method requires the minimization of energy consumption, but also using renewable energy sources. This should enable less developed countries to have access to sufficient quantities of fresh (desalted) water. Different options can be suggested. Systems based on wind energy and solar energy are among the most realistic options (Van der Bruggen, 2003b).

2.5 Common membrane technologies

The growth potential has been observed for membrane systems for various feed TDS, and further discussion is currently focusing on membrane technologies. The ability of these membranes to reject various impurities depends upon the molecular size of the impurities (both suspended and dissolved) and the membrane characteristics (Fig. 2.4). Since these membranes carry different rejection layers, they remove particles of varying nature. Usually they reject all particles greater than the membrane pore size but in some cases their efficiency is not 100% and some solute molecules diffuse towards the permeate side.

2.5.1 Classification of membranes

2.5.1.1 Separation properties of various membranes

The separation processes work differently for different types of membrane and impurities removed from water are usually classified by separation mechanism, applied pressure, driving force and membrane rejection properties (Lee et al., 2006). The portion of the water passed through the membrane is termed 'permeate' whereas the rejected portion of the feed water is known as 'concentrate'. Water flux is the term used to indicate the membrane performance for unit membrane area and in unit time. A few of the most prominent membrane desalination techniques are briefly discussed below.

2.5.2 Reverse osmosis (RO)

RO is now widely being used for seawater desalination, brackish water treatment plants and water reclamation plants. The RO process requires a high pressure to force water molecules from a regime of high solute concentration to a low solute regime through a semi-permeable membrane which allows water to pass through but retain most of the solutes (Fritzmann et al., 2007). There are several types of membranes, including cylindrical or tubular, flat plastic layers, very thin flat membranes and smooth clay fiber (known as the hollow fine fiber), and those with spiral forms (known as the spiral wound). The most commonly used membrane is the spiral wound membrane.

Based on the RO feed characteristics, the pressure requirements vary for various qualities feed water as normal, brackish or sea water. Feed water carrying higher total dissolved solids (TDS) exhibits high osmotic pressure. For these high TDS feeds, the RO system also requires high hydraulic pressure to push water molecules across the membrane. Most of the energy requirements for the RO process originate from the feed pressurization and vary with the feed TDS. Brackish water (2,000 ppm) feed only requires 220 psi operating pressure whereas sea water (35,000 ppm) desalination requires comparatively higher hydraulic pressure of about 900 psi to drive osmosis.

Feed TDS also affect RO recovery because sea water RO typically shows 35–50% recovery (Hafez et al., 2002), which is another limitation of RO. The high applied pressure system also requires very strong equipment to withstand this pressure, which further contributes to higher capital costs for RO plants. Compared to traditional thermal processes, which make use of excessive thermal energy, RO desalination has is relatively cheaper for all water desalination processes while achieving a low feed-water recovery (Reddy and Ghaffour, 2007a). High performance RO membranes have been developed over the last 40 years which are permeable to water, but they are also highly impermeable to salts, organic matters and other pollutants (Zhou and Tol, 2004).

Various concentrate treatment concepts have been proposed to minimise waste and maximise water recovery (Al-Amoudi and Lovitt, 2007, Ang et al., 2006). Using wastewater effluents as sources for water recycling reduces the environmental footprint, particularly the energy demand for water desalination (Al-Amoudi et al., 2008). Although these wastewater reuse processes use the latest treatment techniques, and process and produce high quality water, for aesthetic reasons, wastewater recycle and reuse is still common for non-potable applications.

For operating cost-benefits and adaptability to various feed water sources, membrane-based systems and especially RO have become the primary choice for new desalination applications. They use seawater, brackish water and recycled water as feed. In contrast to thermal desalination, water recycling and reuse are also increasing in various parts of the world as these waters carry lower dissolved solids. Consequently, even low pressure RO operations can be employed to treat this water which requires less energy.

There are still a few concerns such as higher capital cost for high pressure system and energy, and concentrate management (especially for inland brackish water applications) which discourage it from being the sole choice for desalination. Further, sensitivity of RO membranes to fouling by, for example, suspended solids, and damage by oxidized compounds such as chlorine or chlorine oxides is a very serious concern which results in costly membrane replacement (Lee et al., 2006). The risk of more fouling and scaling further prevents RO operation at higher recovery rates of >50% (Lee et al., 2006). Pre-treatment is usually needed to ensure the RO module functions in a stable way.

To overcome these issues, over a short period of time, a number of improvements have been identified in the following areas:

- Development of low pressure RO systems, low fouling RO membranes, high rejection membranes;
- Integration of RO with other membrane-based systems as membrane distillation, nanofiltration, ultrafiltration to reduce the chemical consumption for pre-treatment or post-treatment; and
- Introduction of energy recovery devices, which when combined helped to reduce the overall operating cost for sea water RO desalination in the last few decades.

Apart from these improvements, the existing higher energy requirements for RO desalination are still assumed to be high. New techniques are being devised to reduce water desalination costs (McGinnis et al., 2013).

2.5.3 Brackish Water RO

With the right pre-treatment methods, brackish water RO (BWRO) may be an exceptional choice for producing usable water from any brackish water source. The technology works best to produce water from low and medium salinity fed water with TDS ranging from 500 to 10,000 mg/L and operating at a feed pressure range of 10–15 bar. The recovery rate is in the range of 75% - 85%. The cost of water produced in these systems is very low, in the range of \$0.2 – 0.3/m^3 (Hong and Elimelech, 1997). Depending on operating conditions, BWRO membranes have to be replaced within three to seven years. A significant problem concerning brackish systems is concentrate disposal (Li and Elimelech, 2004). BWRO concentrates contain various impurities especially salts, and currently these concentrates are discharged into the surrounding open surface fields. They are mixed with groundwater using deep well bores and nearby marine water bodies, posing a great threat to these ecosystems (Ang et al., 2006). These methods are not considered safe and environmentally sustainable. Safe disposal of RO concentrate is thus a critical issue for inland desalination plants. The first commercial brackish water RO plant with spiral wound membrane was built at Kashima in Japan in 1969 to cater to the water needs of a power plant (Reddy and Ghaffour, 2007b).

2.5.4 Nano filtration

The nanofiltration (NF) systems treat low salinity brackish or surface water. The NF systems' configuration and economics are similar to brackish RO systems. The NF systems have been applied to reduce concentration-specific components from the feed water, usually divalent hardness ions, iron, organics or colour, removal of low concentration of pesticides while allowing monovalent ions to pass through (Demisch and Pusch, 1976, Baker, 2012). The traditional treatment methods are often not able to reduce the hardness of groundwater to a sufficiently low level but this can be achieved with a NF membrane. The combination of a conventional RO system [conventional what?] with a NF process reduces the fouling problem and requires less chemicals. Due to low salinity, low rejection and high permeability of nanofiltration membranes, the NF systems operate at low feed pressure, usually below 10 bar (Childress and Elimelech, 1996). Many studies have presented successful outcome for the performance of hybrid conventional-NF membrane processes (Bellona et al., 2004, Wang et al., 2005).

2.5.5 Electrodialysis /Electrodialysis Reversal

Electrodialysis (ED) and electrodialysis reversal (EDR) are electrochemical-charge-driven separation processes which have been tested for water treatment in both laboratory and commercial scale brackish water desalination and wastewater reclamation applications. The ED process uses membranes as well, but unlike RO, the salt ions are deliberately carried through the membranes, leaving behind the freshwater (Jin et al., 2009). Two types of membranes are required: one that lets anions through but not cations, and the other that does the opposite. Salt ions are attracted through one membrane or the other depending on their polarity, and by the time the water emerges out of the other side of the stack, it is alternately freshwater and concentrate in the spacer layers. Reversing the polarity of the applied voltage reverses the freshwater and concentrate layers, and this can be done periodically (several times per hour) in order to reduce fouling. This process is termed electrodialysis reversal.

ED was commercialized during the 1960s and is widely used today for desalinating brackish water. For brackish water applications with up to 3000 ppm salt, ED is a membrane technology competing with RO. The energy consumption depends very much on the concentration of the feed water and so ED is rarely used for seawater desalination.

ED/EDR membranes are not as susceptible to degradation by chlorine and can treat surface and wastewaters that have high concentrations of organic materials and microorganisms without significant fouling. The technologies can withstand harsh conditions and are fairly flexible to varying water quality. However, ED/EDR have limited ability to remove non-charged constituents, including organics molecules, silica, and boron. Furthermore, technical skills of a high degree are required to operate ED/EDR systems.

2.5.6 Capacitive Deionisation

Capacitive deionisation (CDI) is an electrochemically controlled method for removing salt from aqueous solutions by taking advantage of the excess ions adsorbed in the electrical double layer region at an electrode-solution interface when the electrode is electrically charged by an external power supply. In CDI, ions are adsorbed onto the surface of porous electrodes by applying a low voltage electrical field, producing deionized water. The negative electrodes attract positively charged ions such as calcium, magnesium, and sodium, while the positive electrodes attract negatively charged ions such as chloride, nitrate, and silica (Huang et al., 2004, Welgemoed and Schutte, 2005).

When the electrode has a high specific surface area, this excess may become significant in terms of number of grams of salt adsorbed on a unit weight of electrode material (Oren, 2008). The major mechanisms related to the removal of charged constituents during water treatment are physisorption, chemisorption, electrodeposition, and/or electrophoresis. Caudle et al. (1966) reported early studies on CDI began in the mid-1960s and they used porous carbon electrodes made of activated carbon powder in a flow-through mode for water desalination. However, despite the vast amounts of intensive CDI-related research activity that has spanned more than 50 years, on developing this technology as an affordable solution for treating various sources (e.g., seawater and brackish water desalination) and for saving water (e.g., municipal and industrial wastewater reclamation), a valid and mature commercial stand-alone technology has not yet emerged (Huang et al., 2004).

2.5.7 Membrane distillation

Membrane distillation (MD) is a hybrid desalination technology that uses both thermal and membrane-based technologies. It is a thermal membrane separation process involving the transport of vapour through microporous hydrophobic membranes and operates on the principle of vapour–liquid equilibrium as a basis for molecular separation (Al-Obaidani et al., 2008). This separation process is driven by the vapour pressure difference caused by temperature gradient imposed between the liquid–vapour interfaces existing between the porous hydrophobic membrane surfaces. The advantages of MD over commercialised desalination technologies are as follows: (i) lower operating temperatures and vapour space required than MSF and MED; (ii) lower operating pressure than RO; (iii) more than 99.9% theoretical salt rejection; and (iv) the performance is not limited by high osmotic pressure or concentration polarisation (Alkhudhiri et al., 2012).

The membrane pore size required for MD is relatively larger than those for other membrane separation processes, such as RO. The MD process, therefore, suffers less from fouling. Along with pore size distribution, porosity, and tortuosity, the membrane thickness is a significant characteristic in the MD system which shows an inversely proportional relationship with the permeate flux. The permeate flux is reduced as the membrane becomes thicker, because the mass transfer resistance increases, while heat loss is also reduced as the membrane thickness increases (Alkhudhiri et al., 2012). Membranes with pore size between 100 nm to 1 µm are usually used in MD systems and these indicate that the permeate flux increases as membrane pore size also increases (El-Bourawi et al., 2006).

The MD system has many advantages and it can be combined with other separation processes to create an integrated separation system, such as ultrafiltration or with a RO unit (Widjojo et al., 2013). Furthermore, MD can utilise alternative energy sources, such as solar energy

(Blanco Gálvez et al., 2009). The MD process has advantages in the desalination of brackish water and sea water (Alkhudhiri et al., 2012). However, it does have some drawbacks such as low permeate flux (compared to other separation processes, like RO), high susceptibility permeate flux to the concentration and temperature of the feed conditions due to concentration and temperature polarization (Martinetti et al., 2009).

2.5.8 Ultra filtration/micro filtration

Although microfiltration (MF) and ultrafiltration (UF) membranes are not directly involved in an actual desalination step, these membrane filtration processes are now widely used as pre-treatments for various desalination systems such as RO and MD. MF and UF are also commonly used as a primary treatment for drinking water treatment plants for removing suspended particles and bacteria. UF membranes have been more widely accepted and is due to their ability to reject suspended organics, silt, pathogens and viruses more efficiently compared to MF (MF cannot remove viruses).

The major issue impeding the widespread use of UF/MF for drinking water production is poor removal of dissolved organic solutes, disinfection by-products and precursors, biopolymers such as algal organic matter and effluent organic matter (Ang et al., 2014). This gives rise to the concept of using MF/UF membranes as integrated/hybrid membrane processes in treating water with the impurities mentioned above as well as water contaminated with wastes that standalone membrane and conventional processes find hard to remove. Currently, most membrane-based pre-treatments in SWRO desalination plants are using integrated/hybrid UF membrane processes.

2.6 Physical appearance of the membranes and modules

Most of the RO and NF membranes are usually configured in spiral-wound modules, where the feed water flows between two flat membrane sheets wrapped around a central tube. These membranes are also alternatively prepared as the hollow fiber membranes, where small dia. membrane tubes are used. However, hollow fiber configurations for NF and RO are very rare. UF, MF and MD come in both flat sheet and hollow fiber configurations whereas ED usually uses flat sheet configurations.

2.7 Forward osmosis - A unique concept development and future trends

All of the above main technologies highlighted a real need for a rigid and low cost desalination technology carrying less fouling potential technology that may be used to produce usable water from various feed water sources at an affordable cost.

Continued research activities for the low cost water desalination process have recently highlighted remarkable low pressure forward osmosis (FO) water desalination technology. FO is considered to be an emerging green membrane desalination technology using the simple concept of natural osmosis. Osmosis is the net movement of water across the semi-permeable membrane from a solution of higher concentration towards a solution of less potential (Mulder, 1996). The concentration difference of solute across the membrane allows water molecules to diffuse through the semi-permeable membrane to achieve equilibrium whereas membrane does not allow solutes to move freely. This movement of water molecules is due to the osmotic pressure difference of the two solutions on opposite sides of the membrane. A solution having high solute concentration is known as a draw solution (DS) and low concentration solution is referred to as feed solution (FS). As water is diffused toward the DS side, DS starts diluting until the system reaches a point of equilibrium. On the other hand, the FS concentration keeps rising slowly with the diffusion of water molecules towards the DS side.

2.7.1 Differences in RO and FO

In any FO process, when a self-constructed DS possessing high osmotic pressure is placed against any feed water across a semi-permeable membrane, naturally, the water starts flowing towards the DS side until the concentrations on both sides become equal. This movement of the water molecules in FO is different from the RO process in which water permeates through membrane under high hydraulic pressure (Fig. 2.6). For this reason, comparison to the RO, the FO process requires less energy because its energy requirements are limited to power pumps which maintain FS and DS cross-flow arrangement to both sides of the membranes.

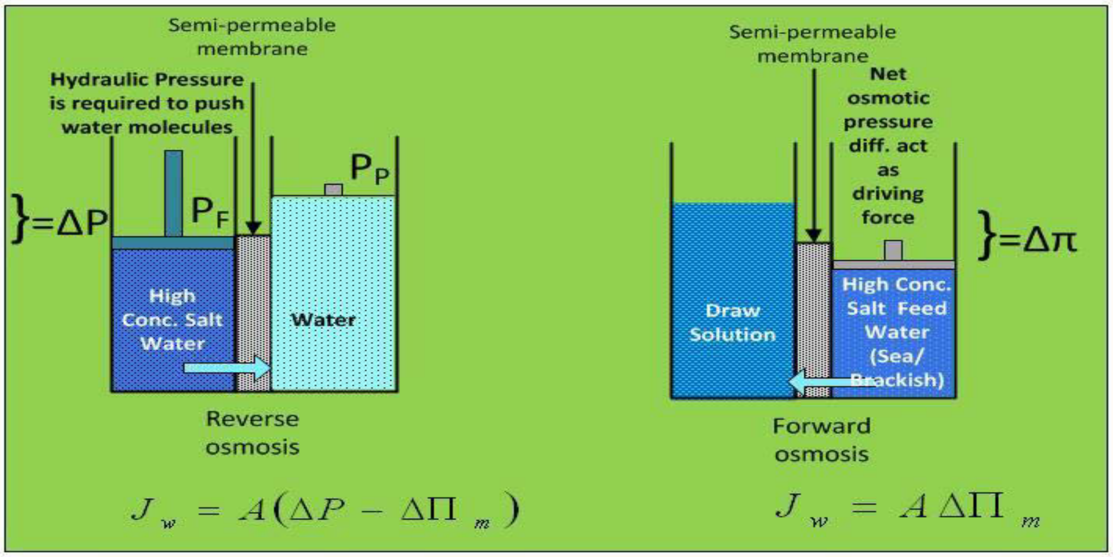

Fig. 2.6. Driving forces for RO and FO desalination

FO harnesses the naturally available power, i.e. osmotic pressure (OP) of DS and therefore it does not require any additional external energy source to pressurize feed water streams as RO requires. It is consequently deemed to be an environmentally friendly desalination technology that leaves a small carbon footprint. Like RO, FO can remove large amounts of many monovalent, divalent, and multivalent inorganic contaminants, and organic contaminates (see Fig. 2.7).

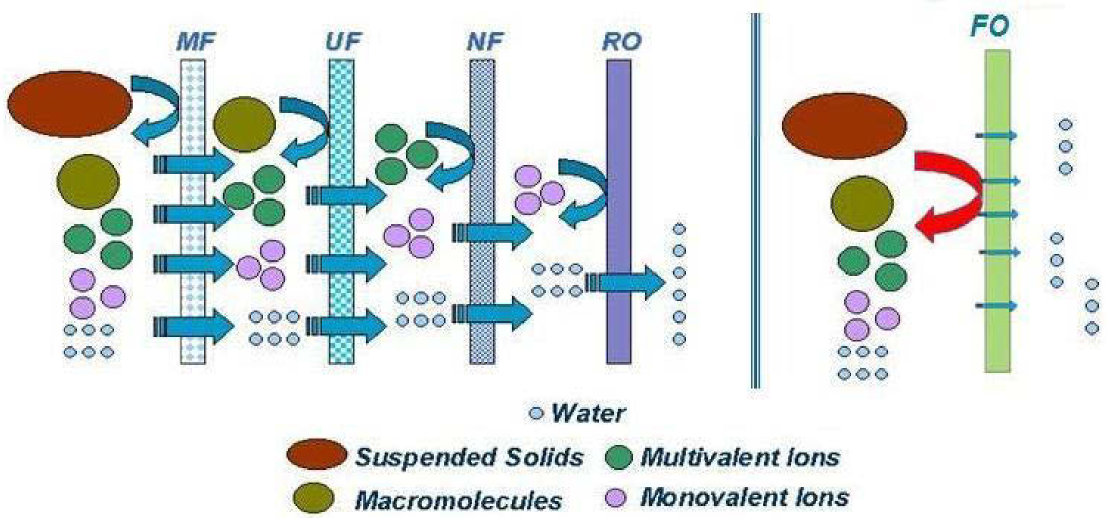

Fig. 2.7. Comparison of the separation processes for the existing conventional membrane processes and FO process

FO differs to RO in that it uses two different solutions on either side of the membrane. For FO, on one side of the membrane, FS is used while on the other side, a higher concentration of DS is used. The solute and water molecules for these solutions also move in different ways for RO and FO. During the FO process, along with the water molecule and FS solute movement from FS side to DS, solutes from the DS are also transported across the membrane in the opposite direction to the water permeation (Fig. 2.8). The diffusion of the DS solutes to the FS occurs due to the available concentration gradient between DS and FS. This phenomenon, which is known as the reverse solute flux, has been investigated in recent studies (Phillip et al., 2010, Zhao et al., 2012b, Yong et al., 2012, Oh et al., 2014) and it indicates a significant impediment to applying osmotically driven membrane processes.

RO and FO processes also differ in respect to the permeate recovery. In most cases, water permeating in the RO process is readily available for any use. However, in the FO process, this is not the case. In the FO process the permeate is available in the form of diluted DS, which depends on the DS used or the intended use of the product that may be used directly or sent for another separation step.

One example of direct usage of the diluted DS is “hydration bag” (Hydration Technologies Inc.), which uses an ingestible glucose and fructose type nutrition as DS. When the bag is immersed in any water source such as a pond or lake, pure water starts to permeate into the bag and make a diluted solution of nutrients. This can then be consumed for any drinking water requirements (HTI, 2013).

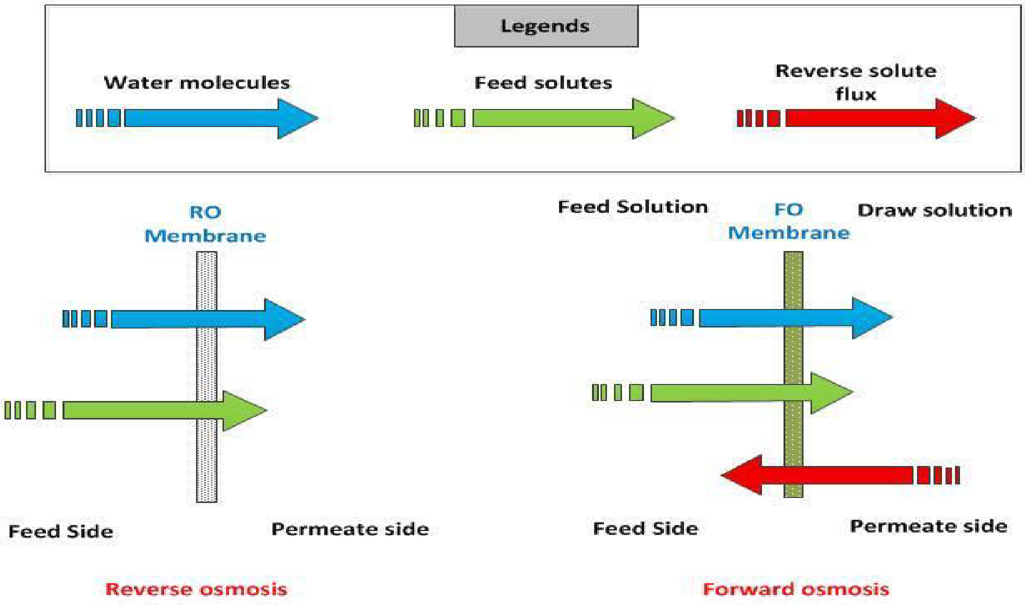

Fig. 2.8 Water and solute molecules movements for RO and FO

In cases when pure water is required for any suitable application, a second separation step is required (Fig. 2.9). In contrast to the actual FO process, this second separation step, does typically require high energy input (McCutcheon et al., 2005).

2.7.2 Brief History

Research on the FO process was began nearly 40 years ago when a a few studies employed different chemicals such as sulphur dioxide (SO_2), glucose or aluminium sulphate ($Al_2(SO_4)_3$)

that were either easily removable or consumable as the draw solution (Kravath and Davis, 1975, Ng et al., 2006). Later, Loeb et al. (1976) and Loeb (1976) did some experiments using a principle of pressure retarted osmosis. This principle was further evaluated by Demisch and Pusch (1976), Kessler and Moody (1976b) and Moody and Kessler (1976). The main focus of these studies was to improve water flux using a better quality membrane and a suitable DS. In later years no significant / prominent activity was noticed regarding the FO process.

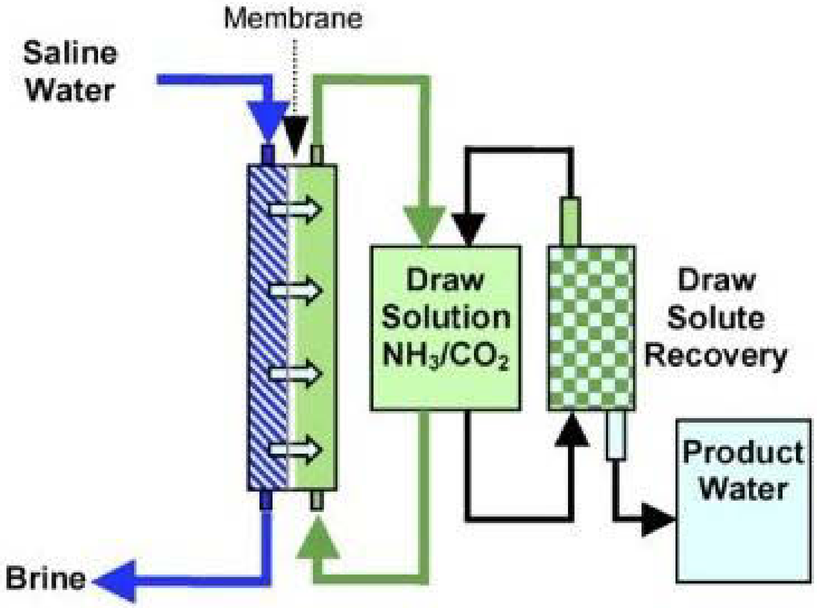

Fig. 2.9 Revolutionary ammonia and carbon dioxide FO process requires more steps in permeate recovery (McCutcheon et al., 2005) (Figure adopted from www.soue.org.uk)

McGinnis (2002) developed and patented a two-stage FO process for recovering water from aqueous solutions. This process takes advantage of potassium nitrate (KNO_3) and sulphur dioxide (SO_2) solutes having highly temperature dependent solubility to desalinate sea water. FO research work experienced a real momentum boost when McCutcheon et al. (2005) presented a novel ammonia carbon dioxide FO process that used either ammonium bicarbonate or a mixture of ammonium bicarbonate and ammonium hydroxide with deionized water to prepare the draw solution. This study utilized a cellulose ester FO membrane and in comparison to RO, much cheaper desalination was possible. This proved to be a major breakthrough for FO and research activities further explored avenues for improving this system.

2.7.3 Potential advantages of the FO process over current desalination technologies

The FO process has many advantages over traditional technologies. A few of the main features of FO are listed below:

- Low operating pressure
- Lower capital cost as high strength construction materials are not required for low hydraulic pressures operation
- Low energy cost
- Suitability of FO operation for both membrane orientations; i.e., active layer - feed solution (AL-FS) and active layer - draw solution (AL-DS)
- Rejection of a wide range of impurities such as suspended particles, dissolved solids, toxic metals, boron, etc.
- Rejection of pathogens and emerging substances
- Extensive pre-treatment systems for FO may be redundant when treating complex feeds
- Low fouling propensity
- Suitability for various dewatering applications
- Useful for a wide range of feed qualities, i.e. surface water, brackish water, sea water, wastewater, other toxic feed such as coal seam gas produce water, oil well water, leachate waste
- Useful for dewatering
- Food /medicine solution concentration where temperature is an issue
- Not just consumes energy but also used to produce electricity

2.7.4 Common concerns with FO

Beside all these aforesaid advantages, FO does have some serious issues that can affect its successful operation (Tang et al., 2011a, Zhao et al., 2012b, Xu et al., 2010b). Some of the important shortcomings of FO include:

- Limited application as a standalone system
- Requires a recovery step in closed loop systems
- Higher impact of concentration polarization on FO performance
- Low water fluxes
- DS leakage through reverse solute flux

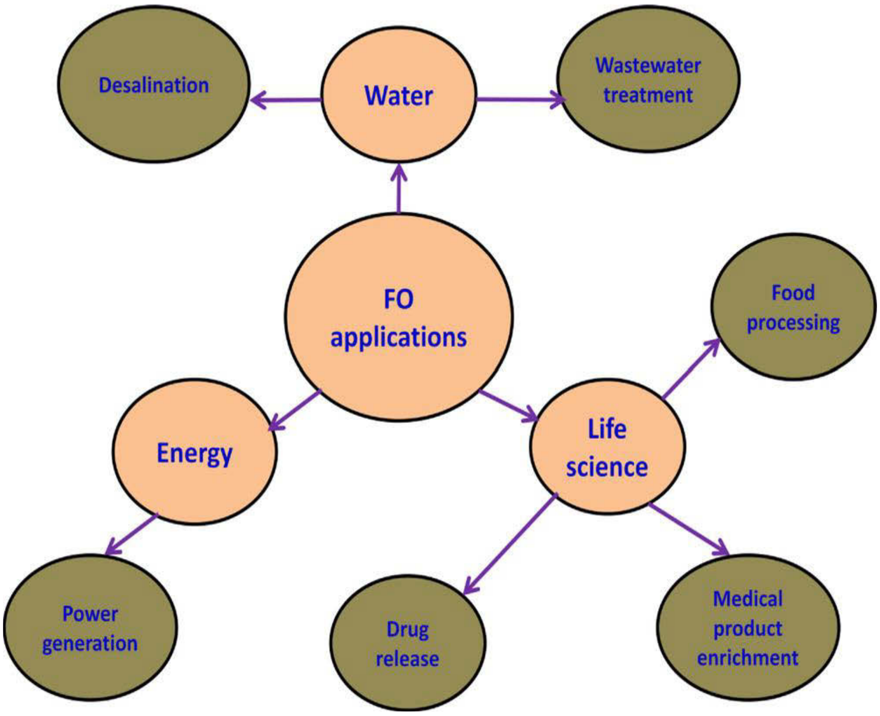

Fig. 2.10 Applications of FO in the fields of water, energy and life science.

2.7.5 Potential FO applications and future trends

To function at low cost, FO has been quickly evaluated for many useful applications. FO is not commonly employed for produced water treatments, but studies have shown its promise in industrial waste stream treatment and enhanced water recovery during brackish water desalination. Zhao et al. (2012b) grouped the main FO directions into water, energy and life sciences (Fig. 2.10). FO has been investigated for a wide range of applications. Some of these are summarized in Table. 2.5.

Table. 2.**5. Major FO applications**

FO application	Source
Sea / brackish water desalination	(McCutcheon et al., 2005, Kessler and Moody, 1976b, McGinnis et al., 2013, Zhao et al., 2012a, Bamaga et al., 2009, Yangali-Quintanilla et al., 2011)
Power generation	(Achilli et al., 2009a, Yip et al., 2011, She et al., 2012b, Statkraft, 2013)
Osmotic membrane biological reactor	(MBR) (Achilli et al., 2009b, Cath et al., 2005, Holloway et al., 2007, Warczok et al., 2007),
Food processing, concentration & recovery of active organic components generation	(Garcia-Castello et al., 2009, Changrue et al., 2008).
Direct fertigation	(Phuntsho et al., 2011).
Oil and gas well hydraulic fracturing waste streams treatment	(Hickenbottom et al., 2013b, Zhang et al., 2014).
Landfill leachate/ Grey water	(Coday et al., 2014, Valladares Linares et al., 2013)
RO pre-treatment	(Ang et al., 2014, Bamaga et al., 2009, Van der Bruggen and Vandecasteele, 2002)

2.8 Forward Osmosis – Theory

2.8.1 Osmotic pressure- The main natural driving force behind FO

Osmotic pressure is the pressure necessary to prevent osmosis entering a given solution when the solution is separated from the pure solvent by a semi-permeable membrane (Siavash Madaeni et al., 2001). The osmotic pressure π of an idea solution with low concentration can be approximated using the Moris equation:

$$\pi = iMRT \tag{2.1}$$

where i is the dimensionless van't Hoff factor, M is the Molarity, R= Gas constant (0.08205746 atm. K^{-1}.mol^{-1}) and T is the thermodynamic (absolute) temperature. This equation gives the pressure on one side of the membrane; the net osmotic pressure on the membrane is given by the difference between the pressures on the two sides.

However, for concentrated salt solutions such as the DS used for FO, the non-ideal solution behaviour must be accounted for and the osmotic pressure is calculated as follows (Klotz, 1964):

$$\frac{\pi}{kT} = c + Bc^2 + Cc^3 + \cdots \tag{2.2}$$

where k is the Boltzmann's constant. The virial coefficients (B, C, D,…) are usually obtained from experimental data (Smith, 1975). The solute number density is defined as:

$$c = \frac{N_A n}{V} \tag{2.3}$$

where N_A is Avogadro's number and the term n/V (moles/volume) represents the molar concentration of the solute.

2.8.2 Water flux model

Fig. 2.8 indicates direction of the water flux for RO and FO processes. The general equation describing water transport, i.e. water flux (J_w) for FO expressed by the same general equation used in RO or other membrane process driven by hydraulic pressure / osmotic pressure is (Cath et al., 2006):

$$J_w = A(\sigma\Delta\pi - \Delta P) \tag{2.4}$$

where A is the pure water permeability coefficient of the membrane, σ the reflection coefficient, $\Delta\pi$ the osmotic pressure difference across the membrane layer and solution and ΔP is the applied pressure or the hydraulic pressure difference across the membrane.

For FO, the net hydraulic pressure difference across the membrane is assumed to be zero ($\Delta P=0$)

Since the only driving force in FO is the osmotic pressure difference, theoretically the water flux in FO can be estimated using the following equation:

$$J_w = A\Delta\pi = A(\pi_{D,b} - \pi_{F,b}) \tag{2.5}$$

Where $\pi_{D,b}$ is the bulk osmotic pressure of the draw solution, $\pi_{F,b}$ is the bulk osmotic pressure of the feed.

The flux equation assuming that the FO membrane is ideally impermeable to the draw solution may be written as:

$$J_w = \frac{1}{K}\ln\left[\frac{\pi_{D,b}}{\pi_{F,b}}\right] \tag{2.6}$$

Where *K* is the resistance to solute diffusion within the membrane porous support layer, and $\pi_{D,b}$ and $\pi_{F,b}$ are the osmotic pressures of the bulk draw solution and feed solution, respectively, neglecting external polarization effects. *K* is defined as:

$$K = \frac{t\tau}{\epsilon D_s} \tag{2.7}$$

where t, τ, and ε are the membrane thickness, tortuosity, and porosity, respectively, and Ds is the diffusion coefficient of the solute. However, it has been recently demonstrated that Eq. (2.6) is valid only for very low water fluxes (Gray et al., 2006).

2.8.3 Concentration polarization

Concentration polarization is a significant problem in pressure-driven membrane desalination processes and has thus been the target of several investigations (McCutcheon and Elimelech, 2006). In osmotic processes, concentration polarization can occur on outer sides of the membrane and within the membrane and support layer structure as well. Two of these phenomena, developed at the outer sides of the membrane are referred as concentrative and dilutive external concentration polarization (ECP). For an asymmetric membrane, concentration boundary layers occur within the porous support layer of the membrane, protecting it from the shear and turbulence associated with crossflow along the membrane surface. This phenomenon as referred as either concentrative or dilutive internal concentration polarization (ICP). These four concentration polarization phenomena are quantitatively described.

2.8.3.1 Concentrative internal concentration polarization

When the feed is placed against the support layer of an asymmetric membrane (as in PRO applications), feed enters the porous support layer and water molecule diffuses across the active layer into the draw solution. The feed solutes cannot easily penetrate the active layer from the support layer side and therefore increases in concentration within the porous layer ad this phenomena is referred to as concentrative ICP (Loeb et al., 1997). Lee et al. (1981) derived an expression describes ICP effects and how they relate to water flux and other membrane constants:

$$\mathrm{K} = \left(\frac{1}{J_w}\right) \ln \frac{B + A\pi_{D,b} - J_w}{B + J_w + A\pi_{F,m}} \tag{2.8}$$

where, B is the salt permeability coefficient of the active layer of the membrane. K is a measure of how easily a solute can diffuse into and out of the support layer and thus is a measure of the severity of ICP.

For high rejection and high flux membranes, B is negligible compared to the other terms in Eq. (2.8). Hence salt flux in the direction of water flux and any passage of salt from the permeate (draw solution) side is ignored. For that, Eq. (2.8) may be written as

$$\mathrm{J}_w = A\left[\pi_{D,m} - \pi_{F,b}\, exp(J_w K)\right] \tag{2.9}$$

Eq (2.10) defines water flux as a product of the water permeability coefficient and the effective osmotic driving force. The exponential term is a correction factor that can be considered the concentrative ICP modulus, defined as

$$\frac{\pi_{F,m}}{\pi_{F,b}} = exp[J_w K] \tag{2.10}$$

Where $\pi_{F,m}$ is the osmotic pressure on the inside of the active layer within the porous support. The positive exponent indicates that $\pi_{F,m} > \pi_{F,b}$ (the effect is CP).

These CP effects for the DS may be presented as

$$\frac{\pi_{D,m}}{\pi_{D,b}} = exp\left[-\frac{J_w}{k}\right] \tag{2.11}$$

From Eq. (2.9) and Eq. (2.11), an analytical model for the effects of ICP and ECP on permeate flux can be described as

$$J_w = A\left[\pi_{D,b} exp\left[-\frac{J_w}{K}\right] - \pi_{F,b}\, exp(J_w K)\right] \tag{2.12}$$

All the terms in Eq. (2.12) can be determined by standard FO experiments.

2.8.3.2 Dilutive internal concentration polarization

For FO operations when the feed solution is placed against the active layer of the FO membrane, the ICP phenomenon now occurs on the permeate side as the draw solution is diluted by the permeate water within the porous support of the membrane. Accounting for the dilutive ICP, Loeb et al. (1997) describe the flux behaviour in the FO mode as

$$K = \left(\frac{1}{J_w}\right) \ln \frac{B+A\pi_{D,b}}{B + J_w + A\pi_{F,m}} \tag{2.13}$$

Again assuming salt permeability is negligible (B=0, σ=0), the above equation for water flux becomes:

$$J_w = A\left[\pi_{D,b} exp[-J_w K] - \pi_{F,m}\right] \tag{2.14}$$

Here, the $\pi_{D,b}$ is now corrected by the dilutive ICP modulus as

$$\frac{\pi_{D,m}}{\pi_{D,b}} = exp[-J_w K] \quad (2.15)$$

Where $\pi_{D,m}$ is the concentration of the draw solution on the inside of the active layer within the porous support. The negative exponent is indicative of dilution at this point that $\pi_{D,m} < \pi_{D,b}$.

From Eq. (2.12) and Eq. (2.15), we get

$$\mathrm{J}_w = A\left[\pi_{D,b} exp[-J_w K] \; - \pi_{F,b}\, exp\left[\frac{J_w}{k}\right]\right] \quad (2.16)$$

This models the water flux for an asymmetric membrane in FO operation. Similar to Eq. (2.12), all the terms in Eq. (2.16) are measureable as well. Note that here, dilutive ICP is coupled with concentrative ECP, whereas in the previous section, Eq. (2.12), concentrative ICP was coupled with dilutive ECP.

2.8.3.3 Concentrative and dilutive external concentration polarization

Concentrative ECP on the surface of the active layer is relatively insignificant when the feed solution is pure water, but it is not negligible in a feed solution with a high solute concentration. Feed solutes would be expected to accumulate at the surface of the active layer and cause an increase in feed concentration $(C_{F,b} \rightarrow C_{F,m})$. As a result, the effective osmotic pressure difference $(\pi_{F,b} \rightarrow \pi_{F,m})$ would decrease. $\pi_{F,b}$and$\pi_{F,m}$ are the osmotic pressures of the bulk feed solution and at the membrane interface. Therefore, determination of $\pi_{F.m}$ would be crucial for analysing CECP. CECP modulus is expressed as Equation (2.17)

$$\frac{\pi_{F,m}}{\pi_{F,b}} = exp\left[\frac{J_w}{k_F}\right] \quad \text{or} \qquad \pi_{F,m} = exp\left[\frac{J_w}{k_F}\right]\pi_{F,b} \quad (2.17)$$

Where k_F is mass transfer coefficient is related to Sh is defined by

$$k_F = \frac{\mathrm{Sh.D}}{\mathrm{d_h}} \quad (2.18)$$

where Sh is Sherwood number, D is solute diffusion coefficient and d_h is hydraulic diameter. The exponent in the Eq. (2.18) is positive which indicates $\pi_{F,m} > \pi_{F,b}$. Concentrative ECP only occurs on the feed side of the membrane. Furthermore, in this equation we assume that the ratio of the membrane surface concentration of feed solute to the bulk concentration is equal to the corresponding ratio of osmotic pressures.

Membrane surface concentration begins by calculating the Sherwood number for the appropriate flow regime in a rectangular channel

$$\mathrm{Sh} = 1.85 \left(Re.Sc\frac{d_h}{L}\right)^{0.33} \quad \text{for laminar flow} \tag{2.19}$$

$$\mathrm{Sh} = 0.04Re^{0.75}\, Sc^{0.33} \quad \text{for turbulent flow} \tag{2.20}$$

Re is the Reynolds number and indicates the transition between the laminar flow and turbulent flow regime at 2300, Sc is the Schmidt number and L is the length of the channel. Dilutive ECP is a phenomenon similar to concentrative ECP, except that in this case, convective water flow is displacing and dragging the dissolved draw solute away from the membrane surface on the permeate side of the membrane. This reduces the effective driving force of the draw solution. A dilutive ECP modulus defined as above, except that in this case, the membrane surface concentration of the draw solute is less than that of the bulk as shown in Eq. (2.11).

Loeb et al. (1997) modelled dilutive ICP by incorporating the solute resistivity resistivity for diffusion within the porous support layer or the inverse of internal mass transfer coefficient, K of Eq. (2.7), which may also be defined as

$$K = \frac{t\,\tau}{\varepsilon\, D} = \frac{ShD}{d_h} = = \frac{I_m}{D} = \frac{S}{D} \tag{2.21}$$

Where, I_m is the intrinsic membrane structural properties, also commonly used as S.

In PRO mode, the corresponding model for the effects of both concentrative ICP and dilutive ECP on water flux can be expressed (Elimelech and Bhattacharjee, 1998, McCutcheon and Elimelech, 2006) by

$$\mathrm{J}_w = A\left[\pi_{D,b}\; exp\left[-\frac{J_w}{k}\right] - \pi_{F,b}\; exp(J_w.K)\right] \qquad (2.22)$$

According to Equation (2.22), it seems that ICP in the membrane support layer is determined by both membrane properties, for instance membrane thickness, tortuosity, porosity, and diffusion solute properties such as the diffusion coefficient of the solute. Based on the membrane orientation, ECP is usually linked with DS and FS concentration whereas ICP is mainly associated with thick dense membrane and support layer structure (Cath et al., 2006).

2.8.4 Estimation of Water Flux

The actual water flux during the FO experiment can be calculated from the volume change of either the feed or draw solution. As the FO process proceeds, the flow of water from the feed solution to the draw solution results in decreased volume of the feed solution with a corresponding increase in the volume of the draw solution. The water flux (Jw) can be calculated as follows:

$$J_w = \frac{\Delta V}{S.\Delta T} \qquad (2.23)$$

where ΔV is volume change of the feed or draw solution, S is the area of the membrane available for flux and Δt is the time interval during which the volume changes by amount ΔV. The specific flux can be calculated by dividing the flux by the driving force, the difference in osmotic pressure (Δπ) in this case:

$$J_{w.sp} = \frac{J_w}{\Delta\pi} \qquad (2.24)$$

2.8.5 Reverse Solute Flux

The solute flux (*Js*) of a particular solute through a semi-permeable membrane is given by Fick's law (Mulder, 1996, Hancock and Cath, 2009)

$$J_s = B.\Delta c = B\left(c_{D,i} - \; c_{F,m}\right) \tag{2.25}$$

where Δc is the concentration differential across the active layer of the membrane, $c_{D,i}$ is the solute concentration at the interface between the support and active layers and $c_{F,m}$ is the solute concentration on the membrane surface of the support layer. Suh and lee (Suh and Lee, 2013b) obtained the following relationship equation to find $c_{D,i}$

$$c_{D,i} = \frac{\left(c_{D,m} + {}^{J_s}\!/_{J_w}\right)}{exp\left(J_w \cdot \frac{\tau_S}{D^S}\right)} - \frac{J_s}{J_w} = \frac{\left(c_{D,m} + {}^{J_s}\!/_{J_w}\right)}{exp(J_w.K)} - \frac{J_s}{J_w} \tag{2.26}$$

and B can be determined from an RO-type experiment (Achilli et al., 2009a) using the following equation:

$$B = \frac{(1-R)A(\Delta P - \Delta\pi)}{R} \tag{2.27}$$

where R is the salt rejection. However, Eq. (2.25) includes the immeasurable variables as $c_{D,i}$ and $c_{F,m}$. In order to remove the immeasurable variables, Eq. (2.25) is substituted for $C_{D,i}$ and $C_{F,m}$. Eq. (2.28) which includes the known measurable variables and the model parameters, was then obtained (Suh and Lee, 2013b):

$$J_s = \left(B\,\frac{\left(c_{D,b} + {}^{J_s}\!/_{J_w}\right)}{exp(J_w.K)\; exp\left({}^{J_w}\!/_{k_D}\right)} - \left(C_{F,b} + {}^{J_s}\!/_{J_w} \right) exp\left(\frac{J_w}{k_F}\right) \right) \tag{2.28}$$

Eq. (2.28) involves the ratio of the reverse draw solute flux to the water flux (J_S/J_W), which is a repetitive term. Yong et al. (2012) noted that when predicting the reverse flux selectivity for highly permeable draw solutes, the reflection coefficient, σ, has to be incorporated to account for the coupling between solute and solvent. Incorporating this additional term yields the following J_w/J_s expression for the reverse flux selectivity:

$$\frac{J_W}{J_S} = \frac{\sigma A n \mathrm{R_g} T}{B} \tag{2.29}$$

where n is the number of dissolved species created by the draw solute (n is 2 for NaCl and 1 for the neutral draw solutes), Rg is the ideal gas constant, and T is the absolute temperature. This is an insightful result as it states that the reverse flux selectivity is independent of the support layer structural parameter *S* as well as the bulk draw solution concentration (Phillip et al., 2010).

2.8.6 Pressure retarded osmosis

Pressure-retarded osmosis (PRO), an osmotically driven membrane process, has the potential to produce electrical power sustainably through the exploitation of natural salinity gradients, such as seawater (as a high salinity solution) and river water (as a low salinity solution). A resulting water flux equation incorporating the effects of ECP, ICP, and reverse salt diffusion are incorporated is presented by (Yip et al., 2011):

$$J_s = A\left[\frac{\pi_{D,b}\, exp\left[-\frac{J_W}{k}\right] - \pi_{F,b}\, exp(J_W.K)}{1+\frac{B}{J_W}\left[exp(J_W.K) - exp\left(\frac{J_W}{k}\right)\right]} - \Delta P\right] \tag{2.30}$$

This equation shows that the solute resistivity (K) behaves as an exponential deterrent to the permeate water flux. Therefore, a smaller K value will result in better membrane performance (Kim and Elimelech, 2012).

2.9 Main components of a FO process

2.9.1 Forward osmosis membranes

FO membrane is one of the main FO system’s components directing the possible outcome for any FO process. Most of the FO membranes carry an asymmetric structure with two different layers; an active layer (AL) and a support layer (SL). The AL is generally the dense selective layer, while the porous SL provides the mechanical support.

Any dense and selectively permeable material can be used as a membrane in the forward osmosis process (Cath et al., 2006). Several membranes have been tested previously for various forward osmosis applications. The following are the desired characteristics of a FO membrane (Gu et al., 2013, Chou et al., 2010):

- High water permeation
- Low reverse salt flux
- High chemical stability
- High mechanical strength
- High salt rejection

Although research is continuing to synthesise new polymeric FO membranes with better transport properties, due to its commercial success, high salt rejection, and reasonable water flux features, HTI's cellulose triacetate (CTA) FO membrane is still the most widely used membrane in FO research.

2.9.2 Development of FO membranes and their progress

The earliest membranes used for forward osmosis were natural materials such as bladders of pigs, fish skin, natural nitrocellulose, rubber, and porcelain (Cath et al., 2006). Later researchers evaluated FO for desalination and osmotic power production (Loeb et al., 1997, Qin et al., 2012) and they investigated the use of FO and PRO in the 1970s. These experiments were being carried out using asymmetric aromatic polyamide RO membranes. In all these cases the researchers observed much lower water flux than expected.

During the 1990s, Hydration Technologies Inc. (HTI, Albany, OR) developed a special FO membrane. This membrane has since then been used extensively in FO applications by researchers and many valuable results on FO intended applications were reported (Zhao et al., 2012b). These studies indicated the characteristics of the FO membrane played a vital role which encouraged the development of improved membranes.

By physical appearance, FO membranes may be divided into the following two types:

- Flat sheet
- Tubular hollow fiber

2.9.2.1 Flat sheet FO membrane

Earlier trials with FO began with HTI's flat sheet membrane which carried a dense selective layer composed of cellulose acetate (CA) and cellulose triacetate (CTA). These membranes highlighted issues such as low water flux and high RSF (Cath et al., 2006, McCutcheon and Elimelech, 2008). Efforts were made to develop an ideal FO membrane having a thin film on a highly porous and very fine support layer, having high water permeability, low salt permeability and enough strength structure layers that result in minimal concentration polarization outcomes, especially ICP (Cornelissen et al., 2008). Polyamide thin film composite polymer and different new materials were also evaluated using various processing techniques for FO membrane development as outlined in Table 2.6.

Table 2.6. Advances in forward osmosis membrane developments, derived from (Zhao et al., 2012b)

Year	Membrane materials and membrane type	Preparation method
	Flat sheet forward osmosis membrane	
2008	Cellulose acetate	Phase inversion and then annealing at 80–95 ◦C
2009		
2010	Cellulose acetate- Double skinned	Phase inversion, and then annealing at 85 ◦C
2010	Polysulfone (PSf) support, Polyamide - TFC	Phase inversion and IP
2011	PSf support modified by polydopamine- Modified RO	Chemical coating
2011	PAI substrate treated by PEI- Positively charged flat sheet	Chemical modification
2011	polyamide PES/ sulfonated polymer substrate, Polyamide - TFC	Phase inversion and IP
2011	PES cast on PET fabric- Nanoporous PES	Phase inversion
2011	Cellulose ester	Phase inversion
2011	PES nanofiber support, polyamide - TFC	Electrospinning and IP
2011	Thin film nanocomposite of polyamide and nano-NaX zeolite (40–150 nm) membranes over porous polyethersulfone ultrafiltration support	Coated via interfacial polymerisation of trimesoyl chloride (TMC) and m-phenylenediamine (MPD) monomers
2012	Zeolite-polyamide thin film nanocomposite (TFN) membranes were prepared on a polysulfone (PSf) porous substrate	Interfacial polymerisation

2012	Super hydrophilic thin film composite (TFC) /functionalised with surface-tailored nanoparticles	(Tiraferri et al., 2012)
2010	Ultra-thin Cellulose acetate (CA) selective layer / interface of polymer	Phase inversion (Zhang et al., 2010)
2013	Polyamide on cellulose triacetate support	(Alsvik et al., 2013)
2012	Thin film composite poly (amide)-carbon-nanotube	(Dumée et al., 2012)
2009	Polyamide/Polysulfone	Interfacial polymerisation
2011	Thin-film composite (TFC)/ sulphonated polymer and macrovoid-free structure in the support layer	
2013	Thin film composite polyamide selective layer / electrospun polyethylene terephathalate nanofibers	Interfacial polymerisation /phase separation (Hoover et al., 2013)
2014	Amine rich thin film composite (TFC) active layer functionalised with poly (ethylene glycol) (PEG) / microporous polysulfone	Interfacial polymerisation, 2nd interfacial polymerisation between ethylenediamine and acyl chloride groups on PA layer (Romero-Vargas Castrillón et al., 2014)
2013	Silver nanocomposite LbL-Ag nanofiltration (NF)	Coating and cross-linkage (Liu et al., 2013b)
2013	Polyamide thin film /polyvinylidene fluoride	Interfacial polymerisation /electrospun nanofiber (Tian et al., 2013)
2013	Thin film composite (TFC)/acetylated methyle cellulose (AMC) support layer	Interfacial polymerisation (Ahn et al., 2013)
2103	Polyamide thin film composite /Carboxylated polysulphones (CPSFs) polysulfone (PSF) microporous support	Interfacial polymerisation/ via direct polysulfone (PSF) functionalisation (Cho et al., 2013)

2011	Modified TFC RO membrane /Support layer modified with polydopamine (PDA)	(Arena et al., 2011)
2013	Thin film nanocomposite (TFN)/amine functionalised multi-walled carbon nanotubes (F-MWCNTs)	Interfacial polymerisation (Amini et al., 2013)
2014	Thin film nanocomposite (TFN) /titanium dioxide (TiO_2) nano-particles in polysulphone (PSF) substrate	(Emadzadeh et al., 2014)
Hollow Fiber forward osmosis membrane		
2007	Polybenzimidazole (PBI)	Dry-jet wet phase inversion
2009	Dual-layer hollow fiber NF- PBI–PES/PVP	Dry-jet wet phase inversion (i.e. co-extrusion technology)
2010	PES substrates, polyamide active layer	Dry-jet wet spinning and interfacial polymerisation (IP)
2010	NF/ Cellulose acetate	Dry-jet wet spinning
2011	Positively charged / PAI substrate treated by PEI	Chemical modification
2012	Poly (amide-imide) (PAI) and polyethersulfone (PES) /Delamination-free ultrafiltration (UF) dual layer hollow fibers	Dry jet-wet spinning /outer layer by polyethyleneimine (PEI) cross-linking followed by multilayer polyelectrolyte depositions (Setiawan et al., 2012)

2.9.2.2 Tubular hollow fibre FO membrane

Work on hollow fiber (HF) forward osmosis membrane development was initiated by various research groups (Wang et al., 2007, Wang et al., 2009) that wanted to create a better performing FO membrane with minimum FO operational issues. Most of the developed HFFO membranes functioned better in terms of flux and RSF when compared to FSFO membranes (Chou et al., 2010, Wang et al., 2010b, Su et al., 2010, Sivertsen et al., 2012b, Xiao et al., 2012, Setiawan et al., 2011, Fang et al., 2012). All these HFFO membranes compared to FSFO membranes have demonstrated their better performance in respect to higher water flux and lower RSF. Some SEM morphologies of the active layer and support layer of the flat sheet and hollow fiber FO membranes are presented in Fig. 2.11.

2.9.2.3 New trends in composite membrane design

The progress in FO/PRO membrane development depends on new design strategies of the materials improving the how well these membranes perform. One strategy is to functionalize the membrane surface and/or embedding functionalized nanoparticles in the polymer. In this way the surface may be tailored to possess properties that may both decrease fouling and enhance water flux (Lutchmiah et al., 2014). Similarly other non-polymer materials as carbon nanotubes, graphine, etc. are also being evaluated for FO functionality.

2.9.3 Draw solution

The performance of the FO process mainly depends on selecting suitable draw solutes because they will provide the main driving force for this process. A suitable draw agent is essential for successful operation and several defined criteria are used for selecting one (Cath et al., 2006, Zhao et al., 2012b). Primarily, in the FO process, inherent osmotic pressure properties are considered to be of key importance for any real potential to emerge (Achilli et al., 2010). DS's higher osmotic pressure than the FS is used as the main criteria for evaluating its suitability for any FO application. The higher the osmotic pressure of the draw solution, the more suitable it is in FO applications (Cath et al., 2006).

Osmotic pressure is a function of solute concentration; the number of species formed by dissociation in the solution, the molecular weight of the solute and the temperature of the solution. Therefore it does not depend on the types of species formed in the solution (Contreras et al., 2009). Eq. 2.1 shows that the osmotic pressure is the function of DS concentration. As the concentration of the DS increases, this raises its osmotic pressure and higher flux for FO is achieved.

Many categories of commercial compounds from gases, nutrients to salts have been explored as draw solutes (Liu et al., 2001) which may be categorized into group for their chemical nature:

Volatile compounds: Ammonium bicarbonate (NH_4HCO_3) solution from ammonia and carbon dioxide, sulphur dioxide (SO_2) -- volatile draw solutes can be separated from produced water by means of heating or distillation

Nutrient compounds: Glucose/fructose are used as draw solutes for various studies. These do not require regeneration and are consumed in their dilute form. Sucrose was also used in wastewater treatment using double- skinned hollow fiber membranes (Su et al., 2012).

Inorganic salts: ($Al_2(SO_4)_3$), ammonium bicarbonate (NH_4HCO_3), fertilizers, NaCl, $MgCl_2$ (Achilli et al., 2010). Draw solutions containing larger hydrated anions such as $MgSO_4$, $KHCO_3$, $NaHCO_3$, Na_2SO_4, $(NH_4)_2SO_4$, and K_2SO_4 showed lower reverse solute flux.

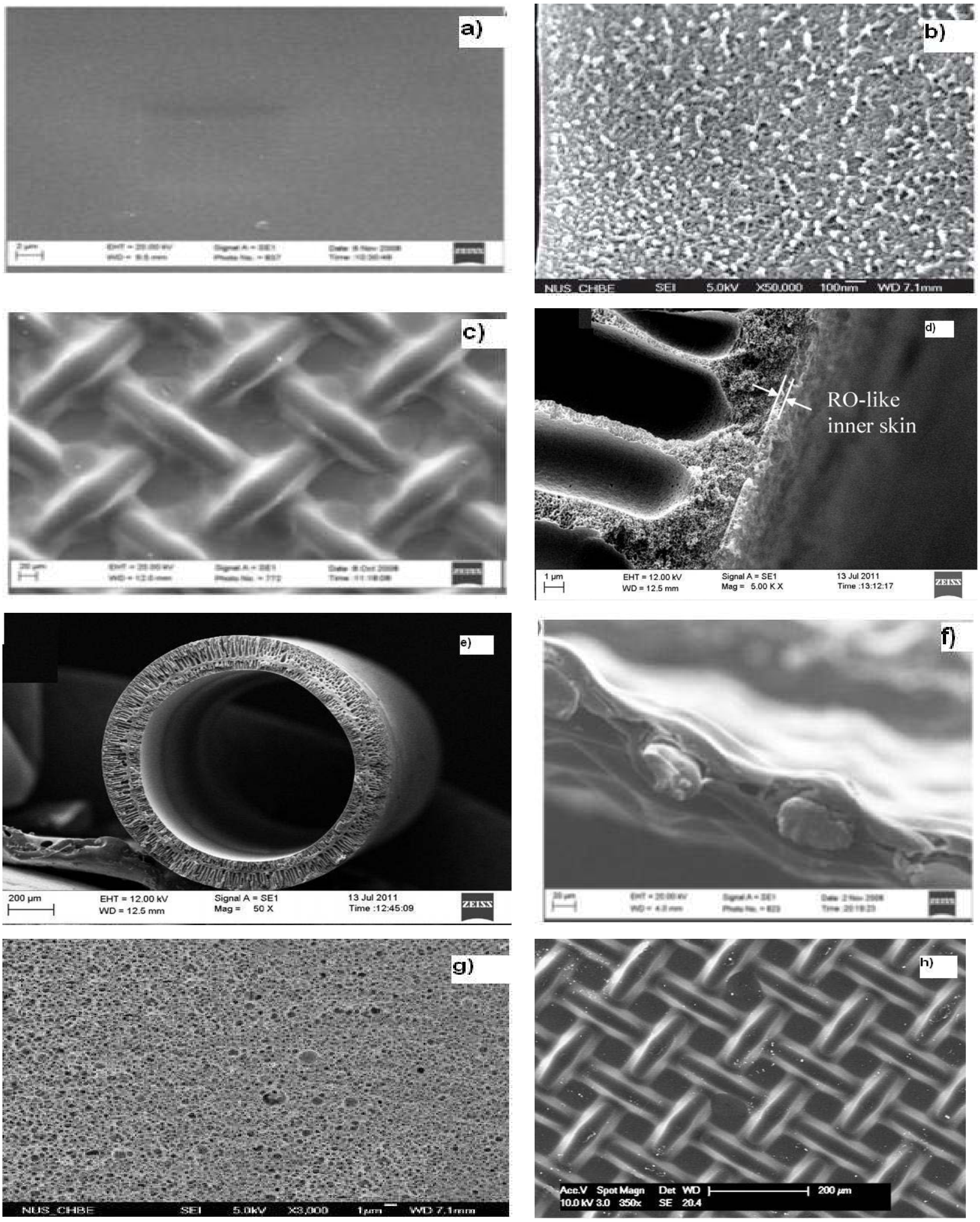

Figure 2.11. SEM images of different FO membranes a) active surface of HTI FO membrane (Tang et al., 2010b) b) TFC PA active layer (Wang et al., 2009) c) PAI hollow fiber substrate d) RO like inner skin for double skinned hollow fiber (Fang et al., 2012) e) cross-section of hollow fiber FO membrane (Fang et al., 2012) f) cross-section of HTI CA membrane (Tang et al., 2010b) g) Sponge middle layer (Su et al., 2010) h) HTI support layer (Zhao and Zou, 2011a)

Organic salts: Bowden et al. (2012) used various organic salts that consisted of an organic anion and an inorganic cation of either Na^+ or Mg^{2+}. These organic salts, namely sodium formate, sodium acetate, sodium propionate and magnesium acetate were selected for further assessments. The advantage of using biodegradable organic salts is that they mitigate the accumulation of draw solutes in OMBR (Bowden et al., 2012);,

Synthetic materials: Hydrophilic magnetic nanoparticles (MNPs) 2-methylimidazole-based organic compounds (Yen et al., 2010), electrolytes of poly acrylic acid sodium (PAA-Na) salts Ge et al. (2012a), polymer hydrogels for FO desalination (Razmjou et al., 2013) have been also investigated as draw solutes. Fig.2.12 illustrates the various types of DS preferably used in FO processes.

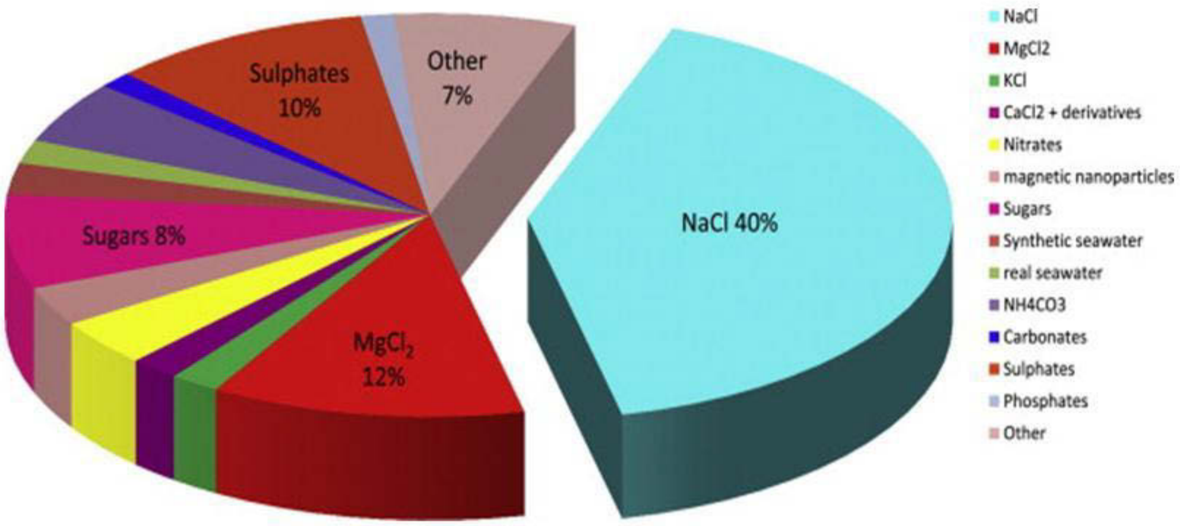

Fig. 2.12 Draw solutions used in FO based on approximately 50% of FO publications. Results are expected to increase in similar ratios when considering all published studies (Lutchmiah et al., 2014).

Polymer hydrogels were successfully demonstrated as draw agents in FO desalination and water could subsequently be released from swollen hydrogels by using temperature, pressure or solar irradiation (or a combination of these) as external stimuli (Li et al., 2011a, Li et al., 2013). An overview of the various draw solutes, their recovery methods and possible drawbacks are summarized in Table 2.7.

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2.9.4 Feed solution

In comparison to other desalination processes, FO uses two streams simultaneously, i.e. DS and FS. Since FO uses the net osmotic pressure difference ($\Delta\pi$) between the DS and FS as the driving force, similar to the important DS characteristic, the properties of the FS as well play a vital role for any specific FO process outcome.

McCutcheon et al. (2005) used DI water as FS for evaluating their NH_3-CO_2 FO desalination process. Hydration packs from Hydration Technologies Innovations (HTI) are designed for various FS types as sea water, brackish water, pond water, etc. (HTI, 2013).

Based on the specific dehydration application, FO uses relevant FS as diluted drugs (Yang et al., 2009b, Nayak and Rastogi, 2010). Similarly FO has used various juices as FS for increasing their concentration (Changrue et al., 2008, Lombard et al., 2008). Lysozyme solutions were enriched by FO membranes using $MgCl_2$ as the draw solution (Yang et al., 2009b, Ling and Chung, 2011b). Garcia Castello et al. (2009) successfully used FO process for the concentration of sucrose solution. Holloway et. al. (2007) demonstrated that FO is able to concentrate both raw and pre-treated centrate and providing high rejection of nutrients of interest. The osmotic pressure difference of the sea water and river water has been used in pressure retarded FO process used for power generation (Achilli et al., 2009a, Chung et al., 2012b, Yip et al., 2011).

Wastewater is also used as FS for various water reuse applications (Valladares Linares et al., 2013). Ge et al. (2012b) used polyelectrolyte-promoted forward osmosis–membrane distillation (FO–MD) hybrid process for treating dye wastewater. The background electrolyte FS representing wastewater effluent carrying either 10 mM NaCl or 1 mM $CaCl_2$ and 7 mM NaCl was evaluated for scaling and fouling (Jin et al., 2012). Cornelissen et al. (2008) introduced an innovative osmotic membrane bioreactor (OMBR) using the forward osmosis (FO) process for activated sludge solution feed. A novel application of FO was tested for treatment and reclamation of water from drilling waste during oil and gas exploration and FS resembling a shale gas field sources was evaluated (Hickenbottom et al., 2013a). Organic fouling studies also used model organic foulants as sodium algenates, humic acid (HA) and bovine serum albumin (BSA) dissolved in DI water (Mi and Elimelech, 2008).

Table 2.7 Summary of the major draw solutes used and their major drawbacks

Year	Researcher (s)	Draw solute (s)	Drawbacks	Ref.
1976	Kessler and Moody	Glucose and Fructose	Not pure water	(Moody and Kessler, 1976)
1997	Loeb et al.	$MgCl_2$	Not pure water	(Loeb et al., 1997)
2005-2007	McCutcheon et al.	NH_3 & CO_2 (NH_4HCO_3) or NH_4OH anf NH_4HCO_3	High reverse draw solute flux Insufficient removal of ammonia	[(McCutcheon et al., 2005, McCutcheon et al., 2006)
2007	Ling et al.	Magnetic nanoparticles	Poor performance, agglomeration	(Jamil, 2013, Ge et al., 2010)
2007	Adham et al.	Dendrimers	Not feasible	(S. Adham, 2007)
2007	Adham et al.	Albumin	Not feasible	(S. Adham, 2007)
2008	McCormick et al.	Salt, ethanol	High reverse draw solute flux and low water flux	(McCormick et al., 2008)
2010	Yen et al.	2-Methylimidazole based solutes	Materials costly	(Yen et al., 2010)
2010-2011	Ling et al. & Ge et al.	Magnetic nanoparticles	Agglomeration	(Ge et al., 2010)
2011	Li et al.	Stimuli-responsive polymer hydrogels	Energy intensive, Poor water flux	(Li et al., 2013)
2011	Ling & Chung	Hydrophilic nanoparticles	Poor water flux	(Ling and Chung, 2011a)

2011	Phuntsho et al.	Fertilizers	Limited application to agriculture only	(Phuntsho et al., 2011)
2011	Lyer and Linda	fatty acid-polyethylene glycol	Poor water flux	(Iyer, 2012)
2012	Su et al.	Sucrose	Relatively low water flux	(Garcia-Castello et al., 2009)
2012	Ge et al.	Polyelectrolytes	Relatively high viscosity	(Ge et al., 2012a)
2012	Noh et al.	Thermo-sensitive solute (Derivatives of Acyl-TAEA)	Poor water flux	(Noh et al., 2012)
2012	Yong et al.	Urea, ethylene glycol and glucose	Low water flux and high draw solute flux	(Yong et al., 2012)
2012	Bowden et al.	Organic salts	Low water flux, energy intensive	(Bowden et al., 2012)
2012	Carmignani et al	polyglycol copolymers	High viscosity, severe ICP	(Ge et al., 2013)
2012	Stone et al.	Hexavalent phosphazene salts	Not economical and practical	(Stone et al., 2013)
2013		Copper Sulphate		(Alnaizy et al., 2013)
2014	Hau et al.	EDTA sodium salt	High energy NF system for DS recovery	(Hau et al., 2014)
2014	Ge et al.	Cobaltous hydroacid complexes	High osmotic pressures, toxic	(Ge et al., 2014). (Hong and Elimelech, 1997)
2014	Ge et al.	Cupric and ferric hydroacid complexes	Low RSF and easy regeneration	(Hong and Elimelech, 1997)

For fouling studies various tough feed water solutions are sued for various studies. FO study was carried out with scaling solution: 35 mM $CaCl_2$, 20 mM Na_2SO_4, and 19 mM NaCl,with gypsum ($CaSO_4 \cdot 2H_2O$) having saturation index (SI) of 1.3 (Mi and Elimelech, 2010a). FS with different bulk gypsum SI from 0.8 to 2.3 were used to investigate gypsum scaling in PRO process (Liu et al., 2012).

Various studies utilised sea water quality FS for different types of flat sheet and hollow fiber membranes (McCutcheon et al., 2006); (Chou et al., 2010, Majeed et al., 2014). Boron and arsenic loaded FS were also employed to evaluate the effectiveness of their rejection by the FO process (Fam et al., 2014, Jin et al., 2012). To employ the advantages of higher net osmotic pressure difference ($\Delta\pi$), most studies used deionized (DI) water for evaluating FO performance. DI water feed also reduces the external concentration polarization effects on FO performance. It also assists in developing a better understanding of the FO process (McGinnis and Elimelech, 2008).

2.9.5 Permeate recovery

FO permeate always end up in the form of dilute solution of the DS. In cases where draw solutes in the product water are not desired, a second separation step is required. The first separation step of FO, driven by an osmotic pressure gradient, does not require a significant energy input (only unpressurized stirring or pumping of the solutions involved). The second separation step, however, does typically require energy input.

The separation and recovery of the DS requires an additional processing phase which in most cases utilizes various thermal and membrane-based techniques. All these techniques consumes energy and therefore DS recovery continues to pose a significant challenge for high quality water especially for drinking water applications. This is another important aspect used for selecting appropriate DS for the FO process. For this reason, the success of FO desalination for potable purposes depends entirely on the selection of suitable DS that can be easily and efficiently separated from the diluted DS to obtain usable water. Fig 2.13 shows the NH_3-CO_2 FO process using heat energy to separate permeate from the DS.

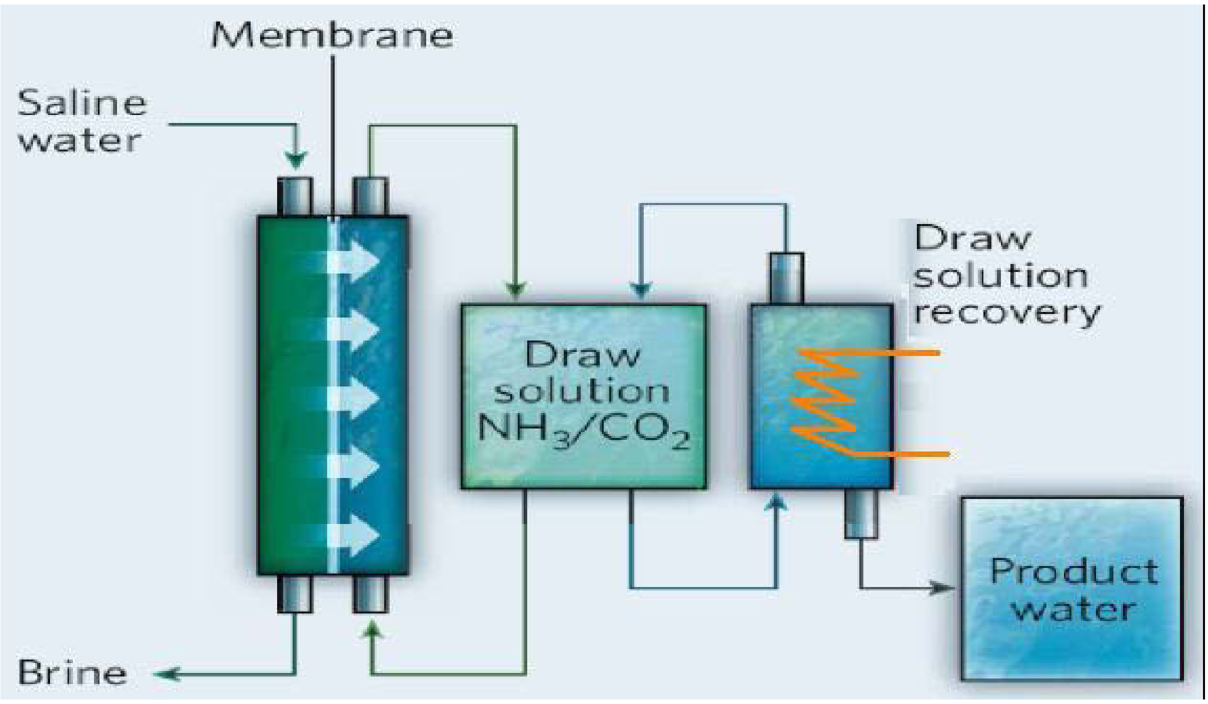

Fig 2.13: Permeate recovery from dilute DS in NH_3-CO_2 FO process (McGinnis and Elimelech, 2007)

Few other FO processes have been developed that do not require separation of the DS from the permeated water. In these processes, the diluted DS is either used as such for any suitable application or may need some dilution to bring its slats level down to some useful limit. A few HTI products such as Hydropack, Hydrowell, X-pack, Seapack, etc. use different nutrients because DS and the permeated water are used as an energy drink (HTI, 2013). Fig. 2.14 illustrates a novel fertilizer drawn forward osmosis process which requires no or minimal DS treatment before using it for some direct applications (Phuntsho et al., 2012c).

FO solute recovery can be made economical by using waste heat (e.g. from a power plant). Similarly, low heating energy requirements can also be met using different renewable energy systems such as solar. Khaydarov and Khaydarov (2007) developed a solar powered direct osmosis desalination process using diethyl ether $(C_2H_5)_2O$ with low boiling point as the osmotic agent and evaporation with a heat exchanger was applied for recovering the osmotic agent. Similarly, solar energy has been effectively used to recover water from swollen PNIPAM-C, hydrogel used in the FO desalination (Li et al., 2011a).

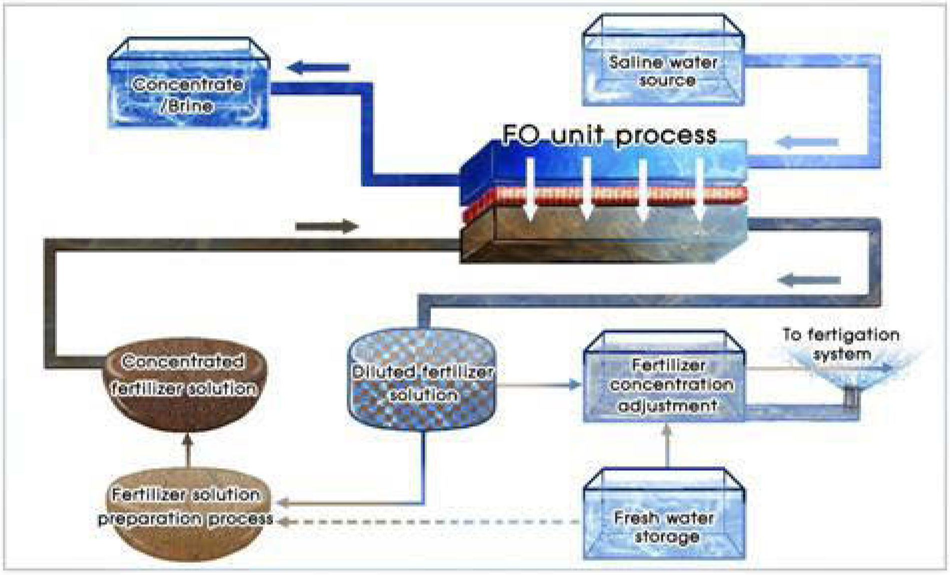

Fig. 2.14: Fertilizer drawn forward osmosis system requires no regeneration of the draw solution (Phuntsho et al., 2012c)

2.9.6 Module configuration

Membrane module configurations imply 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 (Baker, 2012, Mulder, 1996). Selecting a module for any application depends on economic considerations, ease of fabrication into the module design, suitability of the design for specific FO applications and operational performance as flux, RSF, CP effects, fouling propensity, etc. Various commonly available configurations are summarized in Table 2.8.

Similar to RO modules, spiral-wound FO membranes have also been developed and this configuration is commonly used in various FO studies. Spiral wound FO membrane envelopes contain glue lines that create two independent channels inside and outside the envelope, accounting for membrane area loss (Xu et al., 2010b). For such reasons, spiral-wound FO elements have a lower packing density (typically 20 m^2 for 8-inch modules) than sea-water RO elements (typically 30 m^2 for 8-inch) (Mulder, 1996).

When fouling occurs in these spiral wound modules, cleaning can be executed via chemicals, air/water mixing and/or high fluid velocities. Furthermore, it is suggested that to improve the performances of spiral-wound FO, some changes are suggested in the existing membrane module configuration. These include allowance for the back-washing phenomena to allow more effective fouling removal from the membrane surface and feed channels, incorporating short feed channels and wide spacers (Bamaga et al., 2011). Furthermore pilot-scale experiences with SWFO modules are still limited but these are steadily growing in recent years (Hancock et al., 2013, McGinnis et al., 2013, Coday et al., 2014) Xu et al., 2010).

2.10 Important issues and challenges in FO

2.10.1 Draw solution

Solutes carrying higher osmotic pressure are preferably evaluated as DS for FO process because they ensure the availability of the main FO driving force; this reflects higher possible flux outcome. Apart from the higher osmotic pressure characteristics of the DS, it should also have the following additional features if it is to be suitable for the FO process (Contreras et al., 2009):

- Low energy for regeneration or reconcentration and must be easily separated from the pure product water
- Minimum reverse solute flux
- Non-toxic
- Chemically inert to the membrane

- Small molecular weight and low viscosity in its aqueous solution
- Highly soluble

The first two DS features are are the most critical in the success of the FO process of which permeate separation from the DS is the most significant. It requires additional high energy processes that diminish the true advantages of a low cost FO process (Cath et al., 2006). Reverse solute flux further limits the usefulness of FO since it represents a waste of valuable solute, causes CP which reduces the FO performance, and finally adds to the concentrate disposal issues.

2.10.2 Treatment of the diluted draw solution

Permeated water for all FO processes ends up as a diluted DS which for most cases require using additional thermal or membrane-based desalination techniques (Zhao et al., 2012b). As mentioned above, these processes are energy intensive and employing them compromises the low cost desalination advantage of the FO process (Phuntsho et al., 2012b). This further limits its use as a low cost economical desalination strategy. McGovern and Leinhard (2014) recently highlighted that the current level of interest in forward osmosis for seawater desalination is surprising given that FO processes have higher theoretical and actual energy requirements than reverse osmosis, although this is seldom acknowledged or analysed (Semiat, 2008).

With reference to osmotic equilibrium issues, all FO processes using any DS end up with a dilute DS having TDS higher than the initial TDS of any FS. The minimum theoretical energy required for the direct desalination of any stream depends on the feed composition and increases as the feed TDS increases. For treating diluted DS which carries higher dissolved solids level this process is always costly and increases the overall cost of FO desalination (Fig. 2.15).

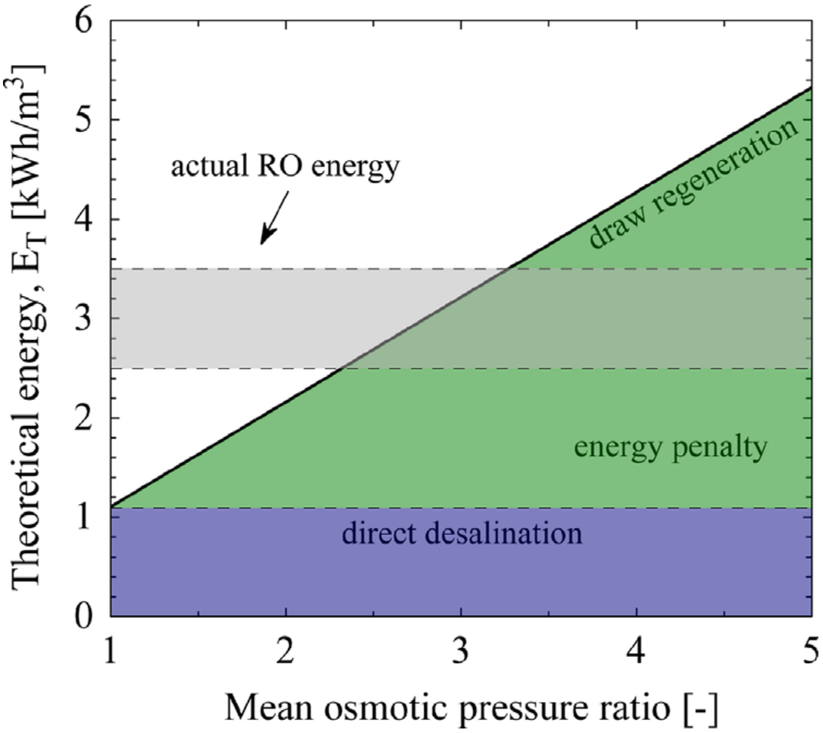

Fig. 2.15 Effect of the mean osmotic pressure ratio upon the energy penalty imposed by draw solution dilution. The theoretical energy penalty is the difference between the theoretical energy required for direct desalination and the theoretical energy for draw regeneration.

This has implications for the amount of energy used, so forward osmosis research is increasingly focused on to develop regeneration-free applications, for example where the draw solution is a nutrient containing drink, a concentrated fertilizer (Hoover et al., 2011). Alternatively, other forward osmosis processes which dilute rather than concentrate the feed stream are a second option, whereby forward osmosis dilutes seawater feeds, prior to RO desalination, by employing a low salinity 'impaired' source of water (Su et al., 2012).

2.10.2.1 Hybrid systems

As described in section 2.10.2, FO receives permeated water in the DS side which needs to be separated to take out desalinated water for any particular application. For that reason and for most applications, FO is not used as a standalone desalination system. Instead it is employed as a hybrid system associated with other thermal or membrane-based technologies.

Sherub et al. (2013) assessed nanofiltration (NF) as an integrated process to FDFO desalination, either as a pre-treatment or post-treatment, to reduce the nutrient concentrations in the final product water and thereby allow direct use of the product water for fertigation without further dilution (Phuntsho et al., 2013a). zNANO FO membranes helped to treat spacecraft wastewater in a variety of layer configurations and electrical charge hybrid[s?] with RO process. Consequently higher flux results were achieved (Kamiya et al., 2013). Another study demonstrated the robustness and treatment ability of a forward osmosis (FO)–

Table 2.8 Various configurations for modules used for FO desalination

Configuration	Advantages	Disadvantages	Reference
Spiral-wound	High packing density Easy cleaning of fouling deposits	Limited pressures in membrane envelop Clogging of spacers	(Xu et al., 2010b, McGinnis et al., 2013, Zhao et al., 2012b, Coday et al., 2014)
Hollow fibre	Self-supported characteristics Appropriate flow patterns Simplicity of fabrication High packing density	Limited mixing at membrane surface In open channels the CP film grows undisturbed in the channel	(Setiawan et al., 2012, Setiawan et al., 2011) (Liu et al., 2013a, Coday et al., 2014)
Plate and frame	Well-suited to wastewater applications Less complicated in design Better backwashing Higher cross-flow velocities	More expensive per m^2 of membrane area	(Achilli et al., 2009b, Bamaga et al., 2011, Gu et al., 2011)

membrane distillation (MD) hybrid system for small-scale decentralized sewer mining, and water recovery of up to 80% was achieved (Xie et al., 2013a).

Hancock et al. (2013) evaluated a long-running FO /RO hybrid system to achieve simultaneous seawater desalination with wastewater reclamation. They operated this system continuously for 1300 hrs (Hancock et al., 2013). Table 2.9 highlights some of the hybrid FO systems that have been evaluated with different DS and feed water sources.

Table 2.9 Various hybrid technologies that used the FO process to separate desalinated water from DS

Hybrid process	Feed source	Product water application	Reference
FO-RO	Wastewater reclamation	Non-potable application	(Hancock et al., 2013). (Xie et al., 2014) (Kamiya et al., 2013) (Childress and Elimelech, 1996)
FO-NF	Sea water	Potable	(Hoover et al., 2011)
FO-NF	Sea water	Agriculture	(Shaffer et al., 2012) (Phuntsho et al., 2013a).
FO-Distillation	Sea water	Potable water	(McCutcheon et al., 2005) (McGinnis and Elimelech, 2008)
FO-Solar	Brackish water	Potable	(Li et al., 2011a)
MD	Sewer mining RO brine Oily wastewater	Non-potable application	(Cath et al., 2005) (Martinetti et al., 2009) (Xie et al., 2013a). (Zhang et al., 2014)
FO-NF	Brackish water Desalination	Potable application	(Zhao et al., 2012a)
FO–PAO–RO	Treated wastewater	Non-potable application	(Oh et al., 2014)

2.10.3 Reverse solute flux

RSF directly affects the suitability of FO for various applications. Efforts are continually being made to develop an ideal semi-permeable membrane that can prevent any dissolved draw solute from permeating into the feed solution. However, since no membrane is a perfect barrier small amount of dissolved solute will always be transported across the membrane (Phillip et al., 2010).

Experimental work with a variety of dissolved solutes demonstrated that solutes diffuse at different rates based primarily on ion solvation and hydrodynamic size (Yong et al., 2012). RSF not only indicates the loss of valuable DS but also contributes to decreasing the osmotic pressure difference across the active layer within the membrane porous surface, i.e. ICP dramatically reduces the flux outcome for any FO process. DS is an expensive strategy so the cost of replenishing lost DS to the FS makes the whole process uneconomical (Phuntsho et al., 2011).

RSF is also detrimental as it may have serious consequences for the concentrate disposal since these RSF solutes may have some serious consequences for the feed concentrate receiving bodies or surrounding environment. This may encourage the decision to focus on additional treatments of the feed solution concentrate that are required prior to discharge.

2.10.4 Lower flux due to concentration polarization

Earlier FO performances indicated smaller flux outcomes for various DS and membranes. Concentration polarization (CP) is considered to be the major serious operational phenomenon directly affecting the flux outcome (McCutcheon and Elimelech, 2006, Li et al., 2011b, Zhang et al., 2010, Cornelissen et al., 2008, Tang et al., 2010a). As the osmosis starts through the FO membrane, pure water permeates from the FS side to DS side, the concentration of the DS starts to reduce with time whereas the concentration of the FS starts rising. These changes affect the concentration of the FS and DS at the membrane surface because the bulk osmotic pressure of the FS and DS differs from the FS and DS osmotic pressure available at the interface of the AL of the FO membrane. Concentration polarization diminishes the available driving force (osmotic pressure gradient) at the membrane surface which results in a sharp decline in flux. Since FO mainly relies on available osmotic pressure across the membrane surface contacting DS and feed solution (FS) to drive osmosis, its performance is more seriously compromised by the CP (Lay et al., 2010, Zhang et al., 2010).

The asymmetric nature (active layer embedded on a porous support layer used to increase the structural strength of the membrane) of the membrane is assumed to be the main contributor to any severe CP build up. This is because it supports the enhancing concentration polarization on both sides of the membrane. Consequently this results in reducing the actual water flux through the membrane.

Four types of concentration polarization i.e., concentrative and dilutive external concentration polarization (ECP), and concentrative and dilutive internal concentration polarization (ICP) significantly affect the FO process output using asymmetric membranes (McCutcheon and Elimelech, 2006, Li et al., 2011b). ICP in the support layer poses a significant obstacle to water permeation across the membrane (Suh and Lee, 2013b). The effects of ICP and ECP on DS and FS available concentrations on the membrane surfaces are shown in Fig. 2.16.

When the active layer of the membrane faces the FS, usually two types of CP are developed, i.e. concentrative external CP (CECP) coupled with dilutive internal CP (DICP) (McCutcheon and Elimelech, 2006). Eq. (2.22) indicates that ICP in the membrane support layer is determined by both membrane properties (e.g. membrane thickness, tortuosity, porosity) and diffusion solute properties (e.g. the diffusion coefficient of the solute). Based on the membrane orientation, ECP is usually linked with DS and FS concentration whereas ICP is mainly associated with thick dense membrane and support layer structure (Cath et al., 2006).

2.10.5 Performance ratio

Performance ratio (PR) is defined as the ratio of the actual FO flux and theoretical flux as shown by the Eq. 2.32

$$\text{Performance ratio} = \frac{J_{Experimental}}{J_{Theoretical}} \qquad (2.32)$$

FO performances with various FO membranes and different DS highlighted issues such as low water flux (J_w) and high RSF (Cath et al., 2006, McCutcheon and Elimelech, 2008) which seriously reduce the adequacy of low energy FO process. Lower PR of 16.48% indicated serious issues with the FO membrane (Phuntsho et al., 2011).

CP mainly contributes to poorer FO performance in that it drastically reduces the available driving force (osmotic pressure gradient ($\Delta\pi$)) at the membrane surface and causes a sharp decline in flux, thus resulting in poor FO operational result functioning. Since FO flux mainly relies on $\Delta\pi$ across the membrane surface contacting DS and feed solution (FS) to drive osmosis, the accumulated CP affects it seriously (Lay et al., 2010, Zhang et al., 2010, McCutcheon and Elimelech, 2006, Li et al., 2011b). External concentration polarization (ECP) is usually linked with DS and FS concentration whereas internal concentration polarization (ICP) is mainly associated with thick dense membrane and support layer structure (Cath et al., 2006).

2.10.6 FO membrane fouling

Fouling is one of the main issues all membrane-based processes face when they are operating. It affects the system's performance in many ways such as decreasing the membrane life, increasing downtime, requiring use of chemicals, and increasing membrane cleaning costs which also consumes additional energy. Regardless of the nature of the membrane process as

NF, UF, MF, RO or MD using different acting driving force such as hydraulic pressure, osmotic pressure or temperature gradient, passive fouling is very common to these membrane-based systems (Holloway et al., 2007).

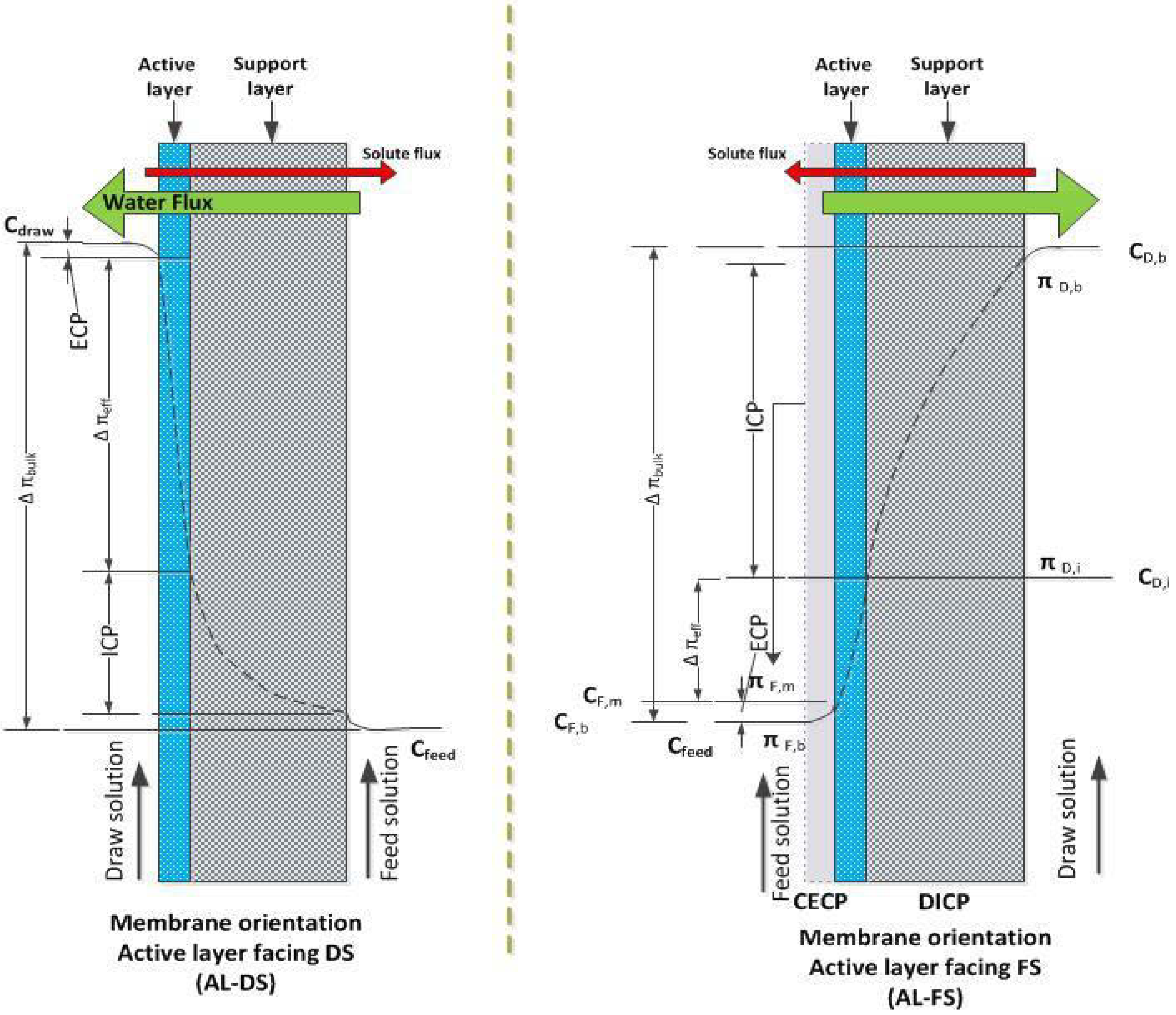

Fig. 2.16 Graphic presentation of external concentration polarization (ECP) and internal concentration polarization (ICP) for AL-FS and AL-DS membrane orientation.

Membrane fouling is a very complex phenomenon as membrane fouling is determined by the coupled influence of physical and chemical interactions between the membrane and impurities coming with the feed water (Kim et al., 2010, Saffarini et al., 2012). Due to the abundance of organic foulants in natural waters and wastewater effluents, it is virtually impossible to completely eliminate membrane fouling in real applications. Aromatic polyamide membranes as used in RO and FO, are prone to fouling due to their hydrophobicity, nano-scale morphology, and the presence of functional groups that can increase the extent of fouling (Elimelech and Phillip, 2011). The nano-scale "ridge-and-valley" structure characteristic of polyamide active layers may lead to enhanced foulant accumulation on the membrane's surface. In addition, negatively charged carboxylate groups on the polyamide surface can promote irreversible binding of natural organic matter through complexation with calcium ions in solution (Rana and Matsuura, 2010).

FO, being a process governed by the osmotic pressure gradient, has been hypothesized to have a smaller fouling propensity than other pressure driven membrane processes like RO/NF (Lay et al., 2010). Various studies that evaluated FO fouling potential for various types of FO membranes and different FS and DS combinations found that the severity of the fouling mechanism for these FO membranes was not so intensive. FO membranes are less susceptible to irreversible fouling and scaling and therefore perform more efficiently with feed streams containing high concentrations of sparingly soluble salts. Cornelissen et al. (2008) further evaluated the influence of various parameters, i.e. operating time, and the specific volume permeated to study the effects of fouling on the FO membrane.

The FO fouling process mechanism is more complex than other membrane-based systems in different ways. For a particular FO application, since the FO membrane can be used in both orientations as AL-FS and AL-DS, the surface properties of both AL and SL sides of the membranes show varied effects of fouling behaviour. Furthermore the FO process carries a simultaneous flow of two different streams as DS and FS on both sides of the membrane, and both are potential candidates for fouling. However, as the DS is produced in a controlled environment using better quality ingredients, then the fouling is usually and mainly governed by the FS characteristics. However, the role of DS properties may not be totally ruled out because Sherub et al. (2014) have shown that the RSF from the phosphate-based DS facilitate fouling on the feed side of the FO membrane.

Cornelissen*, et al* (2008) further studied the effect of fouling on the FO membrane and evaluated the influence of various parameters i.e., operating timeand specific volume permeated through FO (Holloway et al., 2007).

Overall, based on the fouling layer constituents, the fouling is usually divided into the following three main types as Inorganic, organic and biological.

2.10.6.1 Inorganic fouling/scaling

Gypsum scaling on FO membrane in AL-DS orientation is highly prone to internal scaling and calcium sulphate crystal penetrates into the active layer to the support layer (Liu et al., 2012). The scaling rate was increased when DS carrying Ca^{2+} or SO_4^{2-} was used as RSF to enhance their concentration of the FS side and accelerate the incidence of scaling. Similar studies that used chemistry with RSF, different DS and FS solutes mixed with each other, shifted the solubility equilibrium to form insoluble species that enhanced the scaling potential of these solutions (Mi and Elimelech, 2010a, Liu et al., 2012). They also indicated the role and importance of FS and DS chemistry which notably enhanced the scaling potential of the FO system.

Mi and Elimelech (Mi and Elimelech, 2010a) investigated the role of membrane materials in controlling gypsum scaling and cleaning. They found that for CA and polyamide (PA) membranes, gypsum scaling of PA membranes caused more severe flux decline and was harder to clean than the CA membranes. Recently, Sherub et al. (2014) have concluded that FO demonstrated accelerated fouling rates when due to the RSF, phosphate-based fertilizer draw solutes moved to the FS side, reacted with the specific FS species and formed insoluble products.

2.10.6.2 Organic fouling

Cornelissen et al. (2008) and Holloway et al. (2007) studied the FO fouling mechanism in OMBR using activated sludge and discovered that both reversible and irreversible membrane fouling did not occur during the FO experiments using activated sludge solutions and anaerobic digester centrate, respectively. This was possibly due to the FO operation using too low flux conditions, i.e. below the critical flux for membrane fouling. Gu et al. (2013) indicated that in a severe fouling environment, the properties of the membrane surface played a less important role due to foulant-foulant interaction.

Natural sea water fouling potential was studied in detail by Li et al. (2013) who found that the dissolved silica fouling by polymerization mechanism was prominent on the membrane surface (Creber et al., 2010). These fouling layers also contain natural organic matter such as biopolymers that contain bacterial attachment sites. Most of these studies identified that FO performs consistently at AL-FS orientation and avoids severe fouling (Kim et al., 2014, Motsa et al., 2014).

Mi and Elimelech (2008) studied the role of FO fouling for alginate, BSA, and HA. They also investigated the effects of various physical and chemical interactions such as intermolecular adhesion forces, calcium binding, initial permeate flux, and membrane orientation. It emerged in their study found that FO fouling is governed by the dual influence of chemical and hydrodynamic interactions. Li and Elimelech (2004) also confirmed that divalent calcium ions greatly enhanced natural organic matter fouling by complexation and subsequent formation of intermolecular bridges within the organic fouling layer (Li and Elimelech, 2004). Figure 2.17 shows various types of organic and biofouling layers on the FO membrane.

2.10.6.3 Biological fouling

Membrane performance declines markedly through the impacts of different types of fouling including mineral-, colloidal-, organic- and bio-fouling (Motsa et al., 2014). The latter, which results from the deposition of microorganisms (mainly bacteria) and the formation and deposition of extracellular polymeric substances (EPS), is considered to be of special importance in secondary effluents reclamation applications. For these reasons, fouling control has attracted much interest in the research community and various studies have sort to understand the fouling mechanism and develop effective mitigation measures that control fouling (Cornelissen et al., 2008, Lay et al., 2010, Tang et al., 2010b, Creber et al., 2010).

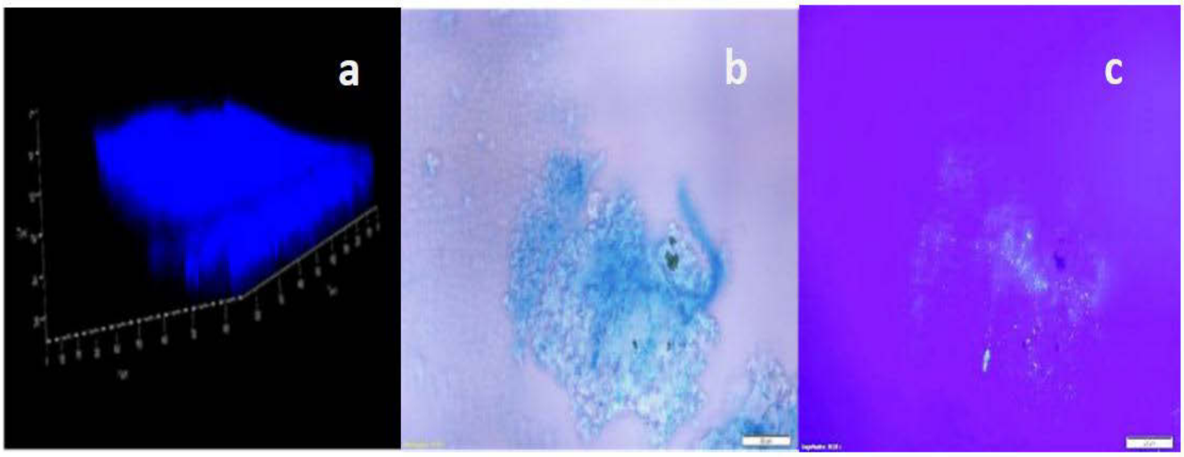

Figure 2.17 Organic and biofouling on the active layer of the FO membrane a) fouling of humic acid; b) fouling of biopolymers and c) adhered bacteria (Li et al., 2012)

2.11 Membrane cleaning

For popular membrane systems such as RO, NF, UF and MF, which use hydraulic pressure as a driving force membrane, cleaning is usually implemented when a significant change occurs in either membrane functioning, for example decreasing permeate flux and/or salt rejection, or operating parameters such as trans-membrane pressure increasing to deliver the same designed water flux. Evaluating the effects of fouling on the FO membrane is complex and difficult to predict in the standard system operations.

To restore membrane performances including flux, subsequent chemical cleaning of the membranes when treating water is often inevitable. Various cleaning techniques such as normal flushing, osmotic backwash, high flow osmotic flushing and chemical cleaning have helped to restore water flux of fouled FO membranes (Li and Elimelech, 2004).

2.12 Effect of operating parameters

Various studies identified that apart from changes in FS and DS properties and membrane characteristics, changes in various process parameters also affect the system's performance and FO system outcomes (Babu et al., 2006, Ng et al., 2006, Jin et al., 2012, Hancock et al., 2013, Oh et al., 2014, She et al., 2012b). A few of the main process parameters indicating changes in FO performance are listed below:

- Membrane orientation (Gray et al., 2006, Jung et al., 2011, Zhao et al., 2011, McGovern et al., 2014, Su et al., 2010)
- DS flow rate (Cochrane and Cochrane, 2007, Jung et al., 2011, Hancock and Cath, 2009)
- FS flow rate (Gruber et al., 2011, Chung et al., 2012b)
- Flow configurations (Sivertsen et al., 2013)
- Temperature (Zhao and Zou, 2011a, Phuntsho et al., 2012e, Xie et al., 2013b)
- Hydraulic pressure (Oh et al., 2014, Coday et al., 2013)

For the same osmosis driving force (concentration of any DS), different membranes have demonstrated different outcomes which indicate that these process conditions not only change the DS characteristics. They also influence the properties of the membrane's AL and SL. Hence there is a need to evaluate the best conditions in which the FO process can operate. These studies revealed that the mechanisms driving various factors, for example membrane structure and orientation, draw solute, co-current or counter-current cross-flow, cross-flow rate, operating temperature, hydraulic pressure, etc., also influence how well the FO process functions. It is clear that this theme needs to be fully studied and well understood.

2.13 Fertilizer drawn forward osmosis (FDFO) process

Fertilizers were initially used as DS in the FO process to extract water from saline water for irrigation (Moody and Kessler, (1976). Later, Phuntsho et al. (2011) presented their innovative concept of fertilizer drawn forward osmosis (FDFO) that concerned various fertilizers such as DS. They could be applied to the FO process using HTI flat sheet membrane and consequently, important outcomes were documented. FDFO is a unique concept using commercially available fertilizers as DS to produce desalinated water for agriculture (Phuntsho et al., 2011). In contrast to other FO processes, the final diluted draw solution does not necessarily require separating the remaining DS and product permeated water which can be used directly for fertigation. DS regeneration or permeate separation is the most expensive part of the FO process but it is eliminated in the FDFO process (Hoover et al., 2011). This helps the latter process take real advantage ofm low cost forward osmosis desalination.

2.13.1 Prospects for the FDFO process

Fig 2.1 near the beginning of this chapter indicates that the demand of water for agricultural application will increase in the near future. Other applications such as drinking, municipal use and industry take up most of the usable water and this means that agriculture misses out. Similarly, the increasing expense of existing desalination processes restricts the use of these technologies in farming, horticulture and other critical areas of the economy that produce food supplies.

Huge quantities of fertilizers are already widely being used in agriculture to create bigger crop yields. This represents a huge leap in the potential of DS to act as fertilizers and indeed for the FO process. It can fulfil the rising demands for usable agricultural water (Phuntsho et al., 2013a). For direct fertigation, diluted fertilizer DS does not require any regeneration, and the FDFO process requires very low energy for water desalination. Sherub et al. (2012b) estimated that the water desalination cost of FDFO for direct fertigation may be less than 0.24 kWh/m^3 which was the main advantage of this application.

Low operating costs make FDFO economical for brackish/sea water desalination. It can provide useable water to the largest water-consuming sectors in agriculture. Communities do have access to abundant reservoirs of sea water along long coastal areas and inland underground brackish water as well. These water resources can be employed using FO and help to reduce the current water deficit, which is proving to be a problem given the rising demand for food in domestic and international markets. In this scenario, the inexpensive FDFO process is an emerging technology that has desalination potential.

2.13.2 Issues with the FDFO process

FDFO has potential not only for sea water but also for large inland brackish water sources which due to their TDS concentration may not be used for irrigation purposes. Higher water salinity on one hand kills roots in the surrounding area, and on the other hand it reduces plants' nutrient intake and this means smaller crop yields (Adams and Ho, 1993, Smith et al., 2000).

Despite its inherent advantage of not requiring DS regeneration for direct fertigation, a few problems do exist in the FDFO process. These include comparative lower lower flux and performance ratio, DS regeneration, high nutrients concentrated in permeated water, the risk of possible nutrients loss to feed solution and membrane fouling (Phuntsho et al., 2012b, Phuntsho et al., 2011). FO flux is directly linked to the FO system's initial capital cost and operating cost. High flux FO operation means producing a small FO plant footprint.

Similarly, and the reduced reverse solute flux (RSF) reflects a reduction in DS leakage to FO waste streams.

2.14 Concluding remarks

The rising demand for water worldwide has emphasised the importance for developing a low cost water desalination process. Forward osmosis using natural osmotic pressure of the DS as a driving force to drive osmosis represents a step in the right direction. Further, the key feature of the FDFO technology in that the diluted fertilizer DS does not require regeneration and it can be used as such for any targeted application. However, the published FO studies that have measured its performance also have highlighted areas where improvements can be made in the FO process. Specifically, they refer to new DS development, membrane modification and establishing better process optimisation conditions.

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Chapter 3

MATERIALS AND METHODS

3.1 Introduction

In order to evaluate the role of the various parameters that were outlined in Chapter 1 (Introduction), the hole study was divided into various small tests. Overall, this study compared the performance of various types of FO membranes by changing the DS and FS qualities and process conditions. Each plan used different types of experimental protocols to obtain the required results.

3.2 Chemicals used in the study

Various types of feed solution and draw solution were used in this study. As osmosis is derived by the net osmotic pressure difference between the FS and DS across the membrane, the characteristics of both the FS and DS played an important role for the FO performance.

Reagent grade chemicals were used to prepare various FS and DS. These chemicals were procured from Sigma-Aldrich, Australia and Chem-supply, Australia. Unless otherwise specified, all the FS and DS were prepared by mixing the weighted quantity of these salts in deionized (DI) water with a magnetic stirrer until all the chemicals were uniformly mixed and fully dissolved in water.

3.2.1 Feed solutions

For most of the basic evaluations, DI water was used as FS. DI water was obtained from a Milli-Q, Millipore lab deionizer which showed EC < 1.5 µS/cm and TOC < 4 ppb. Usually most of the FS and DS used in this study were prepared in DI water. Tap water was also used as FS for the evaluation of FO performance in some of the cases. Table 3.1 shows the water quality parameters of the available tap water used in this study.

Different qualities of model brackish water were also prepared and used in this study. These display an NaCl concentration of 5 g/L, 10 g/L, 20 g/L and 35 g/L. These salt concentrations are later described as BW5, BW10, BW20 and BW35 respectively in the coming chapters.

For different scopes of the study, these BW feed solutions were separately prepared in DI water and tap water and the performance of different FO membranes was evaluated.

TABLE 3.1. Tap water analysis - Adapted from Sydney Water, (2013)

Parameter	Units	Value	Parameter	Units	Value
True colour	TCU or HU	1 - 2	Calcium	mg/L	11.8 -17.1
Turbidity	NTU	0.1 -0.2	Magnesium	mg/L	4.62 -6.04
Total dissolved solids	mg/L	94 -136	Conductivity	mS/m	19 -22
pH	pH units	7.7 -8.0	Potassium	mg/L	1.70 -2.18
Alkalinity	mg $CaCO_3$ /L	35 -46	Sulfate	mg/L	8 – 12
Total hardness	mg $CaCO_3$ /L	51 -65	Chloride	mg/L	26.5 –30.0
Calcium hardness	mg $CaCO_3$ /L	33 -46	Reactive Silica (as SiO_2)	mg/L	1.5 -2.4
Magnesium hardness	mg $CaCO_3$ /L	16 -25	Sodium	mg/L	12.2 –15.0

For scaling and fouling experiments in Chapter 9 and 10, some additional brackish ground water quality FS was also prepared simulating the brackish ground water quality of various points from the salt interception scheme (SIS) wells installed within the Murray Darling Basin (MDB), Australia. These FS go by the nomenclature of BGW in the following study. Simulated BGW was used to evaluate issues related to the fertilizer drawn forward osmosis (FDFO) application in the MDB, and this particularly suited the discharge of water through the existing SIS. The composition of various BGW quality FS prepared for the study is shown in Table 3.2.

Table 3.2: Detailed composition of various synthetic BGW qualities evaluated for the FO fouling study. Osmotic pressure is calculated using OLI Stream Analyzer 3.2 software

	BGW5	BGW10	BGW20	BGW35
Compounds/Concentration	mmol	mmol	mmol	mmol
$CaCl_2.2H_2O$	1.1	2.2	4.3	7.6
NaCl	31.8	63.5	127.1	222.5
$NaHCO_3$	0.6	1.1	2.3	3.9
Na_2SO_4	6.3	12.6	25.3	44.2
KCl	0.9	1.8	3.6	6.3
$MgCl_2.6H_2O$	9.7	19.4	38.8	68
π (atm)	2.74	5.35	10.56	18.56

3.2.2 Draw solutions

Following the development of the FDFO process and attempts to explore the future prospects of this novel application, this study mainly evaluated the influence of various types of fertilizer DS on the FO performance. For specific objectives, both commercial grade and reagent grade fertilizers DS were used for comparison purposes. Continuing the progress of earlier studies (Phuntsho et al., 2011, Phuntsho et al., 2013b), fertilizers draw solutes did not go through the initial screening process and were not evaluated in detail for their physical and chemical properties

3.2.2.1 Commercial fertilizer based draw solutions

Commercially available fertilizers were procured from various local sources in Australia. Each of these fertilizers was initially evaluated for their purity and nutrients content. The results are presented in Table. 3.3.

For the FDFO application for a tomato crop, mixed fertilizer draw solutions (MFDS) were prepared using the following 6 different fertilizers: NH_4NO_3, NH_4Cl, KNO_3, KCl, $NH_4H_2PO_4$

(MAP), and urea. Out of these, 4 fertilizers were categorized as common fertilizers. Among these fertilizers, NH_4NO_3, NH_4Cl and urea were taken as purely N-nutrient source fertilizers, MAP as P and N-source, KCl purely as K-source and KNO_3 as source fertilizer for N and K. Prepared MFDS exhibited specific NPK grades (in % for N, P_2O_5 and K_2O) as 11.5-19-11.5, 15-7-22, 10-0-20, and 15-0-30. This was to directly represent the nutrient requirements for a tomato crop at a particular growth stage as shown in Table 3.4.

Table: 3.3 Chemical analysis of different commercial fertilizers used as DS in this study

Fertilizer			Urea	SOA	MAP	DAP	KCL	KNO3	NH_4Cl	$NaNO_3$	$Ca(NO_3)_2$
Nutrient		Units									
Nitrogen	N	%	47.50	21.30	12.36	20.96	0.11	10.06	13.46	13.56	13.46
Phosphorus	P	%	0.02	0.06	37.55	38.11	0.01	<0.01	0.01	0.03	0.01
Potassium	K	%	<0.01	0.06	0.01	<0.01	61.46	48.48	0.04	0.03	0.04
Sulphur	S	%	0.17	27.97	0.08	0.08	0.10	0.20	0.23	0.16	0.23
Carbon	C	%	20.58	0.08	<0.01	<0.01	<0.01	0.10	<0.01	<0.01	<0.01
Calcium	Ca	%	0.02	0.04	0.01	<0.01	0.01	<0.01	23.52	0.01	23.52
Magnesium	Mg	%	<0.01	0.01	<0.01	<0.01	0.06	<0.01	0.01	<0.01	0.01
Sodium	Na	%	<0.01	0.06	<0.01	0.01	0.40	0.16	0.03	44.87	0.03
pH		-	9.29	5.37	4.05	7.65	6.46	8.81	6.12	8.20	6.12
Electrical conductivity		dS/m	0.07	267.0	74.7	94.9	302.0	205.0	100.6	256.0	100.6
Osmotic pressure (π)*		atm	23.70	46.14	43.80	50.60	44.00	37.20	48.80	41.50	48.80

Except NH_4NO_3, all fertilizer's purity was >95%.

*Based on fertilizer purity of >95%, osmotic pressure of pure reagents was used for flux evaluation, using OLI software (OLI systems, Inc, Morris Plains, NJ, USA)

3.2.2.2 Pure fertilizer based draw solutions

Various reagent grade fertilizers DS were extensively used in this study. Initial properties (as pH) and conductivity were evaluated for different concentration. The osmotic pressure of the DS was also evaluated using OLI software. Except in a few cases, these reagent grade fertizers DS were used in 1-3 M concentrations (Table 3.4).

Table 3.4 Selected fertilizers used to prepare mixed fertilizer DS, showing their nitrogen/ phosphorous/ potassium (NPK) nutrient composition and the osmotic pressure that these fertilizers exert at 1M concentrations

Commercial /Chemical Name /Chemical Formula	N/P/K $N/P_2O_5/K_2O$	Osmotic Pressure (1M conc.) atm	Commercial /Chemical Name /Chemical Formula	N/P/K $N/P_2O_5/K_2O$	Osmotic Pressure (1M conc.) atm
Ammonium chloride; NH_4Cl	25/0/0	43.5	Ammonium nitrate; NH_4NO_3	34/0/0	33.7
Mono ammonium phosphate (MAP); $NH_4H_2PO_4$	18/46/0	43.8	Potassium nitrate; KNO_3	14/0/44	37.2
Urea; $(NH_2)_2CO$	46/0/0	23.7	Potassium chloride; KCl	0/0/60	44
Ammonium sulphate*; $(NH_4)_2SO_4$	21/0/0/(24)	46.14	Calcium nitrate*; $Ca(NO_3)_2$	15.5/0/0/(26.5)	48.8

Reagent grade NaCl was also used as DS in various sections of this study for comparative purposes and baseline evaluations. It was used in 1-5 M NaCl concentrations.

3.2.3 Organic foulants

Three different model organic foulants were used to evaluate their fouling potential on the FO membrane: Sigma-Aldrich sodium alginate (Alginate) which represents polysaccharides that constitute a major fraction of soluble microbial products in wastewater (Mi and Elimelech, 2010b); bovine serum albumin (BSA) which represents proteins and amino acids; and Sigma-Aldrich humic acid (HA) which represents natural organic carbon (NOC) produced by the biodegradation of dead organic matter. Humic substances are refractory anionic macromolecules and these consist of both aromatic and aliphatic components which are primarily applicable to phenolic and carboxylic functional groups.

Alginate represents the hydrophilic fraction of the organic pollutants. Based on the manufacturer datasheet, the molecular weight of sodium alginate ranges from 12 to 80 kDa. Other characteristics of alginate can be found elsewhere (Jin et al., 2012). Alginate is negatively charged within the fouling study pH range 6-8 (Wang et al., 2010b).

A stock solution for each of these model foulants was prepared by separately mixing 2.4 g of the individual foulants in 1 L of DI water. Alginate and BSA (received in powder form) are dissolved in DI water and mixing is continued over 24 hrs to ensure complete dissolution. HA stock solution was prepared by dissolving the HA powder in DI water and adjusting the pH to 8.2 with NaOH. The stock solution was mixed continuously for 24 hrs to ensure complete dissolution. Stock solutions were then stored in amber glass bottles at 4˚C for further use. These model foulants were used in 60 mg/L concentration with various FS qualities. Fouling studies were carried out with FS. These were made from individual foulants and other possible combinations.

3.2.4 Cleaning Chemicals

HCl, NaOH and ethylene diamine tetra acetic acid (EDTA) salt were evaluated to check the performance of these cleaning chemicals for restoration of the fouled FO membrane. HCl was used at pH 2, NaOH at pH 11. 0.01 M EDTA was evaluated at a standard solution pH and 11 pH.

3.3 Forward osmosis membranes

Depending upon the components of the study and the outcome sought, two types of FO membrane were used with the membrane cell or were used to construct modules for the FO set-up. One was cellulose triacetate (CTA) flat sheet and the other was polyamide (PA) hollow fiber. Brief details are summarised in Table. 3.5.

3.4 Evaluation of the membrane properties

Before FO operations, membrane performance with respect to pure water permeability (A) and salt rejection (B) was evaluated as a reference. This used the bench scale NF/RO system as shown in Fig. 3.1.

Table. 3.5 Details of the FO membrane used in this study

Type of FO membrane	Active layer	Support layer	Source
Flat Sheet	Cellulose tri-acetate (CTA) (Tang et al., 2010b)	Polyester mesh (Cath et al., 2006)	Hydration Technology Innovations, LLC, Scottsdale, Arizona, USA
Hollow Fiber	Polyamide (PA)	Sulphonated polysulphone (SPSf)	Samsung Cheil Industries Inc., Uiwang-Si, Gyeonggi-Do, Republic of Korea

3.4.1 Pure water permeability

For the flat sheet FO membrane, the RO was operated at various pressures as 5, 10, 15 and 20 bars for 15 minutes using the DI water feed. Permeate was collected in a measuring cylinder and measured at the end of each test. Water permeability was calculated using the following relationship:

$$Water\ flux\ (J_w) = \frac{Water\ permeated\ (L)}{Membrane\ area\ (m^2)\ x\ Operating\ time\ (h)} \tag{3.1}$$

Pure water permeability ($L.m^{-2}.h^{-1}$/bar) was evaluated by dividing the recorded water flux by the operating pressure (bar).

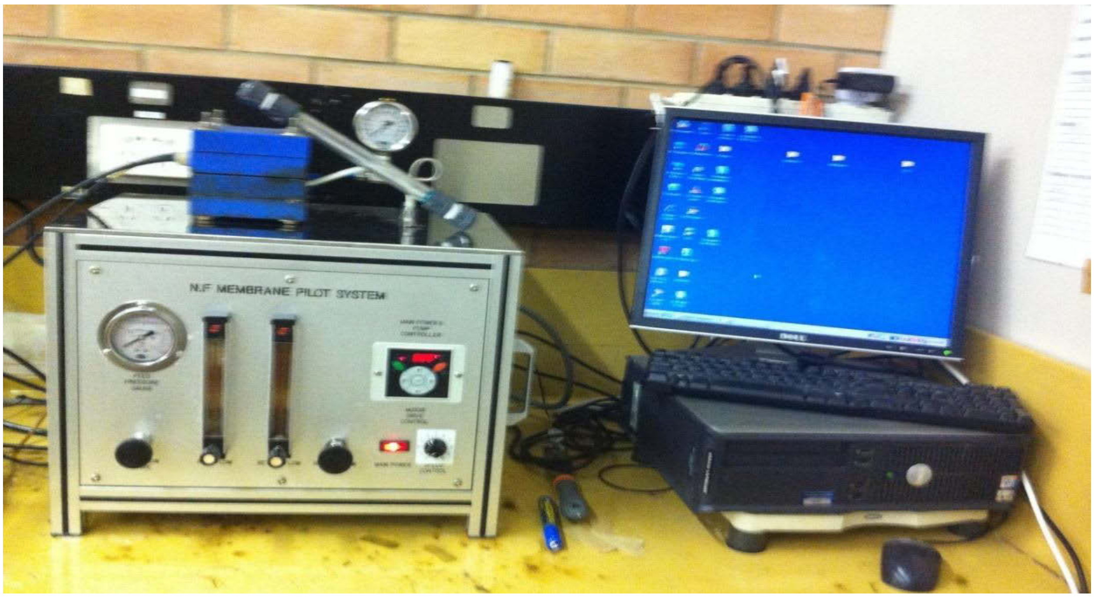


Fig. 3.1. RO system used to evaluate pure water permeability and salt rejection for FO membranes

For hollow fibre membranes, the risk of hollow fibre collapse at higher pressure and pure water permeability was evaluated by operating the RO unit at low pressure (e.g. 0.5, 1 and 1.5 bars). By applying Eq. 3.1 the flux was recorded from the permeate water collection data. Water permeability for the HFFO membrane was later evaluated by dividing the recorded flux (L.m^{-2}.h^{-1}) by the operating pressure (bar).

3.4.2 Salt rejection

Similarly both flat sheet FO and hollow fibre FO membranes were operated in the RO mode for feed water carrying 1000 ppm NaCl. The electrical conductivity of the feed water and the permeate collected in the measuring cylinder was noted. Salt rejection was determined by using the following relationship:

$$\mathrm{R}(\%) = \left[\frac{Cf - C_p}{C_f}\right] x100 \tag{3.2}$$

Where R is the salt rejection in percent (%), C_p is the conductivity of the permeate and C_f is the initial conductivity of the feed water.

3.5 Experimental FO system set-up and configuration

3.5.1 Laboratory-scale FO system

Fig. 3.2 shows the schematic drawing for the low pressure laboratory FO system used in this study. The core FO system is designed for cross-flow arrangements using two variable speed peristaltic pumps (Cole Palmer model 75211-15, 50-5000 RPM and 0.07 HP, Thermo Fisher Scientific, USA). The co-current flow arrangements were mostly used for this study. However, for the purposes of critically evaluating the process conditions on the membrane performances, some parts of the study were executed at a counter current arrangement

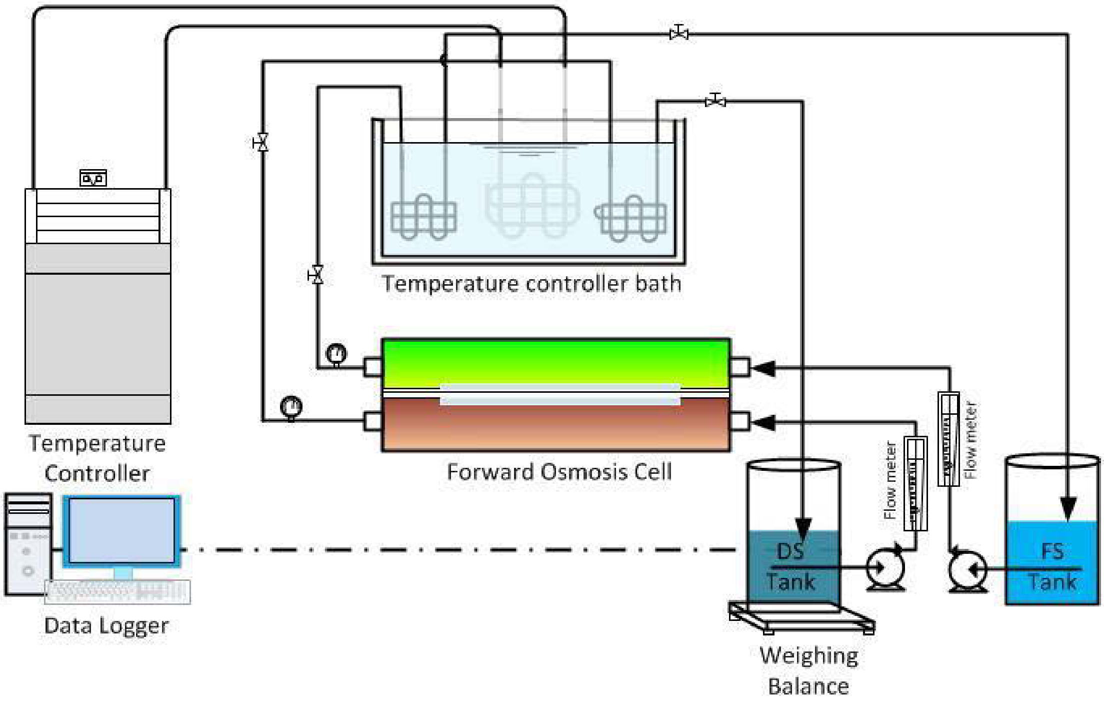


Fig. 3.2: The schematic diagram of the laboratory-scale FO system

3.5.2 Flat sheet FO cell

An acrylic cell was used to evaluate the performance of the flat sheet membrane. The FO cell had channel dimensions of 7.7 cm length x 2.6 cm width x 0.3 cm depth which gave an effective membrane area of 20.02 cm^2. Two channels were provided on both sides of the membrane to allow feed water to flow on to one side of the membrane and DS on to the other side of the membrane.

3.5.3 Hollow fibre FO module

Various hollow fibre FO modules carrying different membrane areas were prepared for this study using different numbers and lengths of hollow HFFO lumens. For most of the evaluations, HFFO modules carrying a membrane area of 25.45 cm^2 and 396 cm^2 were used in this study.

3.5.4 Experimental conditions

FO was operated for two different membrane orientations as active layer–feed solution (AL-FS) and active layer–draw solution (AL-DS). For the flat sheet FO membrane, the AL-FS orientation indicated that the FS flowed at the active layer side of FO membrane and the DS flowed at the support layer side. For the hollow fibre FO membrane, the AL-FS orientation indicated that the FS flowed through the lumens and the DS flowed through the shell side of the module. Similarly, for the hollow fibre FO, the AL-DS orientation indicated that the DS flowed through the lumens and the FS flowed through the shell side (Fig. 3.3).

Unless otherwise stated, for the flat sheet FO membrane, all FO performance experiments in this study were carried out at a crossflow rate of 400 ml/min which indicated turbulent flow with a crossflow velocity of 8.5 cm/s. FS and DS crossflows were mostly operated in counter-current flow directions using two variable speed peristaltic pumps (Cole Palmer model 75211-15, 50-5000 RPM and 0.07 HP, Thermo Fisher Scientific, USA).

The hollow fibre FO membrane was evaluated for 200 ml/min to 1200 ml/min which showed different Reynolds numbers (Re) for FS and DS flowing through either the lumen or shell side of hollow fibre module. These experiments were completed at constant temperature of FS and DS which was maintained at 25±0.5°C by using a temperature water bath controlled by a heater/chiller. For various outcomes, these experiments were continuously operated for various time periods ranging from 1-36 hrs.

3.6 Measurement and analysis

3.6.1 FO performance

FO membranes were operated for the varying combinations of DS and FS and their performance was recorded in terms of flux and RSF, as described hereunder.

3.6.1.1 Evaluation of flux

A digital weighing scale (Model: CUW 4200H by CAS, Korea) connected to a computer was used to monitor the weight of water permeating the membrane from the feed to the draw side. The computer continuously recorded the weight loss after a fixed interval (3 minutes for most of the study). As the specific gravity of the water was one, recorded weight (g) and its corresponding volume (ml) were assumed to be the same. Hence for the sake of simplicity, the value of water volume was used to record the weight loss due to flux. This data was later used to calculate water flux J_w using the relationship given in Equation 3.3.

$$Water\ flux\ (J_w) = \frac{Change\ in\ volume\ (L)}{Membrane\ area\ (m^2)\ x\ Time\ (h)} \tag{3.3}$$

Water flux J_w ($L.m^{-2}.h^{-1}$) was later used to interpret the FO performance outcome. Mostly, the initial volume of 2 L was used for both the FS and DS. However, for some quick performance checks with the DI water feed, flux was also monitored with an initial FS and DS volume of 1 L.

3.6.1.2 Evaluation of RSF

A conductivity meter (Model: H270G-BNDL, Hach) was used to evaluate the changing FS quality. FS conductivity changes for two reasons, one is due to the concentration of the initial feed solutes as pure water permeates towards the DS side and secondly by the RSF movement from the DS side to FS side. The conductivity meter probe was immersed in the FS tank and conductivity of the FS was continuously recorded using data logging features. This data was then used to evaluate the RSF trend.

Reference conductivity curves were also drawn for the various pure chemicals and fertilizers used in this study (Fig. 3.4). These curves were later used to find the RSF values for particular sets of experiment where the DI water was used as feed and the single component solute was used as DS.

When a mixture of salts were used for DS and FS, RSF for the individual salts or elements was determined by analysing the FS samples which used inductively coupled plasma–mass spectrometry or ICP-MS (Perkin Elmer Elan DRC-e).

For experiments involving DS prepared from mixed commercial fertilizer and BW feed, FS samples were collected at the end of each test and analysed for any fertilizer RSF. These samples were analysed for K, P, and N concentration in FS by using the APHA method 3125 protocols.

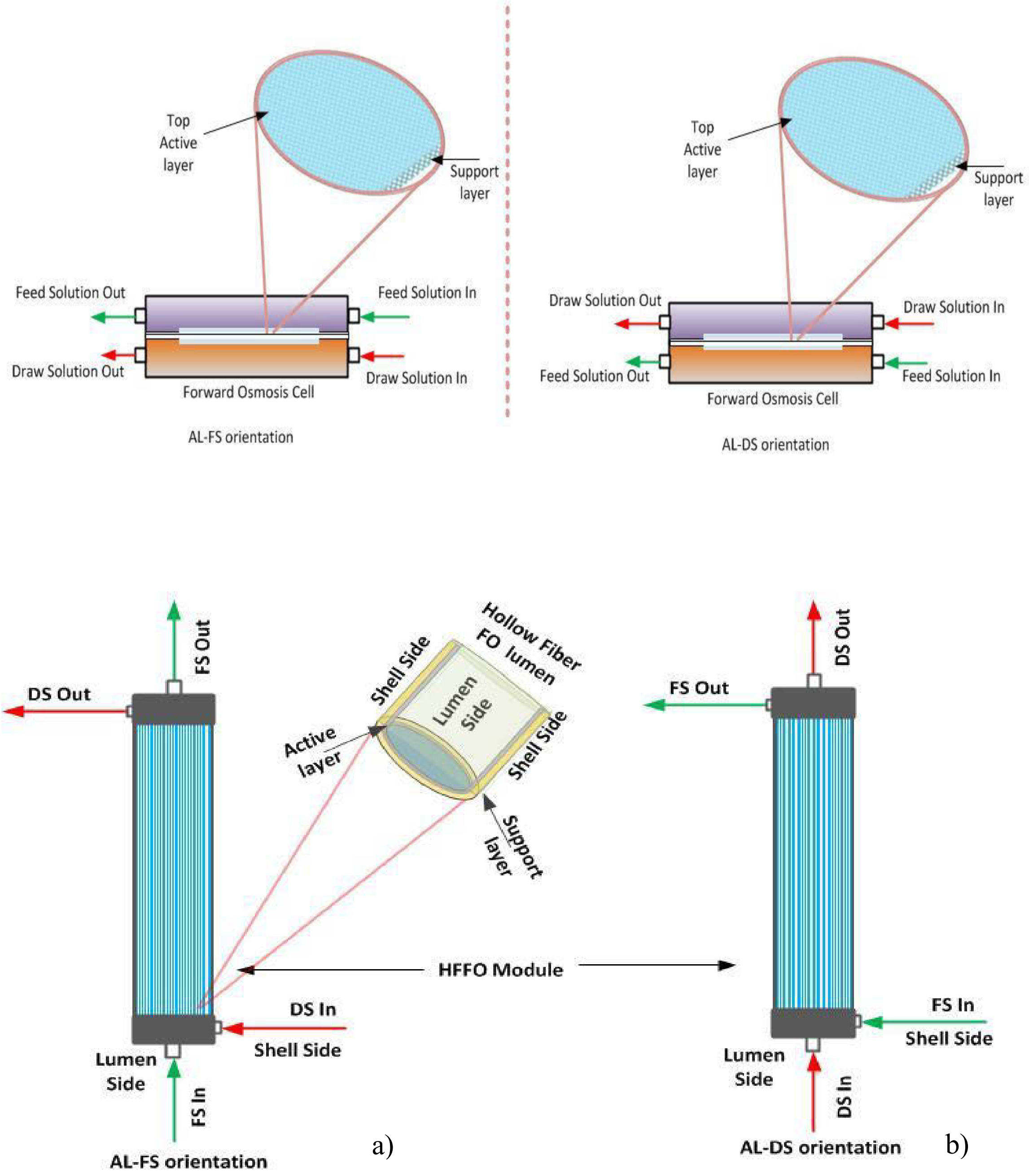
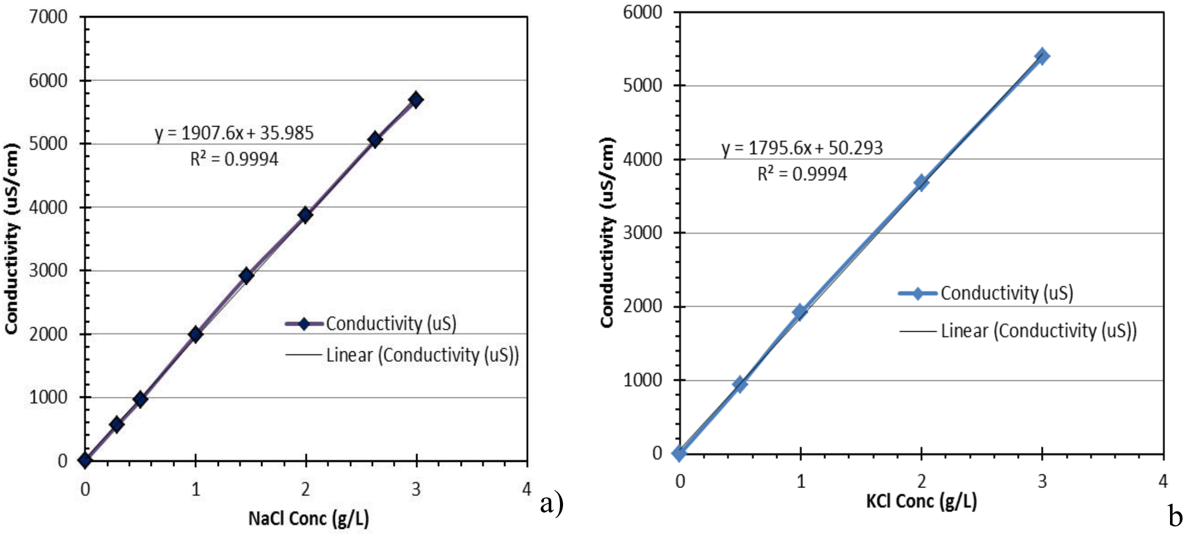


Fig. 3.3. FO orientation in AL-FS and AL-DS a) Flat sheet membrane cell b) Hollow fibre membrane module

3.6.2 SEM observation

A scanning electron microscope (Zeiss Supra 55 VP) or SEM was used to investigate the physical structures and surface morphology of the various membranes involved in the FO process (Fig 3.5 (a)). In this evaluation, a dried sample of membrane was exposed to a narrow beam of electrons in a vacuum. Secondary electrons were liberated from the surface and detected. To observe the intact cross-sections of the membranes, the dried membrane samples were prepared carefully. After dehydration and drying, a direct freeze fracture method (where a membrane was made brittle in liquid nitrogen and then broken to check the cross section) was used. Direct rapid cut was also employed to avoid any damage to the cross section.



a) b)

Fig. 3.4. Reference curves used to evaluate RSF for a) NaCl and b) KCl

Various resolutions were evaluated to visualise the physical structure, thickness, pore size, surface porosity and pore geometry. These images also helped to evaluate the asymmetry of these membranes.

Beside these advantages of SEM images for membrane characterisation, SEM was not used for the fouling layer evaluation of the HFFO membrane as the drying conditions totally modified the fouling layer characteristics and revealed a different physical structure. Further, the drying process also left the DS components attached to the membrane surface which showed their crystallized presence on the membrane. Hence these SEM images left different outcomes corresponding to the actual fouling layer features observed with the magnifying glass.

3.6.3 Contact angle tests

Contact angle is an important index of the hydrophobicity and hydrophilicity of a membrane surface which plays a significant role in delivering specific membrane performances (Fig 3.5 (b)). The hydrophilicity of the both sides of the CTA flat sheet FO membrane was tested by measuring the contact angles using a compact contact angle measurement system (Model: Make). When a de-ionized water droplet is placed on the surface of a membrane sample, the shape of the droplet is determined by balancing the three forces of water, membrane surface and air. The line tangent was drawn at the curve of the droplet to the point where it intersects the membrane surface and forms the contact angle. The image was captured in the computer using a precise camera and tangent lines were determined for the contact angle measurement.

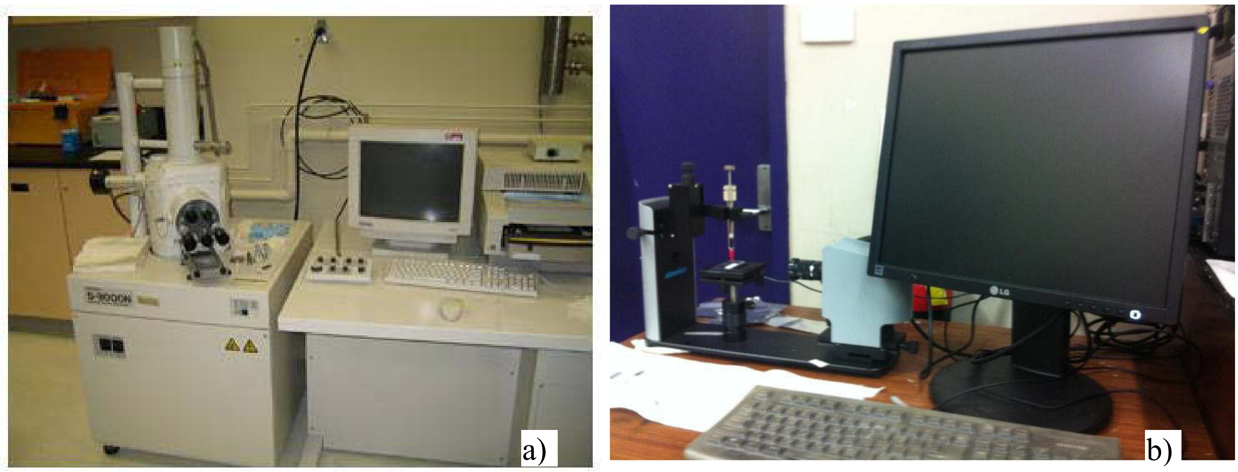


Fig. 3.5. a) Scanning electron microscope (Zeiss Supra 55 VP) b) Contact angle measurement system

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Chapter 4

FDFO- APPLICATION TO TOMATO

4.1 Introduction

The agricultural sector is the largest consumer of fresh water in the world. Like the rest of the world, the agricultural sector uses a major share of the available water resources in Australia. In Australia, the agricultural industry consumes the largest volume of water being 12,191 GL, which represents 65% of water consumption in Australia in 2004-05 (ABS, 2013). Due to recent draughts in the last few years, the agricultural water availability/use has decreased and this has resulted in lower crop areas being harvested and reduced agricultural production. This water scarcity is one of the main reasons for the rising price of agricultural goods/food commodities in our area and across the globe. The effects of water availability on areas harvested and agricultural production are displayed in the statistical data shown in Table 4.1. This data presents the declining trends in tomato crop harvesting and production for Australia in the last decade. As is evident from these statistics, the water shortages directly affected the areas harvested and tomato production. Indeed, both of these have reduced by >30% for this period (FAO, 2013).

Table 4.1 Effects of water availability on agricultural production, tomato harvesting area and production (World/Australia)

Year	2001	2002	2004	2005	2006	2007	2008
Area harvested world (in ,000 Ha)	3,990	4,150	4,478	4,576	4,638	4186	4,244
Production World (in ,000 Tons)	107,977	116,189	127,621	127,977	130,066	137,153	141,119
Area harvested Australia (in ,000 Ha)	10	8	8.4	7.8	7.75	7.29	6.79
Production Australia (in ,000 Tons)	556	435	474	408	450	296	382

Source: FAOSTAT : FAO Statistics division (FAO, 2013)

Every agricultural production site has its own plant life and life cycles. Looking into varying growth patterns and different life spans for common features like growth stage, watering and fertilizer requirements, the whole life period of each crop can be grouped into small periods (Warner et al., 2004). For each of these periods, specific watering schedules are suggested for different crops. Added to this, to ensure the proper development of various plants during each growth stage, these plants require varying quantities of nutrients. Many factors influence the selection, type and quantities of each fertilizer required for these plants. These include, the type of plant, its growth stage, atmospheric conditions, soils type and composition, the nutrients level in the soil, watering systems and the types of water used etc. (Haifa-Group, 2009). Therefore, different types of fertilizers are used in varying concentrations to fulfil the nutrient requirements of these plants for their particular growth stage. For this reason, some specific fertilizers may not be used for all the FDFO applications as no two crops use the same quantity of fertilizer for their whole life period.

Fertilizer requirements for these plants are mostly referred to as their nutrient requirements. Nitrogen, phosphorous, potassium, calcium, magnesium and sulphur are some of the commonly used nutrients required by the plants. Among these, nitrogen (N), phosphorous (P) and potassium (K) are the three main fertilizer nutrients used for agricultural crops which are generally known as NPK nutrients. All available fertilizers are known for their particular NPK values as each fertilizer provides specific quantities of these nutrients to the plant. A specific NPK value represents a percentage of the N, P and K available for that particular fertilizer. For this reason, only the proper dosage of an appropriate fertilizer for a suitable time may assist in terms of getting the required results from the specific fertilizer application.

Earlier work (Phuntsho et al., 2011, Phuntsho et al., 2012a) on FDFO showed that various fertilizers can be effectively used as DS to desalinate brackish or sea water sources for agricultural applications. For other FO applications i.e. drinking water production, FO requires further treatment of the diluted DS to obtain useable product water, thus FO application for potable water use still remains a challenge (McCutcheon et al., 2006). This is because the separation and recovery of the draw solute from the FO product water are not easy and they require additional energy. The FDFO process carries the edge over other FO processes as the resultant low concentration fertilizer DS does not require regeneration and thus can be used directly with some concentration adjustments to irrigate any suitable agricultural crops (Phuntsho et al., 2011, Phuntsho et al., 2012d). As the final energy intensive step of draw solute recovery is eliminated in the FDFO, it is really considered as an effective low-cost desalination technology that may fulfil the low cost irrigation water requirements.

Various types of reagent grade fertilizers have been evaluated and have shown some prominent outcomes in terms of water flux for the different types of FO membranes. The final outcomes of these FDFO processes are diluted fertilizer DS which can be directly used for fertigation without using any further treatment (Phuntsho et al., 2011).

To understand the actual scenario of the FDFO process and unseen practical operational issues, FDFO was applied to one selected crop. Tomatoes were selected as the target crop for this process. The tomato (*Lycopersiconesculentum)* is one of the most popular and widely grown vegetable crops in the world. Its popularity stems from the fact that it can be eaten fresh or used in multiple processed forms. The three major processed tomato products are: i) tomato preserves (e.g. whole peeled tomatoes, tomato juice, tomato pulp, tomato purée, tomato paste, pickled tomatoes); ii) dried tomatoes (tomato powder, tomato flakes, dried tomato fruit); and iii) tomato based food (e.g. tomato soup, tomato sauces, chilli sauce, and ketchup).

Different type of irrigation methods are currently being used for tomato cultivation (Warner et al., 2004, Haifa-Group, 2009). The main growing techniques for the tomato are classified as a) Field grown b) Greenhouse and c) Hydroponic. Again, the tomato plant requires different watering and fertilizer requirements for these three growth techniques. The tomato is usually divided into two main categories a) Fresh and b) Processing. These v processing and fresh market tomatoes also come in different varieties carrying different growth habits and thus require different environmental conditions, soil, water requirements and irrigation patterns. Processing tomatoes are usually grown in the open fields whereas fresh-market tomatoes are grown in greenhouses. This study has been planned for the actual fertilizer and water requirements for the field grown tomatoes.

The tomato responds well to the application of water and fertilizers and is reported to be a heavy feeder of NPK. Balanced irrigation & fertilization regimes ensure optimal nutrition throughout the growth season. Application of top-quality water-soluble fertilizers through the means of the irrigation system is the optimal method for providing balanced plant nutrition throughout the growth season. Tomatoes can tolerate brackish irrigation water up to conductivity of about 2-3 mmho/cm (Cuartero and Fernández-Muñoz, 1999) with a pH above 7.0. This is because acidic water might lead to the dissolution of toxic elements (e.g. Al^{3+}) in the soil (Mitchell et al., 1991). On light soils or when saline water (TDS<1600 ppm) is used, it is necessary to increase water quantities by 20% - 30% (Parida and Das, 2005, Shalhevet and Yaron, 1973). This indicates the limitations of the brackish water application to attain a better yield for the tomato crop.

As 70% or more of the tomato's root system is in the upper 20 cm of the soil, it is advisable to use a drip system equipped with a fertigation device as this will improve the tomato irrigation performance.

The Australian sub-continent has access to abundant reservoirs of sea water along its long coastal areas and it also has inland underground brackish water. FDFO can be effectively utilized to use these huge unusable water resources and convert them to beneficial agricultural water which may help to reduce the current water deficit. This deficit represents a barrier to the increasing food demand in the domestic and international market. As mentioned earlier, these water resources are not being used with the existing uneconomical desalination technologies.

Considering the fertilizer and water requirements for the tomato crop, this FDFO study was planned in two directions. Based on the fertilizer requirements for tomatoes crops at any particular growth stage, various fertilizer based DS were prepared and the performances of FO membrane were evaluated. Sea water quality BW35 FS was used against the fertilizer based DS. This chapter evaluates single fertilizers as DS whereas Chapter 5 discusses FO performances when mixed fertilizers are used as DS. The mixed fertilizer DS represents the NPK nutrient requirements for tomatoes crops at any growth stages. This study is the first serious effort of its kind to help explore commercial applications of FDFO technology for the tomato crop. These outcomes may be easily transformed to suit various other applications in the agricultural sector.

4.2 Experimental

4.2.1 FO Set-up

A small bench scale FO apparatus, as shown in Fig. 4.1 was used to evaluate water permeation through HTI, USA FO. Other process conditions are also outlined in section 3.5.4. A flat sheet CTA membrane was utilised for AL-FS membrane orientation. Table 4.2 summarises process conditions for this FO study.

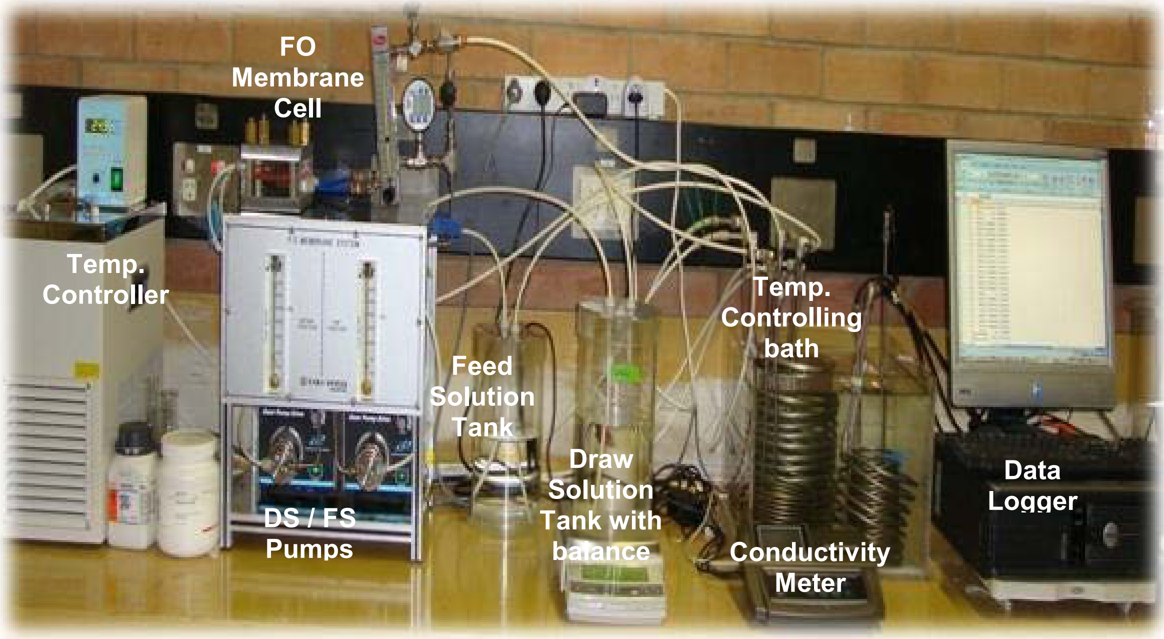


Fig. 4.1. Experimental set-up for FDFO study for tomato

Usually most of the earlier studies on FO were carried out using reagent grade chemicals to prepare DS and FS, thus the effect of the impurities present in the feed and draw solutes was not highlighted properly. For this reason, 9 different commercial fertilizers were selected including ammonium chloride (NH_4Cl), potassium chloride (KCl), calcium nitrate ($CaNO_3)_2$, ammonium nitrate (NH_4NO_3), Urea $(NH_2)_2CO$, mono ammonium phosphate $(NH_4)H_2PO_4$, potassium nitrate (KNO_3) and ammonium sulphate ($NH_4(SO_4)_2$). Mono ammonium phosphate, calcium nitrate and ammonium sulphate are respectively abbreviated in this study as MAP, CAN and SOA. These commercial fertilizers were initially analysed in the lab and the NPK nutrients concentration and level of impurities present were evaluated. A detailed analysis of these fertilizers is provided in Chapter 3. Unlike most of the previous studies (Chou et al., 2010, McGinnis et al., 2013, She et al., 2012a, Phuntsho et al., 2012d), where MQ water was used to prepare FS and DS for FO tests, all DS and FS were prepared by dissolving the DS and FS solutes in tap water. Tap water was used to explore any fouling and scaling issues associated with commercial fertilizers and poor quality water usage (these results are presented in the next Chapter). FS representing highly brackish/sea water osmotic pressure (BW35) was prepared by mixing 35 g/L NaCl in tap water. OLI Stream Analyzer 3.1 software was used to assess the osmotic pressure of these fertilizers (in various concentrations) and the FS. OLI software showed that BW35 FS has an osmotic pressure of 27.38 atm.

4.2.2 Performance and measurements

The water and fertilizer requirements are different for three tomato growing techniques. This study (Chapter 4 and 5) is designed for the water and fertilizer requirements of field grown tomatoes. For field grown tomatoes, about 6,000,000 litres/ha of water is required for the whole crop period of about 120 days (Warner et al., 2004, Brouwer and Heibloem, 1986). Similarly, tomato growth in greenhouses requires up to 10,000,000 litres/ha of water during its crop span (Mitchell et al., 1991, Shalhevet and Yaron, 1973). These water requirements are not uniform for the crop's whole growth period and thus water and fertilizer requirements also vary for different growth stages of the tomato crop. The water requirement increases from germination until the beginning of fruit setting, reaching a peak during fruit development and then decreasing during ripening. In some of the areas a normal period of 3-5 days regular watering is applied. Mild water stress during fruit development and ripening has a positive effect on fruit quality: firmness, taste and shelf-life, but it may result in smaller fruit (Favati et al., 2009, Mitchell et al., 1991). Late irrigation, close to harvesting, may impair quality and induce rotting (Mitchell et al., 1991). Comparing these tomato crop water usage statistics with Table 4.1, it is estimated that in one year, our world consumes about 25,464 ML of water for the tomato crop alone.

4.3 Results & discussions

4.3.1 Selection of suitable fertilizers as DS

4.3.1.1 Fertilizer requirements for various tomato crop stages

The field grown tomato crop has an average age of 120 days. Looking into its plant life cycle, growth stages, fertilizer and requirements, the whole tomato growing period is divided into 4 stages, i.e., Planting - First flowering, Rapid growth - Flowering, Fruit set - Fruit ripening and Fruit ripening - Harvest. Table 4.3 summarises four tomato growth stages with the time period for each stage and the nutrients required in that particular tomato growth stage. Considering the nutrient requirements of tomato crops during its growth stages, various draw solutions (DS) were prepared from a single fertilizer (in this Chapter) and a mixed fertilizer (Chapter 5) was evaluated with respect to pH, FO flux, reverse solute flux (RSF), last essential nutrient concentrations in final DS, membrane fouling trends, etc.

Table: 4.2. Summary of the operating conditions for the bench scale FO process used for the tomato crop.

Description	Details
Single fertilizer draw solutes	NH_4NO_3, NH_4Cl, $(NH_4)_2SO_4$, KNO_3, KCl, $(NH_4)_2HPO_4$, $NH_4H_2PO_4$, $Ca(NO_3)_2$ and Urea
DS concentrations	1- 4 M or mol/kg, Urea was used even at higher concentrations
Feed water types	Simulated highly brackish water/sea water -BW35 (prepared by mixing NaCl in 35 g/L concentration)
Membrane orientation	FO mode (active layer facing FS)
Temperature	25ºC ± 0.5
Parameters evaluated	Fertilizer suitability, compatibility, fertilizer purity, FO flux, RSF and nutrient concentrations in the final diluted draw solutions (FDDS)
FO membrane area	20.02 cm^2

These NPK nutrient's requirements for the tomato crop indicate that about 2300-2450 kg/ha (Claude J. Phene, 2004, Hartz and Bottoms, 2009) of different fertilizers may be available to use as DS for the FDFO process in one crop season for tomato field fertigation.

4.3.1.1 Selection of Suitable Fertilizers

Among the various fertilizers available in the market, the 9 selected commercially available fertilizers were evaluated with respect to their suitability to provide NPK nutrients for tomato growth. The screening of these fertilizers was done for issues such as easy availability, low price, common usage, preference by the tomato growing community, active nutrients (NPK) composition, the purity of commercially available fertilizers, solubility limits, the presence of less suspended/insoluble materials, and the ease in DS preparations. The selected fertilizers were later evaluated for their osmotic pressure and solubility limits for various fertilizer concentrations using OLI software. Some of these fertilizers carry only one nutrient while a few carry two nutrients. For this reason, the selection of a suitable fertilizer was initially done so that the final diluted DS (FDDS) could carry the required nutrients to the tomato plant.

Table 4.3. Nutrients requirements of the open field tomato according to its physical stages (Claude J. Phene, 2004, Hanson, 2008). These fertilizer requirements were used to prepare various forms of DS to meet the varying nutrient requirements for any given growth stage

Days after Planting	Physiological tomato crop growth stages	Days	kg/ha/day		
			N	P_2O_5	K_2O
0 – 25	Planting - First Flowering	25	2.3	3.8	2.3
26 – 45	Rapid Growth -Flowering	20	3.0	1.3	4.4
46 – 70	Fruit Set- Fruit Ripening	25	4.0	0.0	8.0
71 – 105	Fruit Ripening-Harvest	35	5.1	0.0	10.3
Total Nutrients (kg)		105	397.1	120.0	705.7

KNO_3 is a source of both K and N whereas MAP and DAP provide N and P nutrients to the plants.

Fig. 4.2 Impurities observed during DS preparation from various commercial fertilizers a) NH_4Cl b) MAP and c) KCl

N-source Fertilizer: NH_4Cl, NH_4NO_3, CAN, SOA and urea were studies for the DS (single fertilizer based) selection when only N-nutrients were considered. These commercial fertilizers showed various issues in preparing DS (Fig. 4.2). SOA fertilizer presented problems in terms of preparing high concentration solutions. It took a long time to get it dissolved completely using mixing aids and it left black residue/insoluble matter even at the lower fertilizer concentrations (2 M) which are needed for additional filtration. The residue on the filter paper surface was raised with the increase of SOA concentration from 1 M to 3 M. Vacuum filtration did not even perform well for SOA. Removal of these insoluble materials was necessary to reduce the chances of membrane and pump damage and to control fouling during the test run.

Similarly NH_4Cl and MAP left some suspended particles during the DS preparations and their solutions were also filtered before their use with the FO. These two fertilizers comparatively produced less filtration residue than the SOA however the filtration again took a long time even using the standard filter paper with the funnel because the filtration residue was very fine and it quickly blocked the filter paper pores.

Commercially available NH_4NO_3 liquid fertilizer was used in this study as the powder/granular form of NH_4NO_3 fertilizers is not readily available at this time. All necessary NH_4NO_3 solutions were prepared from the available liquid NH_4NO_3 fertilizer. CAN was also studied for single fertilizer DS evaluation only.

Urea is the most popular N-source agricultural fertilizer in the world for crops including the tomato crop. It is cheap, very soluble even at high concentration, easily available, and it is highly enriched with N (up to 46%).

Solubility limits and osmotic pressure for these fertilizers at various concentrations were compared using OLI System Analyzer software. It was found that theoretically, among the above mentioned N-source fertilizers, $Ca(NO_3)_2$ showed the highest osmotic pressure followed by NH_4Cl, $(NH_4)_2SO_4$ and urea. Urea showed the lowest osmotic pressure among all available fertilizers hence a low operating flux was expected from it (which was later proved from the results).

Sodium fertilizers are not encouraged for use in tomato field crops as sodium cations compete with potassium cations for the roots uptake sites, and chloride competes for the uptake of nitrate-nitrogen and will impede plant development (Hebbar et al., 2004). The same problem occurs if the available feed irrigation water has high salinity. If this is the case, the Na^+ ions compete with the potassium ions supplied through K fertilizers and they reduce their intake. Also, calcium effectively suppresses the uptake of sodium. When sufficient calcium is available, the roots prefer the uptake of potassium to sodium, and the sodium uptake is suppressed.

OLI data was also used to get an indication of the solubility limits for these DS fertilizers. Most of the fertilizers showed high solubility in their pure form but when the commercial fertilizers were used, some of the fertilizers such as KCl, NH_4Cl, MAP & SOA showed issues in preparing high concentration DS. Only urea, CAN, and DAP worked well up to 6 M DS concentrations. For this reason, the flux evaluation in this study was restricted to a single fertilizer DS concentration of up to 3 M.

Table 4.4. Shortlisted fertilizers showing their NPK nutrient composition were used to prepare the single fertilizer DS for the FDFO process

Commercial /Chemical Name (with molecular wt.)	Chemical Formula	N/P/K ($N/P_2O_5/K_2O$)	Commercial /Chemical Name (molecular wt.)	Chemical Formula	N/P/K ($N/P_2O_5/K_2O$)
Ammonium Chloride (53.5)	NH_4Cl	25/0/0	Ammonium Sulphate (132.1)	$(NH_4)_2SO_4$	21/0/0/(24)
Ammonium Nitrate (80.04)	NH_4NO_3	34/0/0	Potassium Nitrate (101.1)	KNO_3	14/0/44
Calcium Nitrate (236.15)	$Ca(NO_3)_2.4H_2O$	15.5/0/0/(26.5)	Potassium Chloride (74.6)	KCl	0/0/60
Di Ammonium Phosphate (DAP) (132.1)	$(NH_4)_2HPO_4$	12/51/0	Urea (60)	$(NH_2)_2CO$	46/0/0
Mono Ammonium Phosphate (MAP) (115.0)	$NH_4H_2PO_4$	18/46/0			

Further, since these selected fertilizers had varying solubility and chemical characteristics, the compatibility of these DS fertilizers was checked before other DS fertilizers were used on the FO system. The issue of mixing phosphate and sulfates with calcium based CAN fertilizers were avoided as they immediately produce insoluble residue in the system. Before using these single DS fertilizers one after another, the system was thoroughly rinsed twice with DI to flush out traces of diluted DS from the system tubing. Fig. 4.3 summarises the important issues that were considered in relation to selecting suitable DS fertilizers for FDFO application and for better process outcomes.

4.3.2 Characteristics of fertilizer DS and their effects on osmotic pressure and FO flux

4.3.2.1 Significance of theoretical osmotic pressure of single fertilizer DS

For the selected fertilizers, using OLI software, the theoretical osmotic pressure trends of all of these fertilizers were studied. Osmotic pressure is the driving force for the FO process driving osmosis and it is assumed that when the osmotic pressure difference of the FS and DS ($\Delta\pi$) is higher, the flux would be higher. OLI data showed that the net driving force ($\Delta\pi$) increased with the increase in fertilizer concentration, although, the osmotic pressure of these fertilizers did not show an exact linear relationship. Similarly, each fertilizer showed a varying slope for π when they were evaluated for higher concentrations. DAP showed the highest π at 1 M concentration whereas urea showed the lowest π among these fertilizers for the same fertilizer concentrations. For the lower fertilizer DS concentration (up to 1 M concentration), these selected fertilizers did not show too much difference in osmotic pressure. However, as their concentration was increased over 2 M, these fertilizers started to show significant differences in their theoretical π at particular fertilizer concentrations. Mono-valent cation based nitrate fertilizers such as NH_4NO_3 and KNO_3 showed lower π in 30’s (33.7 and 37.2 atm) respectively whereas divalent cation based CAN fertilizers showed π of 48.8. This indicates that for a set of salts carrying common anions, the cationic part of the salt plays a more important role in π evaluation.

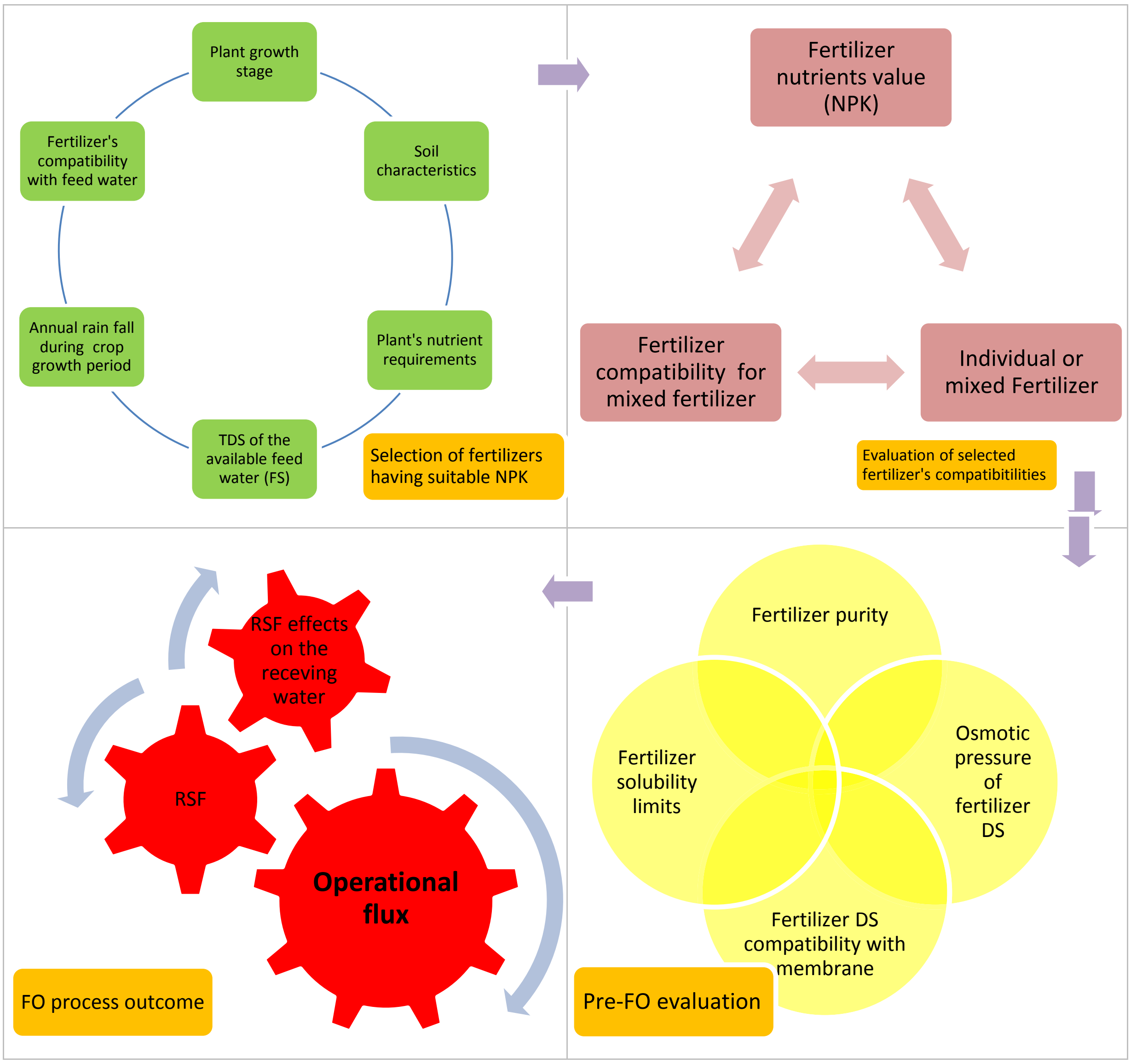


Fig. 4.3. Various important factors effecting the FDFO process design and outcome for particular crops

Comparison of the theoretical π at 3 M concentration for these fertilizers showed that SOA had the highest π followed by a group of four fertilizers CAN, DAP, NH_4Cl & MAP which incurred nearly the same osmotic pressure. NH_4NO_3 and KNO_3 showed the least π among these fertilizers at 3 M concentration. The order for π for the rest of the single fertilizer DS did not change too much at higher concentrations (3 M). This showed that the order of π behaviour at 1 M concentration is a little bit different from π behaviour at 3 M concentration for these fertilizers as the DAP took the second position in their π descending order. The varying π outcome indicated that the resultant flux for the selected fertilizer DS would also be different from changing the DS concentration which was confirmed with the following discussion. It is not yet clear which DS properties caused changes in their π order and this suggests that further investigations are required in this direction.

4.3.2.2 Single fertilizer DS flux against sea water quality FS

Selected fertilizers were evaluated as single fertilizer DS and the FO performances for water flux and RSF were noted for these fertilizer DS. These DS fertilizers were evaluated against BW35 FS.

Fig. 4.4 shows the resultant FO flux for the selected fertilizer DS against sea water quality FS. Urea, NH_4NO_3 and KNO_3 showed negative flux at 1 M fertilizer DS concentration. NH_4NO_3, NH_4Cl and KNO_3 showed positive flux for DS concentrations over 1 M whereas urea continued to show a negative flux up to 5 M concentration. Another important result found is the changing order of DS which results in high flux. At 1 M concentration, CAN shared the highest flux for 2 M and 3 M DS concentrations, while NH_4Cl and KCl gained the top positions for flux outcome. The varying patterns of these results did not follow the osmotic pressure-flux relationship when BW35 was used as FS. These results further indicate that for the FO operation with a high FS concentration, only $\Delta\pi$ does not reflect the resultant flux. Instead the other ionic species show that both the DS and FS sides influence the flux performances through the FO membrane.

These results suggest that NH_4Cl and KCl can be preferentially used for FDFO to obtain a high flux at even low concentrations of fertilizer DS against sea water (SW) quality FS (BW35).

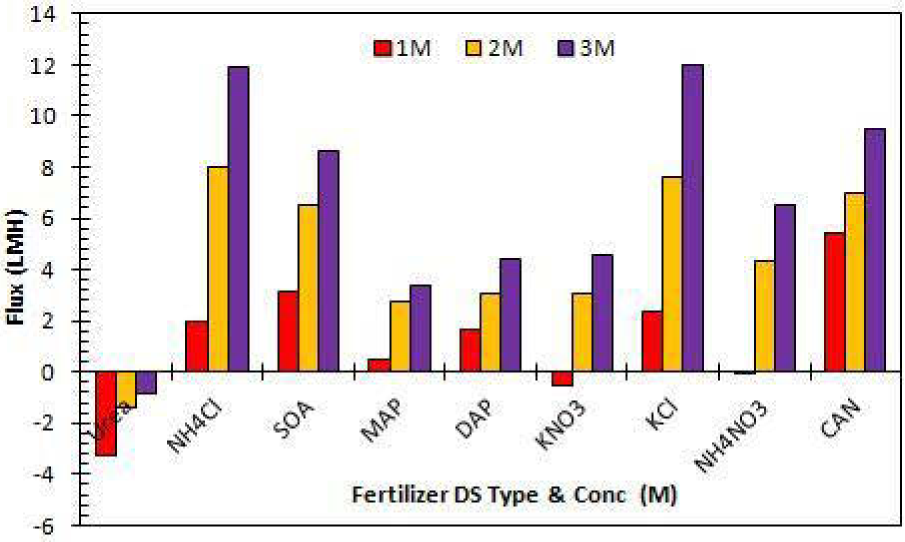


Fig. 4.4. Pure water flux using selected single fertilizers DS with varying molar concentrations. BW35 was used as FS.

4.3.2.3 Osmotic pressure and flux trends for urea

For negative flux outcome for urea DS against SW concentration FS, urea was further evaluated for higher concentrations of up to 6 M and the results are presented in Fig. 4.5. It was observed that it showed negative flux up to 4 M concentration whereas at 6 M concentration, a flux of 1.93 LMH was achieved (Fig. 4.5). Such low flux output seems to be due to its inability to produce a large number of ionic species and this has kept its osmotic pressure low.

Fig. 4.5 further compares the flux trend for varying concentrations of urea DS and the flux outcomes for 1M NH_4Cl and KCl DS. Besides possessing high osmotic pressure at 6 M concentration, urea nearly showed a similar flux to what NH_4Cl delivered at 1 M concentration but less than what KCl showed at 1 M concentration. On the other hand, NH_4Cl and KCl at 1 M concentrations possesses just one third of theoretical osmotic pressure compared to what urea the DS showed for 6 M concentration. But, here, urea at high concentration was unable to give FO flux which linearly corresponding to the theoretical osmotic pressure it was processing at 6 M concentration. Despite having just one third of the osmotic pressure of urea, 1 M NH_4Cl and KCl DS still managed to produce flux which was nearly equal to what urea gave at the 6 M concentration. Sherub et al. (2011) has indicated that the resultant flux phenomena for a particular DS for FO process is linked to the number of charged species generated when salt is dissolved in water (Phuntsho et al., 2011). OLI software showed that in comparison to NH_4Cl and KCl, urea even at higher concentrations produces a smaller number of ionic species. For that reason, urea delivered a lower flux outcome.

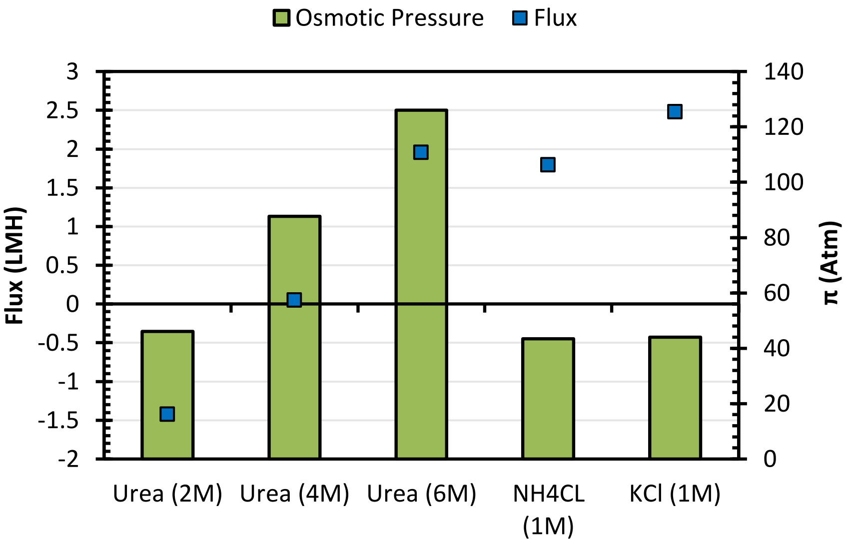
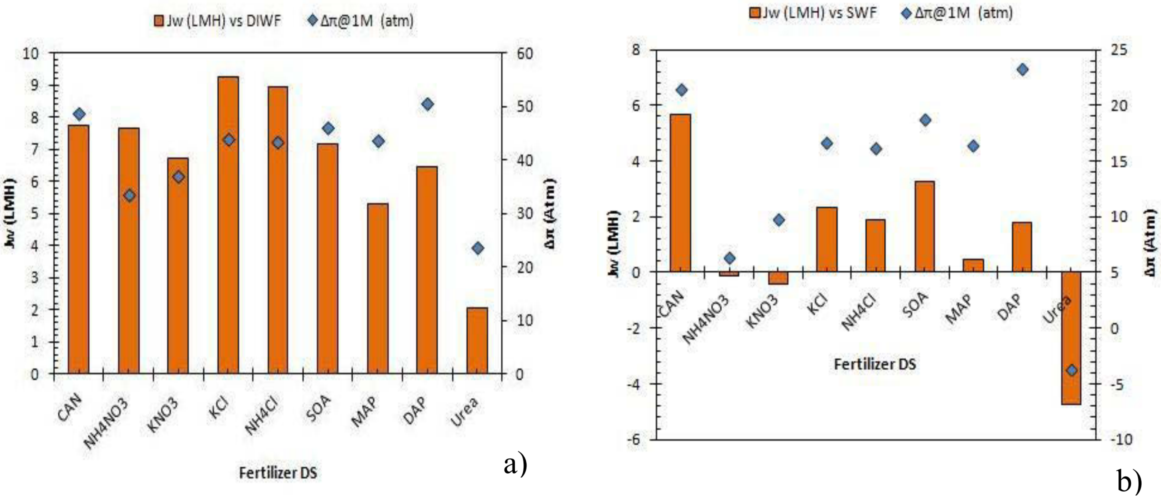


Fig 4.5 Comparison of the flux and osmotic pressure (π) trends for urea DS (up to 6 M concentration) and NH_4Cl and KCl DS (1 M concentration)

4.3.3 Flux variation patterns with changing FS concentration

Fig. 4.4 and Fig 4.5 showed that the flux performance of various DS fertilizers changes with the DS concentration. To understand the effects of FS on the FO flux outcome, a single fertilizer DS outcome against BW35 FS was compared with the flux outcome for fertilizer

DS against deionized water FS, data adapted from Phuntsho et al. (2011) and the results are presented in Fig. 4.6. The comparison shows that the water flux varied for different fertilizers in varying order for different FS qualities. For DI water FS, KCl showed the highest flux followed by NH_4Cl, CAN, NH_4NO_3, SOA, KNO_3, DAP, MAP and urea, whereas this order was changed when the FS was changed from DI water to BW35 concentration (i.e., 35 g/L NaCl). With BW35 FS, CAN showed the highest flux, followed by SOA, KCl, NH_4Cl, DAP, NH_4NO_3, KNO_3, MAP and urea in descending order. For some DS such as NH_4NO_3, NH_4Cl, KNO_3, and MAP, the flux gap for two different FS is increased whereas for the CAN and DAP, the flux gap is decreased when the FS quality was changed from DI water to BW35.



a) b)

Fig 4.6. Flux (LMH) and net osmotic pressure Δπ (atm) trends for various fertilizer DS (1M concentration) with a) DI water FS b) BW35 sea water quality FS

Fig. 4.6 further indicates that few of the fertilizers in low concentration (1 M) may not be used as DS for the FDFO process when sea water quality FS is used as FS. Urea, NH_4NO_3 and KNO_3 exhibited negative flux with BW35 FS. MAP also delivered a very low water flux of 0.45 LMH with BW35 FS.

To understand the effect of the driving force (Δπ) on the FO flux for these fertilizers, the resultant flux per unit driving force was evaluated and presented in Fig. 4.7. The effect of Jw/Δπ (LMH/atm) was plotted for fertilizer DS which shows that these fertilizers give varying flux outcomes against 1 atm of net osmotic pressure applied. Similarly changes in FS concentration showed varying effects on the flux outcome for unit Δπ when these DS fertilizers were applied. Fertilizers carrying nitrate (NO_3) anions with monovalent cations showed inferior flux performances for the same Δπ applied.

Fig. 4.6 and Fig. 4.7 results also indicated that some of the DS fertilizers with higher bulk osmotic pressure show comparatively low experimental flux. This shows that π of DS or Δπ for any particular FS and DS alone does not correctly dictate the resultant flux for the FO process. Apart from the membrane properties, other issues such as FS concentration, FS chemical composition, DS concentration, DS chemical composition, mono & divalent ions, type of mono or divalent ions both in DS and FS also influence the flux outcome for the FO process. These findings make the selection of a particular DS even more complex as it is still believed that the resultant flux output is only governed by the net osmotic pressure available.

4.3.4 Behavior of the Individual fertilizers DS on RSF

To evaluate the loss for these fertilizers through RSF, samples of the FS were collected at the end of each experiment and analysed in the lab for nitrogen, phosphorus and potassium. For FDFO, this RSF indicates the extent of the loss of fertilizer nutrients to the FS stream. Among the 9 fertilizers evaluated in terms of flux, 7 fertilizers were studied for the RSF. Urea was not accounted for RSF as some previous studies have already shown high RSF for urea (Phuntsho et al., 2011). CAN was eliminated for its non-compatibility with P-fertilizers. Flux and RSF results for 7 fertilizer DS are shown in Fig. 4.8.

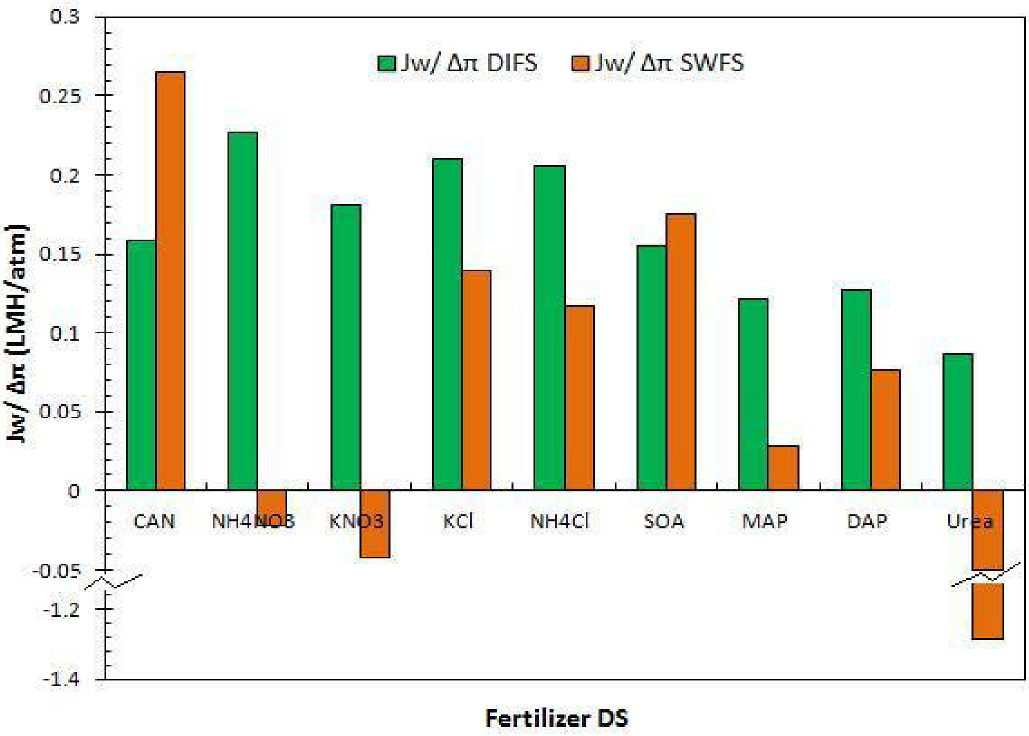


Fig 4.7. Flux outcome for unit Δπ applied for varying fertilizer DS. Fertilizers were used in 1 M concentration as DS for DI water and BW35 quality FS.

Both potassium based fertilizers such as KCl and KNO_3 showed high RSF for K. RSF for these fertilizers showed rising trends with higher DS concentration. N RSF for the KNO_3 showed very little increase with high DS concentration. Instead the N-RSF was the lower value for KNO_3 for DS concentration changes from 2 M to 3 M.

For DAP and MAP, it was observed that DAP showed a smaller value for P-RSF and MAP showed less value for N-RSF. DAP showed varying trends for N-RSF when DAP DS concentration was increased from 1 M to 3 M. However, MAP showed increasing trends for P-RSF when MAP DS concentration was raised from 1 M to 3 M. These two showed the lowest RSF values for P and N among all fertilizers that were used in this study, and these were probably for the larger P^{3+} size.

Results for NH_4Cl, NH_4NO_3 and SOA RSF also showed very interesting behaviours. N-RSF for NH_4Cl nearly remained the same for 1-3 M concentrations and it was raised when the DS concentration was increased to 4 M. Although, the N-RSF value was on the high side for lower DS concentrations (1 M), the NH_4Cl DS showed less N-RSF than other NO_3^- and NH_4^+ fertilizers. NH_4Cl gave better results for N-RSF among other nitrogen source fertilizers. A high value of N-RSF for NH_4NO_3 indicates that it may not be favoured as DS for the FDFO application.

4.3.5 Fouling behavior of FO membrane with commercial fertilizer DS

Sections 4.2 and 4.3 earlier outlined the presence of a large quantity of impurities present in the commercial grade fertilizers. All the DS were prepared by dissolving these fertilizers in tap water. For these reasons the FO membrane was first evaluated with 1 M KCl DS and flux was recorded. At the end of the last experiment, using the same membrane, flux was again evaluated with 1 M KCl DS which gave nearly the same flux outcome. It shows that the CTA flat sheet membrane carries a smaller risk of serious fouling for the commercial grade fertilizer chemicals and tap water solutions.

4.3.6 Application of final diluted draw solution

It was observed that FO flux with these DS fertilizers reduces gradually with time. The DS side is continuously diluted and FS (initially carried 35 g/L NaCl) was concentrated as pure water permeated towards the DS side. For this reason, the net driving force for the FO process was continuously decreased which effected flux outcome. For economic reasons, experiments with single DS fertilizers were carried out up to a flux of 0.5 LMH. At this stage, the nutrients level in the final diluted DS was higher than the suggested value required by the plants. This suggests that the final diluted DS may not be used directly for the crops, rather it requires dilution or some further treatment to reduce the nutrients level before its application as fertigation.

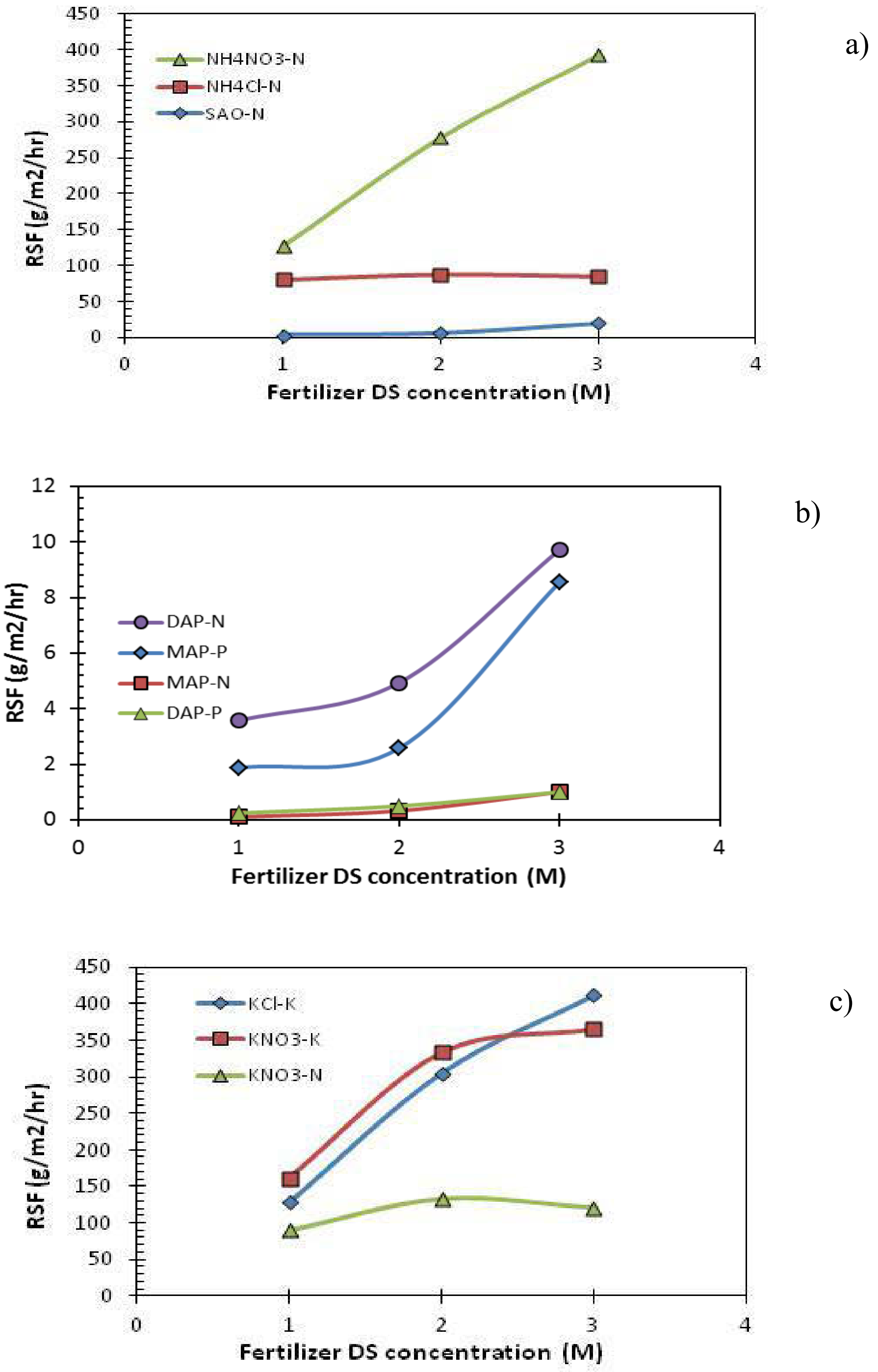


Fig. 4.8. RSF (in g/m^2/hr) for various single DS fertilizers used in the study a) nitrogen source fertilizers as NH_4Cl, NH_4NO_3 and SOA b) phosphate fertilizers as DAP and MAP and c) potassium fertilizers as KCl and KNO_3

4.4 Concluding remarks

This study was designed to evaluate practical issues for FDFO process using commercial grade fertilizers as DS when BW35 FS and DS were prepared in tap water. The tomato was selected as a target crop and the DS were prepared using information on the tomato's water and fertilizer requirements during its various growth stages. Decision pyramids were developed to shortlist a few suitable fertilizers for FDFO application.

- 9 selected fertilizers were used for the FO process evaluation and the water flux and RSF was evaluated for these DS. Due to the impurities present in commercial fertilizers, various issues were observed in the DS preparation. This suggests that to avoid membrane and pump damage and reduce membrane fouling issues, DS prepared from commercial chemicals should be filtered before its use with FO.
- Flux for various fertilizers increased with the increase of DS concentration but not linearly especially when BW35 is used as FS. With BW35 FS, NH_4NO_3, KNO_3 and urea showed a negative flux at 1 M fertilizer DS concentrations. Lower flux for a few DS fertilizers suggests that all fertilizers may not be effectively used as DS against high FS concentrations.
- These fertilizers did not show a uniform flux outcome against the unit $\Delta\pi$ applied. This indicates that apart from the net osmotic pressure and membrane properties, other DS and FS properties also influence FO flux outcome. Experiments with urea DS further confirmed these issues as urea showed a lower flux outcome of 1.98 LMH at 6M concentrations.
- Changes in FS quality effected flux for various fertilizers in different orders.

- MAP and DAP exhibited lower RSF even at higher DS concentrations. Among nitrogen source fertilizers, SOA showed very low RSF whereas NH_4NO_3 demonstrated high RSF value.
- Both KNO_3 and KCl showed high RSF values for nitrogen and potassium.

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Chapter 5

FDFO APPLICATION TO TOMATO (USE OF MIXED COMMERCIAL FERTILIZERS AS DS)

5.1 Introduction

As outlined in the earlier chapters, the higher costs of desalination restrict the existing desalination technologies such as thermal distillation and RO for agriculture applications as these processes are still believed to be highly energy-intensive (Shon et al., 2008, Semiat, 2008). Additionally, the continuous rises in energy prices results in high desalination costs. Accordingly, energy intensive desalination techniques are unlikely to be considered seriously as an ideal solution for agriculture.

On the other hand, in the last few decades, draughts and climate changes have continuously affected the agricultural water availability and this has resulted in reductions to harvested crop areas and lower agricultural yields. Agricultural water scarcity is one of the main reasons for the rising prices in agricultural food commodities across the globe (de Fraiture, 2007) and the current trends show that in the future it may affect world food security even more severely. Both water quality and water scarcity are considered to be the most important challenges in terms of global food production because they directly influence crop yields and food quality (Shalhevet, 1994, Shalhevet and Yaron, 1973). The serious effects of usable water scarcity on harvested areas and production yield are highlighted in Table 4.1.

Due to a low-energy process facet and other additional benefits, it is believed that FDFO can be economically used for brackish/sea water desalination to provide useable water to the heavily water-consuming agricultural sector. FDFO can be easily and economically applied to desalinate abundant sea water reservoirs available along long coastal areas and inland underground brackish water. . The FDFO process uses fertilizer nutrients as DS which are usually applied to different agricultural products in varying ratios. Our current study has been planned to take into account water and fertilizer requirements for field grown tomato crops. In this connection, in Chapter 4, commercial grade single DS fertilizers were evaluated for

FDFO as the DS was prepared from single fertilizer solutes. These DS fertilizers have shown varying outcomes when used individually as DS against BW35 FS.

Chapter 4 further highlighted serious issues for the DS fertilizers that were evaluated. Some of these DS (KNO_3, NH_4NO_3 and urea) showed lower or negative flux outcomes when they were evaluated in 1M fertilizer DS concentration. Urea is the most commonly used fertilizer in the agricultural community but it did not show positive flux for up to 4M concentration. Further, higher RSF results for potassium based fertilizers (KNO_3 and KCl) and nitrogen based fertilizers (NH_4Cl and NH_4NO_3) did not meet expectations.

The objective of this study was to evaluate the synergistic effects of various fertilizer DS mixtures on FO flux and RSF performances. FDFO was evaluated for FO flux and RSF performances using mixed fertilizer DS prepared for various tomato plant growth stages and sea water-quality FS. Commercially-available fertilizers were used to prepare the DS for the FO process. Various combinations of fertilizers were used for nitrogen, phosphate and potassium nutrients. The effects of changing nitrogen-source fertilizers in a particular DS were evaluated to find how one fertilizer affects the performance in a DS mixture. RSF loss was evaluated for DS adjustment to get the required nutrient level in the final DS, cost control, and waste discharge management. Long-terms tests were also aimed to evaluate the process effectiveness and to assess the expected final nutrient concentration in the diluted DS.

5.2 Materials and methods

5.2.1 Forward osmosis performance measurements

Laboratory-made FO apparatus similar to that shown in Fig. 4.1 was used to evaluate the water permeation through the FO membrane. The FO membrane made up of cellulose triacetate (CTA) embedded on a polyester woven mesh (Cath et al., 2006, Tang et al., 2010b) was supplied by HTI, USA. All tests were carried out using membranes in normal FO orientation, i.e., the active layer is facing FS (AL-FS).

The flow through each channel was controlled by a variable speed peristaltic pump drive (Cole- Palmer, U.S.A.) and monitored by variable area flow meters (Blue-white Industries Ltd., U.S.A.). The flow rates were kept constant at 400 ml/min for both FS and DS. Tests were carried out in a co-current flow configuration for FS and DS streams and the temperatures of both DS and FS streams were kept constant at 25°C ± 0.5°C using a water bath controlled by a heater/chiller. A weighing scale (CUW 4200H by CAS, Korea) connected to a computer was used to monitor the weight loss of the FS which was later used to calculate the water flux in the FO operation.

5.2.2 Chemicals and reagents

Commercially-available fertilizers, namely: NH_4NO_3, NH_4Cl, KNO_3, KCl, $NH_4H_2PO_4$ (MAP), and urea were used in this study to prepare the DS, so as to get real application data. These fertilizers were initially analysed to evaluate their NPK ingredients and the level of other impurities. DS were prepared for specific NPK grade (in % for N, P_2O_5 and K_2O) as 11.5-19-11.5, 15-7-22, 10-0-20, and 15-0-30 to exhibit the nutrient requirement for the tomato crop at any particular growth stage as shown in Table 4.3. DS were filtered through a Whatman filter paper to avoid blocking or fouling of the membrane surface.

FO was evaluated against sea water (SW) quality FS which represents the largest source of water available on earth. All FS were prepared using 35 g/L NaCl (representing sea water osmotic pressure) dissolved in tap water. NaCl supplied by Chem-Supply Australia was used to prepare FS. Actual sea water quality FS was not evaluated in this study as Ca^{2+} and Mg^{2+} commonly present in sea water posed a risk of insoluble suspension formation with phosphate fertilizers.

Unlike all other previous studies where MQ water was used to prepare FS and DS for FO tests, here both DS and FS were prepared in tap water. Tap water was used to explore any scaling and fouling issues associated with the use of a commercial fertilizer and poor quality water. Tap water having conductivity, total hardness and alkalinity of 22 mS/m, 65 mg $CaCO_3$/L and 46 mg $CaCO_3$/L, respectively was used in this study.

5.2.3 Performance and measurements

The water flux performance was evaluated using DS prepared from the fertilizer requirements of tomatoes in their different growth stages. FS samples were collected at the end of each test and analysed for RSF particularly the K, P, and N concentration using APHA method 3125 protocols. OLI software was used to access osmotic pressure and other physical and chemical properties of DS and FS. OLI software indicated that 35 g/L NaCl dissolved in tap water showed an osmotic pressure of 27.38 atm.

5.3 Results and discussion

5.3.1 Screening of fertilizers to prepare DS

Eight selected commercially-available fertilizers i.e., NH_4Cl, SOA, CAN, NH_4NO_3, KNO_3, KCl, urea and MAP were initially evaluated for their suitability to provide NPK nutrients for tomato growth. NH_4NO_3, NH_4Cl and urea were taken as purely N-nutrient source fertilizers, MAP as P and N-source, KCl purely as K-source and KNO_3 as a source fertilizer for N and K.

These fertilizers were evaluated and screened for issues such as the farmers' choice and preference for fertilizers, availability, price, NPK nutrients, osmotic pressure, solubility limits, presence of unwanted impurities and previous FO studies (Phuntsho et al., 2011).

Two fertilizers were rejected in the initial screening process. SOA was dropped for issues in preparing DS at higher concentration. SOA was problematic in terms of preparing DS. It took a long time to dissolve it completely despite using mixing aids, and it even left black insoluble matter at 2M concentration which quickly blocked the filter paper pores.

Fertilizer carrying higher osmotic pressure such as CAN was an ideal choice as DS for FO. However, it was abandoned as calcium carried a high probability of forming insoluble suspensions with phosphate fertilizers (Marais, 2004, Haynes, 1985). Furthermore, excessive calcium in the final diluted DS also affected the tomato yield as Ca^{2+} reduced the potassium intake by the plant and the tomato yield dropped drastically due to plant's K^+ deficiency (Hartz et al., 1999, Hebbar et al., 2004).

NH_4NO_3 was considered for comparative purposes due to its non-availability in granular form. All necessary NH_4NO_3 based DS were prepared from the available liquid NH_4NO_3 fertilizer. Urea was evaluated for the FO process as it was considered the most popular N-source fertilizer for the tomato crop. It is cheap, easily available, highly enriched with N (up to 46%) and immensely soluble even at high concentrations. OLI software showed that urea carries the lowest osmotic pressure among all the present fertilizers.

NH_4Cl and MAP also left some residues in preparing concentrated DS but these solutions were filtered easily. Considering their physical and chemical characteristics, NH_4Cl, SOA, KNO_3, KCl, MAP, urea and NH_4NO_3 were shortlisted to prepare DS and evaluated for the FO DS process. An initial amount of four fertilizers were categorized as common fertilizers for DS.

5.3.2 Preparation of mixed fertilizer DS suitable for tomato application

Looking into the average life cycle of processing a tomato plant of 120 days and its watering and fertilizer requirements, a tomato crop span is divided into 4 stages, i.e., planting - first flowering, rapid growth – flowering, fruit set- fruit ripening and fruit ripening-harvest (Claude J. Phene, 2004) hereinafter described as S1, S2, S3 and S4, respectively. Stage S1 indicates the time from planting or seeding during vegetative growth until the first flower appears. Stages S2, S3 and S4 cover the period from flowering to first fruit set, from fruit ripening to first harvest and from first harvest to the end of the last harvest, respectively. Fertilizer requirements for the various tomato growth stages was used to prepare the fertilizer DS. These four growth stages respectively require fertilizers of 11.5-19-11.5, 15-7-22, 10-0-20, and 15-0-30 NPK values. The shortlisted fertilizers were used to prepare fertilizer DS matching the nutrient requirements of the tomato plant for the different stages.

NH_4Cl was selected as the primary N-source fertilizer for preparing the fertilizer DS carrying nutrients. The influence of the other two N-source fertilizers such as NH_4NO_3 and urea was also studied by preparing the DS of the same NPK value and the FO performances were evaluated. NH_4Cl was separately replaced by NH_4NO_3 and urea in the DS mixture without affecting the DS NPK ratio. However, OLI software indicated that all the DS showed varying osmotic pressures. For the P-nutrient source, only MAP was used and for the K-nutrient source, KCl was used with KNO_3 in the entire study. KNO_3 also contributed to N-nutrients.

Compared to the individual fertilizer components, the fertilizer blends showed several changes in the physical and chemical properties of the DS. MAP and NH_4Cl fertilizers produced suspensions and left residue at higher concentrations. Similarly, fertilizers containing the same salt component, i.e., KCl and KNO_3, showed difficulties in mixing as their solubility decreased in the mixture. For these reasons, the fertilizer DS for various NPK values was prepared according to the solubility limits in a given mixture.

5.3.3 Water flux in FO process using mixed fertilizer draw solutes

The performance of fertilizer DS in terms of water flux (J_w) for the FO process is presented in Fig. 5.1. DS were prepared for 4 tomato growth stages namely S1, S2, S3 and S4 representing NPK nutrient values of 11.5-19-11.5, 15-7-22, 10-0-20, 15-0-30, respectively. To prepare the specific NPK value DS, various fertilizers were mixed in pre-determined quantities. Fertilizer DS were prepared for 25%, 33% and 50% NPK fertilizer quantity per hectare for various stages and these are represented by suffix -1, -2 and -3, respectively (in the bracket of the x-axis label in Fig. 5.1). Due to solubility issues, for stage 4, the fertilizer DS were prepared for only 15% NPK quantity per hectare. These fertilizer DS were separately evaluated with FO flux, RSF and ultimate essential nutrient concentrations in the final DS. Flux ranged from 2.51 LMH to 12.54 LMH with seawater FS for the fertilizer DS.

For a solution carrying more than one solute, the expression of total osmotic pressure for a mixture of different solutes can be written as $\pi_{Total} = \pi_1 + \pi_2 + \pi_3 + \pi_4 + \cdots$ where the subscripts 1, 2, 3, 4...represent the various components of the draw solute. The OLI software showed that the resultant osmotic pressure of the DS was the sum of the osmotic pressure of the individual components present in the mixture. It was observed that the flux changed with rising DS concentration but not linearly in all cases (Fig. 5.1). Flux results did not respond proportionally to changes in the respective osmotic pressure. Results showed either positive or negative deviations for linear trends. The main reason for these variations in slope for different DS seems to be due to the type and concentration of individual components present in DS. Each DS behaved differently depending on the concentration of various components present in the mixture.

The basic flux equation (J_w= AσΔπ) reveals that the flux should change linearly with the osmotic pressure gradient available across the semi-permeable membrane as other parameters were fixed for these tests. However, the slope of the flux varies for all the DS in Fig. 5.1(a-f). The above flux equation suits ideal or very weak solutions however, it still accounts for the main driving force (osmotic pressure gradient) for osmosis. From the nonlinear flux results in Fig. 5.1, it can be seen that for non-ideal solutions and high concentration DS, other physical and chemical properties of the solute components served to support these resultant flux variations. The membrane permeability coefficient (A) decreased at high DS osmotic pressures (Mehta and Loeb, 1978b). High concentration DS results further showed notable deviations in the theoretical flux to actual flux which reflects that the other relevant forces increase with the DS concentration.

Furthermore, the dissimilar slope of the flux and osmotic pressure curves for these DS shown in Fig. 5.1(a-f) follow earlier research evaluations and confirm that the rising DS concentration does not change the water flux linearly in FO (Sutzkover et al., 2000, Suh and Lee, 2013a, Sheikholeslami, 2003). Both external concentration polarization (ECP) and internal concentration polarization (ICP) also vary with the changing DS/FS concentrations (Suh and Lee, 2013a, Gao et al., 2013, Mehta and Loeb, 1978a, McCutcheon et al., 2006). High FS concentration also contributed to the increase in ECP which directly caused a high reduction of the resultant water flux (Suh and Lee, 2013a).

The main reason for the variation in slope for different DS seems to be due to the type and concentration of individual components present in DS. Each DS behaved differently depending on the concentration of various components present in the mixture. The effect of membrane properties, DS diffusion coefficients, inter-molecular interactions, and ionization energy have been evaluated by many researchers for FO flux but clear reasoning is lacking for the changes of flux with osmotic pressure (Mehta and Loeb, 1978a, Paul, 1974, Chung et al., 2012b, McCutcheon et al., 2006, Schaep et al., 1998).

Fig. 5.2 summarises the FO flux performance of the various DS in conjunction with the main FO driving forces such as DS osmotic pressure (π) and net osmotic pressure difference available ($\Delta\pi$). The presented data is unable to authenticate the presence of any fixed correlations between the osmotic pressure and the resultant flux for varying DS especially when the DS and FS concentrations are high for the FO process.

To get further insight into the behaviour of the driving force, the FO flux was plotted against the ratio $\Delta\pi/J_w$ (bar/LMH), which depicted the net osmotic pressure required to get a unit value of flux (Fig. 5.3(a)). It shows that several DS require different net osmotic pressures ($\Delta\pi$) to provide a unit flux (LMH) output. This further indicates that the same osmotic pressure of two DS mixtures may not give a uniform flux. Most of DS mixtures show $\Delta\pi/J_w$ values around 10 except S2 (AC-1), S2 (AC-2), and S2 (AC-3), which showed a lower value for this fraction (more effective DS) and S3 (U-1) and S1 (AN-3) showed a higher value for this fraction (less effective DS).

Using OLI software, it was revealed that S2 (AC-1) DS containing NH_4Cl as N-source fertilizer formed a larger number of ionic species than S2 (U-1) DS which used urea as an N-source fertilizer. Accordingly, it can be concluded that the DS forming more ionic speciation delivers more flux. The osmotic pressure should not be taken as the only criteria to select DS for FO operation. For the same osmotic pressure, the DS with higher diffusion coefficient results in higher water flux (Holloway et al., 2007). This further reflects the fact that DS carrying more ionic species presents a higher diffusion coefficient. The role of DS components carrying high osmotic pressure is important but additional study is required to fully explore the phenomenon of DS behaviour.

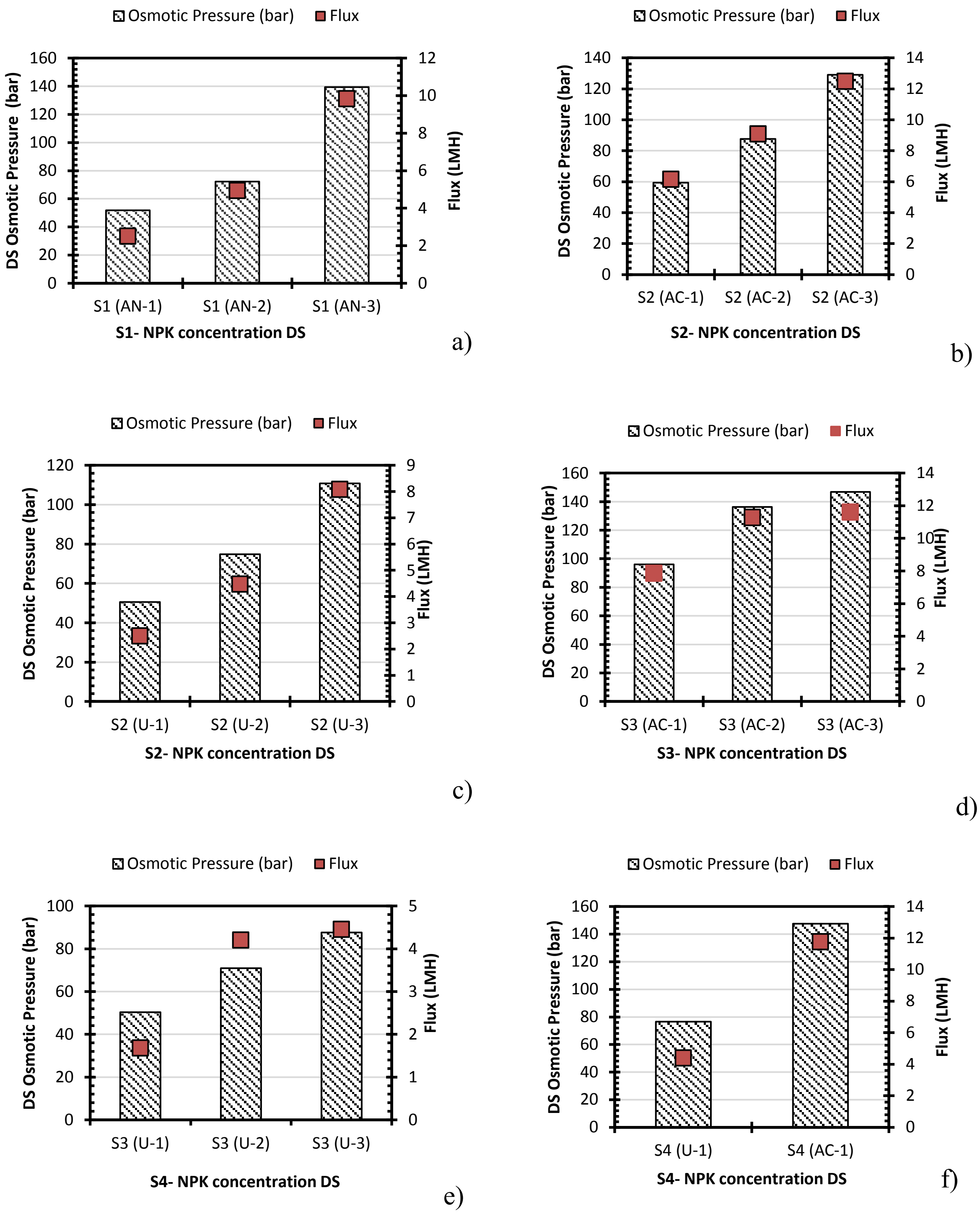

Fig. 5.1. Osmotic pressure and resultant flux changing trends for different DS prepared for various tomato crop growth stages a) S1 stage with NH_4NO_3 as N-source fertilizer b) S2 stage using NH_4Cl as N-source c) S2, urea replaced NH_4Cl N-source in DS, d) and e) S3 stage with NH_4Cl and urea replaced NH_4Cl N-fertilizer source in DS and f) S4 stage DS using urea and NH_4Cl as N-source fertilizers. (AN: Ammonium nitrate, AC: Ammonium chloride and U: Urea represents main N-source fertilizer in respective DS).

Fig. 5.3 (b) also shows similar variations when the ratio of $J_w/\Delta\pi$ was plotted for these DS mixtures. Thermodynamically, the transport of a given species must be directed to decrease the chemical potential for the species (Paul, 1974). So for an FO process, which reduces the chemical potential between the two solutions across the membrane, it is hypothesized that in a mixture of DS, besides the osmotic pressure of DS and FS, the chemical properties of their individual solutes such as inter-molecular interactions, ionization potential, chemical potential, ionic charge, ionic interactions between DS species and FS components and others also plays a vital role in dictating the FO flux outcome.

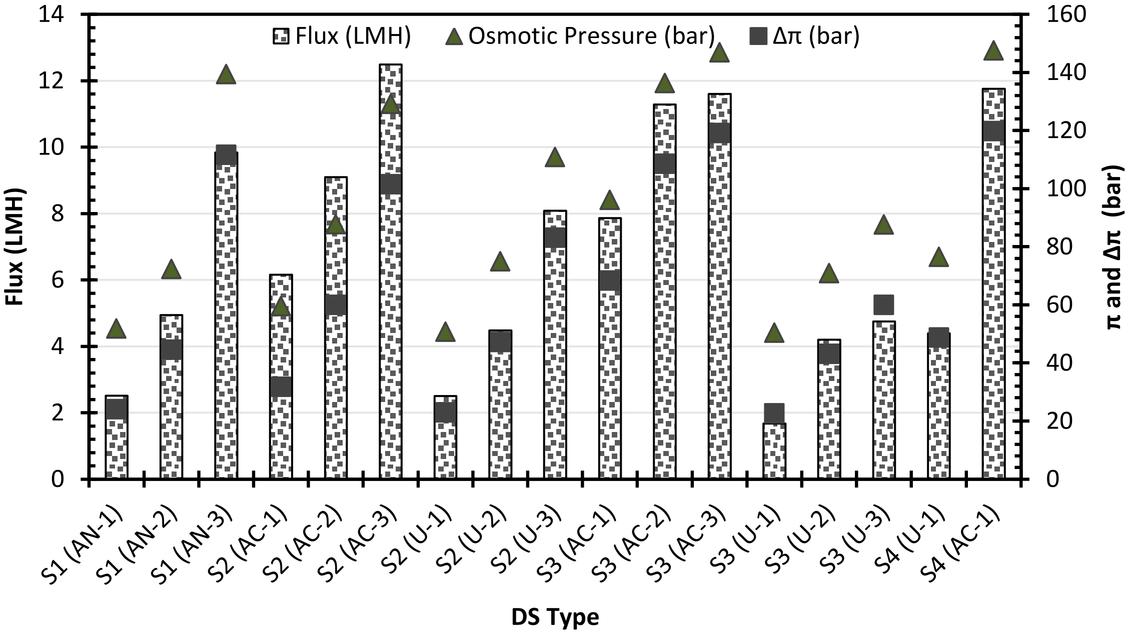

Fig. 5.2. Effect of osmotic pressure and net osmotic pressure on FO flux outcome for various DS mixtures

Fig. 5.3 (b) also shows similar variations when the ratio of $J_w/\Delta\pi$ was plotted for these DS mixtures. Thermodynamically, the transport of a given species must be directed to decrease the chemical potential for the species (Paul, 1974). So for an FO process, which reduces the chemical potential between the two solutions across the membrane, it is hypothesized that in a mixture of DS, besides the osmotic pressure of DS and FS, the chemical properties of their individual solutes such as inter-molecular interactions, ionization potential, chemical potential, ionic charge, ionic interactions between DS species and FS components and others also plays a vital role in dictating the FO flux outcome.

5.3.4 Comparison of flux for changing N-source fertilizer during various plant growth stages

Three N-source fertilizers namely: NH_4Cl, NH_4NO_3, and urea were used to prepare DS to meet the nutrient requirements of S1 tomato growth stage and then evaluated for the FO process.

NH_4NO_3 and urea fertilizers gave low flux and high RSF and may not be favoured for the FO process (Phuntsho et al., 2011). However, these two fertilizers were evaluated for their synergic effects with other DS fertilizer blends, and were compared with NH_4Cl-based mixtures.

The tomato crop stage S1 NPK ratio of 11.5-19-11.5 was further evaluated for the FO process. DS were prepared for NH_4Cl, NH_4NO_3 and urea N-source fertilizers and evaluated for 25%, 33% and 50% fertilizer quantity which is required per hectare at the S1 stage. Fig. 5.4 indicates that the mixtures carrying DS components having less osmotic pressure (π) such as urea and NH_4NO_3 showed a lower flux output. However, DS containing NH_4Cl for the same NPK values showed a higher resultant flux.

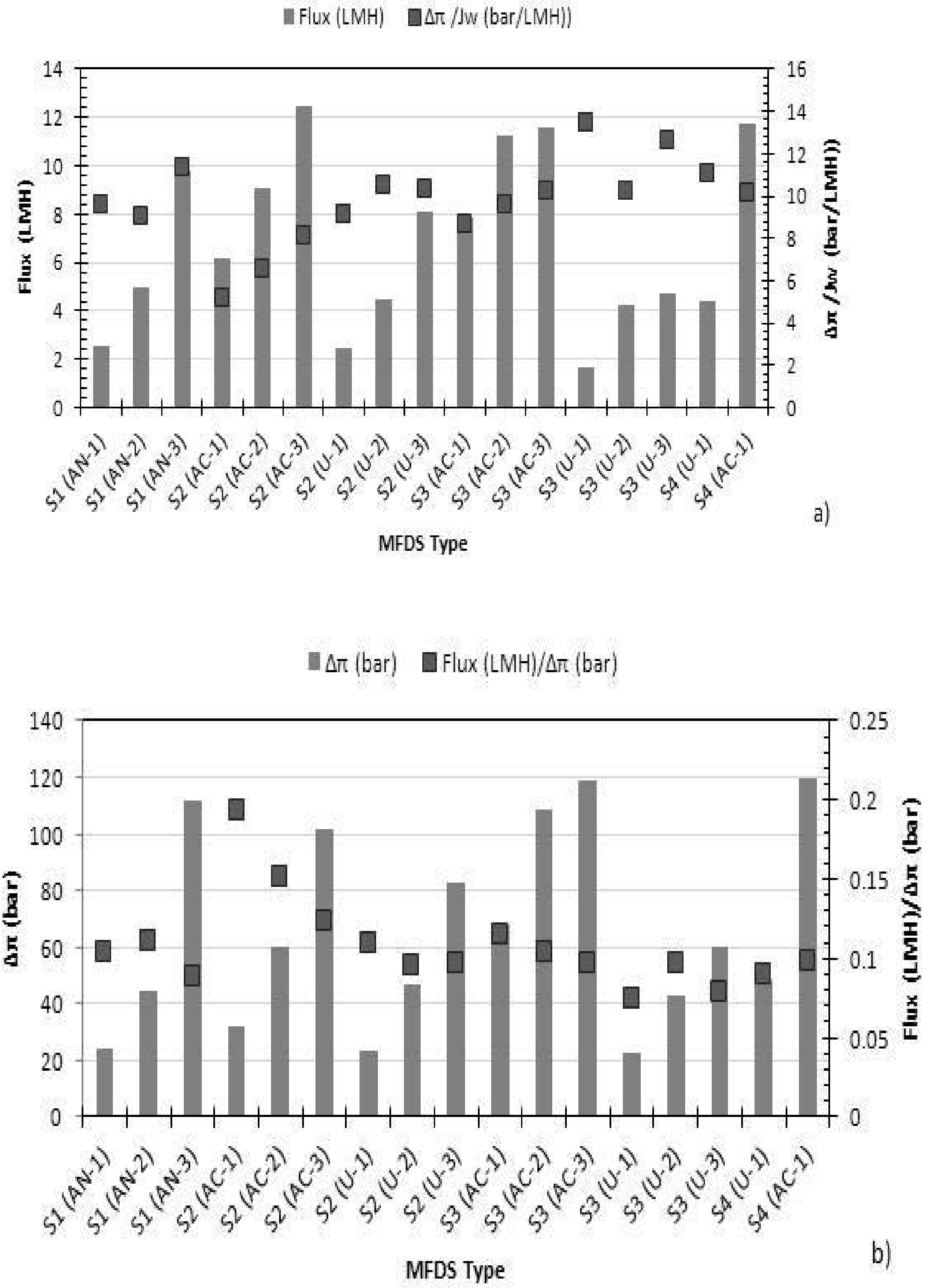

Fig. 5.3. Comparison of a) Flux and $\Delta\pi/J_w$ (bars/LMH) b) Net osmotic pressure gradient $\Delta\pi$ (bars) and J_w(LMH)/$\Delta\pi$(bars) for different mixed fertilizer DS

OLI software further revealed that at 1M concentration, NH_4Cl showed π of 43.5 atm, which is 83% and 29% higher than the π of 1M urea and NH_4NO_3, respectively. This confirms that in a mixture of DS solutes, the higher osmotic pressure value component mainly quantifies π and the flux of the mixed DS. Thus NH_4Cl-based DS showed a higher resultant flux than that of other N-source fertilizer blends. However, the differences in flux outcome vary with their concentration and the presence of other components in any given DS.

In contrast, at 1 M concentration, urea shows π of 23.7 atm whereas NH_4NO_3 shows π of 33.7 atm, which is 42% higher than that of urea. Despite these differences in π, both NH_4NO_3 and urea showed nearly the same flux for two DS prepared for the same NPK ratio. From this, we may conclude that in these DS mixtures, urea and NH_4NO_3 fertilizer fractions exert inconsiderable π in the overall osmotic pressure of the DS. DS carrying KCl, MAP, and KNO_3 as other main components of the DS contributes to a notable portion of the overall π. Due to the lower π contribution of these two N-fertilizers, the resultant flux was not dictated

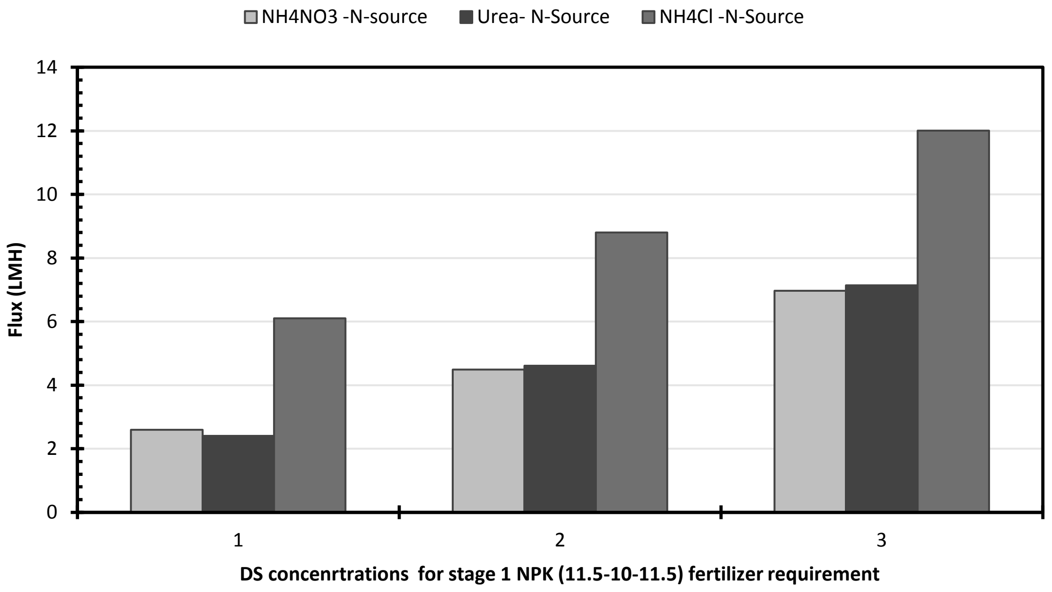

Fig. 5.4. Water flux with varying N-source component in mixed fertilizer DS: NH_4Cl N-source based DS shows the highest flux whereas Urea and NH_4NO_3 based DS gives lower but nearly the same flux (DS were prepared for 1(25%), 2(33%) and 3(50%) concentrations of Stage S1 NPK fertilizer requirements**).**

by the π of urea and NH_4NO_3 components but by other components of DS. These results again may be due to the influence of intermolecular associations between the different components of the DS.

5.3.5 Reverse solute flux using DS blend

FS samples were collected at the end of each experiment and were analysed to evaluate any draw solute diffusion across the membrane to the feed side. Fig. 5.5 and 5.6 compare the flux and net osmotic pressure ($\Delta\pi$) of DS to NPK RSF (in $g/m^2/h$). Similar to the FO flux results, the RSF outcome showed a varying behaviour with different fertilizer DS blends. Apparently, all nitrate-based DS blends indicated high RSF values. Moreover, DS having a high concentration of urea or NH_4NO_3 showed high RSF in terms of nitrogen. Nitrates due to smaller molecular size penetrate deeply into the membrane (Paugam et al., 2003, Wang et al., 2005, Paugam et al., 2004). Some of the DS prepared from KNO_3 also showed high RSF values.

RSF is considered as a loss of valuable DS inputs which work to raise the FO operating cost. RSF was regularly monitored for all DS to collect data for cost control and waste discharge management. Moreover, concentrated FS carrying RSF solutes is normally discarded or dumped back to other receiving bodies, wherein the excessive nutrients present in the FS concentrate create algal bloom and eutrophication problems in the receiving water.

For most of the RSF results for the S1 and S2 tomato growth stages, it was observed that N-RSF was higher than K- and P- RSF, which was probably due to the small size of N–hydrated radii. RSF for K and P always remained on the lower side for nearly all DS blends.

However, the S3 and S4 stage DS results indicated that the K-RSF was higher than N-RSF for these two stages. These results are due to the high potassium concentration (Table 4.3) in the DS mixtures for stages S3 and S4. Phosphate loss was observed at a minimum while using MAP as phosphate/nitrogen nutrient source component. MAP-based DS showed low RSF not only for phosphorus but for nitrogen as well. This suggests that higher MAP concentration in the DS helps keep this nutrient loss at a minimum and improves the overall efficiency of the process.

Tang et al. (Tang et al., 2010b) and She et al. (She et al., 2012a) have presented the following equation to predict the reverse draw solute flux across the membrane for a single solute:

$$\mathrm{J_s} = \mathrm{J_w}\frac{B}{A\beta \mathrm{R_g} T} \tag{5.1}$$

where J_s is the solute flux, J_w the water flux, B is the solute permeability coefficient of the membrane, A is the water permeability coefficient of the membrane, β is the van't Hoff coefficient, R_g is the universal gas constant and T is the absolute temperature. Eq. (4) mainly relies on the solute permeability coefficient (B) to determine RSF, while maintaining all other parameters constant for any particular solution. The membrane structure and DS composition plays an important role in the bi-directional diffusion of solutes across the membrane (Hancock and Cath, 2009). The solute permeability constant varies inversely with the thickness of the membrane (Wijmans and Baker, 1995). The membrane permeability coefficient (A) and solute coefficient (B) are also affected by the membrane thickness. From this equation, we may deduce that RSF (J_s) is proportional to the pure water flux (J_w), and as J_w increases, RSF should also increase. However, a later study by She et al. (She et al., 2012a) has found that for many membrane processes, as J_w increases, RSF is reduced. This was attributed to the high flux that helps push the solute molecules back to the DS (She et al., 2012a), which seems more reasonable and logical.

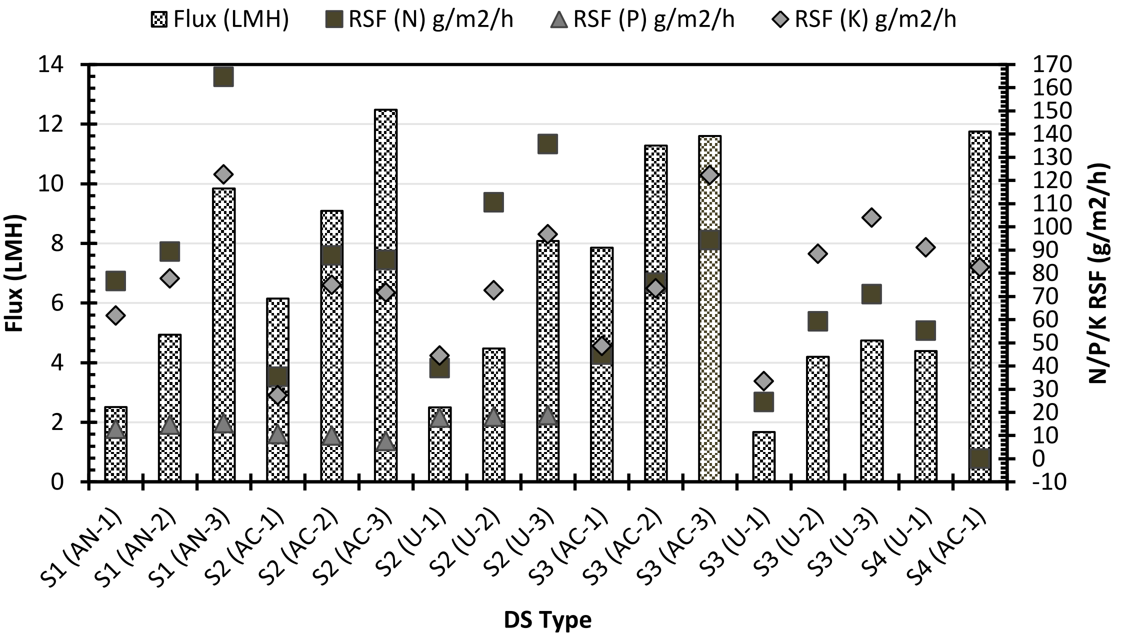

Fig. 5.5. Nitrogen (N), Phosphorous (P) and Potassium (K) RSF behaviour for DS in the FDFO process. All these RSF values are taken as GMH (g/m^2/h). P- RSF shows values for the first two stages S1 and S2 as phosphate fertilizer but it was not used to prepare DS for the S3 and S4 stages.

Fig. 5.5 and 5.6 indicate that the RSF of N-, P-, and K- nutrients rise with the increase in DS mixture concentrations. The resultant high values of flux and RSF are due to the high concentrations of DS in the particular DS. The RSF of N and K responded quickly to the DS concentration changes, whereas the P-RSF did not change much. Indeed, it remained nearly unchanged. Donnan (Donnan, 1924) shows that the ionic equilibrium on both sides of the membrane dictates the diffusion of ions from one side to the other. Osmotic pressures, ionic equilibria and potential differences affect the movement of ions across the membrane (Donnan, 1924). For systems containing two electrolytes with a common ion, one part of the electrolyte moves faster than the other and changes the potential difference of the electrolytes. The diffusion process then slows down and the system returns to the ionic equilibrium. For FO using fertilizer DS against SW quality FS, Cl^- is the common ion in both DS and FS. The other components of the DS such as NH_4^+/NO_3^- and K^+ having smaller hydrated radii move faster than Na^+ ions, which indicates a high N- and K- RSF. The Kirkwood-Buff theory helps to some extent in investigating the changes in associations and interactions by the addition of some common co-solvents (Chitra and Smith, 2002). The diffusion of ions from a solution carrying various solutes is quite complex and still needs answers to many related issues. It is predicted that the uniform P-RSF outcome with these DS fertilizers is due to the size of the PO_4 ions and lower favorable ionic attractions of the ion present on the other side of the membrane.

The RSF results indicate that due to the fertilizer salt losses through RSF, the final diluted DS may not end up with the same NPK nutrient ratio in the final DS as when the tests were started. The RSF outcome indicates the loss of valuable nutrients and possible deviation from the start-up values. To achieve the desired NPK ratio suitable for a tomato crop at any particular crop period, the RSF loss adjustments would be required to prepare the fertilizer DS. For practical use, to account for RSF loss in an FO process, the starting DS is therefore required to have somewhat higher NPK ratios to what is required theoretically so that the final DS may achieve the same NPK nutrient ratio required for any particular growth stage for the tomato or other plants.

The RSF results indicate that due to the fertilizer salt losses through RSF, the final diluted DS may not end up with the same NPK nutrient ratio in the final DS as when the tests were commenced. The RSF outcome indicates the loss of valuable nutrients and a possible deviation from the start-up values. To achieve the desired NPK ratio

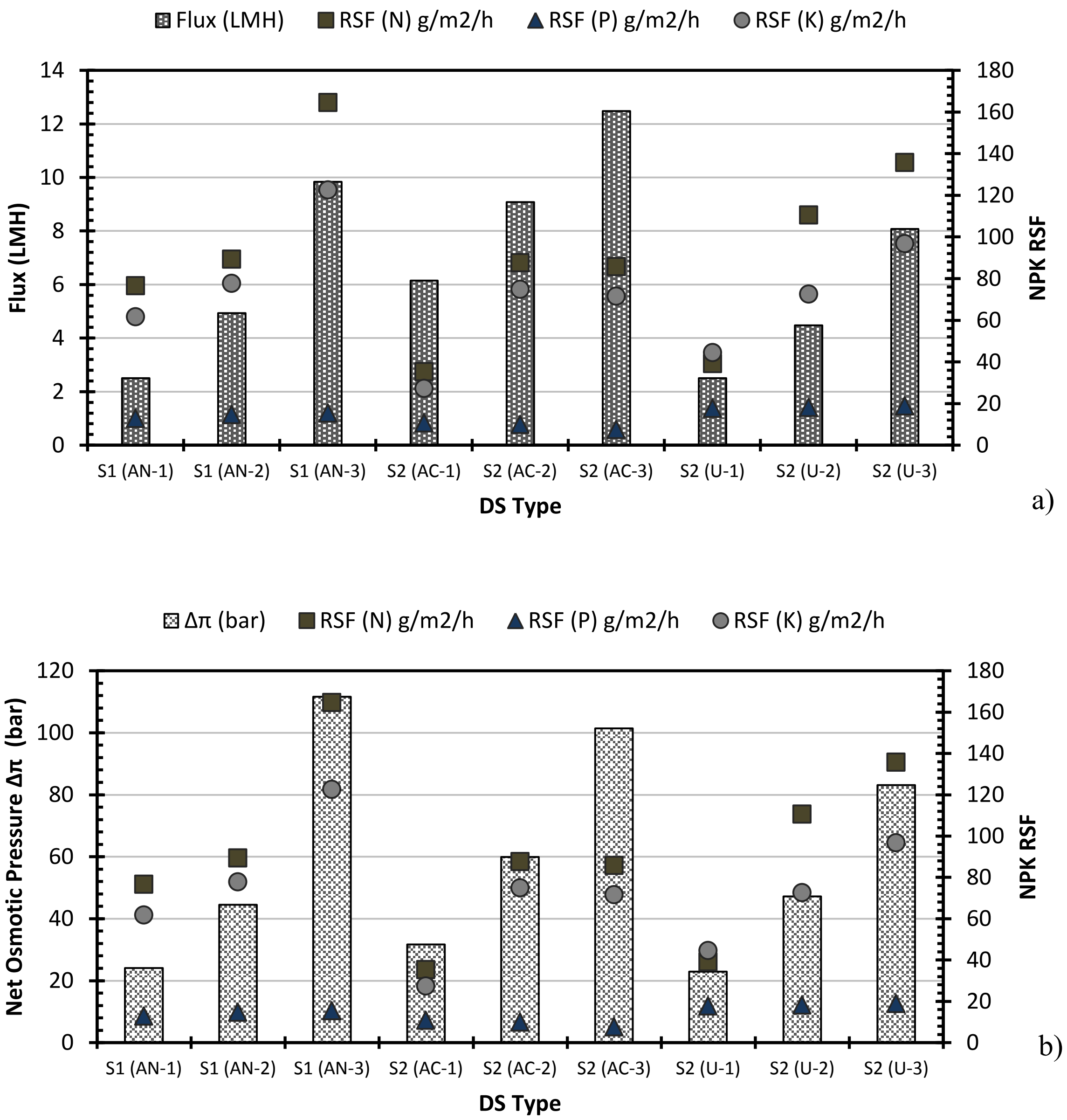

Fig. 5.6. N, P and K RSF for various DS used. a) Flux (LMH) plotted along with RSF for N, P and K b) Net osmotic pressure (Δπ) plotted along with RSF for N, P and K. Along the horizontal axis, the first two letters in the brackets indicate the nitrogen source used to prepare the DS for that particular stage. Similarly numbers 1, 2 and 3 indicate the specific concentrations of particular DS.

suitable for a tomato crop at any particular crop period, the RSF loss adjustments would be required to prepare the fertilizer DS. For practical purposes, to account for RSF loss in an FO process, the starting DS is therefore required to have somewhat higher NPK ratios to those that are required theoretically so that the final DS may achieve the same NPK nutrient ratio required for any particular growth stage of the tomato or other plants.

5.3.6 Long-term run tests for fertilizer DS and expected final DS concentration

Using NH_4Cl and urea N-fertilizers, one DS was prepared for S2 and two DS were prepared for the S4 stage NPK ratio and these DS were evaluated for flux trends for long-term run tests of up to 60 hrs. The NH_4Cl nitrogen source fertilizer was used to prepare DS having a 11.5-19-11.5 NPK ratio (S2 stage). Two other DS were prepared for the S4 stage, one with NH_4Cl as the main N-source fertilizer and the other with urea as the N-source fertilizer for the same 10-0-10 NPK blend (S4 stage).

Fig. 5.7 shows the flux behaviour of DS prepared to meet the S4 stage nutrient requirements. S4-NH_4Cl DS was prepared using KCl and NH_4Cl, having concentrations of 1.2 M and 2.02 M, respectively. Similarly, an S4-Urea DS was also prepared using KCl and urea having individual concentrations of 1.2 M and 0.97 M, respectively. Starting with the same NPK nutrient value for both DS, at the beginning of the test, these DS showed obvious differences in initial water flux. But as the tests were continued for more than 2000 min, their flux gap was observed to become narrower with time. There may be two reasons for this trend. Firstly, the NH_4Cl-based MF blend showed high initial flux, i.e., more water passed towards the concentrated side, quickly diluting the DS. This dilution lowered the available driving force $\Delta\pi$, resulting in a speedy flux decline. On the other hand, as urea-based DS had lower initial flux, water permeation towards DS was slow, so that only a little dilution occurred over the same period of time. Thus, the urea-based DS did not show a sharp flux declining trend. After a certain period of operational run, due to the dilution difference attributed by varying flux, NH_4Cl-based DS possesses lower $\Delta\pi$ as compared to urea-based DS. Thus as the test proceeded towards the final stage, the available osmotic pressure of NH_4Cl-based DS became close to the urea-based DS and showed nearly equal flux.

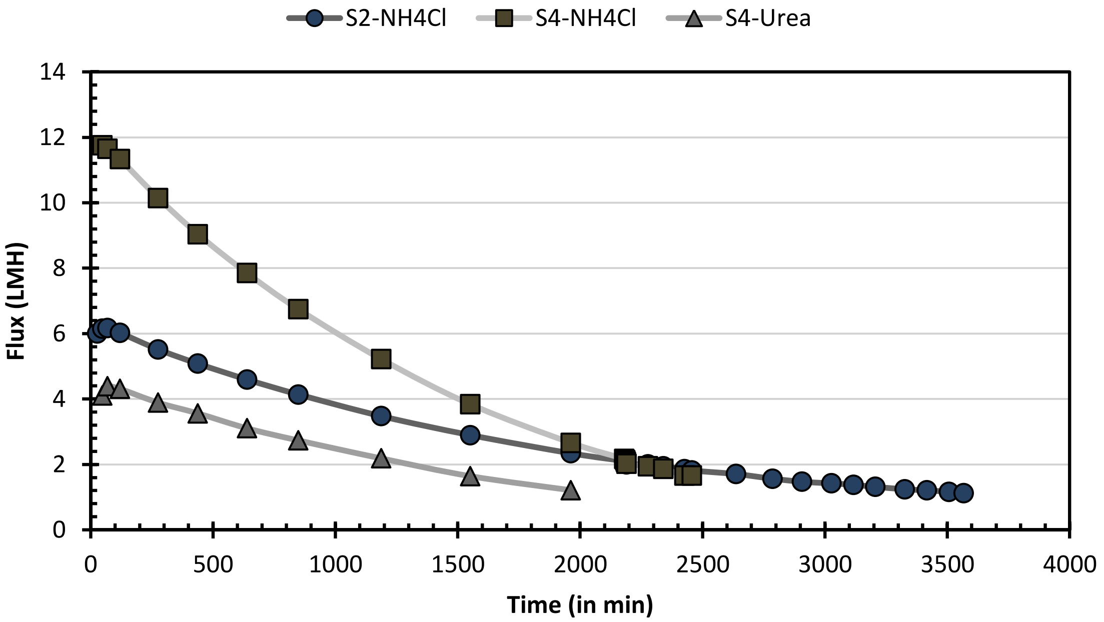

Fig. 5.7. Long run FDFO flux trends for three DS prepared to meet the S2 and S4 stage NPK requirement. Stage S2 DS used NH_4Cl N-source. Two S4 DS were used with different N-source fertilizers. One used NH_4Cl and the other used urea as a nitrogen source fertilizer to prepare DS mixtures.

Additionally, in the recirculation mode FO test, as the test proceeded, the DS kept on diluting due to water permeation through the FO membrane whereas at the same time the FS became concentrated with respect to the solutes present in the FS. The continuous water permeation towards the DS side reduced the total concentration of salts in the DS over time and that resulted in a reduction of the available $\Delta\pi$. By contrast, during the continuous operation run, the FS concentration changed just marginally in comparison to the higher DS concentration, and this did not affect the FS osmotic pressure or contribute to lower the available flux driving force i.e., $\Delta\pi$. As these processes continued for a long duration, the DS dilution brought the driving force down and as a result, the overall flux kept decreasing. The DS dilution played a major role in reducing the net available osmotic pressure (based on the bulk osmotic pressures of the DS and FS) to deliver a resultant flux. On the other hand, concentrating the FS along with RSF support caused an increase of solute concentration on the FS side which in turn affected the $\Delta\pi$ in a longer test run.

The long-term test flux decline shown in Fig. 5.7 was not only due to the decrease of overall osmotic pressure difference ($\Delta\pi$) between the DS and the FS. McCutcheon and Elimelech (McCutcheon and Elimelech, 2006) showed that the concentration polarization (CP) affected the DS and FS concentrations at the membrane active layer and caused a lower actual flux in FO. In either membrane orientation mode (AL-FS or AL-DS), the CP phenomenon developed on both sides of the membrane, which restricted FO to achieve a high theoretical flux through FO operations (Cath et al., 2005, Achilli et al., 2009b, Phuntsho et al., 2012a). Similar CP effects can also be seen in Fig. 5.7 as the flux decline becomes more likely due to the DS dilution and FS concentration effects. Severe CP development is noticed on both sides of the membrane. ECP is severe as high concentration FS is used in this study.

ICP and ECP, along with the dilution and concentrations of DS/FS contributed to the reduced available osmotic pressure across the membrane's active layer, which resulted in a lower flux outcome compared to the high theoretical flux potential. The FO membrane always gives a flux driven by the concentrations present at the membrane surfaces and not by the actual concentrations of DS and FS. As a result of the DS/FS concentration difference at the membrane interface, the resultant lower FO flux was based on the $\Delta\pi_{\text{effective}}$ across the membrane interface instead of the flux based on the $\Delta\pi_{\text{bulk}}$, i.e., the difference in osmotic pressure between the DS and FS themselves. These also helped to reduce the flux in the long term run operation.

5.3.7 Dilution of final diluted DS

After a long-term test run of 60 hrs, the final DS at the end of FO tests was evaluated for nutrient concentrations. The final DS showed high concentrations of TDS compared to that of the final FS. Due to the water flux and solute movement towards the FS side, the FS is concentrated over long-term run operations. For FO operations with a fertilizer DS using an SW quality FS, the final DS ends up highly enriched in NPK nutrients (above the crop's nutrient feed level). Looking into this, it is concluded that the dilution of the final DS will be required for FO using an even lower quality brackish FS (2000 TDS) as the maximum NPK nutrient level allowed in feed water for the tomato crop is only 200/50/300 ppm, which is far below that of the FS initial concentration (Phuntsho et al., 2012a). The fertilizer drawn FO system needs a higher level of dilutions to reduce the nutrient concentration acceptable for direct irrigation of tomato crops. Fig 5.8 summarises the FDFO approach for sea water desalination and techniques for the final diluted DS management for fertigation of the tomato crop.

Nitrogen- and potassium-based DS showed higher N- and K- RSF. However, DS using $NH_4H_2PO_4$ delivered extremely low P-RSF ranging from 12-18.35 $g/m^2/h$. The long term run tests showed that with the use of seawater FS, the FO gave diluted DS enriched in nutrients, and these were higher than the plant's requirement. Higher concentrations of nutrients in the final DS suggest that before applying it to direct end use, dilution of the final DS will be required to bring its nutrient level down to match the crop's acceptable levels.

5.4 Concluding remarks

This study confirms that FDFO can be used effectively to desalinate a seawater feed source using DS prepared from commercial fertilizers.

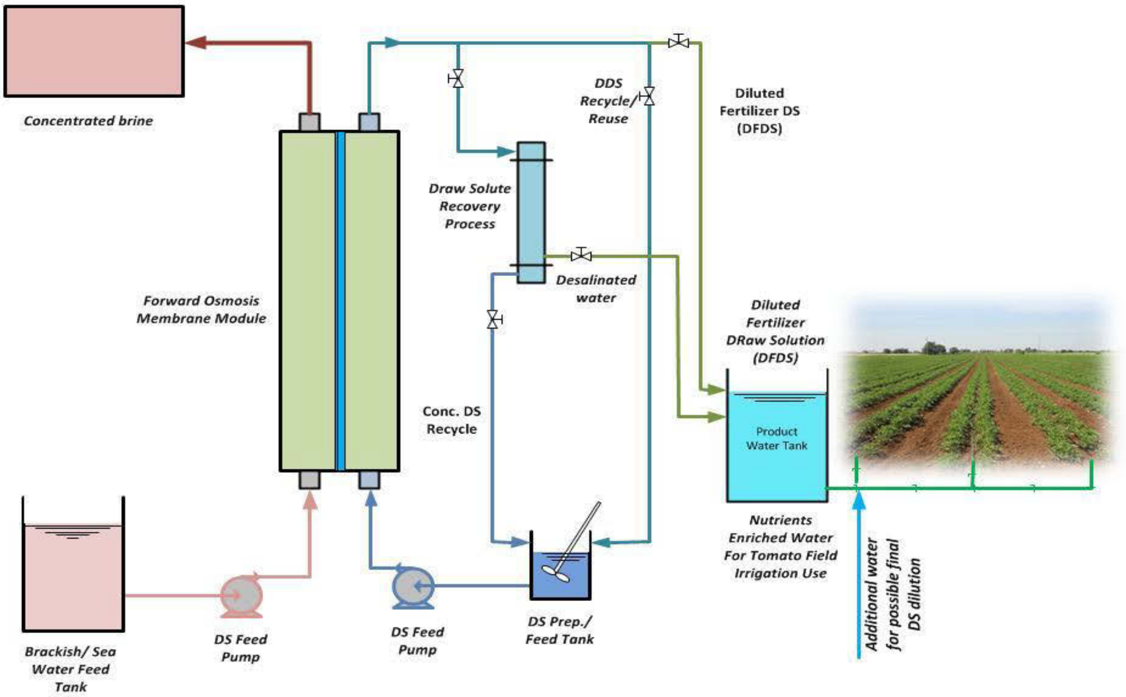

Fig. 5. 8. FDFO approach for sea water desalination for tomato fertigation

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Chapter 6

PERFORMANCES OF THE PA HOLLOW FIBER AND CTA FLAT SHEET MEMBRANE FOR THE FORWARD OSMOSIS PROCESS

6.1 Introduction

Beside the aforesaid inherent advantages of forward osmosis (FO) as outlined in Chapter 2, initial studies with the flat sheet FO (FSFO) membrane show that the DS characteristics and FO membrane properties are considered as the major impediments in the commercialisation of the forward osmosis system (McCutcheon et al., 2006). Membrane characteristics and DS properties play vital roles for any particular outcomes of the FO processes (Lay et al., 2012).

Chapters 4 and 5 have shown the outcomes for the use of the innovative fertilizer drawn forward osmosis process harnessing the natural available power i.e., osmotic pressure of the commercial fertilizer DS. These results indicated that the fertilizer DS naturally induced flux through CTA flat sheet membrane and thus avoided additional energy sources (to develop hydraulic pressure as it did for the RO) to drive sea water desalination. Additionally, in opposition to other FO processes, the final diluted DS did not necessarily require separation of the final diluted fertilizer DS and thus product permeated water can be used directly for tomato fertigation. Different fertilizer DS were evaluated in these studies and a varying nature of outcomes were obtained. NH_4Cl, SOA, CAN and KCl DS showed better flux performances than MAP, DAP, KNO_3, urea and NH_4NO_3 fertilizer DS. Similarly, RSF, MAP and DAP exhibited lower RSF even at higher DS concentrations whereas KNO_3 and KCl both showed high RSF values for nitrogen and potassium.

For these inconsistent outcomes with various DS fertilizers, it is important to evaluate FO for other important aspects i.e., types of membrane. Currently, FO membranes are mainly classified into two main groups 1) flat sheet and 2) hollow fiber. Various earlier studies with CTA flat sheet membranes highlighted issues such as low water flux and high RSF (Cath et al., 2006, McCutcheon and Elimelech, 2008) which also affect the FDFO process directly.

Lower water flux and higher RSF are always considered critical issues hindering the rapid development and transformation of the FO process for commercial applications. A lower performance ratio of 16.48% indicated serious issues with the FSFO membrane (Phuntsho et al., 2011). These issues become more severe when the high concentration FS representing sea water quality was used for the FO process (Majeed et al., 2014). FO flux is directly linked to the operating cost and initial capital cost of the FO system thus efforts are continuously directed to develop and suggest high flux FO operation. Enhanced flux FO operation means a small FO plant footprint and more economical desalination. Reduced RSF reflects a reduction of DS leakage to FO waste streams and decreases the DS replenishment costs.

In the initial FO studies, different types of asymmetric (i.e. active layer embedded on a porous support layer-used to increase the structural strength of the membrane) FSFO membranes were produced and tested for various applications. Resultant flux for any FO membrane was affected by its inherent active and support layer performances and operating issues such as CP buildup during the process. The asymmetric structure of these membranes cause enhancing CP on both sides of the membrane and consequently result in a reduction of the actual water flux through the membrane (McCutcheon and Elimelech, 2006). CP drastically reduces the available driving force (osmotic pressure gradient ($\Delta\pi$)) at the membrane surface and this causes a sharp decline in flux that results in a poor FO operational result performance (McCutcheon et al., 2006).

Since FO flux mainly relies on $\Delta\pi$ across the membrane surface that contacts the DS and FS to drive osmosis, it is suggested that the accumulated CP results in insufficient flux and lower performance ratios for FO (Lay et al., 2010, Zhang et al., 2010, Li et al., 2011b). External concentration polarization (ECP) is usually linked with DS and FS concentration whereas internal concentration polarization (ICP) is mainly associated with the thick dense membrane and support layer structure (Cath et al., 2006). To overcome this issue, efforts have been directed to develop an ideal FO membrane having a thin film on a highly porous and very fine support layer, high water permeability, low salt permeability and enough strength structure layers that give minimum CP effects, especially ICP.

HTI first introduced the commercial flat sheet CTA FO membrane (Cornelissen et al., 2008). During the FO membrane development process, to reduce the intensity of the membrane related issues critical for FO performance outcome, many research groups worked on the development of improved flat sheet and hollow fiber FO membranes. Some of the resultant positive outcomes included novel dual layer hollow fiber membranes (Yang et al., 2009a), well-constructed cellulose acetate FO membrane (Zhang et al., 2010), thin film composite FO hollow fiber membranes (Chou et al., 2012, Wang et al., 2010b), high performance thin film membranes (Yip et al., 2010), thin film nano composites using functionalized multi-walled nanotubes (Amini et al., 2013), double skinned FO membranes (Tang et al., 2011b), acetylated methyl cellulose (AMC) membranes (Kim et al., 2013), cellulose triacetate/cellulose acetate (CTA/CA)-based membranes (Nguyen et al., 2013), etc.

Hollow fiber FO (HFFO) membrane development work was initiated by various research groups (Wang et al., 2007, Wang et al., 2009, Chung et al., 2012b) to produce a better performing FO membrane carrying minimum FO operational issue. In comparison to FSFO membranes, most of the developed HFFO membranes demonstrated proven performance in terms of high water flux and lower RSF (Wang et al., 2010b, Chou et al., 2010, Su et al., 2010, Sivertsen et al., 2012a, Xiao et al., 2012, Setiawan et al., 2011, Fang et al., 2012, Wang et al., 2010a, Yang et al., 2009a).

To date, many studies have been performed to explore FO use for different practical applications using the FSFO membrane (Elimelech, 2007, Martinetti et al., 2009, HTI, 2013, ModernWater, 2013, Statkraft, 2013). Besides improved performances shown by the various HFFO membranes, no serious attempt has been made yet to explore the HFFO membrane potential for any practical application. Hence this study may be considered as a late but genuine first step towards evaluating the HFFO membrane for any commercial applications as FDFO.

As such, the main objective of this study is to categorically compare HFFO and FSFO membrane performances for better outcomes for the FDFO desalination process. The HFFO membrane was evaluated for different DS fertilizers. Flux and RSF performances were compared with the FSFO membrane outcome to identify the role of specific membrane properties that are critical for higher FO process performances. Comparison of the FDFO performance for these two different membranes with multiple DS further provided us with a better understanding in terms of how different DS properties and membrane characteristics manipulate the FO output.

6.2 Experimental

6.2.1 Experimental Set-up

Bench scale HFFO set-ups as shown in Fig. 6.1 and 3.2 were used for this study. Two peristaltic pumps (Cole- Palmer, U.S.A.) were used to supply FS and DS to these set-ups. Cross sectional flow rates were maintained at 400 ml/min for both FSFO and HFFO membrane units. While changing DS, each FO system was washed thoroughly at the end of each test for 30 minutes using distilled water at 400-800 ml/min. The temperature of the DS and FS stream was kept constant at 25°C ± 0.5°C using a temperature water bath controlled by heater/chiller.

Water permeation through HFFO membrane was evaluated by measuring weight loss of FS using a weighing scale (CUW 4200H by CAS, Korea) connected to a computer data logging system which was later used to calculate water flux in these particular FO tests. A conductivity data logger probe was immersed in the FS tank to record changes in FS conductivity at certain time intervals. This data helped in measuring RSF during FO operations. An identical bench scale FO set-up as shown in Fig. 3.2 was used for the FSFO membrane evaluation.

6.2.2 Membranes used

HFFO membrane lumens, supplied by Samsung Cheil Industries, Korea were used in this study. HFFO lumens were composed of an active polyamide (PA) thin film composite (TFC) layer inside a porous polyethersulphone hollow fiber substrate. The inside and outside diameter of these hollow fiber lumens were 0.9 mm and 1.2 mm respectively and the HFFO module carried an average FO membrane area of 396 cm^2.

Simultaneously, a commercially available CTA FO membrane supplied by Hydration Technologies Innovations (HTI), USA was used separately with FSFO lab-setup. The FO lab experimental cell carried a flat-sheet membrane size of 26 mm x 77 mm. Thus the FSFO membrane represented an average membrane area of 20.02 cm^2.

All tests for this study for both FSFO and HFFO were carried out in active layer – feed solution (AL-FS) membrane orientation (Fig. 3.3). A smooth active layer of the FSFO membrane was placed towards the FS side and a rough surface carrying polyester mesh support layer was faced towards the DS side. Similarly, for the HFFO set-up, FS was directed to flow through lumens whereas DS flowed through the FO module shell outside fiber.

6.2.3 Chemicals and reagents

9 commonly used fertilizers including NH_4Cl, $(NH_4)_2SO_4$, KNO_3, KCl, $(NH_4)_2HPO_4$ (DAP), $NH_4H_2PO_4$ (MAP), $Ca(NO_3)_2$, $NaNO_3$, and $CO(NH_2)_2$ (Urea) were selected to use as DS to evaluate and compare the performance of these two FO membranes for the FDFO process.

Membrane performance was evaluated against 1 M individual fertilizer DS concentration. DI water was used as FS for the whole study.

6.2.4 FO operating setup summary

Details of the HFFO and FSFO membrane test set-up are summarised in Table 6.1.

6.3 Results & discussion

6.3.1 HFFO and FSFO membranes comparison

HFFO and FSFO membranes were used for the FDFO process comparison. Physical properties of both membranes are summarised in Table 6.2. Membrane thickness was evaluated using micrometer and its surface characteristics were further assessed using a scanning electron micrograph (*SEM*). The HFFO membrane comparatively shows about 66%

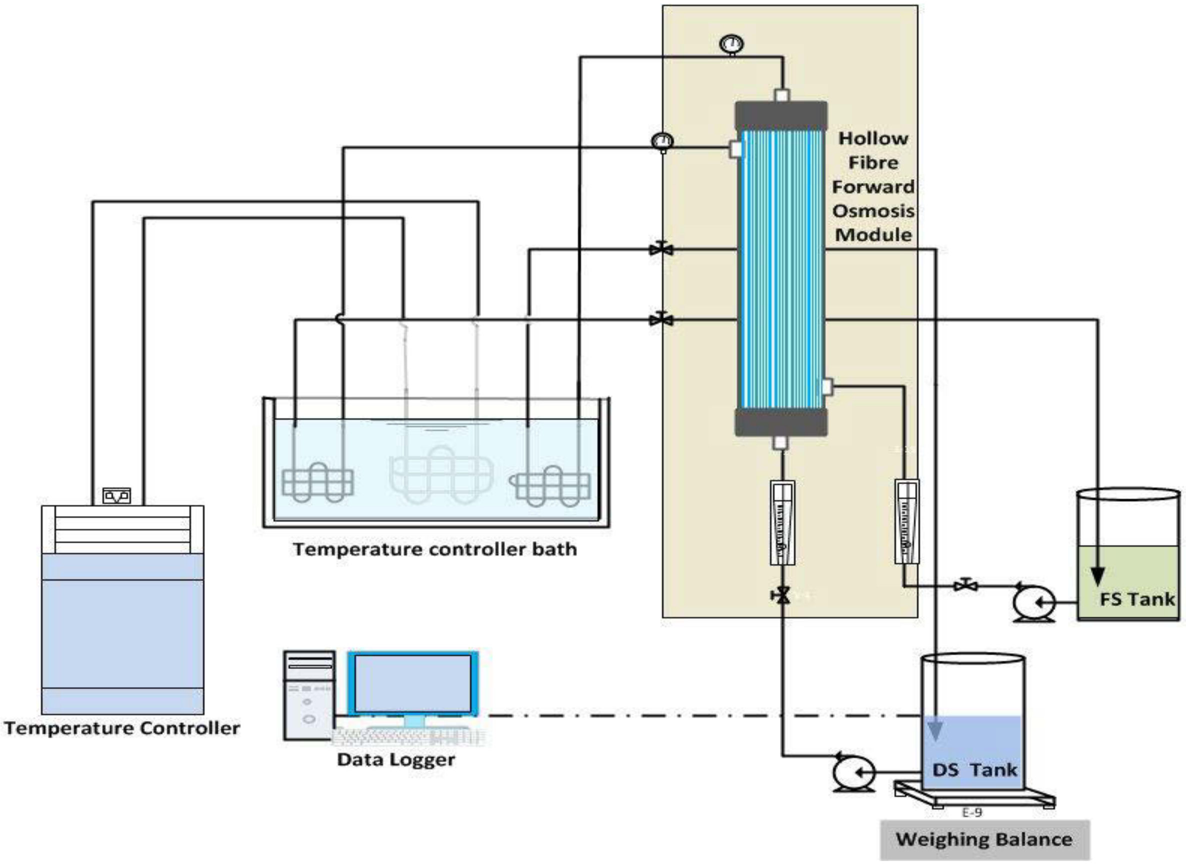

Fig. 6.1. Schematics of lab scale HFFO set-up used in this study

overall higher membrane thicknesses as the HFFO and the FSFO membranes show a thickness of 152±3 µm and 91±2 µm respectively. Thus the HFFO thickness is about 66% higher than the FSFO membrane. Similarly, the thickness of the polyamide active layer of HFFO membrane is also high as compared to the thickness of the active CTA layer of the FSFO membrane

Table 6.1 Summary of the operating conditions for the batch scale HFFO and FSFO membrane systems for the FDFO process comparative study

Description	Details
DS used	NH_4Cl, $(NH_4)_2SO_4$, KNO_3, KCl, $(NH_4)_2HPO_4$, $NH_4H_2PO_4$, $Ca(NO_3)_2$, $NaNO_3$, and $CO(NH_2)_2$
Fertilizer DS concentrations	1 M
Feed water type	Deionized (DI) water
Membrane orientation	AL-FS
Temperature	25ºC ± 1.0
Parameters evaluated	FO flux and RSF
HFFO module type FSFO membrane type	PA lumens based hollow fiber module CTA flat sheet membrane
DS/FS flow rates	400 ml/min for both DS/FS
HFFO membrane active area FSFO membrane active area	39.6×10^{-3} m^2 2.02×10^{-3} m^2

Pure water permeability (PWP) and the salt rejection rate (1000 mg/L NaCl) of both membranes were evaluated in the RO mode. The FSFO membrane was evaluated for higher pressure (5-15 bars) whereas the HFFO was evaluated at extremely low pressure (up to 1.5 bars) to avoid fiber damage. The PWP and the salt rejection of the HFFO membrane were 1.80 $L.m^{-2}.h^{-1}.bar^{-1}$ and 98% respectively while for the FSFO membrane the PWP and rejection were 1.012 $L.m^{-2}.h^{-1}.bar^{-1}$ and 90% respectively. In comparison to FSFO, the HFFO membrane showed a PWP value which was higher by 78% and the salt rejection was higher by 9%.

Fig. 6.2 shows *SEM images* of both the PA HFFO membrane and the CTA FSFO membrane. Both membranes show a huge difference in making and structure. Fig 6.2 (a) shows a top image of a horizontally cut HFFO membrane. A thick PA active layer was seen on top of an outer layer of polyether sulphone. The PA active layer presents excellent intrinsic separation properties with a hydrophilic rejection layer that provides a good mechanical strength to FO hollow fibers.

Table 6.2. Comparison of FSFO and HFFO membrane characteristics and physical properties

	Flat Sheet FO	Hollow Fiber FO
Source	HTI, USA	Samsung Cheil Industries, Korea
Active layer (AL) material	Cellulose Triacetate	Polyamide
Support Layer (SL) material	Polyester mesh	Polyether sulphone
Thickness (Overall) (μm)	91 ± 2	152 ± 3
Thickness (AL) (μm)	45 ± 2	65 ± 3
Thickness (SL) (μm)	46 ± 2	87 ± 3
Pure water permeability (Lm^{-2}h^{-1}bar^{-1})	1.012	1.80
Salt rejection (%)	90	98
Membrane surface charge	Negatively charge [a]	Neutrally charge [b]
Support layer surface charge	Negatively charge	Neutrally charge
Contact angle of the active layer (°)	61 [c]	-
Contact angle of the support layer (°)	87 [d]	-

Sources: [a] (Tiraferri and Elimelech, 2012); [b] (Xie et al., 2013b) ; [c] (Achilli et al., 2010); [d] (Tang et al., 2010b)

Similarly, in Fig. 6.2 (b), a side view of the CTA FS membrane shows a top dense CTA layer embedded on a polyester mesh support layer. Membrane acetate contents (in wt.%) directly affect the pure water permeability and salt permeability as well (Lonsdale et al., 1965). The water diffusion coefficient decreases as the acetate content of the membrane is increased. Similarly, salt permeability is also reduced with any increase of membrane acetate contents which suggests that a better CTA membrane may be made by controlling its acetate contents in the membrane along with the thickness of the membrane.

6.3.2 Comparative performances of FO membranes in terms of water flux and reverse solute flux

Lab FO units for both the flat sheet membrane cell and the hollow fiber module were operated on in similar operating conditions. The FO flux outcome was evaluated for the various kinds of fertilizer DS as used in the FDFO process and these results were then compared for their effectiveness for the FDFO process. These were evaluations in terms of AL-FS membrane orientations. Due to severe ICP issues, the FO operation in this orientation shows relatively less flux output (Wang et al., 2010c).

6.3.3 Overall flux evaluation and comparison

Fig. 6.3 shows the flux performances for the HFFO (PA) membrane and compares it with the FSFO (CTA) membrane flux results. These two membranes showed a mixed trend when the HFFO flux output was compared to the FSFO flux results using 9 different fertilizers including NH_4Cl, $Ca(NO_3)_2$, $NaNO_3$, KNO_3, MAP, $(NH_4)_2SO_4$, KCl, DAP and urea as DS at 1 M concentration. Some of the DS fertilizers showed comparatively higher flux outcomes with the HFFO membrane while others showed a lower flux. Results show that with these two FO membranes, flux varied from -4% to 68% for the different fertilizer DS. Urea showed the highest increase followed by $NaNO_3$, KNO_3, MAP and $(NH_4)_2SO_4$. NH_4Cl, KCl and $Ca(NO_3)_2$ showed lower flux results with the HFFO membrane and the DAP nearly gave the same flux. Urea, $NaNO_3$, MAP, KNO_3 and $(NH_4)_2SO_4$ show that with HFFO, flux increased by 67%, 32%, 25% and 8% respectively whereas NH_4Cl, $Ca(NO_3)_2$ and KCl respectively showed flux decreases of 4.0, 3.0 and 2.0 % for HFFO. Flux for $(NH_4)_2HPO_4$ (DAP) nearly remained the same for both membranes.

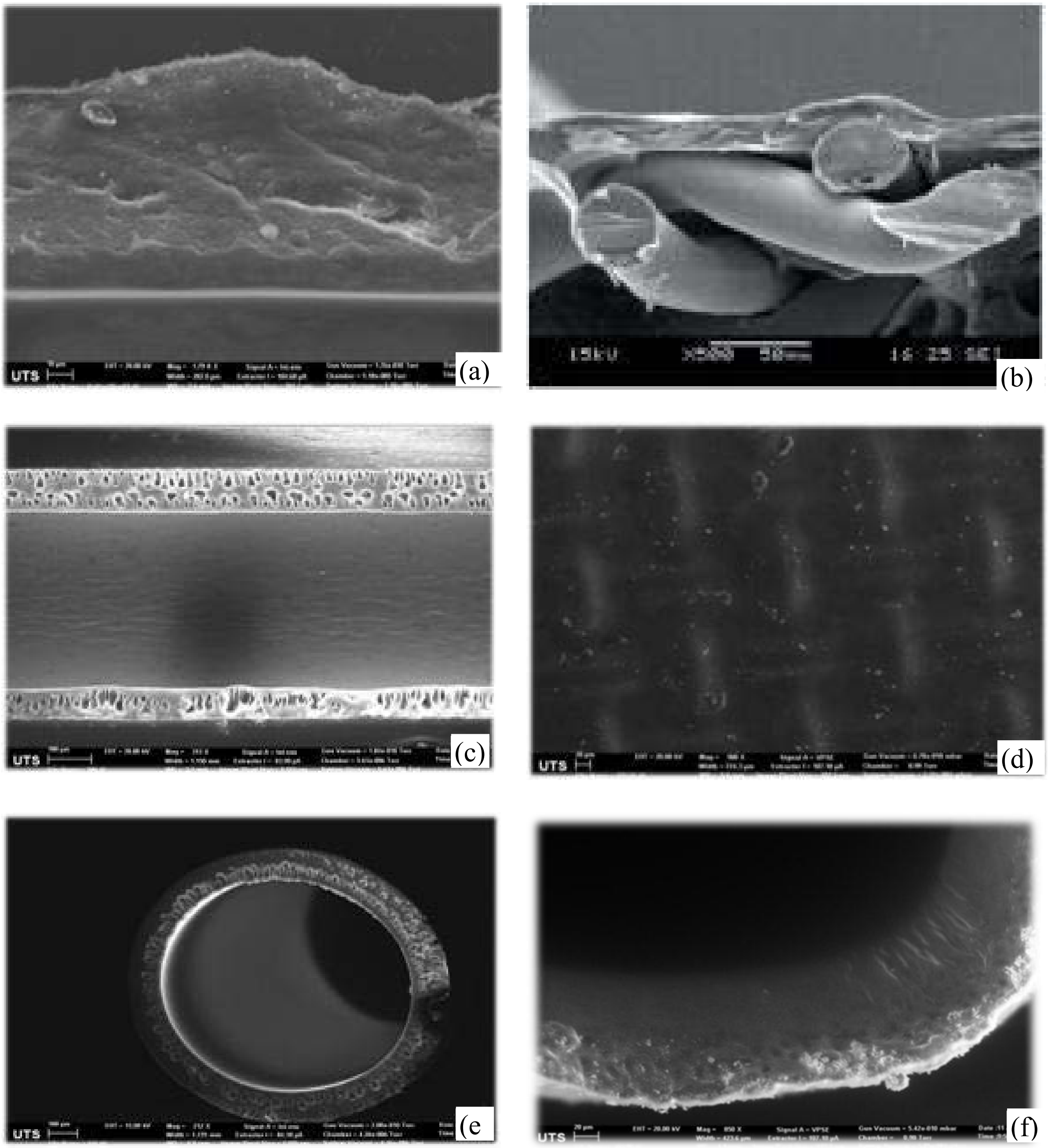

Fig 6.2. SEM images for both FO membranes used in our study. a) cross-section of HF FO membrane showing the inside active PA layer supported by outside PES layer b) FSFO membrane, with CTA active dense layer embedded on polyester mesh c) HFFO horizontally cut, larger view, d) FSFO active layer (top view) e & f) HFFO cross-section. * adapted from (Chung et al., 2012a)

Compared to the physical appearance of the active layer of these two membranes (Fig. 6.2 (a and d)), it is evident that the hollow fiber PA seems to be very porous as compared to a true dense flat sheet CTA membrane. The porous structure of the HFFO membrane apparently helped diffuse water molecules comparatively easily and faster through the PA membrane surface and thus it delivered a comparatively high flux output. From the general theory of permeation and osmosis, it may be concluded that as HFFO substrates seem highly porous with a narrow pore size distribution against a really dense CTA layer of the FSFO membrane, the latter might resist a speedy penetration of water molecules through the membrane active layer and thus deliver a comparatively low flux.

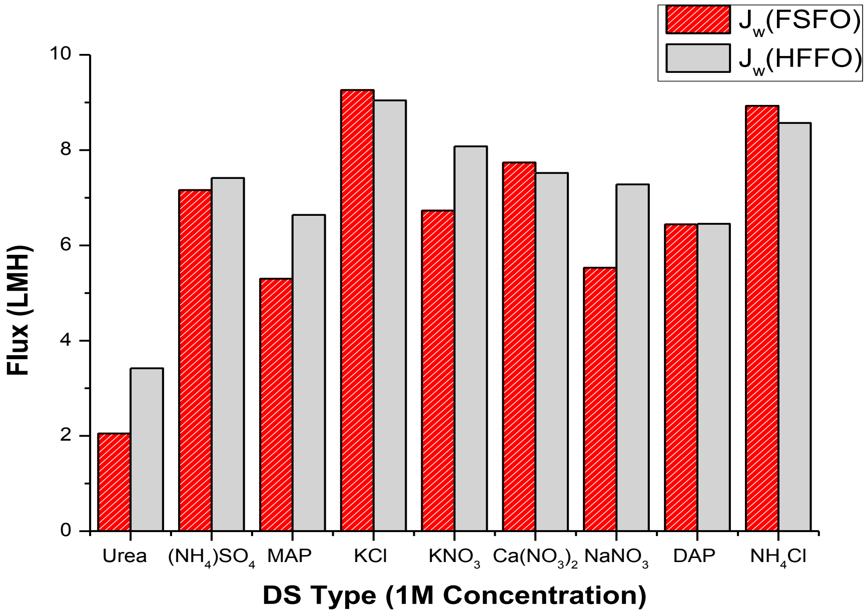

Fig. 6.3. Comparison of flux outcome for FSFO and HFFO membranes

Further, Fig. 6.3 results indicate that for these membranes, the flux variation with a particular DS is affected with the anion part of the DS solute. It was observed that most of nitrate based DS as $NaNO_3$ and KNO_3 gave a higher flux with the HFFO membrane and chloride based DS (NH_4Cl and KCl) provided a higher flux with the FSFO membranes. It is likely that smaller hydrated diameter species have more chance to diffuse through the membrane (Paugam et al., 2004, Kielland, 1937). As the NO_3^- and Cl^- anions carried the smallest hydrated radii size among all anions, they penetrated deep into the support layers of the HFFO and FSFO membranes SL to reach close to the their active layers. However, active layers of these membranes responded differently for DS carrying NO_3^- and Cl^- and delivered an inconsistent flux outcome. The HFFO and FSFO membranes showed varying flux outcomes for the NO_3^- and Cl^- based DS.

Moreover, the associated cationic part of the DS also significantly affects the FO flux for a particular DS. HFFO membrane gave high flux with a mono-valent cation based nitrate DS as $NaNO_3$ and KNO_3 whereas FSFO showed high flux with a di-valent cation based nitrate DS as $NaNO_3$. This indicates that the FO flux for a particular membrane is associated with both DS properties and membrane characteristics.

Dense CTA flat sheet membranes gave lower water flux outputs due to the increased CP phenomenon (Su et al., 2010). Interfacially polymerized TFC membranes on hydrophilic porous substrates show reduced ICP effects and they exhibit high water flux (Sivertsen et al., 2013). The hydrophilicity of porous substrates plays an important role on the TFC FO membranes. These fluctuations in the FO performance have consequences for similar DS and the operating conditions are attributed to the active rejection layer and support layer characteristics.

6.3.4 Reverse solute flux (RSF) evaluation and comparison

RSF of 8 DS fertilizers was evaluated for both the HFFO and FSFO membranes. RSF is an important performance parameter used to evaluate the effectiveness of the FO process as it represents the unwanted loss of valuable DS diffused through the FO membrane towards the feed solution, and it functions as a valuable fertilizer in the FDFO process. The difference of solute concentration in DS and FS on both sides of the membrane drives RSF.

Overall, RSF results indicate that in comparison to the FSFO membrane, HFFO performed extremely well for the RSF outcome for most of the fertilizer DS. Contrary to flux outcome comparisons, irregular behaviour was observed when RSF results of HFFO and FSFO membranes were evaluated and compared for different fertilizer DS (1 M concentrations). Most of the fertilizer DS showed very low RSF with HFFO (Fig. 6.4). $NH_4H_2PO_4$, KCl, KNO_3, KCl, NH_4Cl and MAP DS gave lower RSF values whereas $(NH_4)_2SO_4$ and $Ca(NO_3)_2$ delivered comparatively higher RSF values among these fertilizers.

The results in Fig. 6.4 were evaluated for RSF percentage variation for HFFO and FSFO membranes. The FSFO membrane showed relatively inferior results for RSF. Compared to HFFO, the FSFO membrane showed 1145%, 739%, 650%, 727%, 280% and 1058% higher RSF for $NH_4H_2PO_4$, KCl, KNO_3, $NaNO_3$, DAP and NH_4Cl DS respectively.

Further, NH_4Cl and KCl DS carrying monovalent cations and anions gave similar RSF for the FSFO and HFFO membrane whereas the other DS pair as KNO_3 and $NaNO_3$ also carrying monovalent cations and anions showed significant differences in the RSF outcome (Fig. 6.4). $Ca(NO_3)_2$ and $(NH_4)_2SO_4$ carrying a divalent cation and divalent anion showed less RSF with both membranes. Ca^{2+} thus shows less RSF as compared to Na^+ or K^+. HFFO membrane comparatively indicated the high RSF value for divalent cation and anion based DS such as $(NH_4)_2SO_4$ and $Ca(NO_3)_2$. Divalent cations and anions (Ca^{2+}, SO_4^{2-}) or trivalent anions (PO_4^{3}) have high hydrated radii, hence they exhibit low RSF.

FSFO showed better performance in terms of RSF for $(NH_4)_2SO_4$ and $Ca(NO_3)_2$ DS as it respectively showed 82% and 36% less RSF for these two DS. Low RSF demonstrated by FSFO membrane for divalent ionic compounds could be attributed to ion size exclusion and Donnan electrostatic effect FSFO (Wang et al., 2007, Yang et al., 2009a). Comparative data also proved that divalent cations or anions reduce or slow down the relative permeation of respective mono-valent cations and anions.

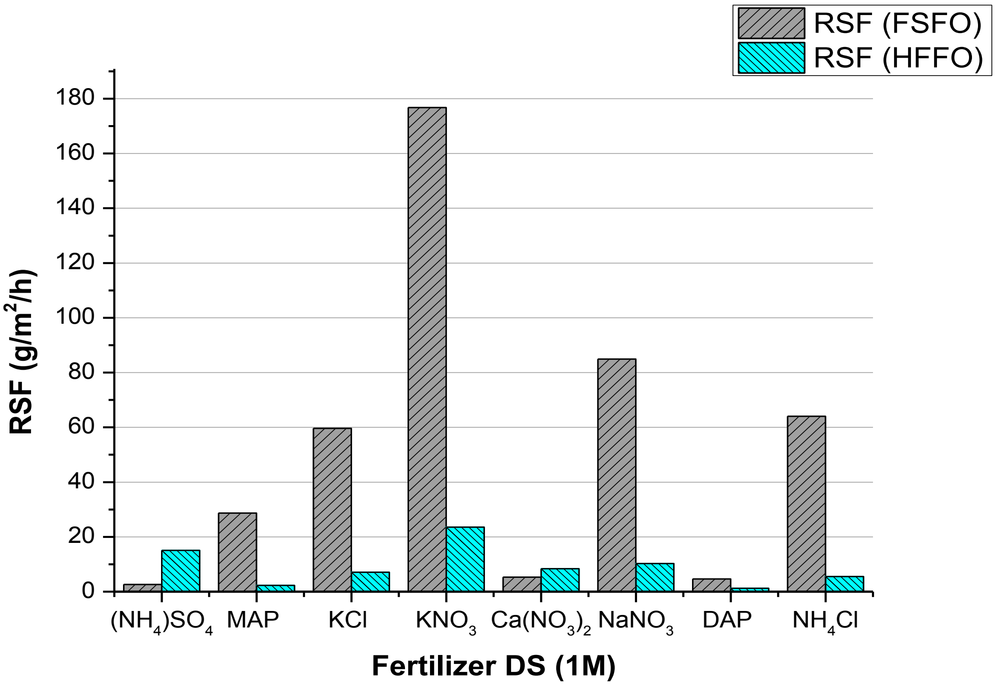

Fig. 6.4. RSF with HFFO and FSFO membranes for fertilizer DS

6.3.5 Flux and RSF behavior with hydrated radii

For water permeation (flux) or a salt diffusion (RSF) through a specific membrane, both the size

of the water molecule and the DS species matter are important. DS ionic size, solute structure and membrane pore shape play an important role in delivering any particular flux through the membrane. FO performance related parameters as flux and RSF have affinity between DS radii, water molecule size and membrane pore size. Ionic and dipole permeabilities are extremely sensitive to the ionic/dipolar radii (Volkov et al., 1997, Conway and Conway, 1981). Large molecules are retained at the membrane surface by electrostatic interactions whereas small, weakly charged ions can enter the pores. Anions hold their hydration shells relatively more strongly than the cations for a given charge density (Tansel et al., 2006).

Fig. 6.3 shows that HFFO membrane exhibited better flux outcomes for a particular DS carrying the same osmotic pressure. For many reasons, solute concentration alone is not sufficient to give good estimates of osmotic pressure (Robinson and Stokes, 1970). Osmotic pressure is not solely a function of the number of solute particles in solution, but it is also related to the solute size (Grattoni et al., 2007). Osmotic potential of organic solutions is largely a function of the size of their solute particles (Cochrane and Cochrane, 2007). Solutes influence osmotic potential by altering the molecular spacing of the free water molecules in solution and therefore different solutes differently influence the osmotic potential (Granik et al., 2002). This also authenticates a close relation between the hydrated radii and membrane pore size.

Results presented in Fig. 6.3 and 6.4 are further evaluated with different prevailing theories to further identify the main issues related to the difference in performance of these two membranes.

Both HFFO and FSFO membranes were asymmetric and permeable to both salt and water. Water flux and salt diffusion seem to be closely linked with each other. Results from Fig. 6.4 indicate the influence of interactions of some strange intermolecular and intramolecular forces which play an important role for the specific diffusion of different solutes through semi-permeable membranes. Characterising DS by their valancy, a comparison of the results in Fig. 6.4 shows that DS containing monovalent cations (NH_4^+, K^+) and anions (NO_3^-, Cl^-) exhibited better results with the HFFO CA membrane. DS containing either a divalent cation (Ca^{2+}) or divalent anion (SO_4^{2-}) exhibited better performance for RSF with the CTA flat sheet FO membrane. Low RSF for divalent cation and anion based DS showed that the CTA FSFO membrane behaves in a similar way to the NF membrane for divalent ions rejection properties. Inconsistent trends for RSF results may only be associated with the membrane active layer properties such as their surface charge, membrane pore size and pore geometry.

Fig. 6.4 indicates that RSF for monovalent cation based NO_3^- and Cl^- DS reduced significantly with the HFFO membrane. AL of HF membrane does not allow nitrates to diffuse through the PA active layer. In comparison to HFFO, FSFO membrane showed 650% and 727% higher RSF for KNO_3 and $NaNO_3$ respectively. Nitrate based DS exhibited high flux and lower RSF with HFFO (Fig 6.3 and 6.4). Furthermore, compared to FSFO, the HFFO membrane showed 739% and 1054% lower RSF for chloride based DS. However, chloride based DS showed higher flux for the FSFO membrane.

The results indicate that in comparison to CTA FSFO, the PA HFFO membrane carries smaller pores with unique configurations which reduce RSF through the membrane. These membrane pores do not allow even the smaller size Cl^- and NO_3^- ions to pass through the HF membrane. However, at the same time a high RSF value for divalent DS indicates that the membrane allows DS carrying large size divalent Ca^{2+} and SO_4^{2-} to move faster through the membrane. It confirms that only hydrated radii size does not direct flux or RSF for any membrane rather membrane properties are more vital for FO performance. Similarly the pore size of membrane AL may not suggest any particular flux or RSF outcome. The PA membrane showed better control of monovalent cationic or anionic DS whereas the CTA membrane showed better control of diffusion for the divalent cation or anion based DS.

In any FO process, RSF and water flux movement through the FO membrane goes in opposite directions (Elimelech and Bhattacharjee, 1998, Su et al., 2013). Water molecules in a high flux FO process push solute molecules backward and result in low RSF. Similar types of opposite forces affect osmosis and diffusion for all flux and RSF outcomes. Fig. 6.3 and 6.4

show that high FO flux outcome reduces RSF. RSF does not reduce linearly with the flux rise for all evaluated DS which indicates that flux rise itself affects the RSF outcome significantly. There is a paucity of data available in the literature which can exactly define the water and solutes molecules movement patterns through the membrane pores as NF, RO, and FO during any membrane filtration processes. Due to these unclear hidden issues, the effects of such a phenomenon are not yet incorporated to derive equations for FO flux and RSF.

It is impossible to have an ideal membrane of zero thickness (Tombs and Peacocke, 1974). All natural and synthetic membranes come with a finite thickness. Table 6.2 shows that the HFFO membrane comparatively carries a thick active layer and support layer. HFFO membrane exhibited the same thickness as he conventional RO membrane (Wei et al., 2011). Water molecules face more obstacles to cross thicker membranes. Higher flux with HFFO membrane indicated that the thin active layer of FSFO has a dense and non-porous membrane structure. Due to smooth pore geometry and structure, water molecules have better chances to move quickly through the micro porous HFFO membrane structure as shown in Fig. 6.2 (a).

Fouling development reduces water flux sharply as fouling makes the water diffusion passage through the membrane thick (Wang et al., 2010c). Fouling tends to increase the thickness of the membrane which hampers the flow of water molecules but flux reduction due to fouling and scaling is mainly attributed to pore blocking (Arkhangelsky et al., 2012). Membrane development work is focused to construct a thinner membrane, however, Fig. 6.3 results indicate that only the thickness of the specific membrane does not effect the FO flux notably. Instead, it highlights the role of other membrane characteristics as pore density, pore size, pore structure and pore depth which are not yet evaluated in detail. These parameters seem more cricitial and relevant than membrane thickness for the FO flux and RSF outcome. However, the influence of AL thickness on FO outcome is not ruled out completely.

CP reduces the net osmotic pressure available across the AL of the FO membrane (McCutcheon et al., 2005). In the FO process, CP increases as the thickness of the membrane or SL increases (McCutcheon et al., 2005, Tang et al., 2010b, Loeb et al., 1997, McGinnis and Elimelech, 2007, Achilli et al., 2009a). ICP effects can be reduced by using thinner and more porous support layers as they reduces mass transfer resistance (Li et al., 2011b). For most of the DS, the higher flux outcome (Fig. 6.3) by HFFO membrane is comprises of thick active and support layers (Table 6.2) which reveal that the thickness of the membrane may not be considered as the main parameter linked to CP. Instead, the AL and SL membrane material characteristics and DS properties together contribute to CP build-up in diverse ways.

Fig. 6.3 and 6.4 results indicate that for different DS, both the HFFO and FSFO membranes showed varying behaviours for the flux and RSF outcome. It is evident from these results that the differences in flux and RSF outcome are because of varying membrane properties and the DS characteristics. Different DS affects flux and RSF performance inconsistently for these membranes as for 1M KNO_3 DS, water flux increases whereas RSF decreases for HFFO membrane. Similar types of varying results were also noticed with other evaluated DS. DS properties seem directly linked with membrane structure, porosity, pore density, pore size, pore structure, solute affinity with water, AL and SL membrane surface charge, membrane thickness, water and solute flow patterns within membrane pores for any particular FO performance outcome. Further studies on these fundamental parameters are recommended to understand and predict any resultant FO flux or RSF outcome for a specific membrane.

6.4 Concluding remarks

- PA HFFO and CTA FSFO membranes were evaluated in this study for the FDFO process. A summary of the main findings appears below:
- The HFFO membrane comparatively gave up to 66% higher flux outcome for different fertilizer DS.
- HFFO membrane performed well for RSF as FSFO showed up to 1184% higher RSF values for fertilizer DS. Most of the DS showed lower RSF values with HFFO except DS having divalent cations or anions.
- FO flux and RSF outcomes for FO membranes are mainly associated with hydrated radii of anions associated with other cations of the DS. Most of the Cl^- based DS gave better flux outcome results with FSFO whereas NO_3^- based DS exhibited better flux results with HFFO. Divalent cationic or anionic parts of the DS significantly affected the RSF and flux results.
- The study confirms close links and associations between the DS properties and membrane characteristics for FO performance.
- A higher water flux and low RSF outcome for the HFFO membrane confirmed that the HFFO membrane is a better choice for the FDFO process.

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Chapter 7

INFLUENCE OF THE PROCESS PARAMETERS ON HOLLOW FIBER FORWARD OSMOSIS MEMBRANE PERFORMANCES

7.1 Introduction

Most of the earlier studies have indicated that the draw solution (DS) properties and membrane characteristics mainly affect the forward osmosis (FO) performances because they directly influence the transport of water molecules through the semipermeable membrane. Various earlier FO studies have shown low performance ratio (a ratio of actual water flux to the theoretical water flux) outcomes. These performances highlighted some serious issues in FO process which are closely linked with the suitable DS selection and FO membrane characteristics (Cornelissen et al., 2008, Costerton, 1999, Chung et al., 2012b, Vrijenhoek et al., 2001, Cath et al., 2006, Phuntsho et al., 2013b). A wide range of both inorganic and organic DS have been evaluated for FO process which indicated varied performance outcome in terms of water flux and reverse solute flux (RSF) (Liu et al., 2001, Jaffer, 1994, Contreras et al., 2009, Bowden et al., 2012, Zhao and Zou, 2011b).

Following Hydration Technology Innovations (HTI) work, which initially introduced a commercial flat sheet FO membrane which has been used in many FO research studies, few other also introduced new types of flat sheet membranes and used them for various applications (HTI, 2013, ModernWater, 2013, Statkraft, 2013, McGinnis et al., 2013). Most of the active layer (AL) of flat sheet membranes were initially prepared using cellulose acetate (CA) and cellulose tri acetate (CTA) followed by poly amide (PA) thin film composite (TFC) materials (Wang et al., 2012). Yip et al. (2010) reported a TFC- FO flat-sheet membrane using polysulphone support. For hollow fiber membranes, most of the attempts were made with PA while few also used CTA active layer.

Performances of the FO outcome were evaluated through improvement of the membrane AL properties (Vrijenhoek et al., 2001) while few others aimed their activities to improve FO outcome through support layer (SL) modification (Ghosh and Hoek, 2009b, McCutcheon and Elimelech, 2008, Widjojo et al., 2011, Tiraferri et al., 2011). These FO studies indicated lower performances results which were attributed to the concentration polarization (CP). It causes lowering of the net osmotic pressure gradient available for osmosis which results in lower permeate flux and low performance ratio during the FO process (Elimelech and Bhattacharjee, 1998, Gray et al., 2006, Zhao and Zou, 2011b). Internal concentration polarization (ICP) is considered as the most critical barrier in getting better performances for different FO.

On the whole, in comparison to flat sheet FO membrane outcomes, hollow fiber FO (HFFO) membranes mostly showed far better results for water flux (Wang et al., 2010b, Yang et al., 2009a, Chou et al., 2012, Su et al., 2010). To understand how the two important components of FO process i.e., characteristics of the FO membrane and properties of the DS collectively result a particular FO outcome, FO was earlier operated for the two main types of membranes, hollow fiber PA and flat sheet CTA FO membranes.

FO performances were evaluated under the same operating conditions for different fertilizer DS and summarized in Chapter 6. These results indicated fluctuating FO performances for water flux and RSF when different fertilizer DS were evaluated for these two membranes for a particular set of process conditions (temperature, crossflow rate and membrane orientation). The outcome indicated that for most of the fertilizer DS, PA HFFO membrane comparatively showed better result than CTA flatsheet FO membrane. However, these results were not at par with the research outcomes for HFFO membrane as referred above.

For FO, although the water transport phenomenon is primarily linked directly with the DS and feed solution (FS) properties and membrane characteristics, but few studies have indicated that it is also effected with the changes in operating parameters. Behaviour of both membrane and DS is affected with the changes in process conditions. These results change in osmotic movement of water molecules through membrane pores.

To get insight into the better membrane performances with the changes in process conditions, it is realized that it is important to understand how the water and solute molecules transport across AL and SL of the membrane is affected. Understanding of water transport mechanisms within the membrane and SL structure may provide solution to challenging flux, RSF and CP issues.

For these reasons, to enhance FO performances, along with the continued efforts to select a suitable DS and improve membrane characteristics, effect of various FO operating parameters such as temperature (You et al., 2012, Phuntsho et al., 2012e), flow direction , membrane orientation (Gray et al., 2006, Zhao et al., 2011, Parida and Ng, 2013), flow rate or velocity (Chung et al., 2012b, Jung et al., 2011, Gruber et al., 2011), viscosity (Cath et al., 2013b) has also been evaluated in some earlier studies and these results demonstrated the room for improving FO performances with the variations in the process conditions. These varying FO performances directed that along with the membrane characteristics and DS properties, specific operating conditions for FO process also exhibit very important roles in delivering improved performances with FO membranes which needs to be explored.

The purpose of this study is to further evaluate how some of the process parameters produce changes in performance outcome for FO process using a HFFO membrane. Parameters including membrane orientation draw solution properties, cross-flow directions and cross-flow rates were evaluated. The HFFO module performance was measured using water flux and RSF as the main indicators.

7.2 Experimental

The bench scale FO system, similar to one described in Chapter 6 was used to evaluate performance of HFFO membrane (Samsung Cheil Industries, Korea). Other membrane characteristics have been presented in earlier chapters. All experiments were conducted using 28 cm long HFFO membrane module carrying 50 fibers with a total membrane area of 396 cm^2(Majeed et al., 2013).

NaCl was used as a primary DS for most experiments while two other monovalent compounds such as KCl and NH_4Cl were also used for comparative studies (all chemicals were reagent grade supplied by Chem-Supply, Australia).

Since this investigation mainly involved comparative studies between each parameter so to avoid the interference of external concentration polarization on the FO performances, deionised water (DI) was used as a FS. Water flux was determined by recording the changes in the mass of the DS tank in unit time using a mass balance connected to PC for data logging.

HFFO operations were performed to assess the influence of three major parameters that affect its performances such as membrane orientation, crossflow directions, crossflow rates and the DS properties. HFFO flux performances were evaluated for different DS and FS crossflow arrangements. HFFO was operated under both co-current and counter-crossflow directions.

In the co-current flow arrangement, DS and FS enter and exit the FO module from the same sides with similar flow directions. In the counter-current flow arrangements however, DS and FS enter and exit the FO module from opposite ends of the module, thereby creating an opposite flow directions as shown in Fig. 7.1. Initially, the study is carried out using DS and FS flow rates were set at 1 L/min representing Reynolds number (Re) of 1300 and 500 respectively (laminar flows). Effects of crossflow directions were evaluated for FO operations under AL-FS membrane orientation.

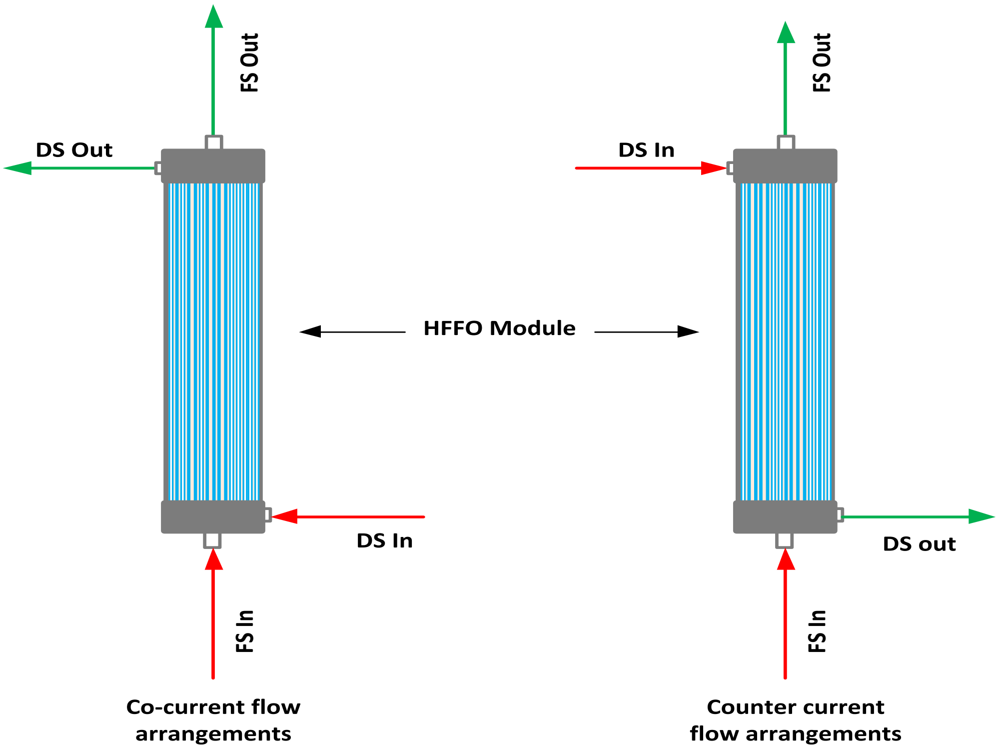


Fig. 7.1. HFFO membrane (in AL-FS orientation) module showing the DS and FS flow directions under the co-current and counter current arrangement for FO experiments

FO was operated for both active layer facing FS (AL-FS) and active layer –draw solution (AL-DS) membrane orientation. Water flux was evaluated from the weight difference evaluated using a weighing balance connected to a computer which measures loss of weight of the FS tank. RSF was measured by recording the change in the electrical conductivity of the FS using HACH conductivity meter (model H270G-BNDL).

FO was further evaluated for varying crossflow rate arrangements representing Re changes for lumen side flow of 100 to 3750 and shell side flow of 300 to 1800. This showed that lumen side was evaluated for both laminar and transition flow zones whereas shell side was operated under laminar flow zone only. For various experiments, lumen and shell sides carried either DS or FS based on FO operation at either AL-FS or AL-DS orientation.

7.3 Results and discussion

7.3.1 Effect of crossflow direction on FO performance

Fig. 7.2 compares flux outcomes under co-current and counter current crossflow directions. FO membrane showed only slightly higher flux under counter-current flow arrangements than the co-current crossflow direction. Jung et al. (Jung et al., 2011) also showed that crossflow direction slightly effected FO flux performance for a flat sheet FO membrane along its module length. It is likely because the net driving force is higher at the DS inlet than at the outlet point of the FO module under the counter-current arrangement. Although the initial water flux under counter-current crossflow mode is slightly higher than co-current crossflow arrangement, however, it was noticed that after a longer run of about 185 minutes, both set of flow arrangements nearly showed similar water flux.

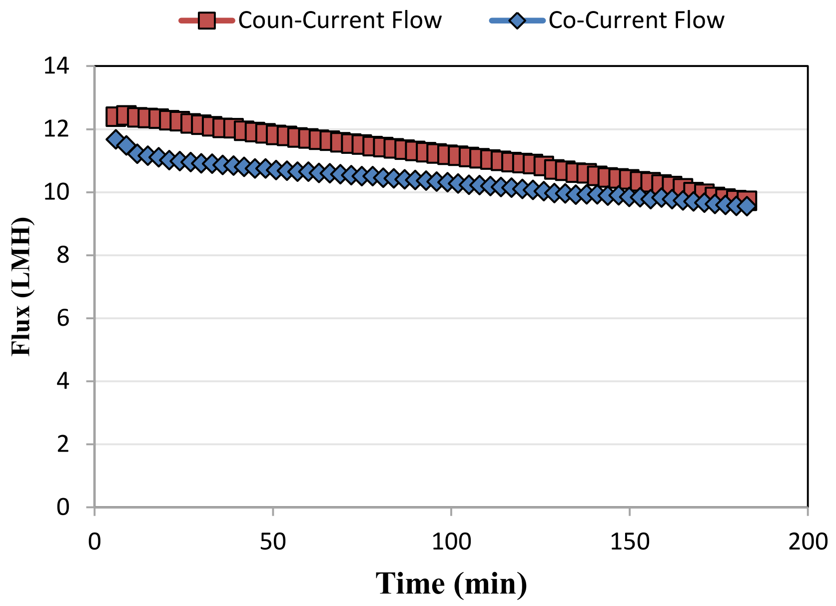


Fig. 7.2. FO performance in terms of water flux under different crossflow directions. Other operating conditions include AL-FS membrane orientation, DS: 2M NaCl, FS: DI, Re for DS: 1300, Re for FS: 500.

7.3.2 Effect of membrane orientation on FO performance

Fig. 7.3 displays water flux outcome when HFFO membrane module was operated under two different membrane orientations i.e., AL-FS and AL-DS. Under the AL-FS mode, PA rejection layer was facing FS whereas for AL-DS mode, membrane PA active layer was facing DS. FO was operated using different DS concentrations (1M, 2M and 3M NaCl) against DI water as FS. Crossflow rate showed Re 500 and 1300 for lumen and shell side respectively. FO results indicated a significant increase in flux outcome under the AL-DS membrane orientation. Compared to AL-FS mode, HFFO membrane under AL-DS mode delivered up to 202%, 293% and 340% higher flux for 1M, 2M and 3M NaCl DS respectively.

Water flux did not vary significantly under the AL-FS orientation for changes in DS concentration as it only showed an increase of 8% in FO flux when DS concentration was changed from 1M to 3M. However, under the AL-DS mode, the flux was increased by 82% when the DS concentration for the similar changes in DS concentrations. By increasing DS concentration, the flux showed more under AL-DS than AL-FS membrane orientation although this increase was not linear at higher DS concentrations. These differences in flux between AL-DS and AL-FS membrane orientation reveal that under the AL-FS orientation, ICP builds quickly in the membrane SL, reduces the available osmotic pressure difference at the membrane interface thus reducing the water flux (Gao et al., 2013, Song et al., 2011, Gray et al., 2006, Tang et al., 2010b). Chou et al. (Chou et al., 2010) further revealed that compared to flat sheet FO, HFFO membrane takes little more time to build-up salt concentration within the substrate and to develop steady ICP. HF membrane flux, therefore, declines sharply at the initial stages of the test run. When a steady ICP is developed in the substrate, HFFO membrane then starts showing steady flux with a gradual flux decline.

Under the AL-DS membrane orientation, water flux declines distinctly initially and then the decline become gradual. This sharp flux drop does not follow the usual flux decline pattern observed with the flat sheet FO experiments (Zhao and Zou, 2011b, Gray et al., 2006, McCutcheon et al., 2006, Mi and Elimelech, 2008). No such sharp decline was also observed with the HF under the AL-FS orientation (Fig. 7.2). This sharp flux decline could be due to two possible reasons. Firstly, as the membrane used in these experiments had much higher area (0.04 m^2), about 20 times higher than the membrane areas used in most of the flat sheet FO studies, more volume of the water was permeated in unit time which quickly diluted the DS and caused a rapid reduction in the osmotic pressure difference and ultimately resulted sharp flux decline. Later, as the flux decreased with time, the rate of DS dilution also slowed down hence the flux declines gradually slowed in the later stages of these experiments

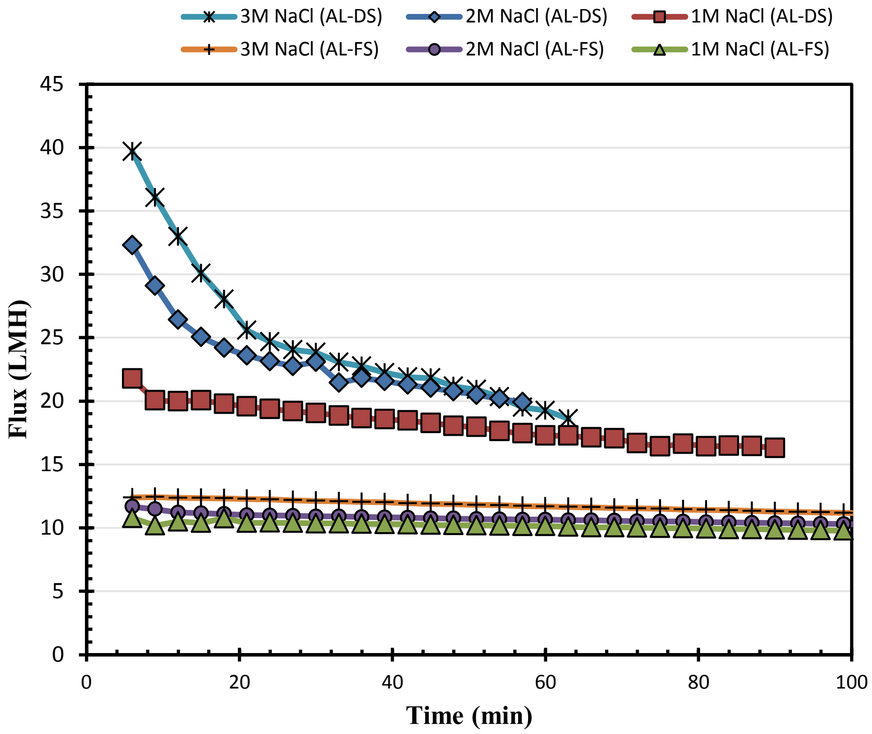
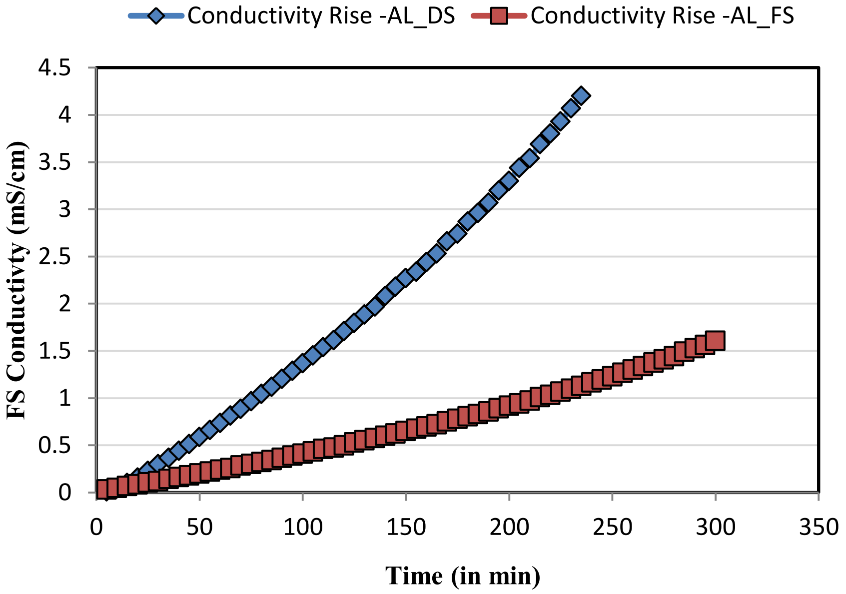


Fig. 7.3. Effect of draw solution concentration and membrane orientation on flux outcome, DI water is used as FS whereas for varying experiments, DS was used in 1-3M NaCl, DS and FS showed Re (AL-FS) of 1300 and 500 and for Re (AL-DS) of 500 and 1300 respectively.

7.3.3 Effect of membrane orientation on reverse solute flux

RSF for two types of membrane orientations was evaluated for 1M NaCl as DS and DI water as FS. These experiments were carried out for crossflow rate representing Re 500 and 1300 for lumen and shell side respectively. FS conductivity was regularly monitored using a bench scale conductivity meter which recorded FS conductivity after a fixed time intervals. Fig. 7.4(a) shows FS conductivity rise due to RSF for two types of membrane orientations. It was observed that in comparison to FO operation at AL-FS orientation, conductivity of the FS rises more quickly in AL-DS orientation and HF membrane showed high reverse salt passage in AL-DS orientation. RSF for HF membrane was observed as 3.6 and 8.88 g/m^2/h for AL-FS and AL-DS orientation respectively (Fig 7.4(b)). Compared to AL-FS, under the AL-DS mode, higher concentration difference between the DS and FS at the AL interface resulted higher RSF (Phillip et al., 2010). On the other hand, under the AL-DS mode, HFFO also showed higher water flux (Fig. 7.3). Due to the high RSF, salt concentration in the FS increased rapidly and caused lowering of the net osmotic pressure which quickly decreases flux with time in AL-DS membrane orientation (Majeed et al., 2014).

In the FO process, water permeation and reverse salt diffusion take place simultaneously but in opposite directions. Water molecules move from FS side to DS side whereas draw solute movement is from DS side to FS side. It might appear that due to this opposite flow directions of water and solutes, water flux and RSF movement should apparently influence each other, probably resist other movement stream and cause slowing down of their movement. Earlier studies have indicated that the increase in DS concentration simultaneously increases flux and RSF for FO process (Achilli et al., 2010). This study also shows similar trends and it was observed that RSF increases as the water flux increases in AL-DS orientation. These indicate that water flux and RSF uses different pores and routes for their flow, independent of each other, hence rising flow of one stream don't effect the other. For this reason, HFFO gives simultaneous rise to both flux and RSF for AL-DS membrane orientation.



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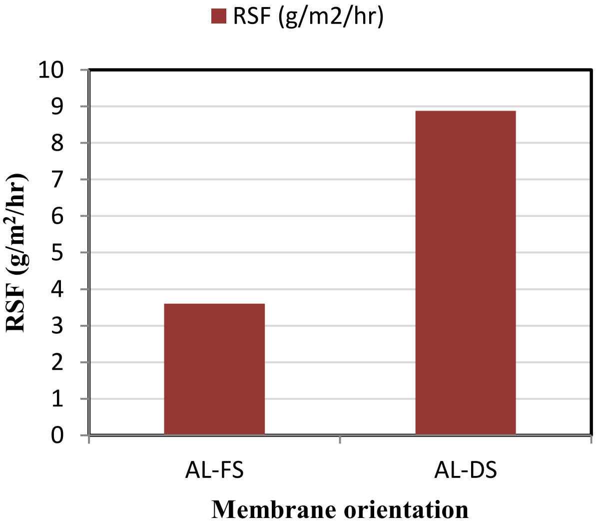


b)

Fig. 7.4. a) Effect of membrane orientation on FS conductivity rise b) Effect of membrane orientation of RSF, DS : 1M NaCl and FS :DI water,

7.3.4 Performance of HFFO membrane in terms of specific reverse solute flux (SRSF)

SRSF was evaluated for 3M NaCl DS under both the AL-FS and AL-DS membrane orientation and the results were compared with the earlier published work (Fig. 7.5). DI water was used as FS for these evaluations and FO was operated for lumen and shell side Re of 500 and 1300 respectively. SRSF is the ratio of RSF to water flux, which indicates the quantity of draw solutes lost by reverse diffusion per unit volume of water extracted from the FS (Hancock and Cath, 2009). Although some of the other's work was evaluated at varying operating conditions using different DS concentrations, the comparison indicate that operating conditions play an important role for SRSF. Compared to available results with lower DS concentration (0.5M NaCl), FO showed lowest value for SRSF for 3M NaCl DS beside the fact that FO delivers higher RSF at high DS concentrations (Tiraferri et al., 2013, Achilli et al., 2010). The comparison shows that with some adjustments in the FO process conditions, HFFO membrane could show the lowest SRSF even when operated at higher DS concentration for both AL-FS and AL-DS membrane orientation.

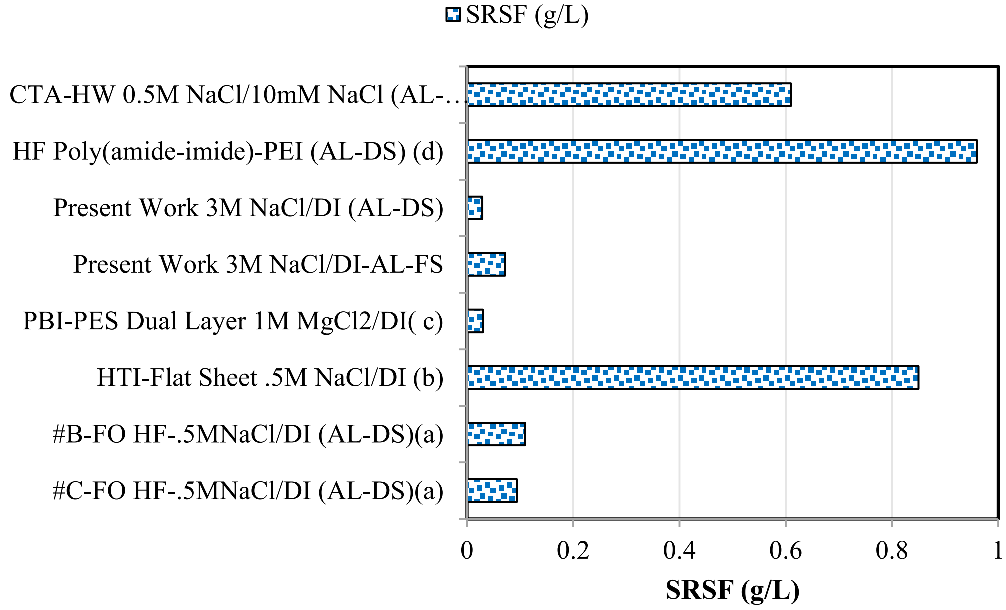


Fig. 7.5. Comparison of the SRSF outcome (present work with the literature data) (a)(Chou et al., 2010), (b)(Tang et al., 2010b), (c)(Yang et al., 2009a), (d)(Setiawan et al., 2011), (e)(Wei et al., 2011)

7.3.5 Effect of DS type on FO performance

Three different types of draw solutes (NaCl, NH_4Cl and KCl) were used to evaluate effect of various DS carrying common anion but different cations on the water flux and the RSF. The results indicate the combined effects of DS properties and the AL and SL characteristics on the water flux and the RSF outcome. Fig. 7.6 shows flux and RSF outcome for HFFO using 1M NaCl, NH_4Cl and KCl as DS and with DI water FS. It shows that for these DS, the water flux and the RSF increase when the membrane orientation was changed from AL-FS to AL-DS. Flux did not change significantly under the AL-FS membrane orientation. Amongst the three DS, KCl showed comparatively highest water flux under the AL-DS orientation.

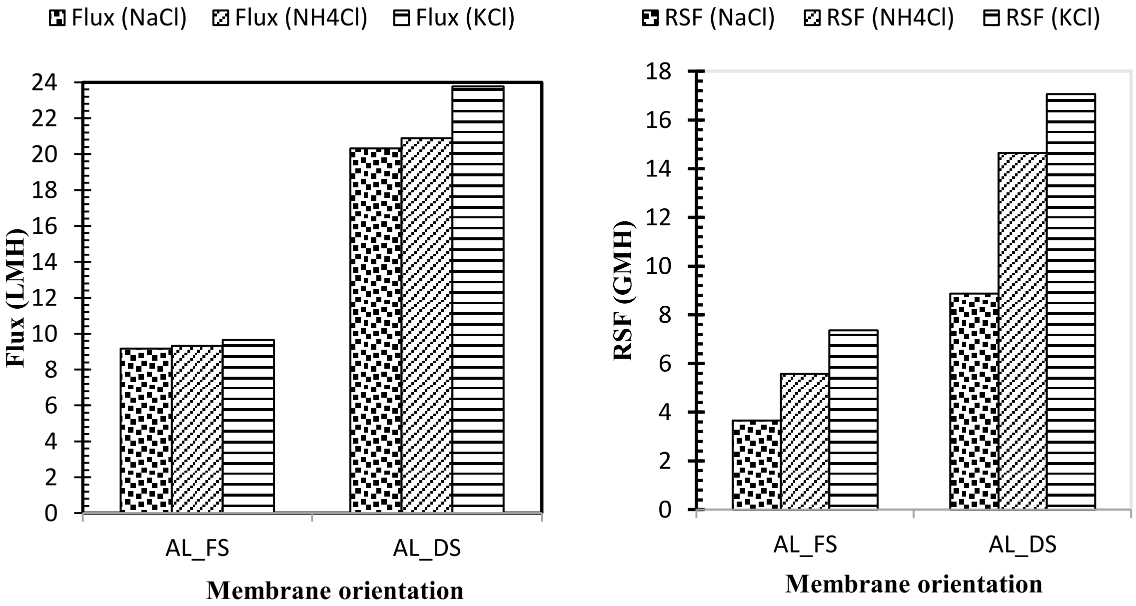


Fig. 7.6. FO performances using three DS carrying same anionic part (Cl^-). a) Flux b) RSF. NaCl, NH_4Cl and KCl DS were used in 1M concentration, DI water was used as feed.

The three DS also showed markedly difference in terms of RSF under both AL-FS and AL-DS orientation. Salt transport through the membrane is influenced by ionic/hydrated radii, charge and size (Schaep et al., 1998). For RSF, Na^+ with higher hydrated radii showed lower RSF than K^+ and NH_4^+. K^+ and NH_4^+, besides having similarly close hydrated radii, showed fluctuating RSF under both membrane orientation and these results indicate that hydrated radii alone may not influence the RSF in the FO process. These results indicate that for FO process using PA membrane, anionic properties of the DS play an important role for the water flux outcome whereas RSF is largely effected by the properties of the cationic part of the DS.

Similar outcomes for various DS carrying similar cation and anion groups have already been reported elsewhere but they were not evaluated for the role of their cationic and anionic parts (Chekli et al., 2012, Achilli et al., 2010). Properties of the cationic and anionic hydrated radii affect the isoelectric point of both membrane surface and these radii radicals which changes membrane surface to form a double layer (Childress and Elimelech, 1996). Varying effects for these DS further indicate that similar undisclosed properties of the membranes and DS are used for the transport of water and solute molecules. The DS properties, such as the ionic size of the cationic part mostly effect the diffusion resistivity to diffusion with the support layer (Achilli et al., 2010).

7.3.6 Effect of crossflow rate on the HFFO performance

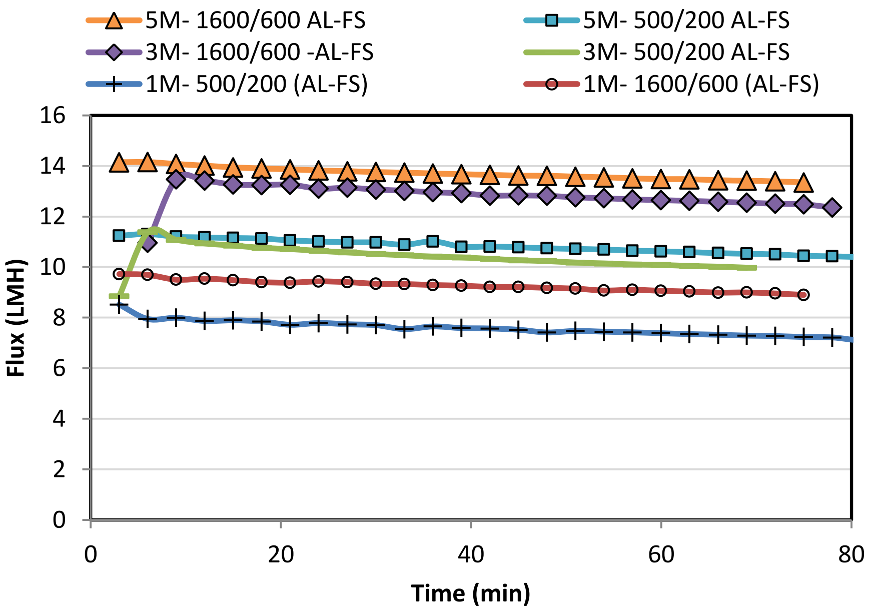
FO was operated under varying FS and DS crossflow rates to evaluate effects of flow velocity or the Reynolds number (Re). These experiments were carried out under both AL-FS and AL-DS membrane orientations. DS concentration was varied from 1M to 5 M NaCl whereas DI water was used as FS throughout. Two crossflow rates representing Re 200/500 and 600/1600 were selected for the tests. First number of the fraction represents the Re for DS and the other represents Re for the FS.

Fig. 7.7 presents the influence of flow rates on the water flux outcome for HFFO membrane. The results indicate better flux outcome when Re was changed from 200/500 to 600/1600 under both AL-FS and AL-DS membrane orientations. Under the AL-FS membrane orientation, the water flux increased by 22%, 18.46% and 28.8% for 1M, 3M and 5M DS concentrations, respectively as shown in Fig. 7.7(a). Similarly, under AL-DS, HFFO membrane showed 37.56%, 31.71% and 17.98% higher flux for 1M, 3M and 5M DS concentration for the above set of Re values (Fig. 7.7(b)).

FO was further evaluated to find which of the solutions DS or FS flow rate has greater impact on water flux. Experiment was started with a specific set of initial flow rates and after short test run, the flow rate of either FS or DS was changed to reflect a new set of Re values for that stream. After short test run at revised Re, both DS and FS flow rates were restored to the initial values. Fig. 7.8 shows flux outcome when HFFO membrane was initially operated at the Re of 600/1600 using 1M NaCl as DS and DI as FS. After about 20 minutes, FS flow rate was reduced to reflect Re. no. of 650 while still maintaining the same Re for DS. It was observed that reducing the FS flow rate only, the water flux decreased sharply. Overall about 60% of the flux decline was observed by reducing FS Re from 1600 to 650. After 20 minutes when the flow rate of FS was again increased to restore to its initial Re, the water flux was restored back to its normal rate.

HFFO membrane was further evaluated using 3M NaCl as DS and DI as FS. FO test was initially started at Re pair of 600/1600. Contrary to the earlier experiment, this time the flow rate of the DS was reduced to represent a lower Re of 250 while FS flow rate was kept same to maintain the uniform Re for FS and the result is displayed in Fig. 7.8. It was noticed that by reducing the DS flow rate, FO flux increased quickly by 8%. However, after 20 minutes when the flow rate was reduced to its initial value, the water flux reduced by 20.2% and followed the initial slope of the line. The results indicate that the HFFO membrane comparatively gives high flux outcome when DS flow rate is reduced. On the other hand, the resultant flux decreases when the FS flow rate is lowered.

To confirm this, FO was further evaluated for 3M NaCl DS at comparatively lower Re pair 250/650 and the water flux outcome was compared with the earlier results (Fig. 7.8). Jung et al (Jung et al., 2011) emphasized the role of flow rate affecting the mass transfer within the external CP layer to optimize FO operations in terms of energy consumption and production recovery. It was noticed that 1M NaCl DS at higher Re pair 600/1600 showed better flux outcome than the 3M NaCl DS at lower Re pair 250/650. These results are important as most of the earlier studies observed that the flux did not vary noticeably by changing DS and FS flow rates using flat sheet FO membranes (Widjojo et al., 2011, Jung et al., 2011, Widjojo et al., 2013, Chou et al., 2012, Wang et al., 2010b). This suggests that the changes in the crossflow rate bring various appropriate modifications in the HFFO membrane pore structures which results improved performances for FO processes. The hydrodynamic conditions leave very little positive influence on the flat sheet FO membrane which may effects the FO flux outcome.



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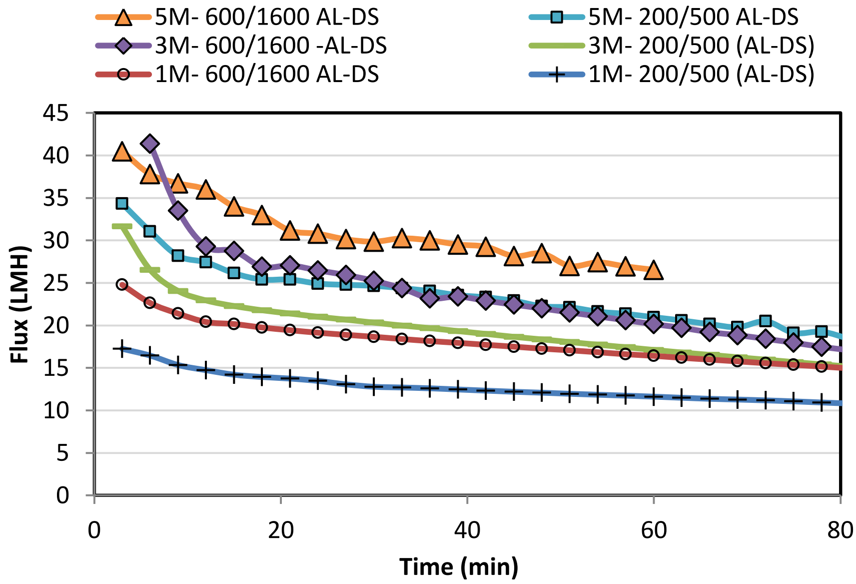

b)

Fig. 7.7. Effect of changing DS/FS crossflow rate on HFFO membrane water flux. a) AL-FS orientation, and b) AL-DS orientation, 1M , 3M and 5M NaCl DS were evaluated DI water FS. Fraction in legends shows Re for DS and FS respectively. For legends, the first term of the fraction represents Re for DS and other Re for FS.

Following the results from Figures 7.7 and 7.8, FO was further operated under AL-DS membrane orientation by varying DS/FS Re pair and results are summarized in Fig. 7.9. It was found that HFFO gave better result at DS/FS Re values of 200/1600 for both 1M and 3M

DS. It was also noticed that the water flux increases with the decrease in ratio of DS/FS Re pair. Fig. 7.9(a) shows that for 1M NaCl DS, flux is increased by 41% whereas Fig. 7.9(b) shows that for 3M NaCl DS, flux increases by 37% when the DS/FS Re pair was increased from 200/500 to 200/1600, which reflect reduction of DS/FS Re pair ratio from 0.4 to 0.125.

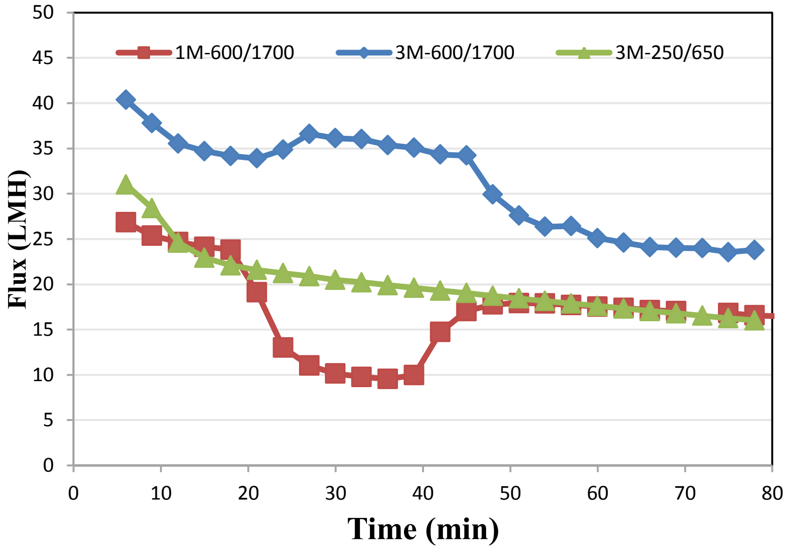

Fig. 7.8. Effect of changing crossflow rate of only one stream (either DS or FS) on FO flux. These tests were performed at AL-DS membrane orientation. 1M and 3M NaCl DS were used with DI water FS.

SEM images of the outer layer of polyamide AL have indicated that it carry a typical ridge valley structure (Ghosh and Hoek, 2009b, Wei et al., 2011). The PA membrane surface shows irregular top surface with non-uniform pore geometry (Fig. 7.10). From the fluctuating flux results for HFFO under AL-DS orientation at different DS/FS Re pairs, we deduce that each DS/FS Re pair develops some pressure or stresses on the polyamide AL of the hollow fiber membrane. These probably results in stretching of the polymeric membrane that could modify the membrane pores ultimately affecting the water flux outcome. We suggest that the variation in the crossflow rates bring similar nature of changes in the membrane structure which are developed during the cross linkage of polymer structure which enhance flux outcome. Higher cross linkage make the membrane surface more hydrophilic, more smoother and compact which enhances membrane performances (Feng et al., 2014). Irregular shaped pores are changed to uniform size pores which allow water molecules easily pass through the membrane and thus high fluxes are obtained. We conclude that with the new pore shape arrangements, the pore structures also becomes align with each other, symmetrical throughout the membrane that facilitate quick movements of water molecules which results higher flux outcome.

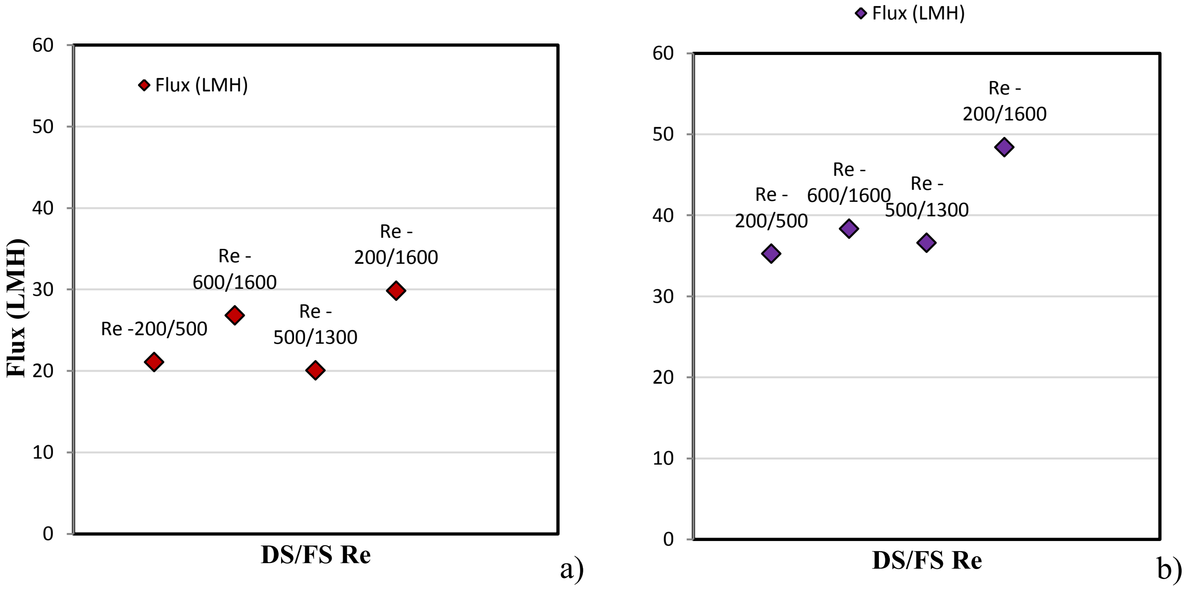

Fig. 7.9. Effect of changing DS and FS flow rates on FO flux performance with a) 1M NaCl DS b) 3M NaCl DS, DI water was used as feed. Flux was evaluated at AL-DS membrane orientation.

Membrane forms a boundary layer with liquids streams in contact with and these boundary layers on either side of the FO membrane induce significant resistance for water permeation and salt diffusion. The transport resistance of this boundary layer may be a function of many factors such as shape of the interface, wettability of the surface to the liquid, hydrophobicity or hydrophilicity, velocity of the liquid at the interface (Yasuda and Lamaze, 1972). Boundary layer resistance is hardly affected within the support layer. The water molecules penetrating into the pores of the membrane and its support layer are barely affected by stirring of the bulk water or turbulence due to water flow. Therefore, in AL-DS mode, dilutive CP is not affected much with crossflow effects. Resultant flux changes are mostly linked to the changes in the properties of the inner and outer layers of the membrane AL.

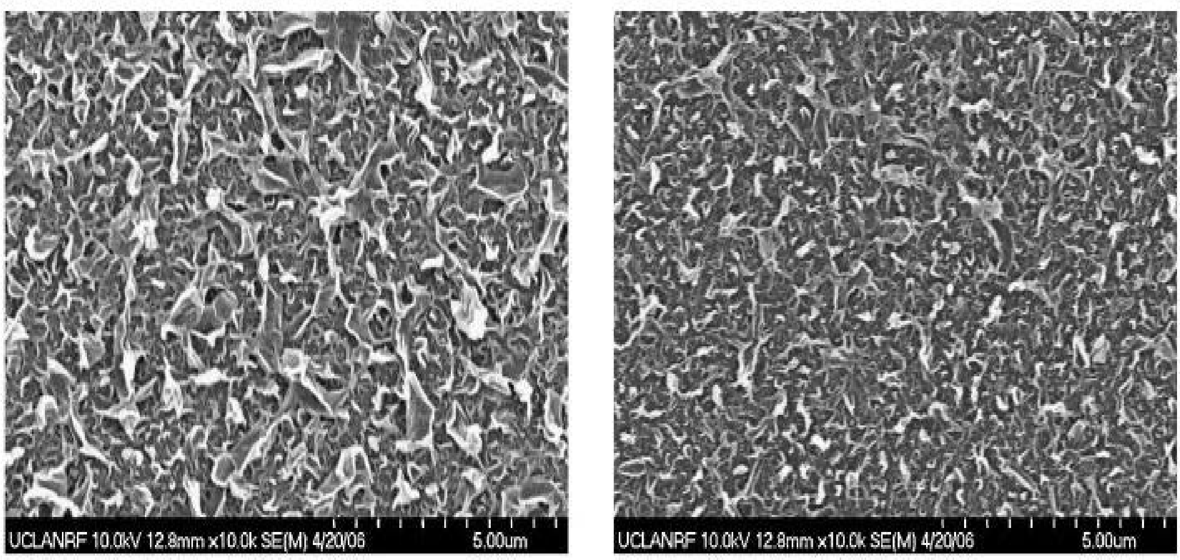

Fig. 7.10. SEM images of polyamide membrane active layer- showing irregular shape of top surface (Adapted from (Ghosh and Hoek, 2009b))

By repeating these experiments at varying DS FS flow rates, it was observed that at there is a particular set of DS and FS flow rate values which help getting highest flux through the FO membrane. Other higher or lower DS and FS flow rates showed comparatively lower flux. From this we may deduce that membrane pores, being made of an elastomeric properties material, change shapes with pressure and flow and at some specific values of these process parameters, they form good arrangement of the pore shapes which facilitates both water and solute flux. By changing operating parameters from these optimum values, the pores again changes back to their disordered structure and which don’t show the same enhanced performance. This further confirms the importance of interfacial polymerization (IP) process of the membrane making step where the polymeric material develops various pore sizes, structures and arrangements of the membrane pores.

7.3.7 Combined effects of process conditions

FO membrane was further evaluated at various other DS and FS flow rates. FO membrane flux outcome for 2M NaCl DS against DI water FS was evaluated for two different operating conditions i.e., for Re. no 200/500 at AL-FS membrane orientation and Re. no 3750/1500 at AL-DS membrane orientation and results are presented in Fig. 7.11. FO membrane in AL-DS orientation showed remarkably high flux of 62.9 LMH when operated at Re 3750/1500. It indicates a flux increase of about 511% for a set of two operating conditions for the same FO membrane. Along with the effect of operating conditions on CP development phenomena, for a better flux outcome, they also help transform membrane pore structure, facilitate DS come closer to membrane, reduce the boundary layer effects and expedite water molecule transport through the membrane AL and SL pores. The variation in these FO flux performances is reflected mainly due to the changes in the membrane characteristics.

7.4 Concluding remarks

HFFO membrane was evaluated to assess the effects of some of the operating conditions in terms of water flux and reverse solute flux. Parameters including membrane orientation, DS properties, cross-flow directions and cross-flow rates were evaluated. It was observed that operating parameters significantly affect the performance of the FO process. Main findings are summarized as follows:

- Properties of the anionic part of the DS were found important for flux outcome whereas RSF was largely influenced by the properties of DS cationic part.
- Results indicated that by adjusting FO processes conditions, HFFO membrane achieve significantly lower specific RSF and higher water flux outcome.

- FO operation at varying DS and FS Re ratio showed better flux outcome as Re ratio for DS and FS decreases and vice versa.
- FO operation under the AL-DS orientation at varying DS and FS crossflow rates markedly showed enhanced performance outcome. It was observed that using 2M NaCl as DS and DI water as FS, HFFO successfully delivered water flux of 62.9 LMH at DS/FS Re of 3750/1500.

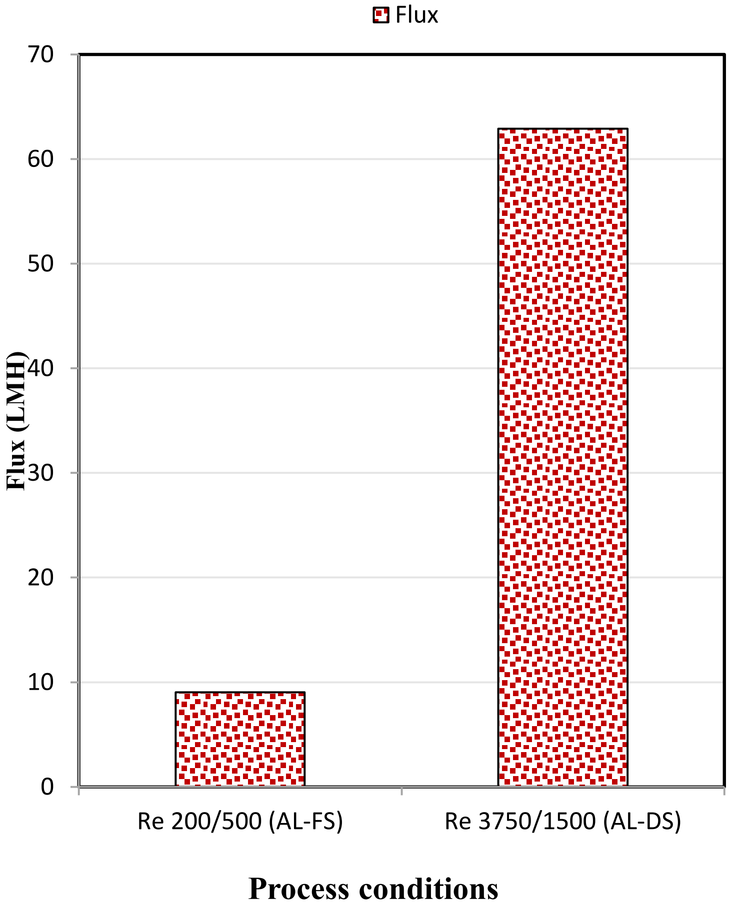

Fig. 7.11. Flux outcome showing effect of operating conditions for the same membrane. Condition Set # 1 (AL-FS orientation, DS Re 200, FS Re 500), Condition set # 2 (AL-DS orientation, DS Re 3750, FS Re 1500), DS: 2M NaCL and FS: DI water.

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Chapter 8

COMBINED EFFECTS OF SCALING AND FOULING FOR HOLLOW FIBER FORWARD OSMOSIS MEMBRANE

8.1 Introduction

Fouling is always considered as a serious operational issue for all membrane based systems as it directly affects the operating cost of water treatment. As the forward osmosis (FO) process has now gone through early lab scale development and is being evaluated for tougher real life applications, FO fouling studies are considered important to help evaluate the risk associated with commercial operations of the FO system. Fouling directly effects the operational costs in terms of downtime, cleaning chemical costs, labour requirements, production loss and frequent and quick membrane replacements (Peng et al., 2004b, Peng et al., 2004a). For these issues, fouling studies, fouling mitigation measures and cleaning strategies are imperative focuses for the researcher's activities.

Various studies have been published earlier which evaluated the FO fouling potential for various types of FO membranes and different feed solution (FS) and draw solution (DS) combinations (Cornelissen et al., 2008, Mi and Elimelech, 2008, Achilli et al., 2009b, Mi and Elimelech, 2010b, Gu et al., 2013). In the few initial studies on FO fouling, the severity of the fouling mechanism for FO membranes was found not so intensive. FO, being a process governed by the osmotic pressure gradient, has been hypothesized to have a lower fouling propensity than other pressure driven membrane processes as reverse osmosis (RO)/nano-filtration (NF) (Lay et al., 2010). Me et al. (2010b) evaluated FO fouling potential with alginate and found that FO fouling is fully reversible with simple rinsing and without the use of any cleaning reagents. Fouling reversibility in FO was attributed to the less compact organic fouling layer formed in the FO mode due to the lack of hydraulic pressure.

Tang et al. (2010b) evaluated that the flux loss in active layer-feed solution (AL-FS) orientation was likely due to the combined effects of the internal clogging of the FO support structure as well as the resulting enhanced internal concentration polarization (CP) in the support layer which was mainly caused by reduced porosity and the reduced mass transfer coefficient in the SL. FO was also tested in AL-DS orientation as this is used to harvest salinity gradient power. Yip and Elimelech (Xu et al., 2010a) evaluated the effect of the organic foulants on FO fouling in the active layer–draw solution (AL-DS) orientation and noticed that osmotic backwash partially helps to restore FO flux (Xu et al., 2010a).

Comparing the fouling evaluation studies for different membranes such as ultrafiltration (UF), microfiltration (MF), NF and RO with FO work, it is apparent that a large difference exists between FO and other membrane system operations and their approach towards these fouling processes. Up to now, all FO fouling studies were carried out in a similar manner to RO/NF/UF fouling studies where performance of these systems was compared with the baseline outcome and any deviation in their flux performance was referred to fouling effects. For performance comparison and fouling evaluation, RO/NF/UF is operated for a fixed driving force (hydraulic pressure). Thus, comparisons of the resultant flux trend with the baseline outcome easily figured out any performance variations which clearly indicated the resultant fouling effect on the membrane performance. Permeate flux and trans-membrane pressure are the best indicators of membrane fouling for RO/NF/UF applications but may not be used well for FO studies.

However, the FO process differs from other membrane based processes in many ways, mainly in the existence of a constant driving force. Unlike RO or NF, it is very difficult to operate FO at a fixed driving force. For FO, at any particular point, continuously changing driving force (varying FS and DS concentrations) with their simultaneous effects on the CP make it really hard to operate two FO processes at the same driving force. As at any fixed time, the FO does not show the same driving force for any two flux data curves, it is difficult to identify the portion of flux change affected actually by fouling. It is noticed that this main concept was ignored for the earlier FO studies which are completed without taking this important issue into account and this makes comparison of these flux performances for FO fouling meaningless (Fig. 8.1).

For a particular FO application, the FO membrane can be used in both orientations as AL-FS and AL-DS. Additionally, as FO manages the simultaneous flow of two different solutions as FS and DS on either side of the membrane it carries varying fouling risks for different sides of the membrane. FS coming from various sources may carry different unwanted impurities which pose severe threats for fouling development on the FO membrane surface. However, as

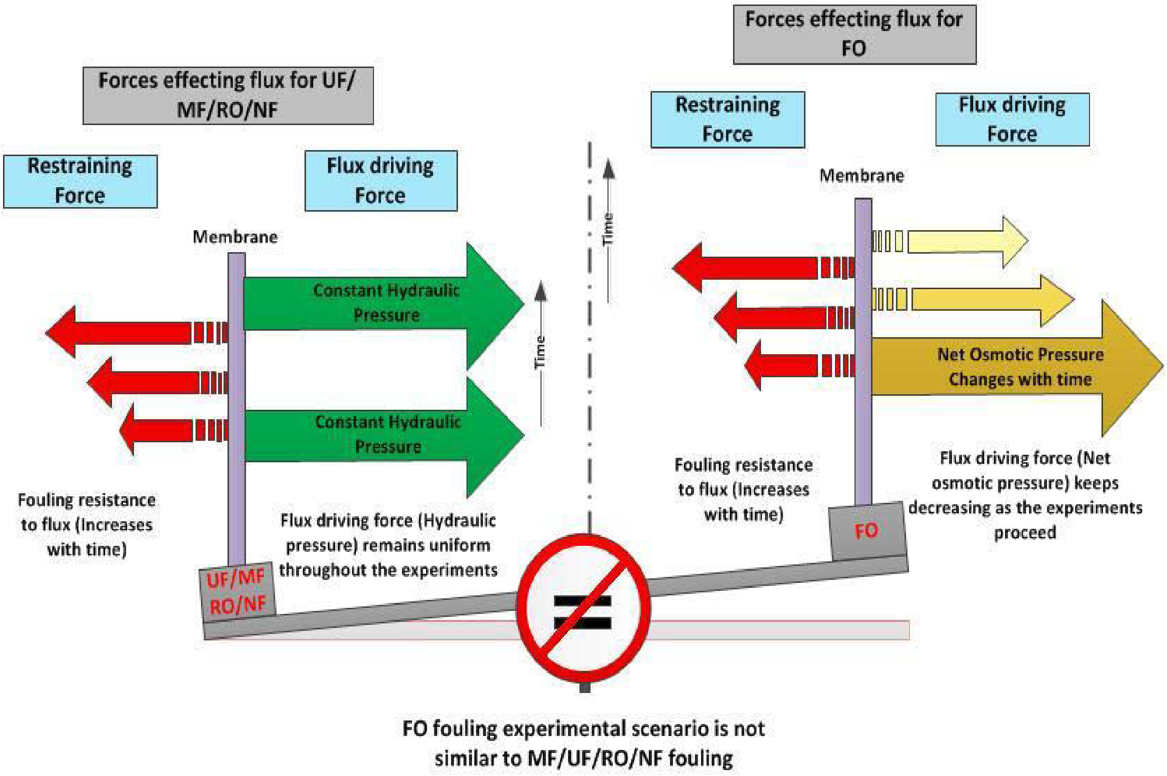


Fig. 8.1. Theme of the study showing that for fouling experiments the overall scenario for FO process is not similar to UF/MF/RO/NF processes. Hence the existing fouling experimental protocol may not be used to evaluate fouling effects for the FO membrane.

the DS is usually prepared in a controlled working environment by dissolving suitable draw solute in high quality treated water, the risk of fouling on the DS side is found to be minimal and thus it has not been seriously evaluated in earlier FO studies (Mi and Elimelech, 2008, Holloway et al., 2007, Cornelissen et al., 2008, Zhang et al., 2012).

This chapter evaluates the possible risks of scaling and fouling for the hollow fiber FO (HFFO) membrane using two different approaches, 1) the existing methodology and 2) an alternate modified approach. The FO membrane was evaluated for flux for FS of various BGW qualities and a combination of model organic foulants such as alginate, humic acid (HA) and bovine serum albumin (BSA).

8.2 Experimental

8.2.1 FO setup

Two identical bench scale HFFO set-ups, similar to one reported by and Majeed et al. (2013) in their earlier FO work were used in this study. Each set-up carried two Cole-Palmer variable speed pumps which were used to circulate DS and FS through the membrane module. A temperature controller unit linked to a water bath was used to maintain the temperature of the DS and FS sides at 25± 0.5˚C during these experiments.

All these fouling tests were performed for crossflow rates representing a Reynolds number (Re) of 1900 and 700 for the lumen side and shell side respectively. These Re values represent the laminar flow through the lumen and shell sides. Fig. 8.2 shows the sequence of experiments performed with each set-up.

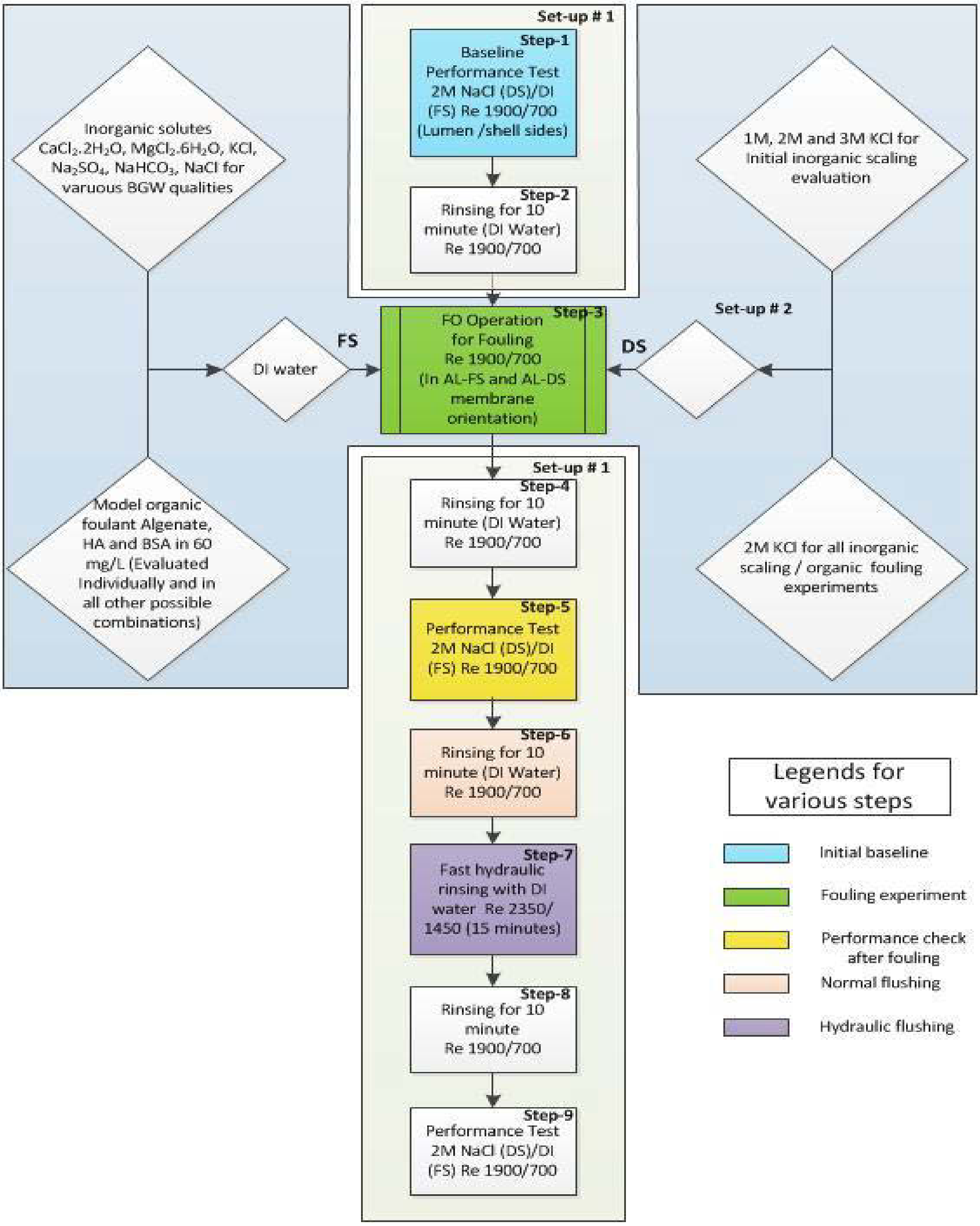


Fig. 8.2. Sequence of operations performed at two side by side FO units (set-up # 1 and set-up # 2) to evaluate the effects of scaling and fouling on the HFFO membrane.

8.2.2 Membrane used

HFFO lumens were supplied by Samsung Cheil Industries, Korea and these were used to construct different modules for the study, each carrying a membrane area of 25 cm^2. FO lumens were made up from aromatic polyamide (PA) thin film composite (TFC) active layer (inside) on hydrophilic sulphonated polysulphone (SPSf) substrate (Chen et al., 2014, Majeed et al., 2013). The PA membrane had a negative charge (at pH=7 the charge is -9.30 mV and contact angle of 55° (Majeed et al., 2013). FO membrane properties such as pure water permeability (A) and salt rejection (B) have been reported in another earlier study (Majeed et al., 2013).

These HF modules were evaluated for AL-DS and AL-FS membrane orientation. For AL-FS orientation the FS was passed through the inner side of lumens and the DS was run outside these lumens. For AL-DS membrane orientation, the FS and DS run the other way.

8.2.3 Chemicals used

8.2.3.1 DS and FS

KCl and NaCl were used as DS for this study. To assess the effects of DS on scaling, KCl was used in 1 M, 2 M and 3 M concentrations as DS for initial baseline tests and the flux was evaluated against DI water FS and specific organic foulant loaded DI water FS. Based on the later flux outcome, all inorganic scaling and organic fouling tests were completed with a 2 M KCl DS concentration. FS showing various brackish ground water (BGW) qualities representing total dissolved solids (TDS) of 5,000, 10,000, 20,000 and 35,000 mg/L were prepared from different analytical grade chemicals and reported as BGW5, BGW10, BGW20, BGW35 respectively in the study. These BGW qualities represent water samples at various salt interception scheme locations in Murray Darling Basins of Australia. NaCl, Na_2SO_4, $CaCl_2.2H_2O$, $MgCl_2.6H_2O$, $NaHCO_3$ and KCl were used to prepare the above mentioned

BGW qualities. Deionized (DI) water was used as FS for baseline (reference line) tests. Further, all other DS and FS for this study were prepared in DI water. All these reagents were supplied by Chem-supply, Australia.

Table 8.1: Detailed composition of various synthetic BGW qualities evaluated for the FO fouling study. Osmotic pressure is calculated using OLI Stream Analyzer 3.2 software

Compounds/Concentration	BGW5	BGW10	BGW20	BGW35
	mmol	mmol	mmol	mmol
NaCl	31.8	63.5	127.1	222.5
Na_2SO_4	6.3	12.6	25.3	44.2
KCl	0.9	1.8	3.6	6.3
$CaCl_2.2H_2O$	1.1	2.2	4.3	7.6
$MgCl_2.6H_2O$	9.7	19.4	38.8	68
$NaHCO_3$	0.6	1.1	2.3	3.9
π (atm)	2.74	5.35	10.56	18.56

8.2.3.2 Organic foulants

Three different model organic foulants were used to evaluate their fouling potential on the FO membrane: Sigma-Aldrich sodium alginate being polysaccharides that constitute a major fraction of soluble microbial products in wastewater (Mi and Elimelech, 2010b), bovine serum albumine (BSA) being proteins and amino acids and Sigma-Aldrich humic acid (HA) being natural organic carbon (NOC) produced by biodegradation of dead organic matter. Humic substances are refractory anionic macromolecules and these consist of both aromatic and aliphatic components primarily with phenolic and carboxylic functional groups, respectively.

Alginate represents the hydrophilic fraction of the organic poulants and based on the manufacturer datasheet, the molecular weight of sodium alginate ranges from 12 to 80 kDa.

Other characteristics of alginate can be found elsewhere (Jin et al., 2012). Alginate is negatively charged within the fouling study pH range (6-8) (Wang et al., 2010b).

A stock solution for each of these model foulants was prepared by separately mixing 2.4 g of individual foulants in 1 L of DI water. Alginate and BSA (received in powder form) are dissolved in DI water and mixing is continued over 24 h to ensure complete dissolution. HA stock solution was prepared by dissolving the HA powder in DI water and adjusting the pH to 8.2 with NaOH. The stock solution was mixed continuously for 24 hours to ensure complete dissolution. Stock solutions were then stored in amber glass bottles at 4˚C for further use. These model foulants were used at 60 mg/L concentration with various FS qualities. Fouling studies were carried out with FS made from individual foulants and their other possible combinations.

8.2.4 Measurement of water flux

Water flux was evaluated by continuously measuring the loss of FS tank weight placed on a weighting balanced directly connected to a computer. FS readings were recorded after a fixed time interval and this data was used to evaluate FO water flux.

FO experiments were carried out for 4-10 hour durations based on targeted evaluation of the FO membrane for scaling or fouling. However, to check the effect of fouling for long run operations, some of the experiments were continued up to 36 hours.

8.2.5 Performance checks and physical cleaning of the FO membranes

At the end of each fouling test, as indicated in Fig. 8.2, performance checks were carried out for all membranes with 2 M NaCl DS and DI water feed. Normal flushing, physical and vibrator shaking and hydraulic backwash were also executed to evaluate flux restoration of the fouled FO membranes by these physical means.

8.3 Results and discussion

8.3.1 Scaling potential of FO membrane in AL-FS orientation

FO was initially evaluated at set-up # 1 for 2 M NaCl DS and DI water FS for AL-FS and AL-DS membrane orientation and baseline flux was recorded. After baseline tests, HFFO modules were shifted to set up # 2 and FO was operated for 1 M, 2 M and 3 M KCl DS and DI water FS and various BGW quality FS for AL-FS and AL-DS. BGW5, BGW10, BGW20 and BGW35 represent water qualities from various salt interception scheme bore holes and their constituent details are summarised in Table 1. Fig. 8.3(a) presents the flux outcomes for AL-FS orientation when the HFFO was evaluated for BGW10, BGW20 and BGW35 FS concentration and DS concentration of 1-3 M KCl. These experiments were continued between 8-30 hours duration. It is observed that the flux inconsistently changes for these changing FS and DS concentrations. Results further indicate that for 1 M and 3M KCl DS concentration, the flux increased by 32% for BGW10 FS, whereas for BGW35 FS, it showed a flux increase of 26%. Similarly changes were observed for flux when the FS concentration was changed because the flux reduces by up to 8 % and 14% for 1 M and 3 M KCl DS at these FS qualities.

The flux curves for the various DS and FS concentrations behave differently and show two distinct performance ranges along the test run. In all cases, the flux declines rapidly in the initial 30 minute period and then shows a steady state flux position. For 1 M KCl DS, the flux changes by 21-28% for various FS concentrations in the initial 50 minute period whereas the flux changes by only 3-8% in the 50-200 minute time. These results indicate that during the initial period, DS and FS take some time to build possible interactions with the AL and SL of the membrane and this affects the flux outcome. It should also be noted that higher flux differences were observed during the initial period. The observed change was higher than the apparent effects of possible DS dilution and FS concentration. We suggest that during the initial experimental time, the higher flux decline is due to the strong interactions between the solute particles and membrane surfaces which help ICP/ECP build up and rapidly reduce the flux. Later as the development of FS and DS solute's association reaches the cusp, the build-up becomes uniform and the flux changes in the remaining test run only appear to be due to the subsequent dilution of the DS and the concentration of the FS side. To confirm this hypothesis, a few experiments were run for 36 hrs, but no serious change was observed in the flux patterns for the long term operations.

8.3.2 Scaling potential of FO membrane in AL-DS orientation

FO performances were further evaluated in AL-DS membrane orientation using the same experiment protocols. DS were used in 1-3 M KCl concentration against BGW5, BGW10, BGW20 and BGW35 FS and the resultant flux outcome is presented in Fig. 8.3(b). It should be noted that the flux curves for these DS and FS combinations showed a different order to the AL-FS orientation which indicates that the ICP and ECP build-up differs for the AL-FS and AL-DS for the given combination of the DS and FS concentration.

In the AL-DS orientation, the FO membrane showed very low flux with the BGW quality FS. Like the AL-FS membrane orientation, the flux patterns showed two distinct types of performance and during the initial test run the flux declined quickly for some time. However, in the AL-DS orientation, the slope of the flux reduced in a shorter time of 20 minutes and became nearly linear. The flux curve at the later stage indicated insignificant flux changes in the FO operations because the driving force did not change remarkably with the DS dilution and the FS concentration along the test run. As mentioned above, in the AL-FS orientation the flux slope took nearly 50 minutes to show a similar linear trend.

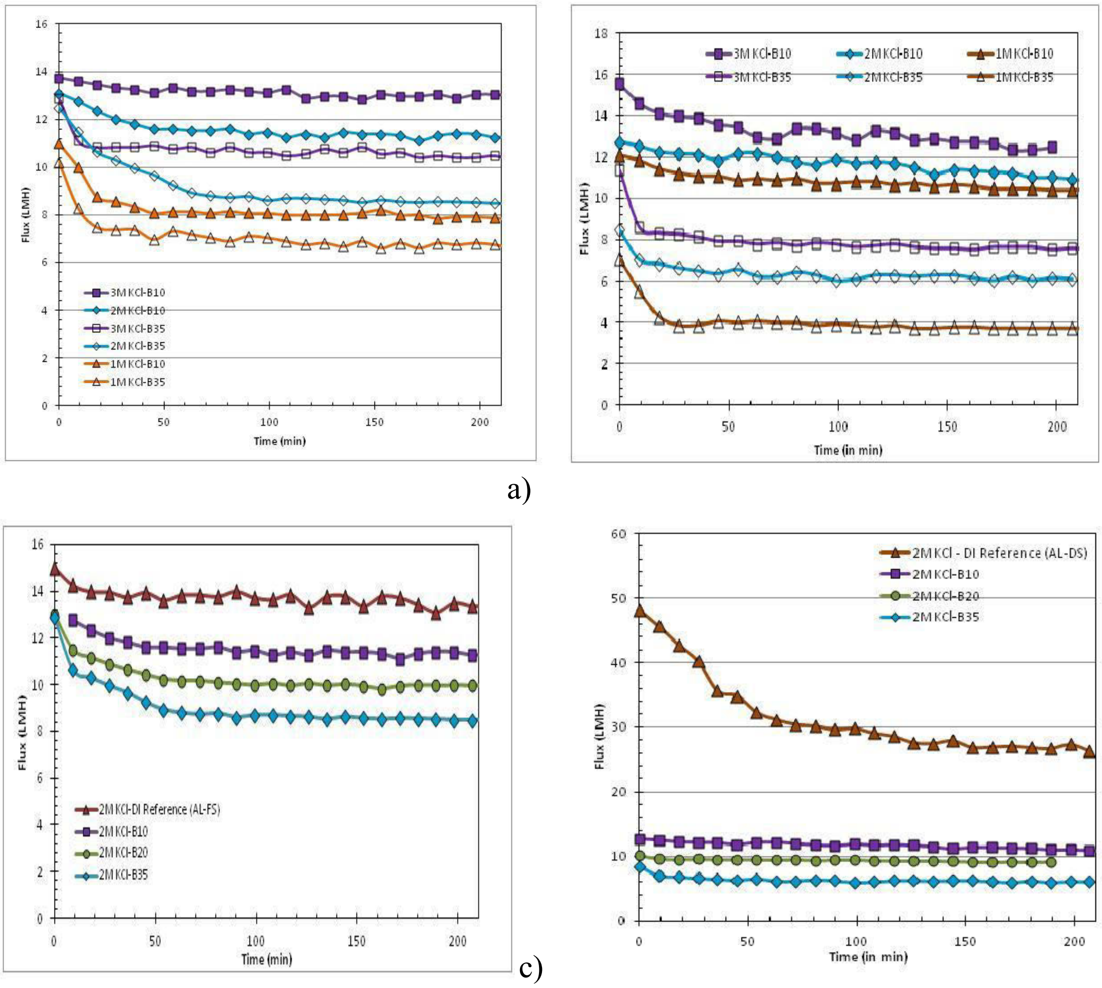
8.3.3 Flux changes with FS concentration.

Based on the flux outcome with earlier tests, the flux was further evaluated for 2 M KCl DS and various BGW quality FS and the comparison is presented in (Fig. 8.3) for both the AL-FS and AL-DS orientation. Water flux was first evaluated for 2 M KCl DS using DI FS and then with 10, 20 and 35 g/L BGW qualities. FO in the AL-DS orientation showed a sharp decline in water flux at the start as the FS concentration was increased. For AL-DS orientation, it was observed that the water flux dropped from 48.2 LMH to 12.7 LMH and showed a decrease of 73.6% when the FS concentration was changed from DI water to 10 g/L BGW (Fig. 8.3(d)). However, the AL-FS orientation showed a flux drop of only 12% as the flux declined from 15.02 LMH to 14.23 LMH with a similar change in the FS concentration (Fig 8.3(c)). Later, the uniform changes in the FS concentration of BGW10 to BGW20 (10 g/L) did not produce similar effects on flux as it declined by 20% and 9.95% for AL-DS and AL-FS orientation respectively. Apart from these initial flux changes, the longer FO operation for varying FS concentrations did not change the flux performance excessively.

Earlier studies have shown that this flux decline is attributed to the enhanced ICP/ECP effect developed by the high FS concentrations (Suh and Lee, 2013b, Tang et al., 2010b, McCutcheon et al., 2006, McCutcheon and Elimelech, 2006). For higher FS concentration, ECP development begins as water permeation starts from FS to DS. As the pure water permeate through the membrane, depending upon the FO membrane orientation, the FS solute enrichment increases at the FS and AL or SL interface. This enhanced FS solute concentration causes a reduction of the net effective osmotic pressure difference for the FO process and as a result, a lower resultant of FO flux output is derived. However, the flux outcome for the AL-DS membrane orientation (Fig. 8.3(d)) indicates that before the concentration of FS solutes can occur due to water permeation, the flux declines immediately and shows a very low outcome. This indicates that apart from the possible ICP and ECP effects, some other forces also play a significant role which dramatically reduces water flux in AL-DS orientation. These results indicate that the divalent FS solutes components such as Ca^{2+} and Mg^{2+} develop further interactions with the functional groups of the membrane SL or at the SL-AL interface and these are mainly responsible for the water permeation. The rapid flux changing phenomena may be further attributed to the SL pore blocking by FS solutes (Majeed et al., 2013). These outcomes stress the need for further studies in this area to track the role of real forces affecting the FO process outcome.

8.3.4 Effect of organic foulants on FO flux performances in AL-FS orientation

Three model foulants such as Alginate, HA and BSA were studied to evaluate the likelihood of organic fouling for the FO process. 2 M KCl was used as DS for these experiments. Alginate, HA and BSA were initially evaluated with DI water FS for organic fouling potential. Later they were also tested with varying BGW FS concentrations to assess the synergic effect of organic foulants and FS solutes on FO performances. Each of these foulants was initially used in individual concentrations of 60 mg/L. Later, they were also evaluated in all their possible combinations in terms of their synergic effect on membrane fouling.



a)

c)

d)

Fig. 8.3. Effect of changing FS (for inorganic fouling) and DS concentration on HFFO flux a) in AL-FS b) in AL-DS c) effect of FS concentration on FO flux for AL-FS d) for AL-DS membrane. 2 M KCl Ds was used. DI water, BGW10, BGW20 and BGW35 were used as FS.

Fig. 8.4 illustrates the effect of the model organic foulant on flux when the FO was operated at AL-FS orientation using DI water and BGW35 FS qualities. To evaluate the long run effect of membrane fouling, most of these experiments were carried out for up to 600 minutes whereas some of the selected experiments were continued for 24 hrs. Fig. 8.4(a) shows the effect of Alginate, HA and BSA FO flux when it is used with the DI water feed in 60 mg/L concentration. It was observed that Alginate, HA and BSA produced similar effects on the FO flux. Compared to 2 M KCl DS and DI water FS baseline, these FS showed a slightly higher flux outcome. Foulants build-up on the FO membrane increasing the negative charge of the membrane surface and this results in a higher flux outcome. FO even showed 5.6% higher flux when FS carrying 60 mg/L each of Alginate, HA and BSA in DI water was evaluated (Fig. 8.4(a)).

The results further indicate that once the fouling layer starts to develop on the FO membrane surface, the net ionic charge and the functional group of these foulants facilitates the passage of water molecules. This further confirms that compared to pressure driven processes, FO in AL-FS orientation shows more stability in flux and this is in good agreement with the earlier findings (Tang et al., 2010b, Achilli et al., 2009b).

Fig. 8.4(b) also showed a similar trend when Alginate, HA and BSA were used with BGW35 quality FS. After 30 minutes of operation, FS carrying organic foulants showed a 9.11% higher flux to the BGW35 quality FS outcome. Interactions between the foulant species and membrane surfaces helped the negative charge on the membrane surface to rise which enhanced the flux through the membrane. Divalent Ca^{2+} and Mg^{2+} ions also attached to negatively charge fouling layers but did not show their effect on flux reduction. Results showed that like RO, neither the attached fouling layers nor the associated Ca^{2+} and Mg^{2+} ions in the fouling layer opposed the FO flux too much. The outcome suggested that with the lower FO operating pressure, the fouling layers remained loose and did not resist the active pores of the membrane driving osmosis. Further, the large size divalent ions associated with the fouling layer did not allow the fouling layer to compact closely, kept it fluffy and did not significantly resist water permeation. Fouling resistance forces did not overcome the earlier mentioned associated advantage of the fouling layer association with the FO membrane.

8.3.5 Effects of organic foulants on FO flux performances in AL-DS orientation

The performance of the HFFO membrane was further evaluated in the AL-DS orientation for various organic foulants and the changing BGW FS quality and outcome is presented in Fig. 8.6. Alginate, HA, and BSA were evaluated in 60 mg/L concentration with DI water and BGW10, BGW20 and BGW35 FS qualities. Based on the specific study objective, these tests were continued for 6-24 hours duration. It was found that in comparison to FO operations in AL-FS, the three model foulants affected the flux in varying order. Fig. 8.6(c) represented the flux outcome when HFFO was operated with various combinations of Alginate, HA and BSA in DI water FS. Contrary to results in AL-FS orientation, the FS carrying combined foulants did not show a higher flux in AL-DS orientation, rather FS loaded with Alginate, /HA foulants showed a higher flux. FS carrying Alginate initially showed a lower flux but it started to show a higher flux after 300 minutes of operation.

FO flux was evaluated in AL-DS orientation for BGW35 FS carrying organic foulant and the results were presented in Fig 8.6(d). FO showed a very lower flux when operated for BGW35 quality FS. Organic foulants with BGW35 FS showed a similar flux behaviour as shown with the DI water FS. Alginate carrying FS showed a higher flux whereas Alginate/HA/BSA loaded FS showed a lower flux outcome. Organic and particulate matter may accumulate inside the porous structure of the support layer and reduce membrane permeability, and reverse salt flux can build up in the support layer and reduce the effective osmotic driving force (Cath et al., 2013a). The above outcome indicated that the developing fouling layers play an important role in the changes in FO performance because they modify some of the membrane properties which have a vital role in the permeation of water molecules through the HFFO membrane.

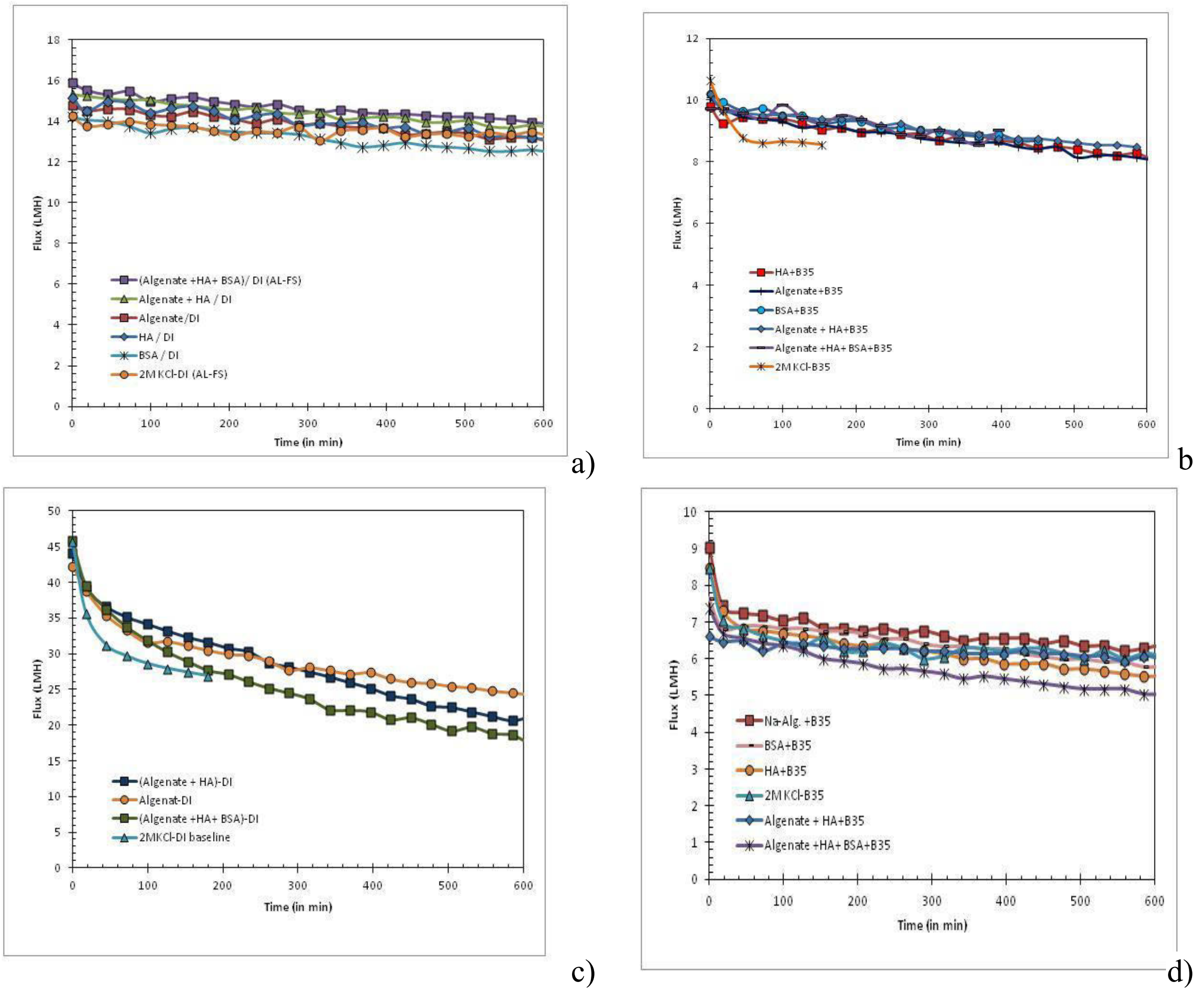


Fig. 8.4. Effect of model organic foulants on flux performance of FO process a) with DI water FS in A-FS b) with 35 g/L BGW FS in AL-FS c) with DI FS in AL-DS and d) with BGW35 in AL-DS orientation. 2 M KCl was used as DS for both AL-FS and AL-FS orientation, crossflow Re DS- 700, FS-1900 and temperature was 25± 0.5˚C

Fig. 8.4 shows that the development of the organic foulant layer slightly enhances the resultant water flux in both the AL-FS and AL-DS membrane orientation. AL and SL membrane characteristics such as membrane surface charge, zeta potential, charge density and hydrophobicity influence the performance of FO. The changes in FO performance with the fouling layer growth indicate that the fouling layer deposition and charge neutralization effects are diverse at different membrane orientations and they strongly depend on the concentration and charge of the foulant species, surface charge and hydrophobicity of the AL or SL of the FO membrane.

In AL-DS orientation, FS carrying foulants induce severe internal clogging on the SL which drastically reduces the flux outcome. This is different to FO operation at AL-FS orientation where fouling phenomena is dominated by cake layer formation on the relatively smooth rejection layer (Mi and Elimelech, 2010b). A higher negatively charged membrane shows a higher flux outcome as it helps the quick and easy penetration of water molecules through the membrane. Negatively charged Alginate and HA foulants increase the negative charge of PA fouled membranes. A higher flux outcome with a highly negatively charged membrane further suggests that the water permeation through the membrane starts with the association of the positively charged (H^+) side of water molecule with the negatively charged membrane as this facilitates the passage of water molecules through the membrane pore.

The higher flux outcome with organic fouling indicates that higher negative charge of the FO membrane helps to facilitate the quick and easy penetration of water molecules through the membrane. It further indicates that the water permeation through the membrane starts with the association of the H^+ part of water molecule with the negatively charged sites of the membrane functional groups. These help water molecules to come closer and pass quickly through the membrane pore.

Results from Fig. 8.3 and Fig. 8.4 indicate that the water flux loss due to fouling on the FO membrane is caused by a combination of (1) the physical blocking of the active pores by the FS components associated with the AL or SL structure; 2) enhanced concentrative ICP which reduces the mass transfer coefficient of the SL; 3) internal clogging in the support structure of the FO membrane which likely reduces the porosity and mass transfer coefficient, enhances the greater structural parameter which results in additional hydraulic resistance; and 4) the enhanced CP development in the attached fouling layer [30]. Initial fouling layer brings about a major impact which can mainly be attributed to pore plugging. Later attachments of the layer to the initial fouling layer do not enhance this effect.

Depending on the type of membrane orientation, the newly formed fouling layer on the FO membrane produces different CP effects. It provides an extra layer on either the AL or SL of the membrane which results in additional ICP or ECP on the FO membrane and it effects the FO flux. The thickness of the fouling layer also helps to enhance the ICP effects which further reduces the flux attributed to cake layer formation (Mi and Elimelech, 2008). Fig. 8.5 shows the varying effects of ICP and ECP on the FO membrane due to the newly developed fouling layer. The FO membrane shows the higher effects of ECP in AL-FS as opposed to the ICP effects on the AL-DS membrane orientation. Fig. 8.3 and 8.4 results further indicate that the higher portion of the flux decline in AL-DS is caused by the pore blocking or cake enhanced resistance whereas for AL-FS, the CP resistance mainly contributes to a flux drop.

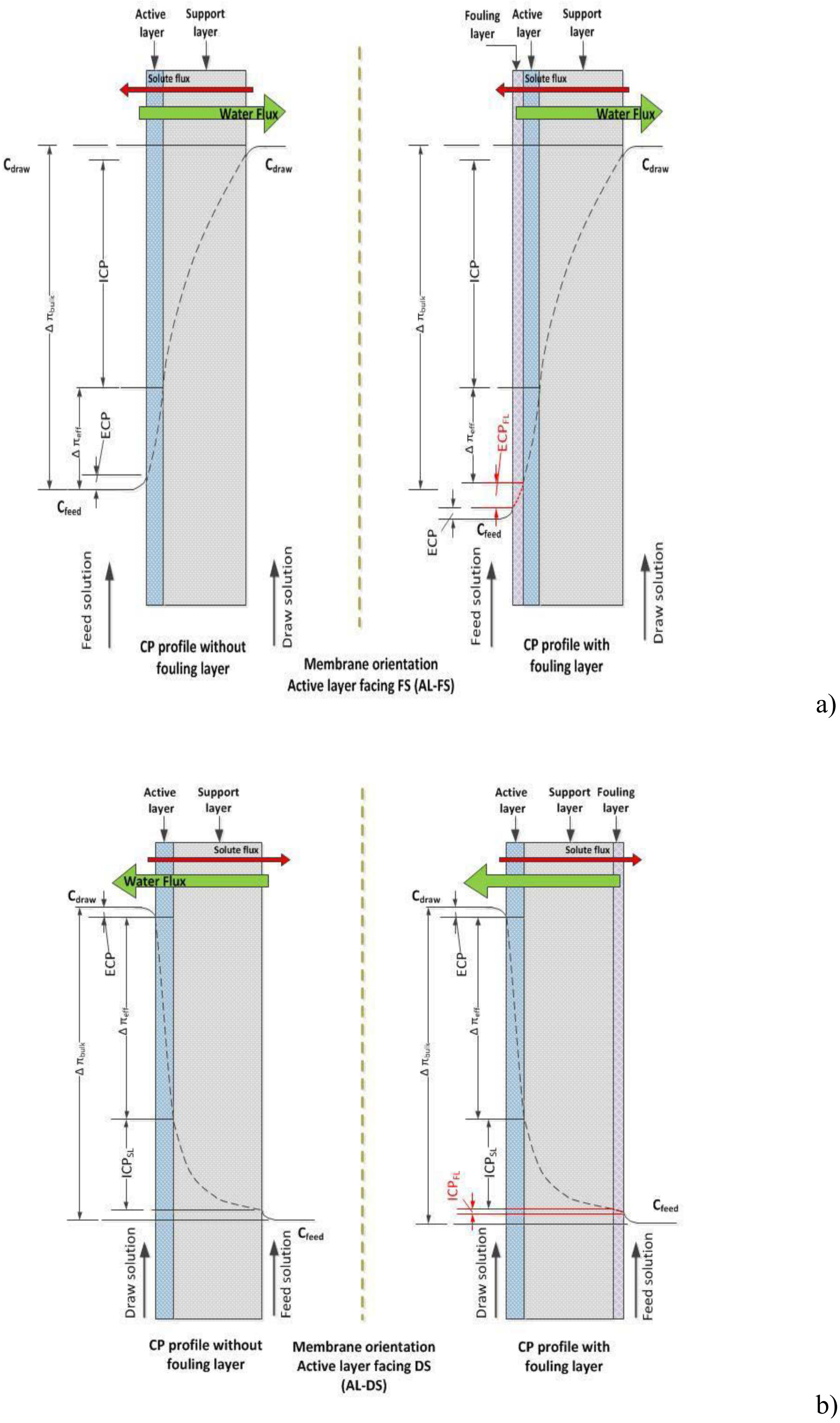


Fig. 8.5. Showing the effects of fouling layer on the ICP and ECP for FO operations a) at AL-FS and b) at AL-DS. Fouling layer has higher effects on ECP in AL-FS than ICP in AL-DS orientation

The formation of a cross linked gel layer was observed when the FO was operated in AL-DS orientation for Alginate, HA and BSA loaded FS. This layer became prominent and easily distinguishable when FS carrying dark brown coloured HA was used for these experiments. Being a linear copolymer of mannuronic and guluronic acids that contain abundant carboxylic functional groups, divalent cation ions especially Ca^{2+} were preferentially attracted to carboxylic groups of Alginate Foulants and these made bridges with the available neighbouring alginate molecules which led to gel layer formation. Ha fouling was also effected by Ca^{2+} but not to the extent that the Alginate showed. BSA also carried similar adhesion forces but due to its low carboxylic contents, it was not affected by the presence of calcium ions and as such did not form complexes and cross linked fouling layers with Ca^{2+} (Mi and Elimelech, 2008). Accordingly, FO shows similar flux trends with all model foulants evaluated in this study.

Fig. 8.6 illustrates the effect of membrane orientation and combined effects of inorganic and organic components of FS on HFFO membrane flux. It summarises the flux outcome for AL-FS and AL-DS orientation for two types of FS i.e., DI water and BGW35, both of which carry Alginate, HA and BSA in 60 mg/L concentrations. Paralleling the earlier results for BGW FS outcome as shown in Fig. 8.3, for Alginate/HA/BSA loaded FS with DI, the HFFO membrane showed high flux in AL-DS orientation whereas the FO showed the lowest flux for Alginate/HA/BSA loaded FS with BGW35. These results reflect the serious pore blocking effect by the FS carrying inorganic solutes which drastically restricts the flux outcomes in AL-DS orientation (Majeed et al., 2014).

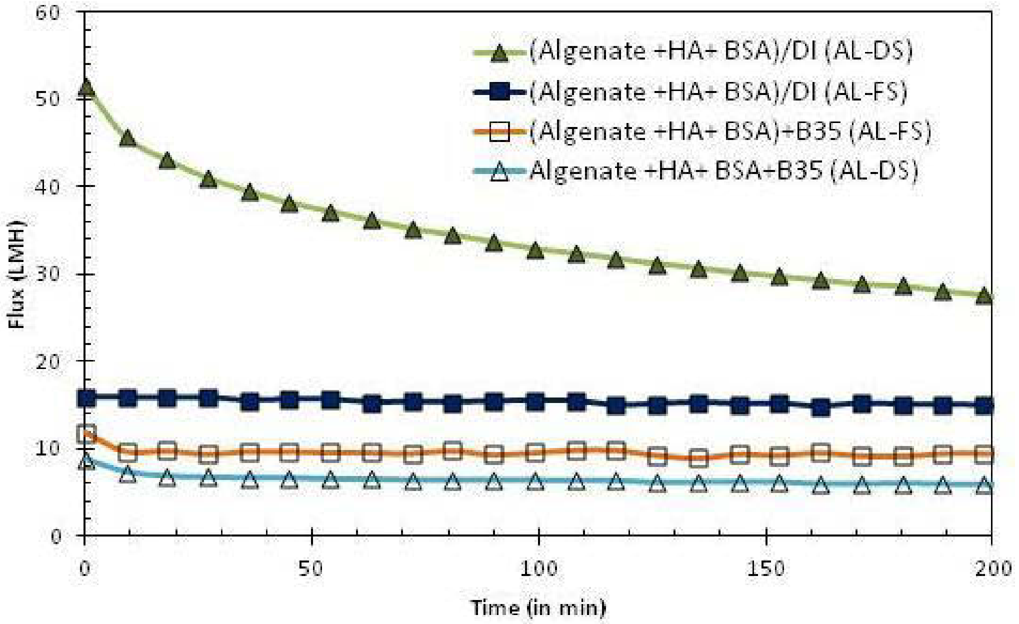


Fig. 8.6. Effect of membrane orientation and FS concentration on FO flux, Conditions: DS: 2 M KCl, FS: DI and BGW35 carrying Alginate, HA and BSA were used in 60 mg/L concentration each, temperature : 25 ± 0.5˚C, membrane orientation: evaluated for both AL-FS and AL-DS

8.3.6 Evaluation of FO scaling and fouling using a distinct alternative approach

In many earlier studies, FO fouling was evaluated in a similar way to RO, NF, UF/MF fouling studies where the membrane performance was purely evaluated for the purposes of the changing performance patterns of the normal permeate flux curve. For any particular study for RO/NF/UF, throughout the experiment, a flux curve indicates the flux performance of the membrane at a uniform driving force (hydraulic pressure), so that the effect of the fouling is easily understood by comparing any flux trend with the baseline outcome. Any difference in the flux is attributed to the effect of the fouling layer. However, in FO, constant changing DS and FS qualities, concentration polarization (both internal and external) and RSF continuously affects the FO driving force (net available osmotic pressure difference) at the AL-FS interface. ICP and ECP also showed enhanced results for the fouled membranes.

These changes in the FO driving force are extremely vital as they seriously affect the flux performance. Hence, from the flux data curve it is really difficult to find how much of the flux is individually affected by the changing driving forces or the fouling and scaling issues (Fig. 8.1).

For similar FO studies, no two points show the similar driving force, hence the flux outcome may not provide a reliable comparison of any two such performances. The same flux declining curves using different driving forces cannot be used to ascertain the fouling potential on the FO membrane surface for any DS and FS. For these reasons, the standard flux curves for FO operation, (like those shown in various earlier fouling studies or those shown in Sections 3.1-3.4) may not be suitable for evaluating the fouling potential of the FO membrane.

The results in Fig. 8.3 have already indicated that when DS and FS qualities are changed, the flux does not change linearly to reflect the changes in the osmotic pressure difference. Some portion of the osmotic pressure increase is offset by the possible changes in the ICP/ECP effects (Fig. 8.5). For higher DS concentrations, the effectiveness of the net osmotic pressure decreases with the higher concentrations of FS. With high solute concentration in BGW FS, CP build-up is high and this results in a lowering of the net osmotic pressure at the membrane interface (Majeed et al., 2014). For this reason, flux difference increases more at high FS concentration.

To overcome this issue, a simple new approach is outlined in Fig. 8.2. To check the absolute effect of fouling on the FO membrane, the FO membrane was initially evaluated at FO set-up # 1 with a different DS (2 M NaCl) and DI water FS and the baseline flux was recorded. FO fouling was evaluated on set-up # 2 for specific DS (2 M KCl) and a varying FS concentration carrying various foulants. On completion of each fouling test, the FO membrane was again placed at set-up # 1 and surface flushing with DI water was carried out using similar crossflow rates on both sides to remove excessive DS and FS from the fouling experiment. Later the FO was evaluated for the same initial driving force using 2 M NaCl DS and DI water FS for any changes in the FO membrane flux performance due to scaling and fouling issues. The average of the initial 10 minute flux was evaluated to compare the membrane performances and the results are presented in the next section.

8.3.7 Actual effects of inorganic fouling on FO performance

Using the experimental protocol outlined in Fig. 8.2, the water flux was monitored for the FO membrane in AL-FS and the AL-DS orientations and results are presented in Fig. 8.7. The results indicate that the changing BGW FS quality somewhat affects the FO flux performance but with minimal margins. FO in AL-FS orientation comparatively showed a smaller flux decline than in the AL-DS orientation. For BGW35 quality FS, in AL-FS orientation, the result shows that the HFFO flux declines by 0.28 LMH (3%). However, in AL-DS orientation, up to a 2.16 LMH (5.6%) flux drop was noticed for similar quality FS (Fig. 8.7(a)).

Although, Fig. 8.3 and Fig. 8.4 show the flux declining trend for various DS and FS combinations, these figures are hardly able to demonstrate flux changes specifically for scaling. To identify the fouling effects for FO fouling, FO was operated using Fig. 8.2 protocols. Fig. 8.7(b) shows the flux outcome for step-1 and step-5 of the FO plan shown in Fig. 8.2 where the FO was operated for 2 M KCl DS and DI and BGW35 FS at both AL-FS and AL-DS membrane orientation. Results show that in AL-FS orientation, for a longer test run with BGW35 FS quality, the FO flux dropped by 0.375 LMH (2.64%) which indicated a minimal effect in terms of fouling. However, HFFO showed a higher flux decline of 2.59 LMH (5.92%) when operated for AL-DS membrane orientation.

Fig. 8.8 shows the consequences of DS and FS steam flowing through the HFFO membrane for scale development and deposition. The given FS crossflow rate produced a high shear force while flowing through the HF lumens and it also generated swirling movements which left fewer opportunities for scale build-up on the inner surface of the FO lumens. Hence a lower flux decline was observed for AL-FS orientation. Higher cross-flow velocity led to a reduction of aggregation of the feed solids in the fouling layer. On the other hand, due to the module design issues, the given FS crossflow rate was unable to deliver the similar swirling effect on the HF outer surface thus leaving a more favourable environment for the scale deposition build-up. The thick scaling layer resulted in a higher flux drop in the AL-DS membrane orientation.

8.3.8 Actual effects of combined fouling on FO performance

Following the Fig. 8.2 experimental protocol, the HFFO flux was evaluated for 2 M KCl DS and various BGW qualities in terms of the FS carrying Alginate, HA and BSA for fouling. The results are summarised in Fig. 8.9. Performance tests were run for 30 minutes and the flux was evaluated using the mean or mode of the initial 10 minute flux reading. These results were then compared to the baseline reference flux obtained for 2 M NaCl DS and DI FS for AL-FS and Al-DS orientation (10 minute average). The results indicated that the fouling potential of the HFFO membrane was accelerated when only organic foulants were used in DI FS whereas the BGW solutes helped to reduce the fouling effects. Fig. 8.9(a) represents the performance of the FO membrane when operated at AL-FS orientation. The FO showed varying fouling effects in relation to different FS qualities.

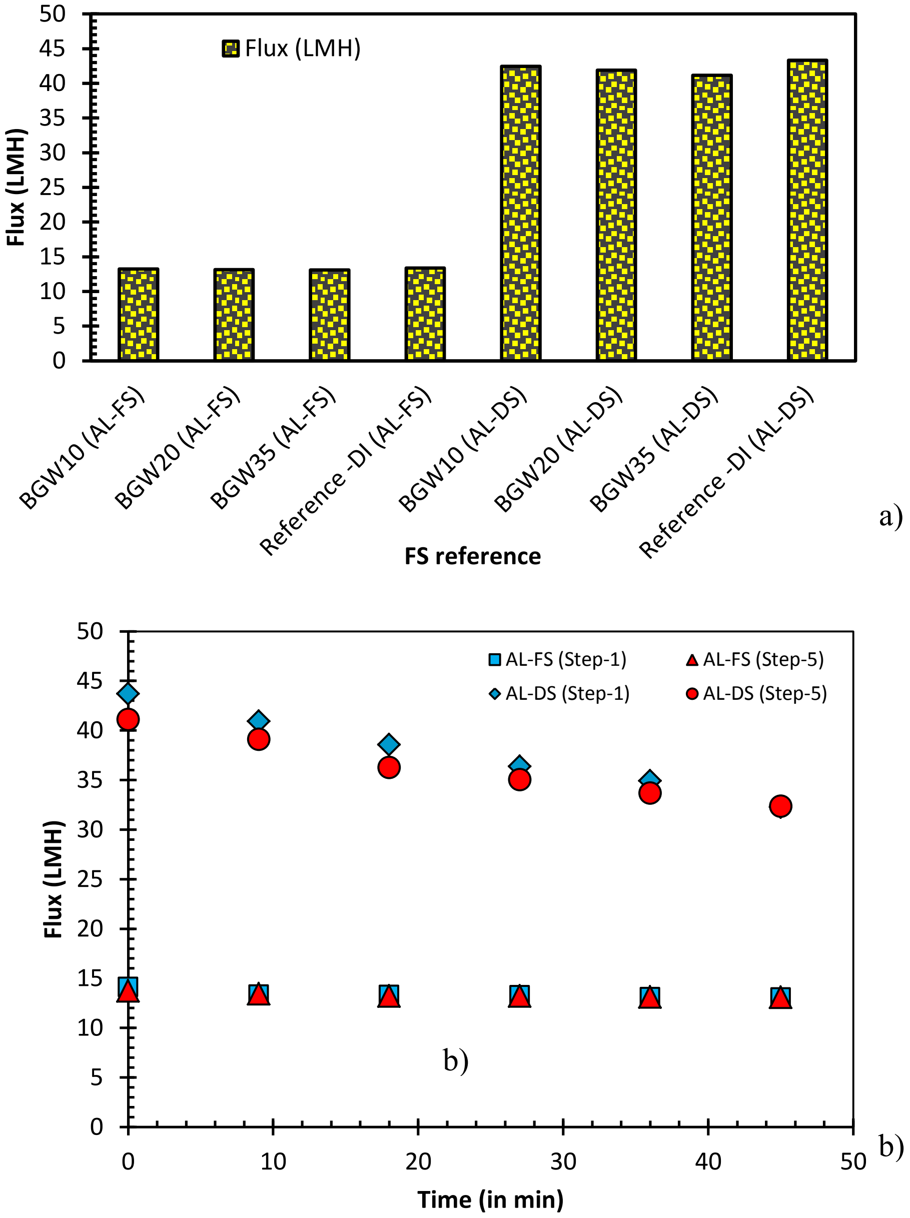


Fig. 8.7. Showing effect of scaling on HFFO membrane performance a) for AL-FS and AL-DS membrane orientation with 2 M NaCl DS and BGW10, BGW20 and BGW35 as FS b) flux performance for step-1 and step-5, 2 M KCl was used as DS against DI water and BGW35 FS, evaluated for both AL-FS and AL-DS membrane orientation, Temp: 25 ± 0.5˚C

Fig. 8.9 further shows that for FS carrying organic foulants, the HFFO flux changes according to the AL-FS and A-DS orientation. The fouling mechanism and fouling layer characterisation were found to be different with the different organic foulants and this mainly depended upon the concentration of the inorganic and organic solutes and their concentration.

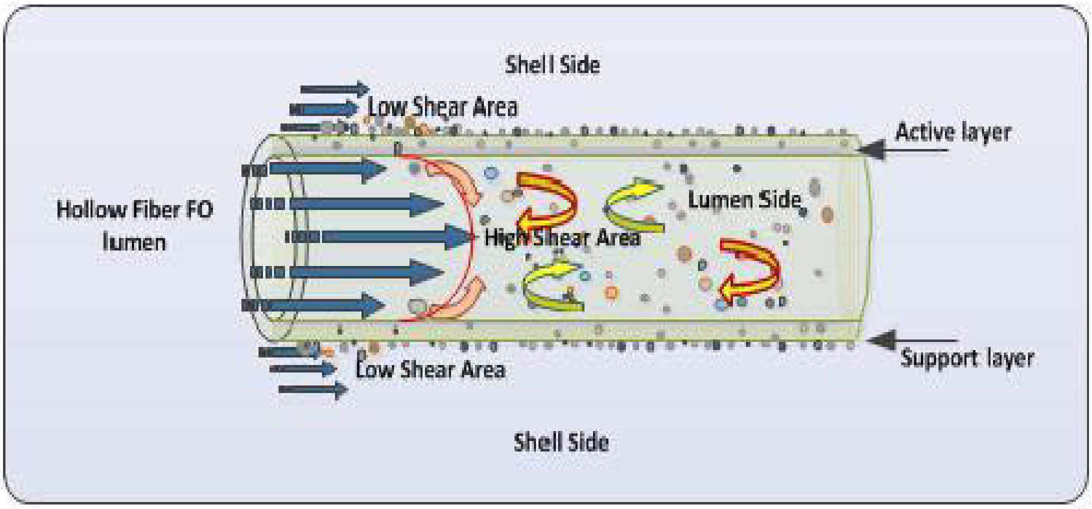


Fig. 8.8. Graphical presentation of the effect of crossflow shear force within and outside the HFFO lumens. The shear force effect with the varying crossflow rate affects the results of the hydraulic cleaning of HFFO membrane.

Organic foulants used with DI water FS display a high flux decline of up to 9% whereas when they are used with various qualities of BGW, there is little evidence of flux decline. A flux drop of up to 4% was also observed for BGW35 FS carrying HA and BSA. In the absence of hydraulic pressure in the FO, the alginate gel layer developed in FO is relatively soft and fluffy and this indicates a loose structure (Mi and Elimelech, 2008). It appears that the bridging of divalent Ca^{2+} and Mg^{2+} ions with the foulants functional groups depresses the adhesion potential of the fouling layer. Indeed, this is pushed out by the shear force generated by the crossflow velocity especially for FS flowing through the fiber lumens. Hence, little or no flux loss can be observed with the combined fouled FS. Surprisingly, in some of the cases, HFFO membranes showed a higher flux outcome owing to the effects of the surface charge modification of the membrane AL with these organic foulants.

Furthermore, when FO was evaluated for its fouling potential in AL-DS orientation using FS prepared with Alginate, HA and BSA foulants mixed BGW, in most of cases high membrane fouling was observed as the flux of the FO membrane was reduced by 16-49%

(Fig. 8.9(b)). This indicates that in AL-DS orientation, the FO membrane is highly prone to a greater risk of fouling. Compared to AL-FS orientation, the FO showed a higher flux decline with higher concentration FS. Among the three model foulants evaluated in this study, the presence of BSA showed more flux decline than HA and Alginate. The observed differences in the fouling rate at different membrane orientations reflects the strong association between the foulants and surface charge, hydrophilicity and zeta potential of the associated layers of the FO membrane.

When FO was operated for FS carrying organic foulants with DI water or BGW quality FS, in AL-DS orientation, the development of gel like fouling layers was observed on the membrane SL and these were quite visible with a magnifying glass. The gel layer also became prominent when HA was added to FS as it showed a dark brown colouring layer on the membrane SL. This fouling layer was found to firmly stick on the membrane surface.

Comparing the FO performance curves presented in Fig. 8.3 and Fig. 8.4 with Fig. 8.6 and Fig. 8.7 and Fig. 8.9, it can be seen that the earlier figures showed a better flux outcome or less fouling for Alginate, HA and BSA loaded FS. This also stands true for AL-FS but it seems misleading for AL-DS orientation. This comparison highlights the severe interference of the interacted forces with the FO performance especially in relation to ICP/ECP. The effects of possible ICP and ECP intensification with fouling layer growth on the FO membrane are unclear. These results indicate that for the FO process, the standard flux performance may not be used to effectively identify the fouling issues for the FO membrane because the behaviour of the FS solutes and various organic foulants on the forces driving osmosis still seem unclear. However, the possibilities in relation to the ICP and ECP intensification of the fouling layer should not be ruled out.

With the same FS and DS, different levels of fouling development and flux decline on AL-FS and AL-DS orientation indicates that the fouling initially starts with the interactions of membrane and foulant macromolecules. Both PA active layer and PES support layers have different functional groups, surface charge, zeta potential, pore size and pore geometry thus they behave differently in different modes of FO operation. Similarly, Alginate, HA and BSA showed the different effect of fouling on AL-FS and AL-DS orientations.

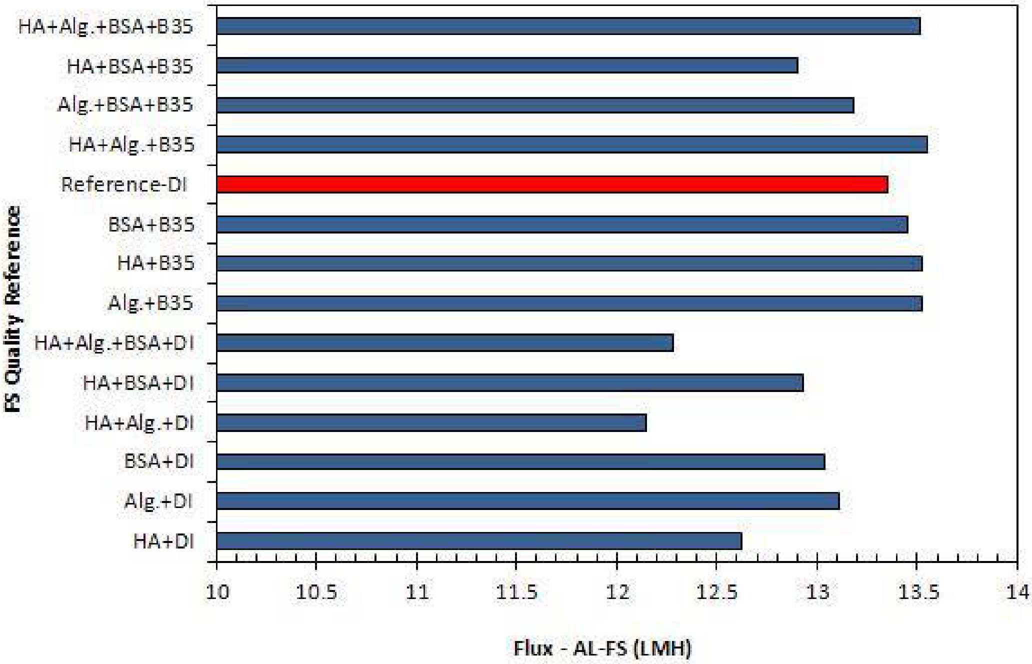
The effect of fouling on membrane performance was also evaluated with reference to the time of operation. FO was separately evaluated for FS carrying 60 mg/L each of Alginate, HA and BSA in DI water and 2 M KCl DS for a period of 2 and 10 hours. At the end of the tests, the membrane was evaluated on another baseline FO unit and the flux performance was recorded. These two membranes showed nearly the same flux decline as flux of 36.56 LMH and 36.58 LMH was recorded for these two tests respectively. A similar flux decline observed for membranes operated at different times indicates that the fouling layer developed on the FO membrane in the first 2 hours of the FO test run mainly contributed towards a reduction in the FO performance. Reduced hydrophobicity and increased electrostatic repulsion led to a lower deposition rate of these foulants onto the membrane surface and thus less fouling (Hong and Elimelech, 1997). The initial fouling layer also blocked the membrane pores which largely caused a flux reduction in the membrane process. Combining the surface charge of the AL and SL, zeta potential, charge of the organic foulants, functional group of the organic foulants, and interactions between the membrane and the organic foulants collectively work to produce effects on the fouling mechanism. The later deposition on the fouling layer seems loose which doesn't appear to contribute to the further plugging of membrane pore. Accordingly, no further flux decline can be observed.

The above results show that due to the multiple parameters affecting the FO performance, the general flux curve comparison does not help us to understand the possible flux losses due to scaling and fouling. Membrane performance evaluated at the conclusion of the fouling test with a standard DS and FS set can give us the actual flux for a membrane at any given time. This comparison with the baseline results successfully represents any actual variation in the FO membrane performance. More detailed studies are required to further evaluate how these FS characteristics affect the FO flux driving forces.

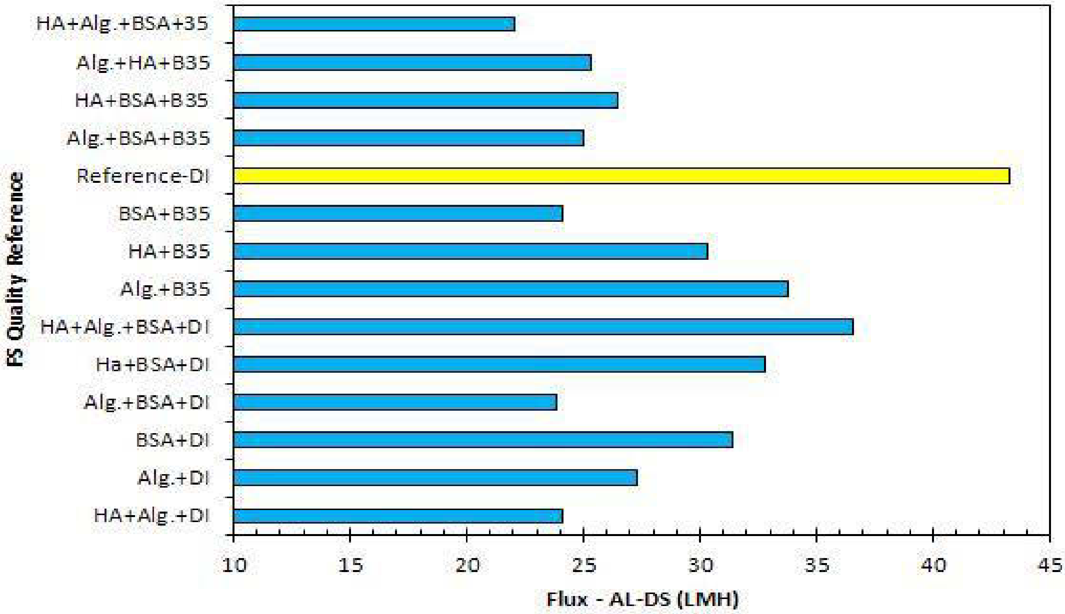
8.4 Concluding remarks

The HFFO membrane was evaluated to assess the effects of fouling using different FS qualities carrying model organic foulants such as Alginate, HA and BSA. The following conclusions are drawn from the outcomes of this study:

- An immediate flux drop at AL-DS orientation in a very short time does not follow the existing concentration polarisation concept where the FS solute becomes concentrated due to the water permeation through the DS. This indicates that the role of possible associations between the FS solutes and active and support layer of FO membrane causes a drop in the net osmotic pressure and flux outcome and this is independent of the general CP and possible scaling or fouling.



a)



b)

Fig. 8.9. Showing the effect of the combined organic fouling on the performance of the HFFO membrane a) flux in AL-FS membrane orientation b) flux in AL-DS membrane orientation

- In the FO process, due to continuous changes in FO driving force and their associated effects on flux outcome, the fouling effects for FO cannot be worked out using similar routine FO fouling experimental methodological approaches. Hence an alternative approach is used to evaluate the actual loss of FO flux due to scaling and fouling and this successfully shows the real impact of the fouling on the FO flux.
- FO performance is severely affected by both inorganic and organic fouling. However, their respective influence on the FO flux is different for both the AL-FS and AL-DS membrane orientation. HFFO showed a higher fouling risk at AL-DS orientation.
- The process conditions, especially the flow rate, severely affect the fouling risk for the HFFO membrane in both the AL-DS and ALFS membrane orientation. Paralleling other membrane systems, the FO membrane also carries nearly the same risk for fouling and this can easily lead to a reduction in the appropriate process conditions for FO operation.

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Chapter 9

PHYSICAL AND CHEMICAL CLEANING OF FOULED HOLLOW FIBER FORWARD OSMOSIS MEMBRANE

9.1 Introduction

Membrane performance can be seriously decreased as a repercussion of different types of fouling including inorganic,colloidal-, organic- and bio-fouling (Mohammadi, 2001). The fouling growth on the membrane surface seriously affects both water flux and permeates quality and thus reduces the efficiency of water treatment systems. For the existing popular membrane systems such as reverse osmosis (RO), nanofiltration (NF) and ultra-filtration (UF), the membrane cleaning is usually initiated when a significant change is observed either in the membrane performance (decrease of permeate flux and/or salt rejection) or operating parameter (rise of trans-membrane pressure) to deliver the same designed water flux.

Various cleaning techniques such as normal flushing, osmotic backwash, high flow osmotic flushing and chemical cleaning have been evaluated to restore the water flux of the fouled forward osmosis (FO) membranes (Li and Elimelech, 2004). To decipher the mechanisms of fouling and chemical cleaning, it is always important to apprehend the foulant-membrane, foulant-foulant, and foulant-cleaning agent interactions. Earlier FO studies indicated little or no fouling on FO, and only physical cleaning practices were experienced to restore flux through the FO membrane. The choice for any physical cleaning technique or specific chemical cleaning plan depends on lowering the foulant-membrane along with increasing the foulant-cleaning agent interaction and foulant-foulant interactions.

Cleaning chemicals clean the membrane by changing the morphology of the foulants, or altering the surface chemistry of the fouling layer. Consequently, proper selection of chemical cleaning agents relies on our mechanistic understanding of the foulants particularly the chemical reactions between the foulant and the cleaning chemicals (Kim et al., 2013, Demisch and Pusch, 1976). Various studies have evaluated these interaction using atomic force microscopy (AFM) (Radu et al., 2012, Vrijenhoek et al., 2001, Mi and Elimelech, 2010b) which helps evaluate the suitability of a particular chemical cleaning reagent or technique. Li and Elimelech (2004) found that the cleaning efficiency is highly dependent on the solution pH and the concentration of the chemical cleaning agent.

Various factors such as the concentration of the cleaning chemicals, contact time, pH and temperature play an important role in the effective cleaning of the membrane. Most of the commercial chemicals used in the market for membrane cleaning are proprietary and the exact concentrations of various ingredients are never disclosed by their manufacturers. For chemical cleaning of fouled membranes, five categories of cleaning agents are commonly used: acids, alkalis, metal chelating agents, surfactants, and enzymes (Chen et al., 2003). Generally HCl, H_2SO_4 and citric acid are the main ingredients for the acid cleaning solutions whereas NaOH is mainly used for alkaline cleaning with some detergents. Sodium hypochlorite (NaClO) and ethylenediamine tetra acetic acid (EDTA) are also used in some cases.

This study evaluates the effectiveness of various physical and chemical techniques for cleaning the fouled hollow fiber FO (HFFO) membrane. Fouling experiments were done with different brackish ground water quality feed solutions and different concentrations of model foulants as alginate, humic acid (HA) and bovine serum albumin (BSA). Membrane cleaning was evaluated for both active layer-feed solution (AL-FS) and active layer draw solution (AL-DS) orientation. General chemical such as HCl, NaOH and EDTA were used to evaluate their cleaning potential.

9.2 Experimental

9.2.1 FO setup

Three identical bench scale hollow fiber FO set-ups, similar to the one reported in Chapter 6 was used in this study. All these fouling tests were performed for crossflow rates representing the Reynolds number (Re) of 1900 and 700 for the lumen side and shell side respectively. These Re values represent laminar flow through the lumen and shell sides. Flushing, and performance checks were carried out at the same Re. Higher crossflow rates were used during hydraulic flushing representing Re of 2350/1450 for lumen side and shell side respectively.

9.2.2 Membrane used

HFFO lumens were supplied by Samsung Cheil Industries, Korea and these were used to construct different modules for the study and each carrying membrane area of 25 cm^2. These HF modules were evaluated for AL-DS and AL-FS membrane orientation. Other details have already been given in Chapter 3.

9.2.3 Chemicals used

9.2.3.1 Feed solutions and Draw solutions

As described in Chapter 8, all inorganic scaling and organic fouling experiments were completed with 2 M KCl draw solution (DS) concentration. Feed solution (FS) showing various brackish ground water (BGW) qualities representing total dissolved solids (TDS) of 10,000, and 35,000 mg/L were prepared from different analytical grade chemicals and reported as BGW10, BGW35, respectively in the study. Complete specifications of the FS quality are provided in Chapter 3.

Deionized (DI) water was used as FS for baseline (reference line) tests. Further, all other DS and FS for this study were prepared in DI water. Normal and hydraulic flushing was also carried out using DI water.

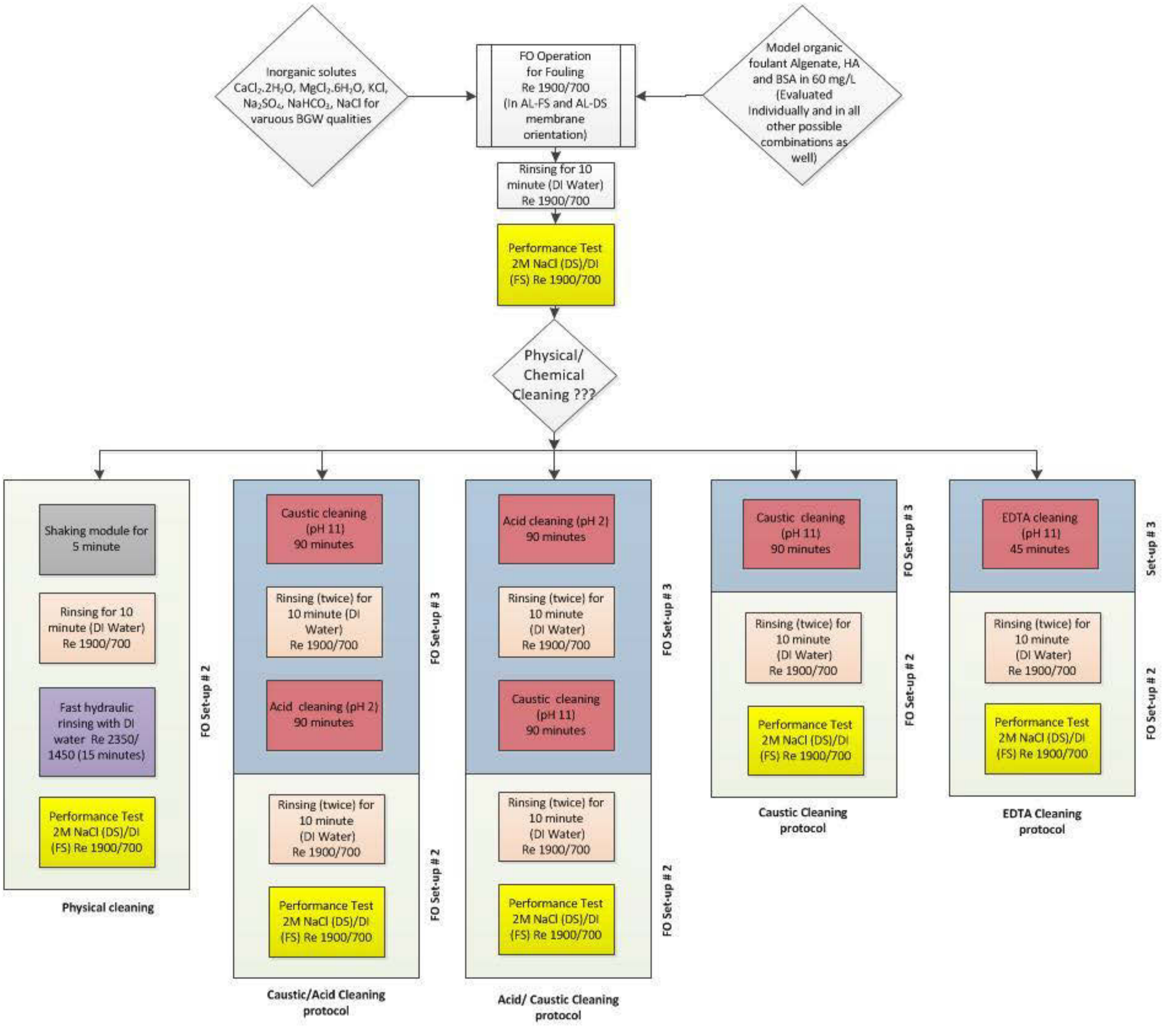

Fig. 9.1. Different physical and chemical membrane cleaning procedures used for this study

9.2.3.2 Organic foulants

Model foulants such as alginate, HA and BSA organic foulants were used with various quality FS for the fouling studies.

9.2.3.3 Cleaning chemicals

NaOH and HCl were respectively used as simple alkaline and acidic cleaning chemicals for the membrane flux restoration. NaOH was used for the organic fouling removal/cleaning whereas HCl was used to clean membranes for inorganic scale deposition. Dilute solutions were prepared from these laboratory grade chemicals supplied by Chem-supply, Australia. NaOH cleaning was carried out at pH 11 whereas HCl solution at pH 2 was used for FO membrane cleaning. pH was regularly monitored and maintained during these tests. EDTA, a metal chelating agent in 1 mM concentration was also used at pH 11 (adjusted with NaOH) for comparing the effectiveness of the chemical cleaning performance.

9.2.4 Measurement of water flux

Water flux was evaluated by continuously measuring the loss of FS tank weight placed on a weighting balanced directly connected to a computer. FS readings were recorded after a fixed time interval and this data was used to evaluate the FO water flux.

9.2.5 Performance checks

At the end of each fouling test as described in Chapter 8, performance checks were carried out for all membranes with 2 M NaCl DS and DI water feed. These results reflected any effects of fouling on the HFFO membrane.

9.3 Results and discussion

9.3.1 Physical cleaning of FO membrane

On completion of the fouling experiments for 600 minutes, the performance of HFFO membranes was carried out to evaluate the effect of scaling and fouling. Based on these evaluations, various simple physical membrane cleaning techniques such as normal flushing, vigorous physical and vibrator assisted shaking, osmotic backwash and hydraulic flushing were evaluated for the flux restoration of the fouled FO membranes (Fig. 9.1).

9.3.1.1 Effects of simple flushing

The fouled FO membrane was subjected to simple flushing with DI water on both DS and FS sides. The same crossflow rates matching experimental conditions were used and flushing was done for 10 minutes. It was observed that normal flushing did not improve the performance of the fouled FO membrane used in the AL-FS and AL-DS orientations.

9.3.1.2 Effects of vigorous shaking

Modules were removed from the FO unit, drained to half and then vigorous manual shaking was carried out to detach the attached fouling layer. The FO module was also placed on a high speed vibrator running at 1000 rpm. Vigorous manual and vibrator assisted shaking helped separate the dark coloured fouling layer attached to the outer surface of the HF lumens. These fouling layers became prominent during the fouling experiments with HA. However, it was noticed that these techniques did not bring any major improvements in relation to the performance of the FO module flux.

9.3.1.3 Effects of fast hydraulic flushing for inorganic fouling

After the application of the initial physical cleaning practices, the FO membrane was further evaluated to check the effectiveness of the hydraulic cleaning for all the inorganic scaling issues. The performance checks with various BGW quality FS indicated a flux loss of 3% and 5.6% for AL-FS and AL-DS orientation respectively.

Hydraulic flushing was used by operating FO for higher crossflow Re. of 2350 and 1450 for the lumen side and shell side respectively. DI water was used as FS and DS and flushing was continued for 15 minutes. It was found that for the FO modules used for fouling experiments with various BGW FS, the DI water flushing at the higher Re successfully restored the flux for modules used in AL-FS orientations. Hydraulic flushing helped dislodge and remove foulants from the membrane surface droplets (Childress and Elimelech, 1996). Unlike RO, the fouling layer is not compact and thus without using any chemicals, hydraulic flushing provides sufficient shear to weaken the fouling layer attachment with the membrane (Mi and Elimelech, 2010b, Setiawan et al., 2012, Park et al., 2013).

As opposed the HFFO membrane used in the AL-FS orientation, the hydraulic flushing for 15 minutes did not provide a satisfactory outcome for flux restoration of the FO used in the scaling experiments at the AL-DS orientation. Flushing was later extended to 30 minutes but only up to 50% of the lost flux was recovered.

Fig 8.8 (Chapter 8) describes the varying effects of crossflow rates of different streams flowing within and outside the HF lumens in the HF module which plays a vital role in cleaning membranes through fast hydraulic flushing. When the crossflow rate wasincreased, higher flow rates produce swirling movements of the cleaning solution with excessive shear forces inside the HF lumens and these help to dislodge any loose scale deposit from the membrane surface. For these issues, inorganic fouling development on the FO membrane was not found to be a very serious issue and whatever scale development occurs on the membrane surface, is easily removed by fast flushing. Due to lower pressure FO operations, the attached inorganic scale on the FO membrane does not compact to form a sticky and hard layer on the membrane surface. Thus, for HFFO used in AL-FS orientation with BGW quality FS, fast flushing representing high Re flow inside lumens helps fully restore flux for the fouled membranes. The flux restoration results with normal flushing further indicate that the inorganic scale does not penetrate inside the AL of membrane pores, rather it just builds up on the smooth outer surface of the AL of the membrane. Hence it is easily removed by hydraulic flushing.

However, with the current FO module design and the operating Re values, the same higher crossflow rates did not produce enough shear force in the shell side of the module which may assist to dislodge scale deposits from the outer surface of the HF lumens. The same crossflow rate showed Re 1450 in the shell side whereas it presented Re 2350 values in the lumen side. Fast hydraulic flushing therefore did not show the same cleaning performance for HF membranes when used for AL-DS orientation. We further suggest that due to comparatively larger SL pores, the BGW solute penetrates deeply into comparatively larger SL pores which are difficult to remove by fast flushing. The flow performances within the HF lumens and HFFO module shell are entirely different and these do not produce enough clipping on both sides of the membrane surface. This results in different cleaning effects for two sides of the HFFO membrane.

9.3.1.4 Effects of fast hydraulic flushing for organic fouling

HFFO modules used for fouling studies with Alginate, HA and BSA loaded DI or BGW FS were also subjected to similar fast flushing. The fouling reduced the flux performances of the HFFO membranes by 9% and 49% for AL-FS and AL-DS orientation respectively. It was observed that the similar hydraulic flushing showed unproductive results for organically fouled membrane cleaning. For the membrane used in AL-FS orientation, normal flushing and fast flushing did not show any improvement for flux whereas for AL-DS orientation it was observed that it recovered 6.24% of the lost flux capacity (Fig. 9.2). This suggests that as the alginate, HA and BSA forms a gel type sticky fouling layer on the membrane surface it requires additional force to dislodge the fouling layer from the membrane surface. For this reason, flux performance of the HFFO wasnot fully recovered for organic foulants loaded FS.

9.3.2 Chemical Cleaning

Chemical cleaning was planned for the membrane where fast flushing did not restore the flux performance of the fouled HFFO membrane affected with combined fouling when operated in AL-DS orientation. Earlier studies have indicated various chemical cleaning protocols for different types of membranes using various acid and caustic solutions (Li and Elimelech, 2004, Ang et al., 2006, Mohammadi, 2001, Siavash Madaeni et al., 2001). For low price and ease of availability, HCl and NaOH were selected for the membrane cleaning.

HCl and NaOH were used in various combination sequences for HFFO membrane cleaning as indicated in Fig. 9.1 and these include acid only, acid-caustic, caustic-acid and caustic only. HCl was used at pH 2 whereas NaOH was used for pH 11. After each acid or alkaline cleaning, both sides of the membrane were initially flushed twice with DI water and then evaluated with 2 M NaCl DS and DI water FS to record the flux outcome.

One chemical cleaning plan consumed about 100 minutes for the following cleaning protocol; flushing with DI water 10 minutes, chemical recirculation 30 minute, chemical stay 20 minutes, chemical recirculation 30 minutes, rinsing twice with DI water (5 minutes each).

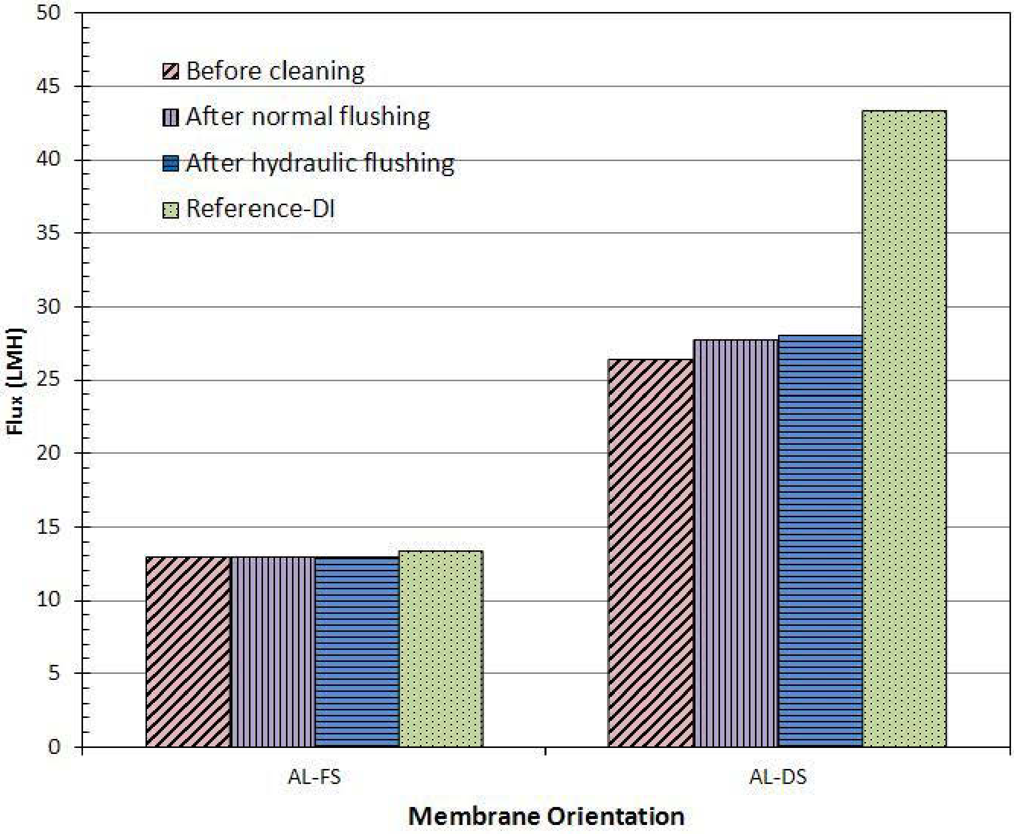

Fig. 9.2. Effect of physical cleaning of HFFO membrane for AL-FS and AL-DS orientation. 2 M KCl DS and 60 mg/L each of HA and BSA were used with BGW35 quality FS for the fouling test. Normal flushing was carried out at crossflow rates representing Re of 1900 and 700 whereas fast hydraulic flux used higher crossflow Re. of 2350 and 1450 for lumen side and shell side respectively.

Also, when both the HCl and NaOH cleaning were used together in different cleaning orders, one after the other, the total chemical cleaning time was extended to 190 minutes.

The uncleaned membrane was then subjected to chemical cleaning. The membrane chemical cleaning was initially performed by circulating chemical solutions on both sides of the membrane. However, the outcomes showed that the chemical cleaning of only the feed side successfully restored the membrane performance. Hence, later, most of the chemical cleaning experiments were just restricted to the FS side cleaning of the membrane (in AL-FS orientation, inner side of HF lumens and in AL-DS orientation, outer side of HF lumens).

9.3.2.1 Acid (HCl) cleaning for HFFO membrane

Looking into the characteristics of various BGW quality FS evaluated for this study carrying inorganic solutes only, FO membrane cleaning was attempted using HCl solution (pH-2). It was noticed the acid cleaning for 90 minutes successfully restored performances of the HF membranes used earlier for inorganic scaling studies at AL-FS and AL-DS orientation. HCl easily dissolved out most of the scale forming solutes deposited on the membrane surface or trapped inside the porous support layer during FO operation in AL-DS orientation and this successfully restored flux.

HCl was used alone and in other combinations for cleaning the fouled membrane. This was used with BGW quality FS carrying on organic foulants. However, it was observed that for FO operated for FS on carrying organic foulants in DI water or various qualities of BGW, HCl cleaning alone did not produce good results to fully restore flux (Fig. 9.3). Nevertheless, the results indicated that when it was used in combination with NaOH cleaning, the HFFO membrane flux was fully restored.

9.3.2.2 Alkali (NaOH) cleaning for HFFO membrane

Fig. 9.3 presents the flux outcome when the HFFO membrane was used with FS carrying on 60 mg/L each of Alginate, HA and BSA with BGW35 and then cleaned for fouling using various cleaning protocols. Among the above chemical cleaning sequences, for membranes fouled with combined foulants (inorganic or/and organic), the optimum results for chemical cleaning were achieved for 90 minutes of NaOH cleaning carried out at pH 11. Results further indicated that for organically fouled membranes, among the various cleaning protocols, NaOH cleaning alone gave the best results to successfully restore the FO flux in the shortest period of time.

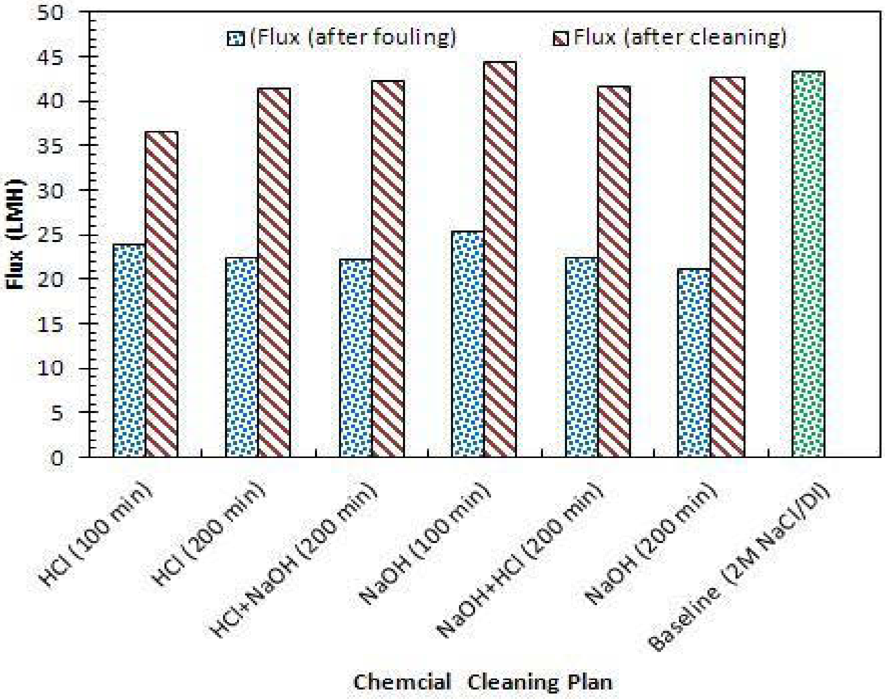

Fig. 9.3. Performances of various combinations of chemicals (HCl and NaOH) for HFFO membrane cleaning. Membrane was used for fouling experiments in AL-DS orientation.

Based on these findings, further membrane cleanings were performed only with NaOH at pH 11 and the results are presented in Fig. 9.4. The FO membrane was evaluated for fouling using various combinations of different BGW quality FS with 60 mg/L each of Alginate, HA and BSA. After fouling tests, the performance was checked with 2 M NaCl and then the membranes were subjected to cleaning with NaOH (pH 11). Fig. 9.4(a) presents few flux performances for NaOH cleaning for the FO membrane which was earlier used in AL-FS orientation. The results indicated that for membranes used with FS with organic foulant, NaOH cleaning uniformly show better outcomes. The results indicate that the chemical cleaning with NaOH successfully restored the FO membrane flux in 95% cases and delivered resultant flux with only ± 1% deviation.

Some of the cleaning results show a higher flux outcome with NaOH, even higher than the baseline flux. This is similar to the higher flux performance for membranes treated with NaOH. Membrane treatment with NaOH adds more OH groups in the polymer chain which results in a decrease of the zeta potential of the membranes (Tang et al., 2007). Membranes with lower zeta potential show improved flux performance for different membranes (Jeong et al., 2007).

Similarly, for the HFFO membrane used in AL-DS orientation, NaOH chemical cleaning successfully restored membrane performance in 86% cases. These membranes earlier showed severe fouling effects as the resultant flux in AL-DS orientation was dropped by 16 to 48%. A resultant flux comparison with the baseline outcome indicates up to ±2% variation in flux (Fig 9.4(b)).

Similar to cleaning results for membranes used in AL-FS orientation, in some cases, FO membranes after cleaning showed an even higher resultant flux than the baseline outcome.

The high negative charge of the membrane (lower zeta potential) helps quick and easy penetration of water molecules through the membrane. Higher flux outcome with a highly negatively charged membrane further indicates that the water permeation through the membrane starts with the association of the H^+ part of the water molecule and the negatively charged membrane and this helps water molecules to come closer and pass through the membrane pore.

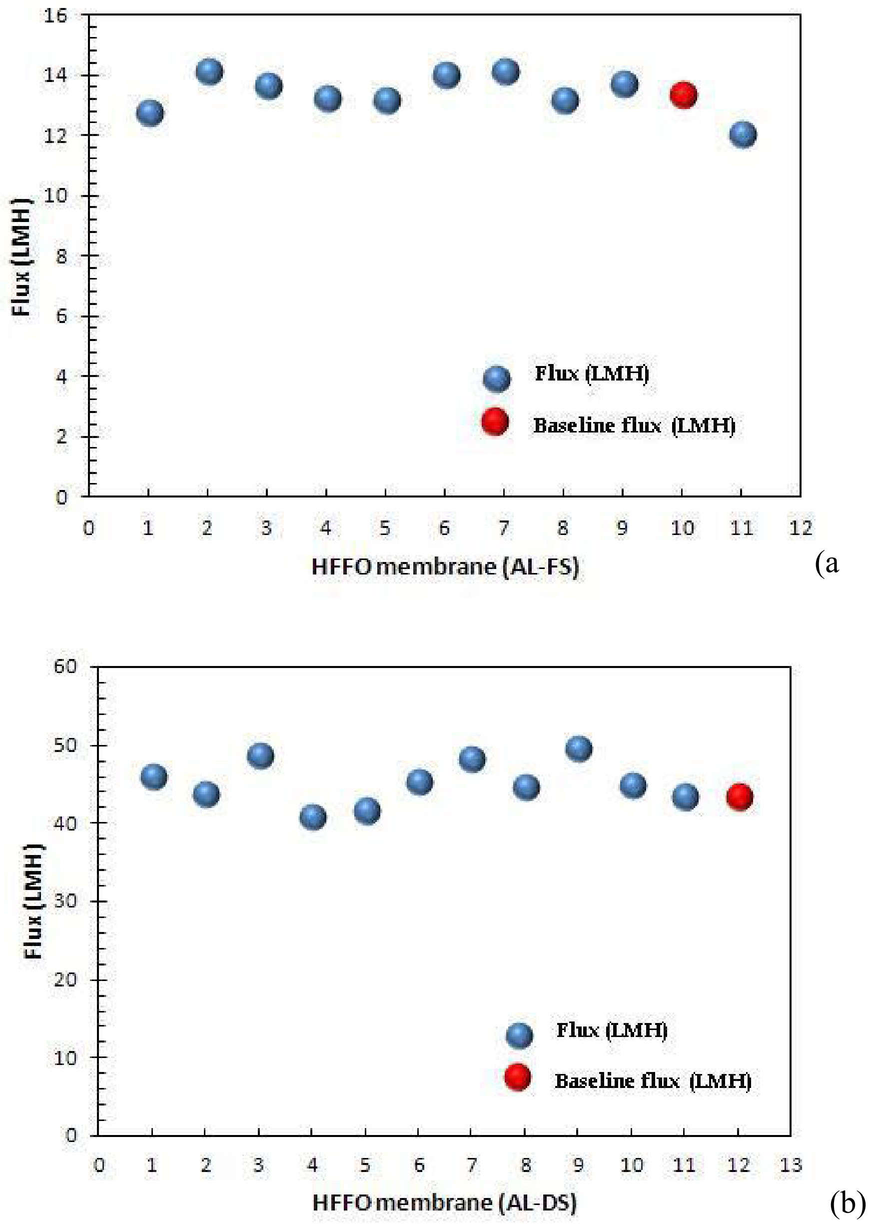

Fig. 9.4. Performances of FO membrane with cleaning a) resultant flux at AL-FS orientation b) flux at AL-DS orientation. Red circle shows the baseline flux

9.3.3 Chemical cleaning with EDTA cleaning

EDTA was further assessed to evaluate the possibilities for improvement in the membrane cleaning efficiency. EDTA has been earlier used in various studies and it showed a remarkable ability in terms of membrane cleaning (Hafez et al., 2002, Li and Elimelech, 2004, Ang et al., 2006). EDTA disrupts the fouling layer structure through ligand exchange between foulants and Ca^{2+} complexes which results in an increase of inter chain repulsion among foulant macro molecules leading to favourable conditions for the desorption of foulants from the fouling layer. 1 mM EDTA was used for FO membrane cleaning with pH adjusted to 11 using NaOH. The following cleaning protocol was used; flushing DI water 5 minutes, chemical circulation 15 minute, chemical stay 5 minutes, chemical cleaning 10 minutes, rinsing twice with DI water (5 minutes).

After the fouling experiments using FS containing 60 mg/L of HA with BGW35 for 3 hrs, FO flux was noted for fouling effects and membrane cleaning was carried out separately with NaOH and EDTA and their cleaning performance in terms of time consumed and flux restoration is presented in Fig. 9.5. The comparison shows that the EDTA demonstrated better cleaning performance as it takes a lesser time of 45 minutes to clean the membrane fouling. EDTA at high pH de-protonated all carboxylic groups and broke down the gel layer more quickly (Al-Amoudi et al., 2008, Ang et al., 2006). EDTA forms associations with the metallic ions in the fouling layer which serve to weaken their association with the membrane surface and reduce the adhesion forces between the fouling layer and membrane surface. This helps the quick detachment of the fouling layer from the membrane surface and thus membrane cleaning is achieved in a short time. NaOH cleaning efficiency was also checked after 45 minutes but the FO membrane showed a lower flux. NaOH cleaning was repeated again for 45 minutes which helped fully restore the FO flux.

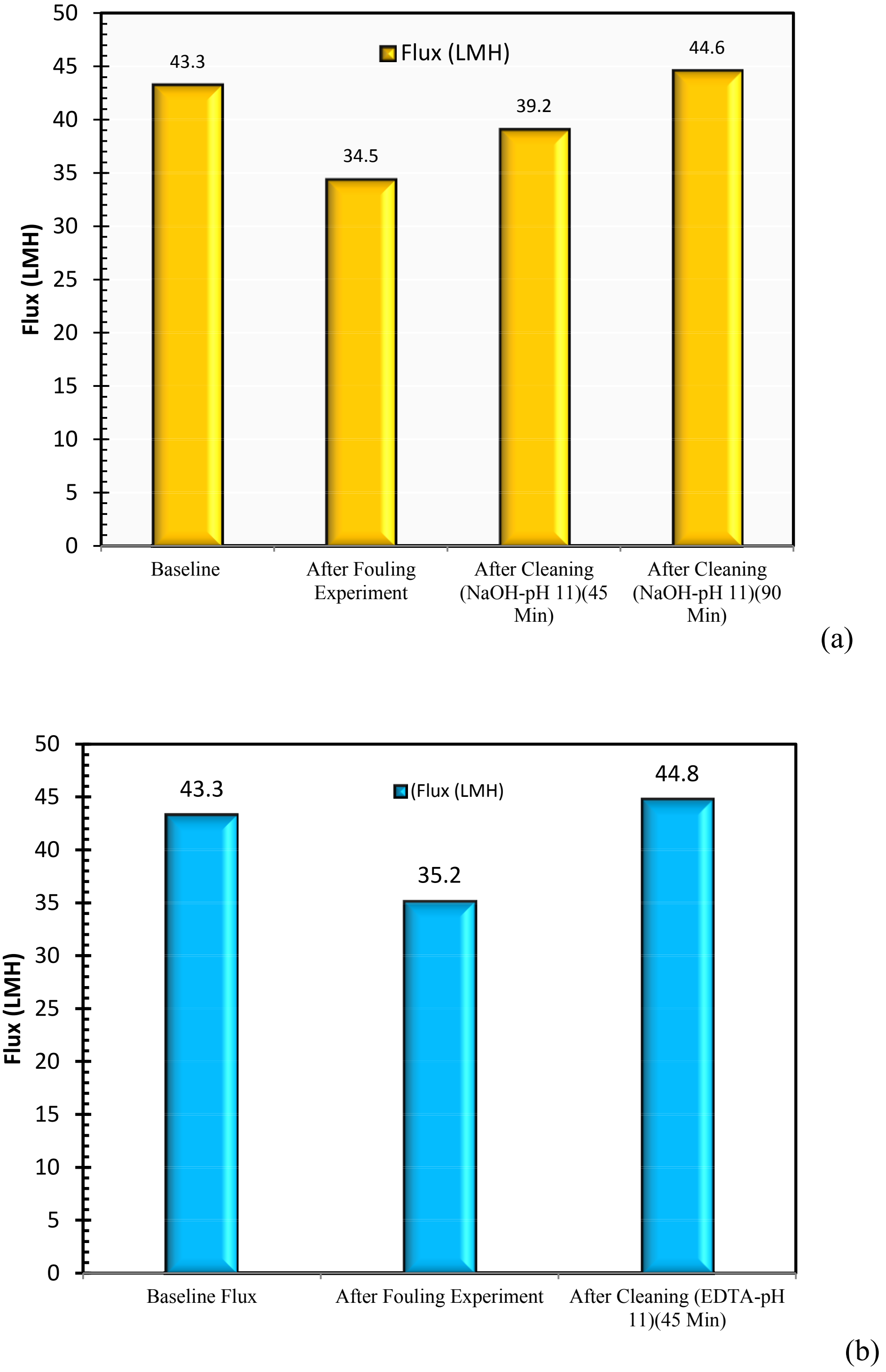

Fig. 9.5. Comparison of the performances of different chemicals for FO membrane cleaning a) Chemical cleaning using NaOH (pH 11) and b) Chemical cleaning using 1 mM EDTA (pH 11)

9.4 Concluding remarks

The HFFO membrane was assessed to evaluate various physical and chemical cleaning techniques for their cleaning efficiencies for membrane fouling which occurred as a result of different FS qualities carrying model organic foulants such as alginate, HA and BSA. The following conclusions can be drawn from the outcome of this study:

1) Hydraulic flushing helped clean HFFO membranes used in AL-FS orientation for fouling with FS with inorganic foulants whereas it did not fully restore the flux for the FS membrane in AL-DS orientation. The higher crosssflow Re values at any particular area seem important for the cleaning.
2) HCl cleaning was found to be more effective for removing inorganic scale whereas NaOH cleaning for a similar period successfully restored the flux for all the membranes used for FS with inorganic and/or organic foulants.
3) Compared to NaOH cleaning, EDTA cleaning (1 mM concentration at pH 11) showed superior results in terms of membrane cleaning as it helped to successfully restore the membrane flux in a very short time.

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Chapter 10

CONCLUSIONS AND RECOMMENDATIONS

10.1 Introduction

One of the most pervasive problems afflicting people throughout the world is inadequate access to useful water. This issue is becoming more serious as the world population rises rapidly and this directly increases the demand for fresh water not only for general applications but for agriculture as well. To meet the rising demand for fresh water, the evaluation of low cost desalination techniques has always been the main focus for the research community in terms of targeting the huge amounts of seawater and brackish water available in reservoirs. Activities to reduce the operating costs for water desalination have gained further importance particularly when the desalination process is considered in the light of agricultural application.

Looking into the low cost forward osmosis (FO) water desalination technique which uses the natural osmotic pressure of the draw solute to drive osmosis rather than hydraulic pressure, fertilizer drawn forward osmosis (FDFO) has recently been introduced as a novel concept for low cost water desalination for agriculture purposes. For its low cost desalination potential, the FO process (which is quickly moving through its various developmental stages) has gained the full attention of the research community in the last decade.

This thesis provides further insight into the FO process and helps to clarify the issues that are directly contributing towards enhanced FDFO performance. This study explores other related important findings as to how various issues can affect the FO performance and it shows how negative consequences can be minimized by using different types of membrane in order to improve the overall FO performance. This study further aims to pinpoint and recommend possible future work directions that can help to further improve the performance of FO in order to gain real benefits in terms of low carbon foot print technology. Additionally, the important operational issues of membrane based systems such as membrane fouling and scaling are evaluated in detail.

10.2 Conclusions

10.2.1 Flux performances:

The FDFO process was assessed for various fertilizer DS's prepared for fertilizer requirements for various stages of the tomato crop growth. These DS's were prepared using commercial grade fertilizers and were evaluated for sea water quality feed solution (FS).

Results confirm that with these fertilizers can be used individually and in mixed form as well for preparing the required NPK quality DS. These DS's can be used for the FDFO process which successfully delivers varying flux outcomes. However, for mixed fertilizer DS's, the FO flux performances vary with the properties of the main fertilizer ingredient in that mixture.

It was observed that the flux for various fertilizers was increased by increasing the DS concentration and/or decreasing the FS concentration as these resulted in a higher net osmotic pressure difference ($\Delta\pi$) available for osmosis. Usually, only the $\Delta\pi$ is taken as the main parameter indicating the possible flux potential of any DS. However this study indicates that the various individual or mixed DS's carrying similar $\Delta\pi$ values do not deliver the same flux which reflects the involvement of some unknown interactions between the DS and membrane surfaces, both active layer (AL) and support layer (SL) for specific outcomes. Similarly, the results with various quality FS and DS concentrations indicate that flux performance does not vary linearly with the changes in $\Delta\pi$. Few fertilizers with high $\Delta\pi$ show lower flux performances to the fertilizer DS which carryies smaller $\Delta\pi$. This issue needs to be explored in detail as this may help us evaluate other DS's which were not evaluated earlier because they possessed smaller osmotic pressure.

With sea water quality FS, the FO showed a significantly lower flux and this highlighted the limitations of the FDFO process for high total dissolved solids (TDS) feed. Against the SW quality FS, few fertilizer DS's in 1M concentration showed a negative or lower flux.

It is observed that the higher feed TDS severely affects the FO flux performance. A little increase in the TDS of the FS results in a sharp reduction in the FO flux performance. Concentration polarization (CP) effects seem to contribute towards delivering these lower flux performances. Results further indicate that besides possessing higher $\Delta\pi$, the FO flux performance decreases comparatively more sharply with the rise in FS concentration and even for the higher DS concentration, the FO shows very low flux performance. With higher TDS feed, the flux outcome declines quickly and it reaches a low level for osmotic equilibrium issues and desalinates less water.

A CTA flat sheet and PA hollow fiber FO membranes flux performance comparison for various fertilizer DS's indicated that urea, $NaNO_3$, MAP, KNO_3 and $(NH_4)_2SO_4$ gave better flux performance with the CTA membrane whereas NH_4Cl, $Ca(NO_3)_2$ and KCl showed a higher flux with the PA membrane. These types of varying behavior for various DS's indicate that the DS properties and membrane characteristics work in tandem to produce particular outcomes for the FO process.

FO performance is usually linked to the thickness of the membrane or S value and this suggests that a high value directly affects the flux outcome. However, the comparison of CTA flat sheet and PA hollow fiber membrane performances indicates that besides the thinner CTA membrane used, the thicker PA membrane shows a better flux outcome for different fertilizer DS's. This indicates that the membrane thickness or S value does not work alone but rather associates with other membrane characteristics for any specific outcomes.

DS carrying similar cationic and anionic components exhibited varying performances for different types of membranes. This indicates that the FO flux for a particular membrane is associated with not only $\Delta\pi$ but rather both DS properties and these membrane characteristics collectively contribute to deliver a specific flux.

Additionally, as the FO process continues, DS concentration continuously decreases with time resulting in a regular flux decline. It is nearly impossible to maintain the same higher initial flux throughout the FO process. Lower water flux reduces the effectiveness of the FO process. This reducing flux also increases the cost of desalination as it requires the FS and DS to flow for a higher time to achieve a higher volume of water permeation.

FO was operated at varying DS and FS flow rates representing different Reynolds number (Re) values. Results indicated that the FO showed better flux outcome as the Re ratio for DS and FS decreased and vice versa. FO operation under the AL-DS orientation at varying DS and FS crossflow rates markedly showed enhanced performance outcome. It was observed that using 2 M NaCl as DS and DI water as FS, the HFFO successfully delivered water flux of 62.9 LMH at DS/FS Re of 3750/1500 whereas the same membrane in AL-FS orientation showed a flux of 9.67 LMH at DS/FS Re of 200/500. This indicated that the same membrane showed a flux increase of 511% which resulted from changes in the process conditions. It is suggested that the cross flow conditions help to modify the structure of PA pores which results in a higher flux outcome.

10.2.2 Reverse solute flux Performances

DS carrying higher valancy cationic or anionic such as Ca^{2+}, Mg^{2+}, SO_4^{2-}, PO_4^{3-} components comparatively showed less reverse solute flux (RSF) which reflects the importance of the size of the DS solute for specific RSF performance.

Paralleling various desalination membranes as reverse osmosis (RO), nano filtration (NF) and membrane distillation (MD), the salt rejection feature of the FO membrane is vital for any particular application. Mostly, these membranes are characterized for their salt rejection properties as these come with salt rejection rates of up to 99.5% (evaluated at lower feed water TDS of 500 mg/L). When operated with sea water TDS of 35,000 to 45,000 ppm or higher TDS feed, these membranes usually display a deteriorating performance. This is true for the FO membrane as well.

Different membrane and support layer pore properties as pore size, pore density and pore geometry play an important role for RSF. However, these are not the only parameters reflecting any RSF for the FO membrane, rather other properties of the membrane such as surface charge, zeta potential, functional group etc. seem to play their particular role in delivering specific RSF and flux outcomes.

Higher reverse solute flux (RSF) with many fertilizers was found at alarming rates especially with Nitrogen and Potassium fertilizers. This needs to be managed as the higher fertilizer RSF not only results in a eutrophication problem in the receiving waters but also increases the cost of desalination as additional fertilizer solutes are required to replenish the wastage. It is thereby suggested that additional efforts be made to keep the RSF in lower limits or zero. This may ease these operational issues and help avoid additional process related concerns for the environment as the RSF represents a great threat for the inland brackish water FO desalination.

Unlike the RO membrane, the FO controls two types of critical solute movements a) FS solutes towards the DS side and b) DS solutes towards the FS side. Thus FO membranes with inferior salt rejection properties deliver useless outcomes and are not required by the industry. On the other hand, most of the research for FO membrane development is focused on developing membranes which show a higher flux performance. No serious effort has been made to enhance salt rejection and reduce RSF. Besides the exisiting lower FO flux outcomes, the low cost FO can be operated for a number of other applications if the RSF is kept under control.

It was further observed that various DS's showed changing RSF performances for various membranes. DS carrying divalent ions as $(NH_4)_2SO_4$ and $Ca(NO_3)_2$ showed better performance with the CTA membrane whereas KCl, KNO_3, $NaNO_3$ and NH_4Cl performed well for RSF with the PA membrane. These further indicated a close association between membrane characteristics and DS properties for any given RSF outcome. It is of importance to understand the behavioral relationships between these two key components of the FO system.

From these results, it is concluded that the properties of the anionic part of the DS were found to be important for flux outcome whereas the RSF was largely influenced by the properties of the DS cationic part.

10.2.3 Use of final diluted DS

For all fertilizer DS used, the FO showed a higher value nutrients concentration in the final diluted DS which was over the recommended level for any particular crop use and hence it was not found to be suitable for any direct fertigation application. The concentration of final diluted DS increases further for FO operated with high TDS feed. To bring the nutrients level down to any acceptable level, the final diluted DS requires additional dilution with the available fresh water source or it needs to link with any hybrid desalination technique such as NF, MD or RO.

The separation of the FO permeated water from the DS is a serious concern as the final diluted DS may not be used for any particular application. In comparison to the existing desalination technologies, the success of the FDFO desalination process as an ideal low energy desalination process requires that FO, as a stand-alone process, must produce water quality acceptable for direct fertigation. For osmotic equilibrium issues, with higher TDS feed, the FO process always ends up with the nutrients concentration higher than the initial TDS of the FS which requires additional process input to bring it down to an acceptable level to make it useful for any particular application. FDFO thus may not be used as a stand-alone system that may directly meet the water and nutrients requirements for any crop. To increase the acceptability of FDFO system, serious efforts either through process improvement and modifications are required to limit the final concentration of the DS.

10.2.4 Limited desalination capacity

Depending upon the fertigation plan of any specific crop, FDFO always uses a limited quantity of fertilizer DS to drive osmosis through the FO membrane. Each fertilizer DS carries a specific water extraction capacity which also drops sharply with the increasing feed TDS. With the given water extraction capacities of these fertilizers, it is observed that these fertilizers may be used as DS to produce desalinated water which may fulfill about 10-15% of the whole crop water requirements. This further raises questions for the sole use of FDFO for any agricultural application. Since the gap for the FDFO potential to desalinate water and total crop water requirements increases as the feed TDS increases, FO use for agricultural application becomes questionable and this seems to be another limitation of the FDFO process. FO definitely requires the support of additional sources of freshwater or another hybrid desalination technique that may help to manage additional water and bring the nutrients concentration in the diluted DS down to meet the irrigation requirement of any crop.

10.2.5 Membrane fouling and cleaning

Hollow fiber FO membrane was evaluated for its behavior for inorganic scaling and organic fouling risks and it was found that the FO, like the RO membrane, also poses potential operational risks in terms of scaling and fouling. During these FO fouling studies, it was noticed that the commonly used FO fouling protocol which is similar to the RO fouling protocol may not be successfully used to evaluate FO fouling. The RO fouling was evaluated against a fixed driving force (hydraulic pressure) and any changes in the flux performance may be referred to the fouling impact. However, in FO, as the driving force (net osmotic pressure difference between the FS and DS) keeps on changing constantly, it is really difficult to predict any flux changes associated particularly with the scaling or fouling. For any two tests, at any particular time, FO does not show the same driving force and hence for the evaluation of fouling, the flux comparison for two different curves may not be useful. Accordingly, a new protocol is suggested for FO fouling studies.

The HFFO membrane indicated varying degree of fouling potential for membrane use in AL-FS and AL-DS orientation. The FO showed a lower fouling risk for the membrane used in AL-FS orientation. However, it was found that these variations in the fouling effects are not related to membrane properties. Instead the hydrodynamic conditions employed for the process affects the fouling potential for the membranes used. Shear force developed due to higher Re flow used in the AL-FS which reduces the chances of fouling development on the membrane surface.

It was also observed that scaling and fouling are not fully reversed for the HFFO membrane used in the physical cleaning pratices of theAL-FS and AL-DS orientation as they depend totally on how the cleaning is attempted at various cross flowrates. Results indicated that the higher crossflow rate helps to clean inorganic scale from the membrane. This is similar to the flat sheet FO cell operation where the physical cleaning is carried out at higher flowrates which results in jet pressure water discharge on the membrane surface in the flatsheet FO cell. During hydraulic cleaning, this higher jet pressure also easily takes off the fouling layer from the membrane surface. The cell design of the flat sheet FO membrane and hollow fiber module displayed different aspects for membrane fouling and cleaning. However, for organic fouling, physical /hydraulic cleaning did not restore flux for the fouled membrane.

Chemical cleaning with HCl (pH 2), NaOH (pH 11) and EDTA (pH 11) was evaluated for membrane fouling for model organic foulants as sodium alginate, humic acid and BSA. It was found that EDTA (pH 11) showed a better outcome for membrane cleaning and it restored HFFO membrane flux in just 45 minutes time whereas NaOH (pH 11) cleaning took 90 minutes for similar membrane cleaning activity purposes.

The cell design of the flat sheet FO membrane and hollow fiber module indicated different aspects for membrane fouling and cleaning. Fouling rates and physical cleaning were affected with the hydrodynamic condition of the FO process. Membranes operating at higher Re values indicated less fouling whereas higher fouling rates were observed where the active layer of the membrane was subjected to lower Re flow. Similarly, the physical cleaning also helped to restore membrane performance when a higher shear force was applied using a higher Re flow rate.

10.2.6 Concentration polarization:

The concentration polarization (CP) affeceds the DS and FS effective concentrations at the membrane active layer and caused a lower actual flux in FO. FO showed lower flux performance to theoretical flux. The FO membrane always gives a flux driven by the concentrations present at the membrane AL interface and not by the actual concentrations of DS and FS. In either membrane orientation mode i.e., AL-FS or AL-DS, the CP phenomenon developed on both sides of the membrane, which reduced the net osmotic pressure available at the AL interface and restricted FO to achieve a high theoretical flux through the FO operation. However this study showed that flux started to decline sharply from the start which indicated that CP quickly builds up on the membrane surface and results in flux decline.

This CP build-up does not seem to develop for possible theoretical DS dilution and FS concentration effects as the FO process proceeds. The sharp flux decline in the initial stages of the FO run indicates that the CP develops not just for the concentration of FS solutes. Rather the DS and FS solutes develop associations with the AL and SL of the membrane which in turn cause a rise in the solute concentration at the membrane interface. We also predict that the FS solute particles develop loose associations with the functional groups of the membrane polymer responsible for the osmosis.

Long run batch FO operations indicate that the role of CP weakens with time. FO operation carried out for longer periods until the concentration of both DS and FS becomes similar indicates that the flux at those particular times is not seriously affected by CP and the FO gives an actual flux which is closer to theoretical flux. This observation needs some further investigation to understand how the higher CP value shown in the initial stage of experiments declines to a very low value. The overall CP at the later stages is not found to be so intensive.

10.3 Recommendations and future work

Better performances for flux and RSF from the hollow fiber FO module suggest that the HFFO is more suitable for the commercial FO application.

While in a few studies, for lower FS TDS application, the HFFO showed a better outcome for AL-DS orientation, it is recommended that the FO should be used in AL-FS orientation for commercial applications at a higher TDS feed. At AL-FS membrane orientation, the FO showed a better flux for high TDS feed and it also processed lower fouling risks.

The wide variations in the FO performance for changes in process operating conditions suggest that these issues should be seriously considered initially for the module design and later for the regular operation.

The study highlighted some practical limitations of the FDFO process along with issues such as lower flux with high TDS feed, higher RSF especially for N and K fertilizers and elevated nutrients concentration with all FS qualities. For the limitations of the osmotic equilibrium, the nutrients concentration in the final diluted DS further exhibited elevated values at a higher TDS feed.

The natural osmosis principle indicates that the net movement of water across the membrane towards the DS cannot extend beyond osmotic equilibrium, and the osmotic equilibrium is limited by the osmotic pressure or TDS of the feed solution. Further, for all batch type experiments in this study, with the continuous osmosis of pure water molecules towards DS, the concentration of the FS further increases. The RSF movement towards the FS side also increases the salts concentration in the FS. FO operation in such an environment shifts up the equilibtium towards higher values. This phenomena ends up with a higher nutrients concentration in the final diluted DS. This effect may be reduced by using once through FS as feed where FS concentration build-up or RSF may affect the FS quality. However, it may increase the chances of fouling as fresh FS may continuously bring new foulants to the membrane.

The above mentioned process inadequacies highlight the roles of major inherent process issues which directly diminishes the true advantage of this low cost desalination approach. Membrane characteristics and DS properties play vital roles for any particular outcomes of the FO process but their influence for any specific FO outcome still needs further investigation.

Studying membrane properties and their role in water movement in any membrane process should be identified in detail. From the available literature sighted and the current study outcomes, it is observed that no clear cut theory presents the mechanism of actual water movement through any membrane. It is really difficult to describe how the water molecule really permeates through the membrane pores. Various studies have indicated the role of various membrane properties such as pore size, zeta potential, and the surface charge of the membrane. The two types of membrane used in this study delivered varying performances which indicates the active role of the membrane characteristic in terms of delivering any flux performance.

Chapter 6 and Chapter 9 indicate that the FO membranes shown higher flux for the negatively charged membrane or membranes carrying higher OH functional groups. In FS, water is usually present in an ionized form with a partial negative charge on oxygen and a partial positive charge on hydrogen. Looking into the repulsion of same charge species and attraction of opposite charge species properties, we may conclude that for the negatively charged membranes or membranes carrying –ve functional group, the water molecules permeation starts from the opposite charge side of the water molecule i.e., the H^+ side. The H^+ side of the water molecule is attracted by the OH functional group of the membrane and it initiates the osmosis process. This theory needs to be explored further as a detailed understanding may help research groups working towards delivering various new innovative membrane materials.

Hydrated radii of the various salts have been commonly used with various membrane processes to understand the possibilities of solute movement or salt rejection through the membrane. Again similar to the flux outcome for various levels of $\Delta\pi$ applied for the FO process for flux outcome, the study indicated varying RSF outcomes but failed to indicate any direct relationship of the pore size and hydrated radii for any specific RSF outcome. Further research is still required to ascertain the role of hydrated radii and membrane pore size for solute movement through the membrane.

FO uses the difference in the osmotic pressures of the DS and FS as a driving force. To get maximum flux outcome, various DS's are used in high concentrations. However, for any FO membrane possessing lower specific salt rejection, the risk for high RSF increases with the DS use at elevated concentrations. It seems very difficult with the existing low rejection FO membranes to overcome the higher RSF outcomes. Accordingly, this suggests that further work should be done to develop membranes showing 100% salt rejection performance.

It is suggested that for the success of the FO process, limiting RSF may provide opportunities for quick FO commercialization. In most of the real life desalination and other useful FO applications, RSF's serious consequences for FO operations were found to be the only issue. An FO process using a better quality membrane and an appropriate DS may accelerate FO acceptance and help commercialize FO application.

HFFO showed better flux performance at AL-DS orientation using DI water feed. However, its flux decreases as it was operated with high FS concentration. For SW quality feed, the FO membrane showed an even higher flux at AL-FS orientation. On the other hand, in comparison to the FO application at AL-FS orientation, the HFFO showed a higher scaling and fouling risk when the membrane was used in AL-DS orientation. Combining these outcomes, to get better results with high TDS feed and lower fouling risks, it is recommended that FO should only be used in AL-FS membrane orientation.

Chapter 7 indicated that the changes in the process parameters resulted in wide variations in the flux outcome. For this reason varying FO outcomes by various research groups operated at different process parameters does not clearly indicate which of the DS properties or membrane characteristics are involved in the delivery of any specific outcome. Hence research work is not particularly focused in one direction. For this reason, these studies failed to identify any improvement of flux or RSF performance within these membranes.

Looking into these variations, it is recommended that the uniform process conditions for evaluating FO performance should be adopted and followed. This may really help us to understand and evaluate any difference in the FO performance when there are varying DS and FS qualities in different membranes.

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