

A NOVEL FERTILISER DRAWN FORWARD OSMOSIS DESALINATION FOR FERTIGATION

by

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A Thesis submitted in fulfilment for the degree of

Doctoral of Philosophy



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CERTIFICATE OF AUTHORSHIP/ORIGINALITY

I certify that 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 acknowledge within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of candidate

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LIST OF ABBREVIATIONS

FO	: Forward osmosis
FDFO	: Fertiliser drawn forward osmosis
RO	: Reverse osmosis
SWRO	: Seawater reverse osmosis
PRO	: Pressure retarded osmosis
BW	: Brackish water
BGW	: Brackish groundwater
RSF	: Reverse solute flux
SRSF	: Specific reverse solute flux
DS	: Draw solution
FS	: Feed solution
SIS	: Salt interception scheme
MDB	: Murray-Darling Basin
MDBA	: Murray-Darling Basin Authority
CP	: Concentration polarisation
ICP	: Internal concentration polarisation
ECP	: External concentration polarisation
GL	: Giga litre
CTA	: Cellulose triacetate
TFC	: Thin film composite
CA	: Cellulose acetate
PWP	: Pure water permeability
HTI	: Hydration Technology Innovations
NF	: Nanofiltration
TDS	: Total dissolved solids
DI water	: Deionised water
NPK	: Nitrogen Phosphorous Potassium
PR	: Performance ratio
EC	: Electrical conductivity
MSF	: Multi stage flash
MED	: Multi effect distillation
DAP	: Diamminium phosphate or $(\text{NH}_4)_2\text{HPO}_4$
MAP	: Monoammonium phosphate or $\text{NH}_4\text{H}_2\text{PO}_4$
SOA	: Sulphate of ammonia or $(\text{NH}_4)_2\text{SO}_4$
MW	: Molecular weight
PAO	: Pressure assisted osmosis

List of Symbols

A	: Pure water permeability coefficient ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$)
B	: Salt permeability coefficient (m.s^{-1})
C	: Solute concentration (mg/L or Moles or M)
D	: Diffusion coefficient (m^2s^{-1})
d_h	: Hydraulic diameter (m)
J_s	: Solute flux ($\text{mmoles.m}^{-2}.\text{h}^{-1}$ or $\text{g.m}^{-2}.\text{h}^{-1}$)
J_w	: Water flux ($\text{Lm}^{-2}\text{h}^{-1}$)
k	: Mass transfer coefficient
K	: Resistance of solute diffusion within the membrane support layer (s/m)
L	: Length of the channel (m)
M	: Molar concentration of the solution (M)
M_w	: Molecular weight (mol/g)
n	: Van't Hoff factor
P	: Applied hydraulic pressure (bar)
R	: Universal gas constant ($0.0821\text{ L.atm.mol}^{-1}\text{K}^{-1}$)
Re	: Reynolds number
R_s	: Salt rejection (%)
Sc	: Schmidt number
Sh	: Sherwood number
T	: Absolute temperature (in K)
π	: Osmotic pressure (atm or bar)
σ	: Reflection coefficient

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ABSTRACT

Agriculture consumes maximum water of up to 70% of the total fresh water withdrawn in the world for consumptive purposes. Rapid population growth is further driving fresh water demand and putting tremendous stress on limited fresh water resources. This increasing demand can only be met by improving the current water use efficiency and by creating new water sources. Desalination could therefore play a significant role in creating a new water source by using unlimited saline water sources. However, current desalination technologies are energy intensive and energy has a significant impact on climate change. If low cost desalination technologies were made available, their impact on agriculture sector would be significant for many water stressed regions of the world.

Recently, forward osmosis (FO) has been recognised as one of the most promising low energy processes for desalination. The FO process is based on the principle of natural osmotic process driven by the concentration gradient and not by hydraulic pressure like the reverse osmosis (RO) process and hence requires significantly lower energy. In the FO process, a concentrated draw solution (DS) extracts fresh water from the saline water using special membranes. The issue of membrane fouling in FO process is less challenging than the RO process where fouling constitutes a major operating issue. However, the lack of a suitable DS has limited the application of FO desalination for potable water. The separation of draw solutes from the diluted DS after desalination requires additional post-treatment processes that still consume energy, making FO uncompetitive with the already established RO desalination technology.

The FO process offers novelty for those applications where the complete separation of draw solutes is not necessary and where the final diluted DS can be used directly if the presence of draw solutes adds value to the end use. Fertiliser drawn forward osmosis (FDFO) desalination for fertigation is therefore proposed based on this concept. When fertilisers are used as the draw solutes in the FDFO desalination process, the diluted fertiliser solution after desalination can be directly applied for fertigation because fertilisers are essential for plants. This concept avoids the need for an additional post-treatment process for the separation and recovery of draw solutes. The objective of this study is therefore to investigate the performance of the FDFO desalination process for fertigation, identify its limitations and investigate options to overcome these limitations. The study has been presented in eleven chapters that include a definition of the detailed

concept and an assessment of the performance of eleven selected fertilisers as the DS under various conditions, through both simulation and bench-scale experiments.

The energy required for FDFO for direct fertigation was estimated to be less than 0.24 kW/m³ of fertigation water, which is comparatively lower than the most efficient current desalination technologies. As such, FDFO can also be easily powered using renewable energy sources, such as solar and wind. Since fertilisers are extensively used for agriculture, FDFO desalination does not create additional environmental issues related to fertiliser usage. In fact, FDFO desalination could add more value to irrigation water, thereby providing opportunities for improving the efficiency of water and fertiliser uses. FDFO desalination can be operated at very high feed recovery rates: higher than 80% using a feed of seawater quality. However, FDFO desalination has its own process limitation. Based on the principles of natural osmosis, the net movement of water across the membrane towards the DS cannot theoretically extend beyond osmotic equilibrium, which in turn is limited by the total dissolved solids (TDS) content of the feed solution (FS). Therefore, it is not possible to achieve a concentration of the diluted DS that is lower than the equivalent concentration of the FS without external influence.

Based on the models for osmotic equilibrium, the water extraction capacities of eleven selected fertiliser DS were calculated for FS, simulated for different ranges of TDS. The water extraction capacities of the fertilisers were observed to depend on the molecular weight and osmotic pressure of the draw solutes, as well as on feed concentration. Based on the water extraction capacity, the expected fertiliser nutrient concentrations in the final FDFO product water was estimated in terms of nitrogen phosphorous potassium (NPK) concentrations. The expected final nutrient concentrations for simulated brackish water (BW) feed (TDS 5,000–35,000 mg/L) failed to meet acceptable NPK concentrations for direct fertigation of crops. Hence, achieving acceptable nutrient concentrations for direct fertigation will be a major challenge for the FDFO desalination process. The rest of the study therefore focussed on investigating processes and options that would help reduce the nutrient concentrations in the final FDFO product so that the final FDFO product water could be used for direct fertigation.

Before the experimental investigation on the FDFO desalination, the influence of major parameters on the performance of FO desalination process was investigated. The

thermodynamic properties of the DS play a more influential role on water flux than the thermodynamic properties of the FS at higher temperature. Although water flux comparable to the RO desalination process was obtained by increasing the fertiliser DS concentrations, the internal concentration polarisation effects played a significant role in the performance of the FDFO desalination process. It was observed that any soluble fertilisers with osmotic pressure in excess of the FS can draw water in FO process; however, only eleven different chemical fertilisers commonly used for agriculture worldwide were selected and their performances studied. The performance of the fertiliser solutions as DS were assessed in terms of water flux, reverse draw solute flux, water extraction capacity and nutrient concentrations in the final product water.

Blended fertilisers as the DS were able to achieved significantly lower NPK concentrations by FDFO desalination than the straight/single fertiliser as DS. However, it was observed that blending fertilisers generally resulted in a slightly reduced bulk osmotic pressure and water flux compared to the sum of the osmotic pressures and water fluxes of the two individual fertilisers when used as DS alone. An integrated FDFO-NF desalination process was investigated to reduce the nutrient concentrations in the final product water. Nanofiltration (NF) as pre-treatment or post-treatment was found to be effective in reducing the final NPK concentrations to acceptable limits for direct fertigation although it required second NF pass, especially when monovalent fertiliser was used as the DS or when a high TDS feed was used. NF as post-treatment was more advantageous in terms of both nutrient reduction and energy consumption because high quality, diluted DS was used as feed.

Finally, this study has recommended a pilot test of the integrated FDFO-NF desalination process in the Murray-Darling basin. Recommendations for further investigations on reducing nutrient concentrations include pressure assisted FDFO desalination and the concept of using osmotic fillers as the DS with fertilisers. The study also recommended evaluating the potential for fertiliser drawn pressure retarded osmosis (FD-PRO) desalination for simultaneous desalination and power generation, and for self-powering the FO desalination process. The other recommendations include a study on membrane fouling and scaling issues for FDFO desalination operated at high recovery rates, boron rejection and, finally, a life cycle analysis of the FDFO desalination process.

CHAPTER 1



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INTRODUCTION

1.1 Introduction

The United Nations estimates that the world population, which stood at 6.8 billion in 2009, has already crossed 7 billion in 2011 and is expected to reach about 9 billion by 2050 (UN, 2009). Therefore, one of the most crucial challenges of the 21st century is to meet the increasing demand for potable water and adequate food supply to meet this enormous population growth (Ward and Pulido-Velazquez, 2008). The current estimate is that more than one third of the world's population lives in water-stressed countries and this figure may rise to nearly two thirds by 2025 (Service, 2006). Water shortages are exacerbated by the impact of climate change resulting in frequent drought and unpredictable rainfall events in many parts of the world, creating further uncertainty about water availability and food security (Whetton et al., 1993; Mearns et al., 1996; Hughes, 2003; McDonald et al., 2011).

Measures such as water conservation, infrastructure repair, improved catchment and distribution systems may alleviate water stress to a certain extent; nevertheless, these measures only help to improve existing water sources and do not create new water resources (Elimelech and Phillip, 2011). In the face of climate change and the increasing global water crisis, the prospey of scientific solutions playing a crucial role in solving water issues is increasing (Jury and Vaux, 2005), including making water available from non-conventional sources such as saline water. One such area is through the application of membrane technologies for water purification (Shannon et al., 2008). The current generation of membrane technologies, particularly reverse osmosis (RO), has significantly improved the scope for the use of saline water and impaired wastewater effluent as an alternative source of water to augment fresh water or to reduce pressure on freshwater resources. Desalination technologies are therefore seen as a promising alternative in alleviating water scarcity in arid and densely populated regions of the world (Service, 2006; McGinnis and Elimelech, 2007).

While desalination for drinking water supplies has become part of the commonly adopted water management policies of many governments all over the world, desalination for large-scale irrigation is rarely studied. In fact, a survey of literature on desalination for irrigation purpose indicates that desalination technology for irrigation is comparatively less studied than desalination for potable purposes. Desalination using

currently available technologies such as distillation and RO is still seen as an energy intensive process and therefore not an economically viable option for large-scale irrigation purposes (Sturdivant et al., 2007). Depending on the cost of the power, energy accounts for 30 to 45% of the total cost of the final product water from a desalination plant (Sturdivant et al., 2007). Moreover, the economic competitiveness of the desalinated water for irrigation is normally compared against fresh water which is available at almost negligible cost from natural sources. Given dwindling freshwater supplies and the competition from other beneficial uses, desalination for irrigation could become a viable option for irrigation of high value crops. However, when water, energy and environmental issues are interrelated (McGinnis and Elimelech, 2008; Semiat, 2008), a desalination technology that consumes much lower energy is essential, especially for large scale irrigation purposes. Addressing global water scarcity problems therefore calls for extensive investment in research to identify robust and new methods of purifying water at lower energy and cost (Shannon et al., 2008). If low cost desalination technologies were made available, their impact on the agriculture sector would be significant for drought stricken countries like Australia where saline water is abundant in the form of seawater in coastal areas and brackish groundwater in inland areas.

Recent efforts have focused on developing new desalination technologies that require much lower energy than conventional technologies such as RO. Forward osmosis (FO) is one such emerging technology that promises low energy consumption (McGinnis and Elimelech, 2007; McGinnis and Elimelech, 2008; Choi et al., 2009; Achilli et al., 2010; Lay et al., 2010; Tang et al., 2010). Unlike the RO process, which separates water from salt using a semi-permeable membrane at very high hydraulic pressure, FO separates saline water sources by simply using a concentration gradient. A highly concentrated draw solution (DS) that generates high osmotic pressure is used to draw water from a saline water source. Depending on the end-use of the product water, the diluted DS is usually further processed to separate and recover the draw solutes. Recent studies indicate that membrane fouling in the FO process is not as problematic as it is experienced in the RO process (Cornelissen et al., 2008; Mi and Elimelech, 2008; Lay et al., 2010; Mi and Elimelech, 2010).

Although the novel concept of FO desalination using a natural osmotic process was conceptualised as early as 1968 (Popper et al., 1968), it has not been advanced since mainly due to a lack of suitable FO membranes and draw solutes. The current asymmetrical membranes used for pressure based filtration result in concentration polarisation (CP) effects that severely decrease the net driving force or osmotic pressure between the two solutions and hence lower the water flux across the membrane significantly (Cath et al., 2006; Gray et al., 2006; Tan and Ng, 2008; Tang et al., 2010). Several research breakthroughs have been reported recently in FO membrane fabrication, however, particularly with thin film composites, carbon nanotube and few other composite membranes (Wang et al., 2010a; Zhang et al., 2010; Chen et al., 2011) that may provide lower CP effects (Gethard et al., 2010; Schnorr and Swager, 2010; Wang et al., 2010b; Yip et al., 2010). These recent developments in FO membrane fabrication have significantly elevated research interest for the application of the FO process for various purposes.

Challenges remain in finding a suitable draw solutes for the application of the FO desalination process for potable water. In the FO desalination process, water is extracted using a highly concentrated DS however, the draw solute has to be separated once water is drawn from the saline water for reuse and recycling. The presence of draw solutes in the water is undesirable for human consumption. Separation and regeneration can be an energy-intensive process in an otherwise low energy process, and is one of the major limitations that prevents wider use of the FO process for drinking water applications (McGinnis and Elimelech, 2007; Hoover et al., 2011). The success of FO desalination in the future, especially for drinking purposes, will largely rely on how easily and efficiently the DS can be separated and recovered from the desalinated water (McCormick et al., 2008).

Where the fate of the DS after desalination by the FO process is irrelevant, or when a DS is used that adds value to the product water, FO offers a promising scope of applications over RO desalination (Hoover et al., 2011). In such cases, the diluted DS can be used directly as is, and fresh draw solutes can be added to the system to create additional product, thereby avoiding the need for additional separation and recovery steps. Eliminating the draw solute separation and regeneration steps can save a significant energy cost in FO desalination technology (Hoover et al., 2011). This merit

of the FO process has been exploited to provide a nutritious energy drink that uses sugar as the draw solute (Cath et al., 2006; Hoover et al., 2011) and for agriculture which uses fertilisers as the DS (Moody and Kessler, 1976). This process for nutrient-rich drinks has already been commercialised and used for life-saving equipment in the boats or during emergencies such as natural calamities (Cath et al., 2006). Other FO applications of non-potable purpose include the concentration of industrial wastewater (Anderson, 1977), the concentration of anaerobic digester (Holloway et al., 2007), sucrose concentration (Garcia-Castello et al., 2009) and dewatering of press liquor derived from orange production (Garcia-Castello and McCutcheon, 2011), all of which have the potential to use seawater or RO concentrate as the DS without the need for a separation process. Recently, FO desalination has been investigated for drinking water augmentation using a hybrid FO system using seawater as the DS and impaired water as feed water (Cath et al., 2010). Recently, the first commercial FO desalination plant with a capacity of 100 m³/day (Thompson and Nicoll, 2011) was built and operated in Oman since 2010 while another 200 m³/day was recently commissioned in the same country (Modern Water plc, 2012).

The same advantage has been capitalised in the proposed fertiliser drawn forward osmosis (FDFO) desalination process based on the concept initially proposed by Moody and Kessler (1976). In this concept, fertiliser solutions are used as DS to extract water from the saline water sources by FO process. The novelty of FDFO desalination is that the diluted fertiliser DS, after desalination, can be directly used for fertigation (fertilised irrigation) because it contains essential nutrients for plant growth. This avoids the need for the separation and regeneration of draw solutes and therefore represents an additional gain in terms of energy savings. The FO process is already a low energy technology and the avoidance of an additional separation and recovery process is another milestone in achieving irrigation water quality using much less energy. This would revolutionise the agricultural industry in arid regions such as much of Australia, where water scarcity is acute and there are no alternative sources of water for food production.

1.2 Research motivation

The following subsections outline the motivation behind this particular research.

1.2.1 Science & technology as a solution to water scarcity issues

The fresh water resources of the world are depleting, while world population is deemed to increase every year. This calls for science and technology to play a significant role in solving water scarcity issues, which are becoming increasingly evident in many parts of the world. Desalination technology in particular is expected to play a crucial role in solving the water issues in the future, because it can provide additional new water from an unlimited saline source on the planet.

1.2.2 Desalination as an alternative source of water for food production – essential for supporting the world's growing population

As much as water is important for potable use, it is equally important for food production to sustain the livelihoods of a rapidly growing population. Agriculture accounts for the highest water usage of up to 70% of the world's total fresh water consumption (Jury and Vaux, 2005). In Australia, agricultural usage varies between 50% and 70% while household use, including sewerage and drainage, uses less than 30%, and industry the remaining 20% (Khan, 2008; ABS, 2010; Rutherford and Finlayson, 2011). As fresh water becomes more scarce, priority for the water supply usually goes first to domestic water supplies, while agriculture is a lower priority. For the same reason, most of the efforts in developing technologies for desalination currently remain focussed on domestic supplies and a few industrial applications, not on food production. If low cost desalination technologies could be made available, even a small saving of fresh water from agricultural water use might make substantial quantities of water available for other beneficial uses for communities and the environment (Ward and Pulido-Velazquez, 2008; McDonald et al., 2011). The current cost of desalinated water is still comparatively higher than the cost of natural fresh water resources however; recently the cost of desalinated water has been falling gradually driven by the increased adoption of desalination technology and increased efficiency. This study is an initiative towards increasing the prospects of desalination technology for high value food production.

1.2.3 Need for a novel low energy desalination technology for sustainable use of brackish groundwater for food production in the Murray-Darling Basin

Australia's food production supports a population of more than 20 million within Australia and another 40 million in other countries through food export. About 40% of the nation's food production comes from the Murray-Darling Basin (MDB). The basin, known as the food bowl of Australia, is a strategic region for Australian national economy (MDBA, 2010b). MDB receives only about 6% of Australia's annual rainfall and yet 75% of Australia's total irrigated land is concentrated here (MDBA, 2010b) indicating the acute stress the fresh water resources are subjected to within the basin. Besides, the basin is a significant indicator of Australia's ecological health, because it is home to the country's most diverse and rich natural environments. However, it has suffered from major environmental issues due to the over- allocation of river water for consumptive use for several decades (Goss, 2003; MDBA, 2010b; Wentworth Group, 2010). Given the significance of the basin to the environment and the long-term sustainability of the basin's economy, the MDB authority (MDBA) released a guide to the Basin Plan in late 2010 which includes a proposal to reduce water allocation for consumptive use and make more water available for adequate environmental flows for a sustainable river ecosystem (MDBA, 2010b). This proposed water restriction will have a significant impact on Australia's agricultural economy, at least in the short-term, because 40% of Australia's food and fibre production comes from the basin.

Besides access to coastal saline water, Australia also has 25,780 GL of groundwater but some 28% of this groundwater has salinity levels higher than 1200 mg/L of TDS (total dissolved solids), rendering it unfit for direct irrigation. Much of the saline groundwater is located within the MDB (ANRA, 2009). This brackish groundwater in the MDB is now generally considered to be an environmental problem because its seepage and intrusion into the rivers contributes to rising river water salinity. To prevent the intrusion of this brackish groundwater, the water is currently pumped out under the salt interception scheme (SIS) to help control the increase in river water salinity. Although this SIS scheme has significantly reduced the salinity downstream (Goss, 2003), the brackish groundwater resource is simply lost through evaporation and does not involve sustainable use of groundwater. A sustainable SIS is required in the MDB, which not

only serves for salt interception but also allows the sustainable use of saline groundwater.

One way of doing this is by making full use of the brackish groundwater for irrigation as an alternative source to river water by desalination. Since current desalination technologies are energy intensive, low cost and low energy desalination technologies are essential for large-scale irrigation purposes. FO is an emerging low energy technology for desalination. Since the quality of water for irrigation is lower than for potable water, FDFO desalination is proposed as a very suitable desalination technology for fertigation. FDFO desalination has the potential to solve several issues facing the MDB, as follows:

- FDFO desalination technology can be suitably integrated with the current SIS
- It can lead to sustainable use of the brackish groundwater for irrigation
- It can make irrigation water available from alternative sources and reduce dependence on river water. allowing improved environmental flows and the interbasin transfer of water
- The technology is low cost and low energy and therefore can deliver irrigation water quality at substantially lower cost than current desalination technologies
- FDFO technology has the potential to revolutionise the agricultural industry in arid regions such as Australia where water scarcity is acute and there are no alternative sources of water for food production. The potential for such technology has been reflected as a very promising and practical application to make much-needed water available for high value food production (Hoover et al., 2011).
- While potential application outlined above is specific to the MDB, FDFO is applicable universally where freshwater resources limited and saline water is abundant.

1.3 Objectives and scope of the research

The concept of using FO desalination for irrigation was first proposed by Moody (1977), part of which was published in an earlier article that includes mathematical models for osmotic extractors (Moody and Kessler, 1976). Since then, there has been no detailed study related to this particular field. The main objective of this study is

therefore to advance the concept of FDFO desalination and evaluate its suitability for practical application as a low energy desalination technology for fertilised irrigation or fertigation of agriculture crops. The following are some of the specific objectives of this particular study:

- Elucidate the concept of the FDFO desalination process as a low energy desalination for irrigation and identify its limitations for direct fertigation
- Screen candidate fertilisers for use as DS for the FDFO desalination process for fertigation and assess their performance using basic models and simulations
- Evaluate the performance of the commonly used fertilisers as draw solutes through bench-scale experiments using a commercially available FO membrane
- Conduct fundamental studies on the FO desalination process, such as the factors responsible for influencing the performance of the FO desalination process
- Propose measures or options to lower the nutrient concentrations in the final FDFO to achieve water quality standards for direct fertigation
- Evaluate the performance of these options for achieving acceptable nutrient concentrations in the final FDFO product water so that the desalinated water can be directly applied for fertigation without requiring further dilution

1.4 Structure of the Study (Thesis outline)

This Thesis consists of eleven chapters with the background, research motivation, objectives and scope of the study included in Chapter 1 (Introduction). Chapter 2 presents a comprehensive literature review of the subject matter.

Detailed explanations of the experimental investigations common to all the chapters are described in Chapter 3, while an experimental description of specific studies can be found in their respective chapters.

The novel concept of FDFO desalination is elaborated in Chapter 4 in relation to its potential application in the MDB.

Chapter 5 concerns the screening of fertilisers as draw solutes and estimates their water extraction capacity based on the osmotic equilibrium models. The main challenges of

the FDFO desalination process for fertigation are also discussed and the options are briefly described.

Chapter 6 evaluates how some of the major factors (such as membrane properties, DS properties, feed solution concentrations and the operating parameters) influence the performance of the FO desalination process in general.

The influence of the operating parameters on the performance of the FO desalination process are included in Chapter 6, while more detail on the influence of temperature and temperature differences (or gradient) in the FO desalination process is included separately in Chapter 7.

Chapter 8 evaluates the performances of selected fertilisers as draw solutes for the FDFO desalination process through bench-scale experimental investigations.

Chapter 9 evaluates the blending of different types of fertilisers to prepare a DS containing all the major nutrients, N/P/K (nitrogen/phosphorous/potassium), required for the plants.

Chapter 10 evaluates the integrated FDFO - nanofiltration (NF) desalination process to achieve the acceptable final nutrient concentrations in the product water for direct fertigation without requiring dilution. NF is evaluated either as a pre-treatment or post-treatment option to reduce the fertiliser concentrations in the final product water.

Conclusions and recommendations are presented in Chapter 11.

CHAPTER 2



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LITERATURE REVIEW

2.1 Introduction

This chapter includes a brief review of literature relevant to this research on fertiliser drawn forward osmosis (FDFO) desalination for fertigation. It begins with a brief review of global water issues in general, followed by water issues in Australia, with particular emphasis on the Murray-Darling Basin. The review also identifies the critical roles desalination can play in solving water issues while at the same time acknowledging the issues and challenges of the different types of current desalination technologies. Energy has been identified as being strategically important to any new technology because conventional sources of energy are directly related to greenhouse gas emission, the recipe for global warming and climate change which in turn affect the water cycle, water availability and food security. Later in the review, the principles of forward osmosis (FO) and its various potential applications, including desalination, are discussed. A detailed discussion on the challenges of the FO desalination process is also covered. Since this research covers desalination for irrigation using fertilisers, a brief discussion on types of fertilisers and their applications are also discussed at the end.

2.2 Global scenario of water issues

Water and energy, which are increasingly interdependent, are essential for human habitation on earth (McMahon and Price, 2011). An estimated 1,386,000,000 km³ of water is found on the earth, occupying more than two thirds of its surface; however, about 97% of this water is in the form of saline water and is not useful for direct human consumption (USGS, 2010). Of the 2.5% total fresh water available on the earth, about 2% is locked up in the form of icecaps and glaciers and therefore unavailable for human consumption, leaving only about 0.5% of the total fresh water available for human use (Khawaji et al., 2008). Fresh water is a necessity for the survival of all species on the earth, but the modern need for water is complex because it includes water for the economy and increasing the livelihood of the growing human population.

Even as water fresh water resources are limited, the demand for water supply is increasing each year; of the variety of reasons given for this, rapid population growth has been cited as the main one. The world is currently in the middle of the most significant demographic upheaval in human history which has resulted in the doubling of world population between 1960 and 2000. (Bloom, 2011). The world's current

population of 7 billion is projected to reach 9 billion by 2050 (UN, 2009) with population growth mostly occurring in developing and under-developed countries. Currently, 1.4 billion people in the world lack safe drinking water supplies, while 2.6 billion people have no access to proper sanitation (Shannon et al., 2008). Because of the lack of access to clean and adequate drinking water coupled with poor sanitation, millions of people die annually, including 3,900 children a day, from diseases transmitted through unsafe water or human excreta (Montgomery and Elimelech, 2007). Therefore, lack of adequate access to clean water and sanitation is one of the most significant and challenging issues worldwide (Shannon et al., 2008; Vorosmarty et al., 2010).

The issue of worldwide water problems is well known and well documented, and the problem is expected to grow worse in coming decades, especially in developing countries where population is growing more rapidly and economies are expanding swiftly (Shannon et al., 2008; Vorosmarty et al., 2010). The current estimate is that more than one third of the world's population lives in water-stressed countries, but that this figure may rise to nearly two thirds by 2025 (Service, 2006). Population growth brings increased demand for water supplies for drinking, food production and industrial needs. The increasing demands placed on the global water supply has put tremendous stress on our limited fresh water resources, thereby threatening biodiversity and the supply of water for food production and other vital human needs (Pimentel et al., 2004). One of the most crucial challenges of the 21st century, therefore, is to meet the increasing demand for potable water and food supplies to cater for this enormous population growth (Ward and Pulido-Velazquez, 2008). The majority of these issues affect people living in the developing and underdeveloped regions of the world (Ashbolt, 2004). Climate change due to anthropogenic activities has created further uncertainty regarding water availability and food productivity by altering the global hydrological cycle (McDonald et al. 2011).

Agriculture consumes the largest share of fresh water resources of up to 70% in the world, and even more in the United States. For example, approximately 1,000 litres (L) of water are required to produce 1 kilogram (kg) of cereal grain, and 43,000 L to produce 1 kg of beef (Ashbolt, 2004). However, food availability may soon be limited

by water availability and the optimum management of global water resources presents a crucial challenge (Jury and Vaux, 2005; McDonald et al., 2011).

2.3 Water issues in Australia

Australia covers an area of 7.7 million square kilometres with a population of only 22.5 million (ABS, 2011; DFAT, 2012). Despite its vast land size and small population, Australia is referred to as the driest continent on Earth, with a climate often marked by recurrent droughts and extreme floods which cause river flow and groundwater recharge to be extremely low and variable, making water a critical issue (McKay, 2005; Khan, 2008; Vlotman and Kulkarni, 2012). Only 12% of the surface runoff in Australia is collected in the rivers and the country therefore has one of the lowest overall runoff per unit area and rainfall-runoff ratios, with one of the highest river flow variabilities in the world (ANRA, 2001; Khan, 2008). Australia has struggled to adjust to the droughts and flooding rains, to the impoverished soils, to the different types of native plants and animals (Thom and McKenzie, 2011). Despite this, Australia has abundant water when expressed on a per capita basis, although this is unevenly distributed around the continent (Rutherford and Finlayson, 2011).

The Australian annual mean rainfall recorded in 2008-2009 was 522 mm and in 2009-10 it was 503 mm (ABS, 2012a). The total volume of water extracted from the environment for use within the Australian economy was 64,076 GL (gigalitres) in 2009-10, up from 59,839 GL in 2008-09. This is much higher than the 23,300 GL of water estimated by the comprehensive water audit for the period 1996-97 in 2000 (McKay, 2005). The agricultural industry consumed the largest volume of water in 2009-10, accounting for 52% of Australia's water consumption (ABS, 2012a), but this share of irrigation is down from an estimated 75% in 1997 (ABS, 2012a; ABS, 2012b) mainly due to the prolonged drought that plagued Australia for several years (McKay, 2005). Therefore, even small savings from agricultural water use through improved efficiency might make substantial quantities of water available for the community and the environment (Ward and Pulido-Velazquez, 2008; McDonald et al., 2011). Surface water was by far the greatest source of water for the water supply industries in 2009-10, with 96% of total distributed water being derived from this source, and groundwater and desalination providing the rest.

The water issue in the Murray-Darling Basin in Australia is typical of an issue faced by many countries in the world. Over-allocation of water from rivers and groundwater and difficulties in water management for rural and, to a lesser extent, urban Australia have sparked several public policy debates on water in Australia (Cullen, 2004; Thom and McKenzie, 2011). Even as the current debate over how much water should be returned to the river reached fever pitch with the October 2010 release of the *Guide to the Proposed Basin Plan* of the MDB Authority (MDBA, 2010), the environmental conditions of the MDB continued to decline, as highlighted in successive State of the Environment (SOE) reports (SOE, 2001; Beeton et al., 2006; Thom and McKenzie, 2011).

2.4 Water issues in the Murray-Darling Basin

2.4.1 The MDB, the food bowl of Australia

The Murray-Darling Basin (MDB) is 3,375 km long, drains one-seventh of the Australian land mass, and is currently by far the most significant agricultural area in Australia (Figure 2.1). The basin is host to Australia's most iconic river system, defined by the catchment areas of the two major river systems of the Murray and Darling rivers and their many tributaries. The MDB, consisting of 23 river valleys and an area of more than one million km², covers approximately 14% of the Australian land mass which is mostly flat, low-lying and far inland, and receives little rainfall (MDBA, 2010b). Although the MDB receives only 6% of Australia's annual rainfall, a very large proportion of Australia's irrigation resources is concentrated there and the MDB contains around 65% of Australia's irrigated land area and approximately 40% of Australia's farms. Therefore, the basin is critical to the Australian economy and food security as it produces some 39% of the nation's food and fibre, contributing about \$15 billion worth of agricultural produce annually mainly from commodities such as grain (\$3.4 billion), meat cattle (\$2.8 billion) and sheep and other livestock (\$1.7 billion).

Some of the key features of the MDB (MDBA, 2010b) are that it:

- forms about one seventh of the Australian total land mass
- contains 65% of Australia's irrigated land area and around 40% of Australia's farms

- produces 39% of Australia's food and fibre, contributing \$15 billion worth of agricultural produce annually
- was responsible for 45% (\$5.5 billion) of Australia's total irrigated production (\$12.2 billion) in 2005-06
- produces 90% of the nation's cotton yield
- produces 56% of Australia's total grape crop
- produces 42% of Australia's total fruit and nut crop
- produces 32% of Australia's total dairy output
- provides critical water supplies to more than 3.3 million people

Agricultural activity, mainly irrigated agriculture, is the key economic driver of local industries and regional activities. Irrigation in the Murray-Darling Basin has an economic multiplier of 3.5, indicating that for every \$1,000 of farm gate revenue generated there is an additional \$3,500 of dependent economic activity (Meyer, 2005; NPSI, 2011).

Several varieties of crops and pasture are grown in the MDB for food, fibre and bio-fuel for domestic consumption and export (MDBA, 2010b) such as:

- cereals (e.g. wheat, barley, rice, sorghum)
- cotton
- legumes (e.g. field peas)
- fruit and nuts (e.g. apples, oranges, almonds)
- grapes
- vegetables (e.g. tomatoes, onions)
- canola
- livestock fodder (e.g. pasture for grazing or hay/silage).

The MDB is therefore a significant factor in Australia's ecological health, because it is home to the country's most diverse and rich natural environments, including a World Heritage site and 30,000 wetlands of national and international importance, including many RAMSAR listed wetlands, which provide critical habitat for 95 basin state and Commonwealth-listed threatened inundation-dependent fauna species (MDBA, 2010b).

The MDB covers four states and drains roughly three-quarters of New South Wales (including all of the Australian Capital Territory), half of Victoria, a substantial portion of southern Queensland, and a small part of eastern South Australia. In general, the climate is hot and dry in summer, and mild in winter (MDBA, 2010b). Much of the terrain is semi-arid and nearly all of it is only a few tens of metres above sea level. Typically, tree-lined watercourses meander slowly through Mulga or Mallee scrub, grasslands or chenopod shrublands.

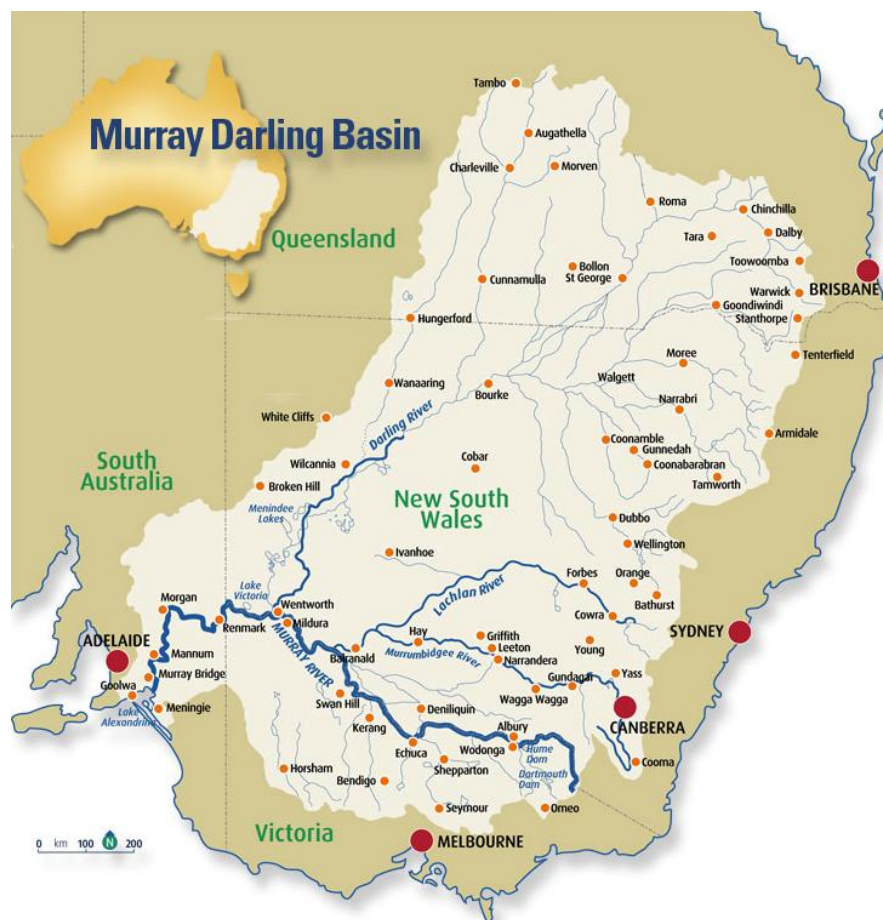


Figure 2.1: Murray-Darling Basin map (Source: MDBA)

2.4.2 Hydrology of the Murray-Darling Basin

Rainfall is highly unpredictable and varies from place to place, as well as from year to year, but is typically 250 to 300 mm a year. Rainfall records (1895–2009) suggest that the long-term average rainfall across the basin is in the order of 500,000 GL/y (MDBA, 2010b). However, only a very small percentage (6%) of the rainfall becomes an inflow (31,780 GL/y) ending up as water in surface-water streams and underground aquifers,

while the rest of the water is lost through evaporation and transpiration. The basin receives some 1,000 GL/y of additional surface water from the Snowy Mountains and this gives a long-term average of 32,780 GL/y of surface-water inflows. Figure 2.2 shows that 19,100 GL/y or 58% of the total inflow, currently remains in the environment, while 13,680 GL/y or 42% of the total inflow is extracted for consumption purposes. The consumptive use includes 10,940 GL/y for irrigation together with urban supplies from watercourse and floodplain diversions (collectively termed watercourse diversions), and 2,740 GL/y which is intercepted by farm dams and forestry plantations that intercept run-off before it reaches watercourses (termed 'interception') (MDBA, 2011a).

A tiny proportion of rainfall (26,500 GL, or 5%) finds its way into the groundwater system as groundwater recharge. Since surface water and groundwater are connected in many parts of the basin, some of this volume discharges to streams and forms part of the surface-water inflow. Around 1,700 GL of groundwater is consumed each year from the basin's water resources. This volume is much smaller than the amount of surface water consumed across the basin, but some areas rely heavily on groundwater for supply. However, high salinity in some aquifers can mean the groundwater is unsuitable for many uses (MDBA, 2011a).

Currently, the average outflow from the MDB at the mouth of the Murray River is 5,100 GL/y, which is 41% of the 12,500 GL/y that might be expected if water were not extracted for consumption (MDBA, 2010b).

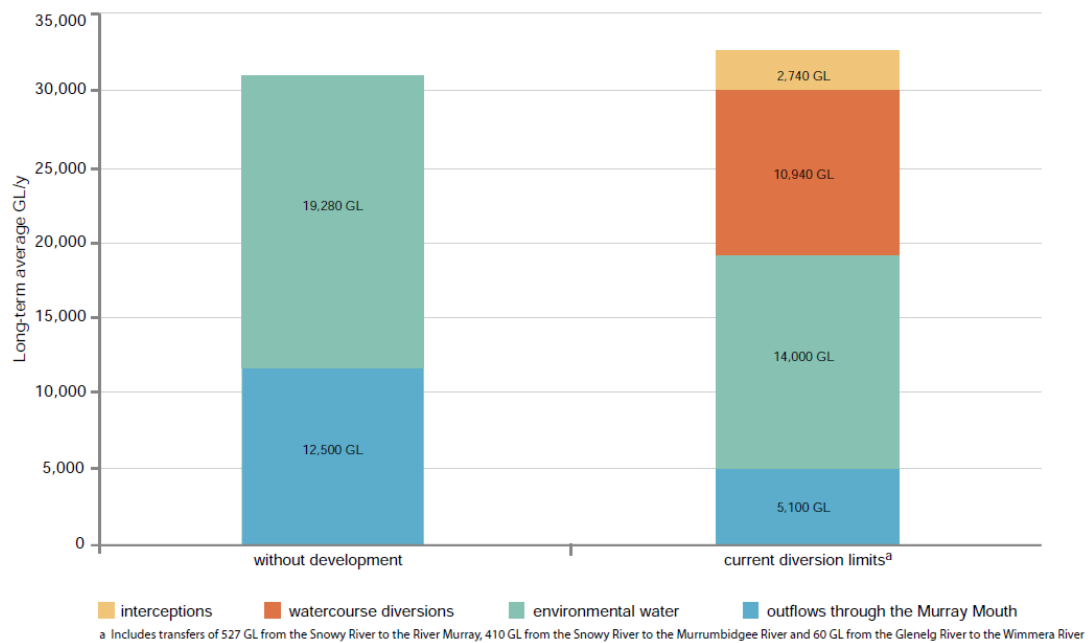


Figure 2.2: Use of long-term average surface-water inflows in the MDB. (Source: (MDBA, 2010b))

2.4.3 Environmental issues of the basin

2.4.3.1 Over-allocation of water and poor river ecosystem

The surface water diverted for consumptive use such as in towns, industry and irrigation has increased from 2,000 GL/y in 1920 to approximately 11,000 GL/y of entitlements in the 1990s. The combination of drought and prolonged diversions through over-allocation means that the flows through the Murray Mouth since 2002 have been significantly reduced. Therefore, the basin is under enormous environmental stress because of over-extraction of water inflow and severe and prolonged drought, which is compounded by natural climate variability and anthropogenic climate change (Goss, 2003; McKay, 2005; MDBA, 2010b; Wentworth Group, 2010). The ecosystems of 20 of the 23 catchments in the basin are rated as ‘poor’ to ‘very poor’ in health (MDBA, 2010b). The problem of water quality has been increasing in the past decade with more frequent outbreaks of blue-green algae blooms.

A major issue in the basin is the reduced volume of water that flows in the river system due to over-allocation of water for consumptive use, which significantly affects the fragile river ecosystem within the basin (Goss, 2003). Over-allocation of river water within the basin for consumptive use has been widely documented and agreed, not only within scientific communities but also across the wider community (Goss, 2003;

MDBA, 2010b; Wentworth Group, 2010). It is genuinely believed that there is an urgent need to lower the water allocation to maintain adequate environmental flow for a sustainable river ecosystem (MDBA, 2010b; Wentworth Group, 2010). With further water use restriction imminent as a result of the proposed Basin Plan (MDBA, 2010b; MDBA, 2011c), alternative sources of water must be explored if the agricultural production within the region, on which Australia significantly depends, is to survive. The groundwater source within the basin is plentiful; however, this groundwater cannot be used directly for irrigation because of the high salinity content within most of the basin area.

2.4.3.2 Salinity issues

Dry land salinity and river water salinity are major environmental issues in Australia, affecting millions of hectares of land (DSEWPC, 2008). Salinity in Australia has damaged natural resources and infrastructure, and is also impacting terrestrial biodiversity (Goss, 2003). Salinity refers to the presence of soluble salts in the soil or water, which can cause stress or toxicity to crops and vegetation, increase sodicity and soil erosion, pollute drinking water and damage roads, fences, railways, buildings and natural ecosystems. The primary cause of salinity is the natural occurrence of salts in the Australian landscape. The salts come from the weathering of rocks, from groundwater and from salt deposited over many thousands of years by precipitation (cyclic salt). Salinity in Australia is therefore one symptom of a much bigger landscape problem; secondary salinity is the result of human activity and changes in land use such as urbanisation and extensive agriculture (DII, 2009).

Salinity is also a major environmental issue in the MDB (Jolly et al., 2001). The increase in river-water salinity level is due to both natural and human actions, with the cumulative effects of these actions resulting in increased salinity levels at the mouth of the river at Lake Alexandrina in SA (MDBA, 2011a). This increase in river salinity has several causes: a slow-moving river leading to more evaporation loss, saline groundwater intrusion, drainage flows from irrigation areas and rising groundwater levels due to irrigation, and recently, more extensive areas of dry land farming. The substantial extraction of river water for consumptive use has significantly reduced the volume of river flow and exacerbated the river salinity problem in the basin (McKay,

2005; MDBA, 2010b; Wentworth Group, 2010). There is also a clear relationship between river flow and river salinity levels: the lower the flow the higher the level of salinity in the rivers, particularly caused by the intrusion of saline groundwater in the basin (Ife and Skelt, 2004). The Murray-Darling River salinity is monitored by salinity measurements at Morgan. Figure 2.3 shows a typical variation of river salinity at Morgan and the variation of river water salinity along the length of the Murray River.

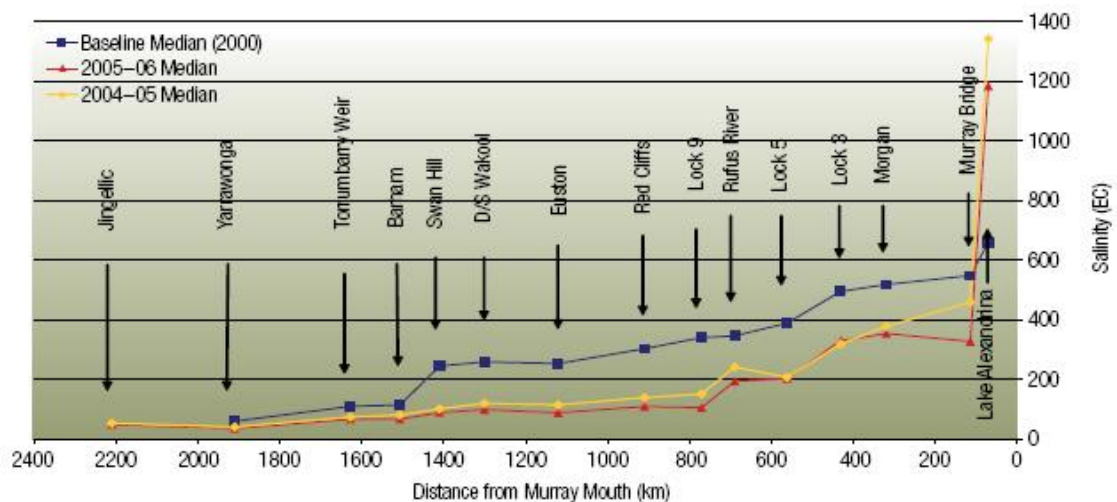


Figure 2.3: The Murray River salinity profile – Baseline medians for the Benchmark Period of 1975–2000 and 2005–06 medians (MDBC, 2007)

2.4.3.3 Salt Interception Scheme (SIS) in the MDB

Since 1988, the Australian Federal Government together with the basin states has funded and installed a number of Salt Interception Schemes (SIS) to control river water salinity. An SIS consists of large-scale groundwater pumping stations and drainage projects that intercept brackish groundwater flows and dispose of them, generally through open pond evaporation. Salt interception is achieved by designing bore fields that create a zone of pressure in the aquifer which is equal to or slightly less than the pressure at the river. This causes a flattening or local reversal of the hydraulic gradient between the bore field and the river, causing the saline groundwater to flow towards the bore wells rather than to the rivers and thus preventing the salt from entering the river system. The aim of the design process is to maximise the interception of the salt while minimising the induced flow from the river to the bore field, resulting in more than half a million tonnes of salt being kept out of the River Murray each year. Salt interception schemes, together with other actions such as improved irrigation practices and river dilution flows, have reduced the salinity in the Murray River by approximately 200

electrical conductivity per year at Morgan in SA. The SIS has significantly reduced the salinity downstream of the MDB (Goss, 2003), although the groundwater is simply lost through evaporation and therefore does not enable the sustainable use of groundwater.

2.4.4 The Murray-Darling Basin Plan

2.4.4.1 The proposed plan

The need to maintain the Murray-Darling Basin as a healthy, working river system has long been recognised (Wentworth Group, 2010; MDBA, 2011c). The basin has a long history of over-allocation of water for consumptive use, which has seriously affected the basin's river eco-system. Frequent drought in the basin has further worsened the plight of the environment within the basin, so an environmentally sustainable level of water allocation would ensure that sufficient water was left in the river system to meet the environmental needs for a healthy river ecosystem.

The Australian Government and the basin states have recognised the need for a water reform process for the basin since the basin plays a significant role in the environmental, social and economic wellbeing of Australia. The Australian Government and the basin states passed the 2007 *Water Act* (Cwlth) that agreed to a referral of certain powers and recognised the need for urgent action (2007). An action was initiated under this act to redress the imbalance between water for the environment and water for consumptive purposes, and to avoid the risk of the basin facing an irreversible environmental, economic and social decline.

The Murray-Darling Basin Authority (MDBA) released a major document titled *Guide to the Proposed Murray-Darling Basin Plan* in October 2010 outlining its plan to secure the long-term ecological health of the basin (MDBA, 2010b). It was the first part of a three-stage process to address the problems that have plagued the system for years. A significant component of the guide was the setting out of discussions on environmental water requirements, and the volumes of water that can be taken for consumptive use — known as long-term average sustainable diversion limits (SDLs) for surface water and groundwater. The analysis in the guide indicated that the long-term average water flow for a healthy environment is between 22,100 GL/y and 26,700 GL/y, whereas the average flow was only about 19,100 GL/y. The guide proposed additional water

between 3,000 GL/y and 4,000 GL/y to be made available for improving the ecological health of the basin's environment.

Although the guide is intended to improve the environmental health of the basin, it received fierce criticism, particularly from the basin's farming community, because the proposal included reducing water allocation between 27-37% spread over the whole basin. The farming community expressed their concern that the proposed cut in water allocation by 3,000-4,000 GL/y would have a significant social and economic impact not only within the basin but for the whole of Australia since the basin provides about 40% of Australia's agricultural produce. The guide was, however, welcomed by most of the scientific and environmental community, who considered the plan to be long overdue.

The *Proposed Basin Plan* released by MDBA in November 2011 proposed cutting water entitlements by 2,750 GL/y, lower than the 3000-4000 GL/y initially proposed in the guide (MDBA, 2011c). The current plan has received criticism from both by the farming community and the scientific community, although for opposite reasons. Members of the scientific community such as CSIRO (Commonwealth Scientific and Industrial Research Organisation) have expressed concerns that the water volume of 2,750 GL/y is not based on available science and therefore will not achieve the expected environmental objectives and targets because it will not return enough water to the environment (Young et al., 2011). The farming community is still not happy and considers that 2,750 GL/y is still too much water for the environment. The proposed plan has been submitted to the Federal water minister and is expected to become law before the end of 2012.

2.4.4.2 Social and environmental benefits of the proposed basin plan

By limiting the water allocation for consumptive use, the basin plan intends to provide a balanced and sustainable use of surface water and groundwater both for the economy and the environment. The basin plan expects to significantly improve the overall health of the basin by improving its key ecosystem functions and the health of its key environmental assets. As more water is made available for the environment, it is expected to improve the resilience of water-dependent ecosystems and allow them to withstand short-term and long-term changes in watering regimes, particularly in light of

the increasing variability in climate conditions due to climate change. Lastly, a reduction in water allocation could allow the Murray Mouth to remain open most of the time (MDBA, 2010b; MDBA, 2011c).

The above improvements in environmental outcomes are likely to lead to increases in socio-economic benefits for a range of industry sectors such as flood plain agriculture, recreational and commercial fishing, recreational boating, reduced cost in salt interception, improved water quality, soil erosion prevention and tourism (Arche Consulting, 2010; Ernst & Young, 2011; MDBA, 2011c; CSIRO, 2012).

2.4.4.3 Social and economic impacts of the proposed basin plan

Although, the proposed basin plan claims that the impact of the plan on the basin economy will be modest, it has been acknowledged that those communities that depend largely on irrigation will experience greater impact from the proposed plan (MDBA, 2011c). The flow-on impacts for total agricultural production, gross regional product and employment will be significant (MDBA, 2011c). For example, ABARES (ABARES, 2011) estimated that the regions most likely to experience the largest reductions in value of agriculture production are the Murrumbidgee, New South Wales Murray and Goulburn–Broken regions. While this regional pattern is influenced by trade and commodity price assumptions, these are also the catchments where the greatest volumes of water are available. These communities will be exposed to changes in water availability because there are larger proposed reductions in diversions, and/or because water trade is likely to result in large amounts of water leaving the community. These changes will be manifested through impacts on local economies associated with reduced production and possible flow-on effects to local businesses (Arche Consulting, 2010). Impacts will be felt as social as well as economic issues (EBC et al., 2011; MDBA, 2011d).

2.5 Roles of science and technology in water issues

The world population will continue to grow while fresh water resources may remain the same or simply decrease, with the latter most likely to be the prevailing scenario. To support the growing population and its economic needs, water demand must be met and this raises the prospect of scientific solutions playing a crucial role in meeting the

increasing water demand (Jury and Vaux, 2005). This calls for a extensive research efforts to identify robust and new methods of purifying water using less energy and at lower cost, while at the same time minimising the environmental impact (Shannon et al., 2008). Three major options are usually implemented to solve the increasing water crisis: demand management and improvement of water use efficiency including rainwater harvesting; wastewater reclamation and reuse; and desalination. These options are briefly discussed below.

2.5.1 Demand management strategies and water use efficiency

Demand management is any program that modifies the level and/or timing of demand for a particular resource with the main objective of achieving water use efficiency, economic efficiency, social equity and development, environmental protection, and sustainability of water supply (White and Fane, 2002). Water demand management strategies are designed primarily to promote water conservation either through changes in consumer behaviour or by changes to the stock of resource-using equipment (Greenberg and Harshbarger, 1993). Demand management strategies comprise a combination of *measures* and an *instrument* (White et al., 2003).

Measures in water demand management include water use efficiency, conservation, using dual water supply systems and influencing behaviour around activities such as watering times. Water use efficiency includes the use of more efficient water equipment and distribution systems to control leakage and water losses (Beecher, 1996). Water conservation includes the use of alternative sources (source substitution), such as the installation of rainwater tanks. Dual water supply systems involve combining two alternative systems, as in a grey water reuse system for toilet flushing, gardening and other non-potable purposes.

Instruments are used to assist in achieving the adoption of a measure and can be categorised as regulatory, economic or communicative. The behavioural change of consumers can be promoted via communicative instruments such as education campaigns, or through economic instruments such as pricing, including incentives. Demand management should be subjected to economic evaluation and compared under a least cost planning (LCP) framework so that investment in the options with the least total cost to the community can be made. Effective planning and implementation of

demand management strategies could substantially reduce average water demand (White and Fane, 2002), reduce costs by 25–45%, and pressure management increases savings by a further 20–55% (Burn et al., 2002).

2.5.2 Water reclamation and reuse

A large portion of the fresh water withdrawn from natural fresh water sources for consumptive use is returned to the environment after usage. For example, about 30-40% of the water used for agricultural and livestock is returned, 80-90% after industrial use, 95-98% after power generation, and 75-85% from domestic users, while the rest is lost to the atmosphere or consumed in biological or chemical processes (Shannon et al., 2008). The reclamation and reuse of water involves capturing water directly from these non-traditional sources and restoring them to potable water quality (Miller, 2006; Shannon et al., 2008). It has been acknowledged that wastewater reclamation and reuse is an efficient and valuable way to cope with water scarcity and the severity of water pollution (Po et al., 2003; Chu et al., 2004). However, the impaired water or wastewater contains a wide range of contaminants, including pathogenic micro-organisms which must be removed before the water can be used for potable purposes (Toze, 2006; Shannon et al., 2008).

Decades of research effort have produced technological options that can produce treated wastewater of reusable quality including treatments using membrane processes. Although the significance of community acceptance for a successful water reuse program is widely acknowledged, there is still a lack of social research on understanding the basis of public perceptions of water reuse and the psychological factors governing their decision making processes (Po et al., 2003). Nevertheless, treated wastewater has already been used for indirect potable reuse, such as being mixed with fresh water and ground water recharge (Miller, 2006) and non-potable applications such as irrigation (Toze, 2006). Tertiary effluent from a wastewater treatment plant can suitably be used for the irrigation of ornamental plant nurseries where the nutrient content in the effluent provides food for plant growth (Lubello et al., 2004).

2.5.3 Desalination

Measures such as water conservation, infrastructure repair, improved catchment and distribution system can help to alleviate water stress to a certain level, but these measures only improve the existing water use efficiencies of water sources and do not create new water resources. Desalination is the only available option that can create new water from saline and impaired water sources which are otherwise unusable waters. Desalination is the process of converting saline water, such as seawater or brackish water, into potable or fresh water by removing the salt from the salt solution.

The concept of separating salt from water is an ancient one and dates back to a time when salt, not water, was a precious commodity (Cooley et al., 2006). Desalination was used for thousands of years by Greek sailors who boiled water to evaporate fresh water away from the salt, and Romans used clay filters to trap salt. The first patent for a desalination device was granted in 1852 in Britain (Simon, 1998; Cooley et al., 2006). In the early days, desalination was mostly based on a thermal distillation process (Chen et al., 2008), and a major seawater desalination plant was built in 1938 in what is now Saudi Arabia (Cooley et al., 2006). Most research on desalination was conducted during World War II to meet the need for water for the military in water scarce regions. An early version of the modern distillation plant was built in Kuwait in the early 1960s (Cooley et al., 2006).

On the basis of the development of desalination technologies, the past four decades can be divided into three phases (Chen et al., 2008):

- 1950s: discovery of desalination technologies
- 1960s: research on desalination technologies
- 1970s-1980s: commercialisation of desalination technologies

In the early 1970s, the industry began to concentrate on commercially viable desalination applications and processes, and the first reverse osmosis (RO) water treatment plant of significant size was constructed in the 1970s in Florida (Chen et al., 2008). During the last three decades, there have been significant advances in membrane materials and RO desalination technology has greatly improved the cost effectiveness and performance capabilities of the processes. RO membrane processes are increasingly

used worldwide to solve a variety of water treatment problems. In the USA desalination industry, RO membrane technology is the most popular technology. Seawater desalination represents 60% of the globally installed desalination capacity (Cooley et al., 2006; Carter, 2009).

2.6 Available desalination technologies and their challenges

There are four adopted desalination technologies: reverse osmosis (RO), multi-stage flash (MSF), multiple-effect distillation (MED) and mechanical vapour compression (MVC). RO and MSF processes account for 50% and 40% of the entire desalination market, respectively (Ettouney and Wilf, 2009). The RO desalination process continues to grow quickly because of advances in the technology, especially in the development of a more efficient and less expensive membranes, and also due to significant reductions in the energy requirement compared to two or three decades ago (Fritzmman et al., 2007). In some countries such as the USA, Spain, Cyprus and Malta, the RO process is the only technology used for desalination (Ettouney and Wilf, 2009).

2.6.1 Thermal based desalination

In the early 1960s, the only process available for seawater desalination was the thermal based distillation process (Schliephake et al., 2005). Thermal processes consume large amounts of heat energy for their operation, however, because the latent heat of water is very high; for this reason, thermal based desalination technologies are mostly concentrated in the countries of the Middle East where oil is cheaply available for heating (Semiati, 2008; Elimelech and Phillip, 2011). Thermal desalination includes Multi-stage Flash Distillation (MSF), Multiple Effect Distillation (MED) and Vapour Compression Distillation (VCD).

2.6.1.1 Multi-stage Flash Distillation (MSF)

The MSF distillation process is based on the principle of flash evaporation in which seawater is boiled and evaporated by reducing the pressure using multiple stages, as opposed to raising the temperature (Khawaji et al., 2008; Mezher et al., 2011). MSF plants may contain between 4 and 40 stages, but usually they comprise 18 to 25 stages (Mezher et al., 2011). The MSF plant consists of heat input, heat recovery, and heat

rejection sections (Al-Radif et al., 1991; Khawaji et al., 2008). MSF desalination technology has proved to be a highly reliable process, especially in those countries where oil is cheaply available, such as those in the Middle East (IDA, 2006; Ettouney and Wilf, 2009).

2.6.1.2 Multiple-Effect Distillation (MED)

The MED process is one of the oldest technologies is now a well-established desalination technology (Al-Shammiri and Safar, 1999; Khawaji et al., 2008; Ettouney and Wilf, 2009). This process permits the seawater feed to undergo multiple boiling without supplying additional heat after the first effect (Khawaji et al., 2008). It also allows efficient use of thermal or mechanical vapour compression, where the vapour from the last effect is re-compressed over a temperature range of 30–40 °C (Ettouney and Wilf, 2009). In MED desalination, the process of evaporation and condensation is repeated from effect to effect, each at a successively lower pressure and temperature (Michels, 1993).

2.6.1.3 Vapour Compression Distillation

The MVC desalination process was developed in the early 1980s mainly motivated by the need to have a thermal desalination system that utilised solely electric power (Matz and Fisher, 1981; Ettouney and Wilf, 2009). In the VC process, the external heating energy comes from compression of part of the produced vapour (Khawaji et al., 2008; Mezher et al., 2011). The VCD process takes advantage of the principle of reducing the boiling point temperature by reducing the pressure (Khawaji et al., 2008). The vapours can be compressed using either TVC or mechanical vapour compression (MVC) (Mezher et al., 2011). However, the energy required for VC is estimated to be about 7.5–13 kWh/m³ and the actual cost of water produced using VC is in general higher than it is for MSF and MED because the VC unit capacity is smaller (Khawaji et al., 2008; Mezher et al., 2011).

2.6.2 Membrane based desalination technologies

In the membrane based desalination process, semi-permeable membranes are used for the desalination process. The processes include the RO process, the currently emerging

Forward Osmosis and the Membrane Distillation Process. They are briefly described below.

2.6.2.1 Reverse Osmosis

The details of osmosis and osmotic pressure are discussed in Section 2.8. Reverse osmosis is a process in which a hydraulic pressure higher than the osmotic pressure of the salt water is applied to drive the water across the membrane, thereby separating it from the salt solution. In the late 1950s, the work of Reid showed that cellulose acetate membranes were capable of separating salt from water by reverse osmosis, even though the water fluxes obtained were too small to be practical at that time (Reid and Breton, 1959; Ferguson, 1980; Lonsdale, 1982; Applegate, 1984). RO became practical in the early 1960s after Loeb and Sourirajan developed a method for synthesising asymmetric cellulose acetate (CA) membranes that have relatively high water flux and salt rejection (Loeb and Sourirajan, 1963; Loeb, 1981). Since then, a new-generation of thin-film composite (TFC) membranes for the RO process have been developed that not only perform well in terms of water flux and salt rejection but also offer other advantages over CA RO membranes (Williams, 2003). TFC membranes are resistant to wide ranges of pH and temperatures and even resistant to harsh chemical environments. Besides seawater and brackish water desalination, other modern applications of RO membranes include wastewater treatment, the production of ultrapure water, water softening, and food processing, as well as many others (Bhattacharyya et al., 1992).

Recently, significant advancement has been made in the RO technology for desalination, particularly in terms of the properties. The salt rejection property of the RO membrane has increased seven-fold over the last 30 years and its water permeability has increased significantly. The current generation of RO membranes have high mechanical, biological and chemical strength and high fouling resistance. All these properties have contributed to more than tenfold reduction in the membrane cost per unit volume of water produced since 1978. Today, the RO process is the most widely used desalination technology in the world and has overtaken all other commercial desalination technologies (Lee et al., 2011). Due to continuous improvements in RO technology, including energy recovery devices, the energy consumption for RO desalination has decreased significantly. Thirty years ago, the energy required for

seawater desalination was 5-10 kWh/m³, whereas modern state-of-the-art RO systems need only around 3.0 kWh/m³ (Schiermeier, 2008; Elimelech and Phillip, 2011). However, the energy efficiency of RO desalination has already reached a plateau and efforts to further enhance energy efficiency are likely to be incremental (Schiermeier, 2008; Semiat, 2008; Elimelech and Phillip, 2011).

2.6.2.2 Forward osmosis

The forward osmosis (FO) process is a recently emerging technology for the membrane separation process, including for desalination. Since the process is based on the natural osmotic process using a concentration gradient across a semi-permeable membrane, it has been termed a novel process, particularly for desalination as it does not require high pressure such as in the RO process. FO desalination has been said to have the edge over the RO process in terms of energy consumption and fouling resistance (McGinnis and Elimelech, 2007; McGinnis and Elimelech, 2008; Choi et al., 2009; Achilli et al., 2010; Lay et al., 2010; Tang et al., 2010).

Unlike the RO process where high hydraulic pressure is required, the FO process simply uses the intrinsic osmotic pressure differential between the two solutions of different osmotic potential (highly concentrated draw solution and saline feed water) separated by a semi-permeable membrane to desalinate water. Although literatures on FO membrane fouling are still scarce, recent studies indicate that membrane fouling may not be a significant issue for the FO process, which is another significant advantage for FO over the RO process. In the absence of hydraulic pressure, membrane fouling during the FO process is reported to be physically reversible, indicating that pre-treatment and chemical cleaning may not be essential for the FO process, as it is in the RO process (Cornelissen et al., 2008; Mi and Elimelech, 2008; Lay et al., 2010; Mi and Elimelech, 2010). More details on the FO process, including its fundamental principles, are discussed in Section 2.8 of this chapter.

2.6.2.3 Membrane distillation

Membrane distillation (MD) is a combination of membrane technology and thermal process in one unit (Findley, 1967; Weyl, 1967). It involves the transport of water vapour through the pores of hydrophobic membranes via the temperature difference

across the membrane (Tomaszewska, 2000). A temperature difference is maintained across the membrane that results in a vapour pressure difference. The vapour molecules are transported from the high vapour pressure side to the low vapour pressure side through the pores of the hydrophobic membrane (Drioli et al., 1987; Godino et al., 1996). For several decades, MD has been considered an alternative approach to conventional desalination technologies such as MSF and RO, as these processes involve high energy and high operating costs (Drioli et al., 1987; Lawson and Lloyd, 1997). MD operates at normal atmosphere pressure and low temperatures between 40°C and 70°C and has high salt rejections, therefore offering a number of advantages over RO and the simple distillation process (Srisurichan et al., 2006).

Recently, efforts have been made to tap renewable energy sources such as solar energy, geothermal energy, or waste heat to achieve cost and energy efficiency (Chen and Ho, 2010; Guillén-Burrieza et al., 2011). The other major limitation of the MD process is the pore wetting of the hydrophobic membrane which reduces both the permeate flux and separation performance (Khayet, 2011; Alkhudhiri et al., 2012). Figure 2.4 shows the lab scale MD setup.

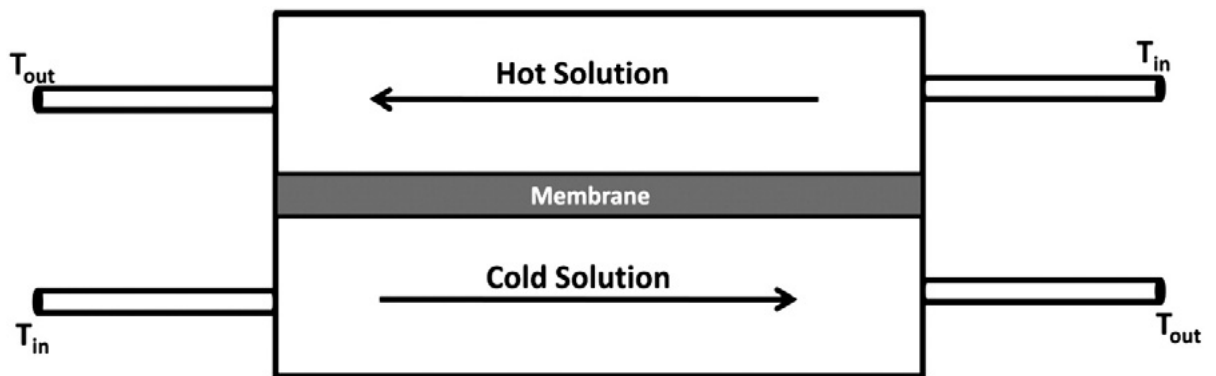


Figure 2.4: Direct Contact Membrane Distillation process. Direct Contact Membrane Distillation process. (Source: (Khayet, 2011; Alkhudhiri et al., 2012))

2.6.2.4 Electro-dialysis (ED) and electro-dialysis reverse (EDR)

Electro-dialysis (ED) is a technique that transports ions through selective membranes under the influence of an electrical field. ED has a high recovery as long as the sparingly soluble salts do not precipitate and hence used in Japan to pre-concentrate seawater prior to evaporation for salt recovery. ED has proved its feasibility and high performance in the desalination of brackish water (Sato et al., 1995; Kesore et al., 1997;

Ortiz et al., 2005; Ortiz et al., 2006; Zhang et al., 2011). ED was commercially introduced in the mid 1950s (Cooley et al., 2006; Mezher et al., 2011).

When an electrical potential difference is applied between these electrodes containing a stack of cation and anion exchange membranes placed alternatively, the ions move towards the oppositely charged electrodes facilitated by the presence of ion exchange membranes. The movement of ions raises the ion concentration in some compartments (concentrate compartments) and causes a decrease in the adjacent compartments (diluate compartments) (Ortiz et al., 2005). The transport of charged ions in a conventional ED for NaCl solutions is presented in Figure 2.5.

The energy required for seawater ED is 17 kWh/m³; brackish water ED requires 3–7 kWh/m³ (Mezher et al., 2011). ED is primarily applied on brackish water with low TDS and ED has a high recovery of 85–94% producing a concentrate of 140–600 mg/L TDS (Eltawil et al., 2009). However, the practical application of ED is effected by concentration polarisation, by incomplete current utilisation and by osmotic and electroosmotic water transport through the membranes, with the first two phenomena affecting process efficiency (Strathmann, 2010).

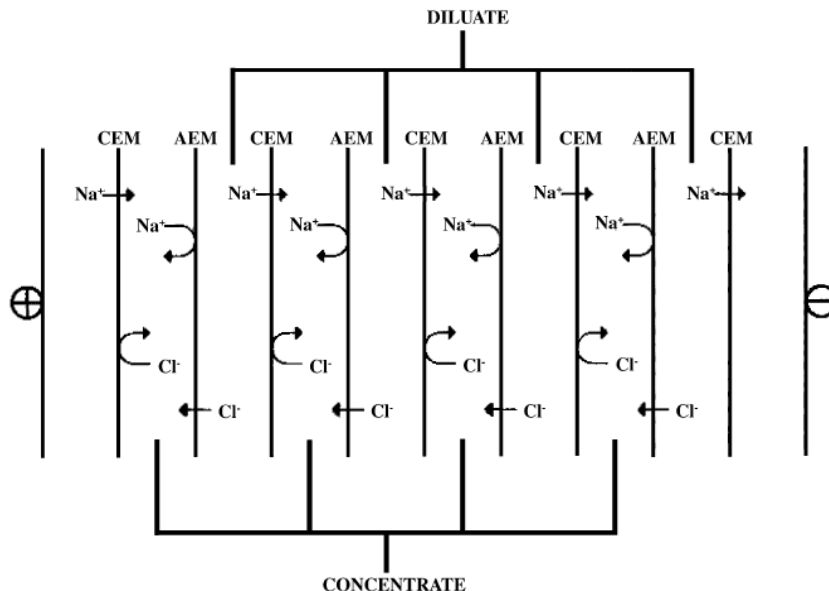


Figure 2.5: Charge transport in the electrodesalination stack. Cation-exchange membrane is indicated as CEM, and anion-exchange membrane as AEM. (Source: (Ortiz et al., 2005))

2.6.3 Other desalination technologies

2.6.3.1 Capacitive deionisation

Capacitive deionisation (CDI) technology uses high-surface-area electrodes which, when electrically charged, adsorb the ionic components from water, desalting the saline water in the process (Oren, 2008). CDI therefore works by sequestering ions, or other charged species, in the electrical double layer of ultra capacitors. On applying a voltage difference between the two electrodes of 1.2 – 1.5 V, cations are attracted in electrostatic double layers inside the negatively charged cathode while the anions are removed by the positively charged anode (Anderson et al., 2010; Porada et al., 2012). The key parameter for CDI is the salt adsorption capacity of the electrodes which uses electrode materials such as porous activated carbon particles or carbon aerogels (Anderson et al., 2010; Porada et al., 2012). Figure 2.6 shows the schematic diagram of CDI and explains the removal of charged ions using two charged electrodes.

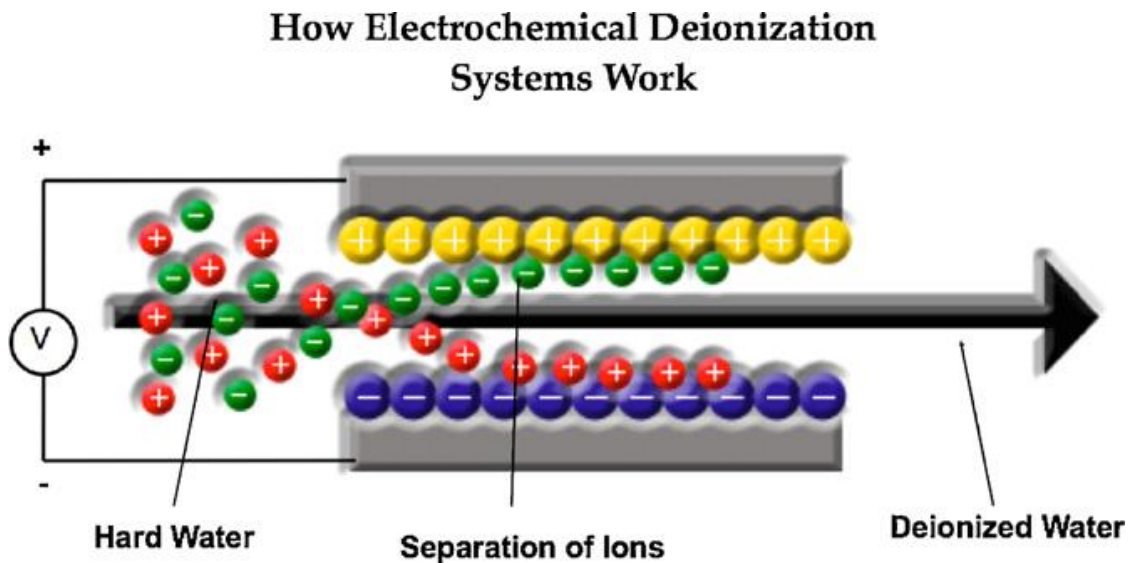


Figure 2.6: Schematic diagram of capacitive deionisation showing the removal of charged ions or species by two charged electrodes. (Source: (Anderson et al., 2010))

2.7 Desalination for irrigation

Water desalination is a well-established technology used mainly for drinking-water supply in water scarce regions. With agriculture accounting for up to 70% of all water withdrawals, however, desalination is an alternative source of water for many water scarce countries (Beltrán and Koo-Oshima, 2006). Irrigation with brackish water is a widespread practice in regions where freshwater is in acute shortage and where ample

brackish water resources exist, but such practices have severe soil degradation consequences due to increased salinity and sodicity (Ghermandi and Messalem, 2009). Desalination for agricultural irrigation will be an important contributor to satisfying growing water demands in water scarce regions (Shaffer et al., 2012).

Desalinated water is more expensive than conventional water resources and is only affordable for high value crops, especially where subsidies on capital costs are provided (Beltrán and Koo-Oshima, 2006). The cost of desalinated water has been reported to be about 3.5 times higher than the cost of natural fresh water (Schiermeier, 2008) and is an inhibiting factor in the application of desalination for large-scale irrigation. Based on the cost considerations, brackish water desalination is more suitable for agricultural production than seawater desalination (Beltrán and Koo-Oshima, 2006). However, with water demand expected to rise unabated in the future, competition for limited fresh water resources will also rise, driving up the cost of available fresh water resources. With more countries adopting desalination as a reliable option, technological improvements will decrease its cost significantly over time, the assumption being that desalinated water may eventually achieve near cost parity with available fresh water resources (Reddy and Ghaffour, 2007).

As desalinated water is comparatively more expensive than the natural fresh water resources, irrigation with desalinated water will provide an incentive to improve water use efficiency, thereby driving a more innovative and efficient irrigation system in the market. Only 3% of the world's total desalinated water in 2000 was used for irrigation, mostly in countries such as Spain (Beltrán and Koo-Oshima, 2006; Downward and Taylor, 2007), the United Arab Emirates (Sanza et al., 2007), and Israel. In these countries, the integration of the national water carrier of the large desalination plants located along the Mediterranean coast ensures that large quantities of desalinated water are delivered to farmers for irrigation (Yermiyahu et al., 2007; Dreizin et al., 2008; Ghermandi and Messalem, 2009).

2.8 Forward osmosis process

2.8.1 Fundamental principles of the FO process

2.8.1.1 Osmosis and osmotic pressure

Osmosis is the term that describes the spontaneous passage or diffusion of solvents or water through a semipermeable membrane while preventing the passage of solutes, and it is ubiquitous in all living cells. Although this phenomenon was first studied in 1877 by a German plant physiologist, Wilhelm Pfeffer, the general term ‘osmose’ (now osmosis) was introduced in 1854 by a British chemist, Thomas Graham (Britannica, 2012). When a solution and a pure solvent are separated by a semipermeable membrane, the solution tends to become more dilute by absorbing the solvent through the membrane. If a hydraulic pressure is applied on the solution to stop the movement of pure solvent across the membrane and maintain a condition of equilibrium, this equivalent pressure is termed ‘osmotic pressure’ (Robinson and Stokes, 1959b). Osmotic pressure is a colligative property which indicates the chemical potential of the solvent in the solution, or alternatively it includes vapour pressure lowering, boiling point elevation, freezing point depression and osmotic pressure (Rudin, 1999).

Osmosis therefore describes the natural diffusion of water through a semi-permeable membrane from a solution containing lower salt concentration to a solution containing higher salt concentration (Cath et al., 2006). The osmotic pressure (π) of an ideal dilute solution is given by Van’t Hoff’s (1887) equation shown below.

$$\pi = nMRT \quad (2.1)$$

Where n is the Van’t Hoff factor (accounts for the number of individual particles of compounds dissolved in the solution, for example $n=2$ for NaCl, $n=1$ for glucose), M is the molar concentration (molarity) of the solution, R is the gas constant ($R=0.0821 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and T is the absolute temperature (in K) of the solution. The osmotic coefficients of a few commonly available salts such as NaCl and KCl, etc. are provided in the work by Robinson and Stokes (1959b).

The Van’t Hoff equation is applicable only to ideal and dilute solutions where ions behave independently of one another and it is generally used for the determination of the molecular weight (MW) of large molecules (Yokozeki, 2006). However, at higher

ionic concentrations, the electrostatic interactions between the ions increase and it becomes a non-ideal solution. This ultimately reduces the activity coefficient of each ion and the osmotic pressure of the solution (Snoeyink and Jenkins, 1980). For general solutions, the osmotic pressure can be given by the concentration dependence osmotic equation (Stigter and Hill, 1959; Rudin, 1999), also known as the virial equation, as follows:

$$\frac{\pi}{c} = RT \left[\frac{1}{M_w} + Bc + Cc^2 + Dc^3 + \dots \right] \quad (2.2)$$

Where c is the concentration in terms of grams of solute per litre (g/L), B , C and D are the osmotic virial coefficients which are functions of the temperature and the chemical potentials of the species in the salt solution (Stigter and Hill, 1959). The virial coefficient can be determined empirically by fitting experimental osmotic pressure data and generally the determination of B and C is sufficient to reproduce observed data (Yokozeki, 2006). A solute with small MW combined with high water solubility can generate higher osmotic pressure (on an equal mass basis) and therefore can lead to higher water fluxes (McCutcheon et al., 2005).

The alternative way of determining the osmotic coefficient of a solution is by measuring the osmolality of the solution using an osmometer. An osmometer measures osmolality in osmoles/kg of water based on the freezing point depression method, but the application of osmoters is limited to solutions with infinite dilutions and therefore is not suitable at higher concentrations. Osmolality can be converted into osmotic pressure (π) based on the following equation (Zhang and Song, 2000):

$$\pi = 19,300 \times \text{Osmolality (in mmof Hg)} \quad (2.3)$$

2.8.1.2 Forward osmosis process

Water containing dissolved solids such as saline water generates osmotic pressure and this osmotic pressure depends on the concentration of the solutes in the solution. When hydraulic pressure is applied in excess of the osmotic pressure of the solution, the clean water moves through the semi-permeable membrane, leaving behind the dissolved solids. This process is traditionally known as the reverse osmosis desalination process

(RO) and this process needs a large amount of energy to separate water from the salt solution.

The other way of making the water move through a semi-permeable membrane from the dissolved solution such as saline water is to put a solution with a concentration much higher than the saline water on the other side of the membrane. Because of the concentration gradient between the two solutions, the water from the saline water will move towards the concentrated solution by natural osmosis. The FO process is in fact an engineered osmotic process in which an artificially high concentrated solution, termed a draw solution (DS), is used on one side of the semi-permeable membrane and the water to be treated is on the other side of the same membrane. Although FO is based on the principle of osmosis, the term ‘forward osmosis’ (FO) has been probably coined to distinguish it from RO, which is the term that has generally used for the membrane desalination process for many decades. The semi-permeable membrane, usually made from polymeric materials, acts as a barrier that allows small molecules such as water to pass through while blocking larger molecules such as salts, sugars, starches, proteins, viruses, bacteria, and parasites (Xu et al., 2010).

Both the RO and FO processes use a semi-permeable membrane to separate water from dissolved solutes effectively, although their driving forces are different. The main difference between the two processes is that the driving force in the RO process is created by hydraulic pressure, while the driving force in the FO process is created by the concentration or osmotic gradient.

Pressure-retarded osmosis (PRO) is a closely related process and it has been tested and evaluated since the 1960s as a potential process for power generation (Loeb, 1976; Loeb et al., 1976; Loeb and Mehta, 1979; Loeb, 1998; Loeb, 2001; Loeb, 2002a; Loeb, 2002b; Cath et al., 2006; Achilli and Childress, 2010; Yip and Elimelech, 2012). PRO uses the osmotic pressure difference between seawater, or concentrated brine, and fresh water to pressurise the saline stream, thereby converting the osmotic pressure of seawater into a hydrostatic pressure that can be used to produce electricity. PRO is viewed as an intermediate process between FO and RO (Cath et al., 2006); however, the net water flux is still in the direction of the concentrated draw solution (similar to FO).

The general equation describing water transport in FO, RO, and PRO is given by the following equation (Cath et al., 2006).

$$J_w = A(\sigma \Delta\pi - \Delta P) \quad (2.4)$$

Where, J_w is the water flux, A is the water permeability constant of the membrane, σ is the reflection coefficient defined as the ratio between the negative solute-water phenomenological coefficient divided by the pure water permeability (Mulder, 1997; Hancock and Cath, 2009) and ΔP is the applied hydraulic pressure.

The following conditions describe each process of the equation:

For RO process, $\Delta P > \Delta\pi$

For FO process, $\Delta P = \text{zero}$

For PRO process, $\Delta\pi > \Delta P$

Figure 2.7 describes the flux directions of the permeating water in the RO, FO and PRO processes, while the different points each describing the RO zone, point of FO process and PRO zone along with the flux reversal point are illustrated in Figure 2.8. The flux directions and driving forces for these three processes were characterised by Lee et al. (1981) and are described later in greater detail.

The main feature of the FO process is that the water transport across a semi-permeable membrane does not require hydraulic pressure, therefore the energy consumption is significantly less (compared to conventional desalination processes) (Moody, 1977; McCutcheon et al., 2005; McGinnis and Elimelech, 2008; Elimelech and Phillip, 2011). Moreover, due to the absence of hydraulic pressure, the severity of the fouling problem in the FO process is also less likely to be a major issue, unlike the RO process in which fouling is often a major problem. Fouling in the FO process is observed to be physically reversible; hence, chemical cleaning may be only seldom required in the FO process (Holloway et al., 2007; Cornelissen et al., 2008; Mi and Elimelech, 2008; Lay et al., 2010; Lee et al., 2010; Mi and Elimelech, 2010; Zou et al., 2011). Depending on the properties of the membranes used, FO offers similar advantages to RO desalination in processing the rejection of a wide range of contaminants and lower membrane-fouling propensities. In addition, for food and pharmaceutical processing, FO concentrates the

feed streams without requiring high pressures or temperatures, which become detrimental to the quality of the solutions under treatment. Hence, there has been a growing interest in exploiting this natural process for various applications, particular for desalination, because it has advantages over traditional processes in terms of energy consumption (McGinnis, 2002a; McCutcheon et al., 2005; Cath et al., 2006; McCutcheon et al., 2006; Miller and Evans, 2006; Ng and Tang, 2006; Hancock and Cath, 2009).

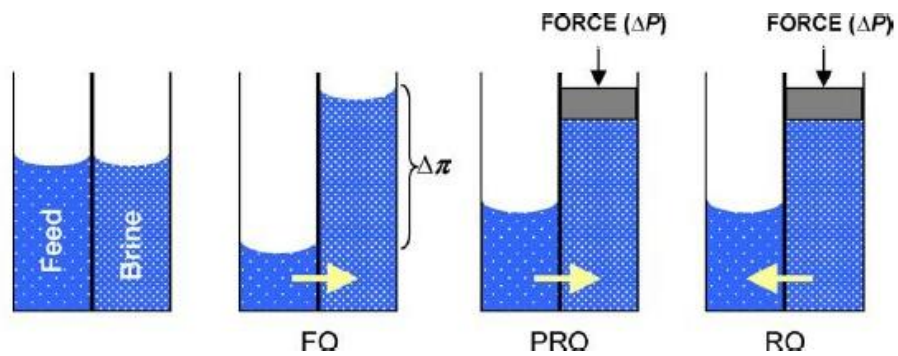


Figure 2.7: Principles of osmotic processes: forward osmosis (FO), pressure retarded osmosis (PRO) and reverse osmosis (RO). Adapted from (Cath et al., 2006)

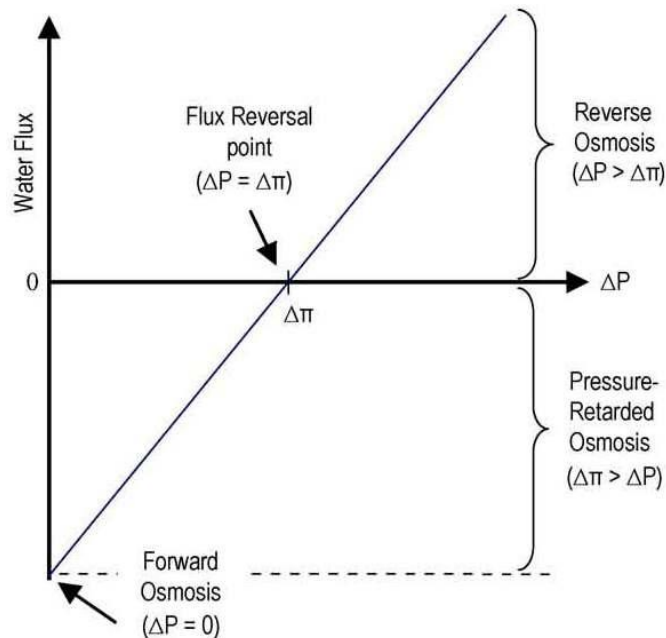


Figure 2.8: The direction and magnitude of water flux as a function of applied pressure in FO, PRO and RO (Lee et al., 1981). Adapted from (Cath et al., 2006).

2.8.2 Draw solutions for FO process

A draw solution (DS) is any aqueous solution which exhibits high osmotic pressure. In the FO process, the DS should provide sufficient driving force to cause a net flow of water through the membrane and therefore form an integral part of the FO process. As the osmotic pressure of the DS is the driving force in the FO process, it is crucial to select an appropriate concentrated solution prior to any application (Achilli et al., 2010). From equations (2.1) and (2.2), it is clear that the osmotic pressure is a function of solute concentration; the number of species formed by dissociation in the solution, the MW of the solute and the temperature of the solution and therefore does not depend on the types of species formed in the solution (colligative properties). A solute with small molecular weight combined with high water solubility can generate higher osmotic pressure and therefore can lead to higher water fluxes (McCutcheon et al., 2005). The performance of the FO process also depends on the selection of suitable draw solutes because it is the main driving force in this process. The draw solute must be highly soluble and must generate osmotic pressure that is much higher than the feed solution.

Many types of DS have been studied in the past and they can be generally classified as inorganic-based DS, organic-based DS and other compounds such as magnetic nanoparticles. The sub-classification includes electrolyte (ionic) solutions and non-electrolyte (non-ionic) solutions depending on whether the solution is made up of charged ions or neutral/non-charged solutes respectively.

2.8.2.1 Classification of draw solutions

2.8.2.1.1 Inorganic-based DS

The majority of FO studies have investigated inorganic-based compounds as the DS and these are still extensively utilised today. Inorganic based DS are mainly composed of electrolyte solutions, although non-electrolyte solutions are also possible. The most recent and comprehensive studies of inorganic DS have been made by Achilli et al. (2010) and Tan and Ng (2010). Achilli et al. (2010) tested and compared 14 inorganic-based compounds as DS for the FO process. These solutes were chosen from amongst more than 500 inorganic compounds because of their higher water solubility, osmotic pressure, lower specific cost and toxicity, all of which are crucial criteria that impact greatly on FO performance and end use. Table 2.1 provides a list of inorganic

compounds commonly used as DS for the FO process.

Numerous studies have used sodium chloride as the DS in a wide range of applications. For instance, it has been applied in food production (Petrotos et al., 1998; Garcia-Castello et al., 2009) and water and wastewater treatment (York et al., 1999; Holloway, 2006; Achilli et al., 2009b; Martinetti et al., 2009). The main reason that NaCl is used as the DS for many FO studies is that saline water is abundant on earth, making seawater a natural and cheap source of DS. NaCl is also often utilised because it is relatively straightforward to reconcentrate to high concentration with the RO process without the risk of scaling, and it has high water solubility and exhibits high osmotic pressure. Moreover, the thermodynamic properties of NaCl have been widely investigated, making it easier to study.

Other inorganic DS which are commonly studied include magnesium chloride (Yang et al., 2009; Zou et al., 2011), ammonium bicarbonate (mainly as a thermolyte solution that can be recovered and reused) (McCutcheon et al., 2005; McCutcheon et al., 2006; Ng and Tang, 2006; Hancock and Cath, 2009) and calcium chloride (Petrotos et al., 1998; Wallace et al., 2008; Achilli et al., 2010; Tan and Ng, 2010).

Table 2.1: Physicochemical properties and experimental water fluxes of inorganic compounds tested as DS. Adapted from Zhao et al. (2012c)

DS tested	MW	Osmotic pressure ^a at 2.0 M (atm)	pH ^a at 2.0 M	Max. solubility ^a (g/mol)	Scale precursor ions	Experimental water flux ^b ($\mu\text{m/s}$)	References
CaCl ₂	111.00	217.60	6.29	7.4	Yes (Ca ²⁺)	2.64	(Achilli et al., 2010; Tan and Ng, 2010)
KBr	119.00	89.70	6.92	4.5	No	2.84	(Achilli et al., 2010)
KHCO ₃	100.10	79.30	7.84	2.0	Yes (CO ₃ ²⁻)	2.25	(Achilli et al., 2009b)
K ₂ SO ₄	174.20	32.40	7.33	0.6	Yes (SO ₄ ²⁻)	2.52	
MgCl ₂	95.20	256.50	5.64	4.9	Yes (Mg ²⁺)	2.33	(Achilli et al., 2009b; Martinetti et al., 2009)
MgSO ₄	120.40	54.80	6.70	2.8	Yes (Mg ²⁺)	1.54	(Achilli et al., 2009b; Martinetti et al., 2009)
NaCl	58.40	100.40	6.98	5.4	No	2.68	(Achilli et al., 2009b; Martinetti et al., 2009)
NaHCO ₃	84.00	46.70	7.74	1.2	Yes (CO ₃ ²⁻)	2.47	(Achilli et al., 2009b)
Na ₂ SO ₄	142.00	95.20	7.44	1.8	Yes (SO ₄ ²⁻)	2.14	(Achilli et al., 2009b; Martinetti et al., 2009)
NH ₄ HCO ₃	79.10	66.40	7.69	2.9	Yes (CO ₃ ²⁻)	2.04	(Achilli et al., 2009b)
(NH ₄) ₂ SO ₄	132.10	92.10	5.46	5.7	Yes (SO ₄ ²⁻)	5.391	(Achilli et al., 2010)
NH ₄ Cl	53.50	87.70	4.76	7.4	No	5.348	(Achilli et al., 2010)
Ca(NO ₃) ₂	164.10	108.50	4.68	7.9	Yes (Ca ²⁺)	5.022	(Achilli et al., 2010)
KCl	74.60	89.30	6.80	4.6	No	6.337	(Achilli et al., 2010; Tan and Ng, 2010)

^aOsmotic pressure, pH and solubility data were calculated by OLI Stream Analyser.

^bExperimental water fluxes were taken from (Achilli et al., 2009b) for the first ten DS for an osmotic pressure of 2.8 MPa and the other experimental fluxes were taken from (Petrots et al., 1998) at 2.0M concentration of DS.

2.8.2.1.2 Organic-based DS

Over the past four decades, organic compounds – particularly fructose and glucose solutions – have been tested as DS, especially for seawater desalination and food production applications. Although organic DS usually consists of non-electrolyte compounds, they have the potential to generate high osmotic pressure as they generally exhibit high solubility (Ng and Tang, 2006), as shown in Table 2.2..

Kravath and Davis were the first to test organic compounds as DS. They studied the use of glucose as a DS in FO desalination for emergency water supplies in lifeboats. Soon after, Kessler and Moody (1976) used a combination of glucose and fructose for similar applications. Glucose was also investigated as a potential DS by Petrotos et al. (1998) for the concentration of tomato juice, and more recently by Ng et al. to extract water from a saline feed source. Fructose was also suggested as the DS in many studies. Stache (1989) proposed to use fructose as a DS to produce nutritious drinks using a saline feed water source, especially for emergency relief situations. Fructose was also used for the concentration of red raspberry juice (Wrolstad et al., 1993) and for dewatering a saline feed solution (Ng and Tang, 2006). A concentrated sugar solution such as sucrose has also been tested as the DS to produce concentrated beverages and liquid foods (Beaudry and Lampi, 1990; Herron et al., 1994; Petrotos et al., 1998).

Other organic DS include polyethylene glycol 400 (PEG) to concentrate tomato juice (Petrotos et al., 1998), ethanol for the recovery of water from highly impaired sources (McCormick et al., 2008), albumin for dewatering RO concentrate (Adham et al., 2009) and 2-methylimidazole-based compounds (Yen et al., 2010).

Table 2.2: Physico-chemical properties and experimental water fluxes of some organic compounds tested as DS.

DS tested	MW	Osmotic pressure ^a at 2.0 M (atm)	pH ^a at 2.0 M	Max. solubility ^a (mol)	Experimental water flux ^b	References
Ethanol	46.1	43.93	7.00	Miscible	Not/A	(McCormick et al., 2008)
Sucrose	342.3	56.81	6.18	6.1	0.35 LMH 0.24 LMH	(Petrotos et al., 1998) (Kravath and Davis, 1975; Petrotos et al., 1998; Ng and Tang, 2006)
Glucose	180.2	55.03	7.01	800.0		
Fructose	180.2	55.02	7.01	22.4	7.5 LMH	(Stache, 1989; Ng and Tang, 2006; Adham et al., 2009)

^aOsmotic pressure, pH and solubility data were calculated by OLI Stream Analyser.

^bExperimental fluxes were taken from (McCutcheon and Elimelech, 2006) for fructose at 6M fructose concentration and from (Yang et al., 2009) for sucrose and glucose at 58.29% (w/w) and 62.86% (w/w) respectively.

2.8.2.1.3 Other Draw Solutions

Magnetic nanoparticles as DS: Nanoparticle research is currently an area of intense scientific interest due to a wide variety of biomedical applications such as biocatalysis and drug delivery. In the context of the global water shortage problem, recent studies have put forward the idea of using nanoparticles as the DS in FO. Three recent studies (Ling et al., 2010; Ling and Chung, 2011b; Ling and Chung, 2011a) have focused their works on hydrophilic magnetic nanoparticles (MNPs). Three different types of MNPs were investigated as potential DS: the polyacrylic acid magnetic nanoparticles (PAA MNPs), the 2-Pyrrolidone magnetic nanoparticles (2-Pyrol MNPs) and the triethyleneglycol magnetic nanoparticles (TREG MNPs). Although they are non-electrolytes, the main advantage of MNPs is their extremely high surface-area-to-volume ratio and their bigger sizes compared to inorganic salts and organic molecules which facilitate recovery using magnetic fields and low pressure membrane processes such as MF or NF. Moreover, they are capable of producing very high osmotic pressure, up to 70 atm (for PAA MNPs), which is far higher than the seawater osmotic pressure of 26 atm, and makes them very attractive for desalination (Ling and Chung, 2011a).

Concentrated RO brine: The disposal of concentrated brines from a RO desalination plant is a significant environmental issue. RO concentrate is made up of waste flow with highly concentrated organic and inorganic compounds (Ng et al., 2008). Hence, there is

a need to sustainably manage the RO concentrate to avoid any adverse effects on the receiving environment. Recent studies have focused on the potential use of the FO process with RO brines as the DS to solve concentrate issues. Ling and Chung (Ling and Chung, 2011b) designed a novel dual-stage FO process where MNPs are used as the DS in an up-stage FO process to concentrate proteins, and RO brine is used as the DS in a down-stage FO process to reconcentrate MNPs. Bamaga et al. (Bamaga et al., 2011) designed a hybrid FO/RO process where the first FO process is used as a pre-treatment for RO desalination to minimise scaling risk during the desalination process. The second FO process, using the RO brine as the DS, is utilised to concentrate the impaired water to minimise its volume for further treatments. Hence, in this application, the FO process combining with RO brines as the DS is used to lower the energy requirement for desalination. In the context of seawater desalination, the use of concentrated RO brines as the DS has the advantage of using a compound with a very high osmotic pressure (much higher than the osmotic pressure of seawater) without the need for reconcentration. Moreover, there are several benefits to coupling the FO and RO processes. The RO process is proved to be an efficient reconcentration and recovery process, capable of producing very high quality product water. Using this concept of coupling processes, Modern Water successfully designed and deployed the first commercial FO desalination plant with a capacity of 100 m³/d of produced water in Oman on the Arabian Sea (Thompson and Nicoll, 2011).

Ionic polymer hydrogel particles: Li et al. (2011a) recently studied the development of a new class of DS: polymer hydrogel particles for FO desalination. Hydrogels are three-dimensional networks of polymer chains that are linked by either physical or chemical bonds and are able to catch large volumes of water attracted by the highly concentrated hydrophilic groups. Their sizes generally range between 50 and 150 µm. Hydrogels with ionic groups are able to attract an even larger amount of water, which increases their osmotic pressure and makes them attractive for desalination applications. One important and advantageous aspect of polymer hydrogels is that they undergo reversible volume change or solution-gel phase transitions in response to environmental stimuli, including temperature, light, pressure or even pH. One particular interesting response to these stimuli is the change from hydrophilic to hydrophobic (generated by heating or pressure stimuli) which induces hydrogel particles to release water. This unique characteristic makes the recovery of this novel DS very easy and less costly than

thermal or membrane processes. In a more recent study (Li et al., 2011b), it was demonstrated that combining the polymer hydrogel particles with light-absorbing carbon particles enhances the heating and dewatering of the particles. In both studies, the polymer hydrogel particles delivered high osmotic pressure of about 2.7MPa at 27 °C. Water fluxes ranged from 0.55 LMH to 1.1 LMH depending on the polymer used.

Dendrimers: Adham et al. (2009) proposed the use of dendrimers as a novel DS for dewatering RO concentrate. Dendrimers are symmetrical spheroid or globular nanostructures that are precisely engineered to carry molecules. These macromolecules consist of a highly branched tree-like structure linked to a central core through covalent bonds. Because they are macromolecules, they can provide a high osmotic pressure up to 330 psi, much higher than RO concentrate. Moreover, they can be readily regenerated by conventional membrane processes such as ultrafiltration (UF). In this study, two types of dendrimers were tested: ethylenediaminecore dendrimers with sodium succinamate terminal groups, and pentaerythritol core dendrimers with sodium carboxylate terminal groups.

2.8.2.2 Criterion for selection of suitable DS

Based on past and current studies of the FO process, it is clear that the selection of a suitable DS depends on many criteria. In the next paragraph, useful information for the selection of a suitable DS is provided. This information is general to any FO application, so it is important to understand that for some specific applications, further criteria need to be evaluated before the selection of an appropriate DS.

Before running bench scale experiments, an initial screening of DS is carried out. Thermodynamic modelling software can be useful for determining basic properties, such as water solubility, pH, speciation and osmotic pressure; these are important criteria that greatly affect FO process performance, as discussed earlier. It is important to ensure that the DS is inert, of near neutral pH, stable and non-toxic, especially when FO is used for drinking water production. Another important factor to assess is that the DS should not chemically or physically alter the membrane through reaction, adsorption, dissolution or fouling. Lastly, to ensure the economic viability of the process, the DS should not be expensive.

Once this preliminary screening has been carried out, experiments can be conducted to assess DS performance in terms of water flux, reverse salt transport and water recovery – the three main parameters used to assess the performance of the FO process. Another important criterion in most FO applications is the separation and recovery of the DS after it has been diluted. This process should be able to reconcentrate and recover the DS at a low energy cost, otherwise full-scale implementation will not be financially viable compared to other pressure-driven processes that have already been commercialised.

Finally, the FO process should be tested at full-scale with the selected DS, and a life cycle assessment should be conducted to ensure that each stage of the process (from the production of raw materials to the treatment of waste) has little or no impact on the environment. A flow diagram that displays the DS selection criteria, as described above, is illustrated in Figure 2.9.

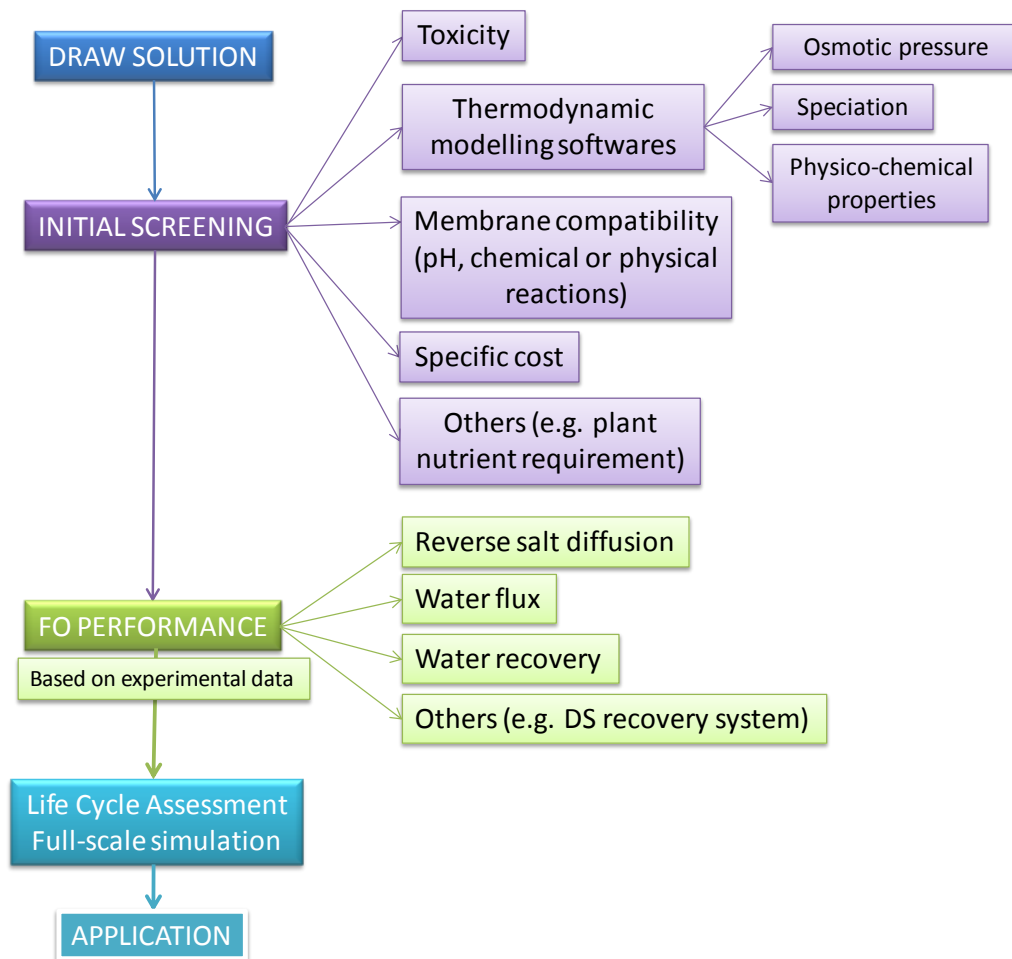


Figure 2.9: Flow diagram describing the criteria for selecting the DS in FO process

2.8.3 Concentration polarisation phenomenon in the FO process

As described earlier, water transport through any membrane process is described by the following standard equation (Cath et al., 2006):

$$J_w = A(\sigma \Delta\pi - \Delta P) \quad (2.5)$$

All the variables have been defined previously. For the FO process, ΔP is zero while for the RO process, $\Delta P > \Delta\pi$ and for the PRO process, $\Delta\pi > \Delta P$. Therefore, the following standard equation applies for the water flux in the FO process:

$$J_w = A \Delta\pi = A [\pi_{D,b} - \pi_{F,b}] \quad (2.6)$$

where $\pi_{D,b}$ is the bulk osmotic pressure of the DS and $\pi_{F,b}$ is the bulk osmotic pressure of the FS. Eq. (2.6) predicts flux as a function of driving force only in the absence of concentrative or dilutive ECP, which may be valid only if the permeate flux is very low for very dilute solution. When flux rates are higher, this equation must be modified to include both the concentrative and dilutive CP effects.

Many studies have demonstrated that, although a high driving force in the FO process ($\Delta\pi$) can be obtained using highly concentrated draw solutions, the actual water flux is observed to be very low compared to the traditional RO process. The lower than expected water flux is attributed to the modification of the solute concentrations at the boundary layer with the membrane surface, known as concentration polarisation (CP) effects (McCutcheon and Elimelech, 2007; Choi et al., 2009; Hancock and Cath, 2009; Xu et al., 2010). Equation (2.2) is therefore valid only when the DS is very dilute or when the water flux is very low. At a higher osmotic gradient, higher water flux is obtained and therefore the flux must be modified to account for the CP effects at the membrane boundary layer.

In the FO process, two independent solutions are involved: the DS and the FS on each side of the membrane. The presence of two independent solutions on each side of the membrane results in two different types of concentration polarisation (CP) effects: concentrative CP on the membrane surface facing the FS and dilutive CP on the membrane surface facing the DS. In any pressure based membrane processes,

depending on the water flux, the feed solute concentration at the membrane surface is higher than the bulk solute concentration which enhances the osmotic pressure of the feed solution at the membrane surface, thereby decreasing the net transmembrane pressure and the water flux. This phenomenon is called a concentrative CP effect, and a similar phenomenon exists in the FO process on the feed side of the membrane.

In addition to the concentrative CP effects on the feed side, the FO process experiences additional CP effects known as dilutive CP that occur on the membrane surface facing the DS. As water passes through the membrane from the feed towards the DS, the solute concentration at the membrane surface facing the DS decreases due to the dilutive effect of the incoming water. This phenomenon is known as a dilutive CP effect and it lowers the DS concentration at the membrane surface below the bulk DS concentration, thereby decreasing the net driving force or the osmotic gradient. Both concentrative CP and dilutive CP significantly influence the water flux across the membrane in the FO process. Concentrative CP occurs only on the feed solution side of the membrane, while dilutive CP occurs on the DS side of the membrane (McCutcheon and Elimelech, 2006). The dilutive CP phenomenon is unique to the FO process, whereas the concentrative CP effects are similar to any pressure based membrane process. Figure 2.10 illustrates the concentration polarisation effects in the FO process using a symmetric membrane.

The CP effects model in Figure 2.10 is true only if the membrane used in the FO process is a symmetric membrane. The existing polymeric dense and salt rejecting membranes such as RO membranes or nanofiltration membranes are made up of a thick support layer on which a thick and dense salt rejection layer is seated. Because of this asymmetric membrane design, two distinct CP phenomena occur depending on the orientation of the membrane to the two solutions during the FO process. The CP phenomenon that occurs within the support layer of the asymmetric membrane is termed an internal CP or ICP, and that which occurs on the active layer side of the membrane is termed an external CP or ECP.

2.8.3.1 Concentrative and dilutive ECP

As in any other pressure based membrane process, the concentrative ECP also occurs in the FO process when the osmotic process is operated in FO mode (FS placed against the active layer side of the membrane). When the water from the FS permeates the

membrane towards the DS, the concentration profile of both solutions at the membrane boundary layer changes. In the case of FS, the solute concentration increases at the active membrane surface ($C_{F,m} > C_{F,b}$) and is known as concentrative ECP Figure 2.10(b). Determination of the concentration of the feed at the active layer surface is not easy, though it can be calculated from experimental data using boundary layer film theory (McCutcheon and Elimelech, 2006). For a rectangular channel, the Sherwood number has been found to be useful to derive the concentrative ECP (Mulder, 1997; Baker, 2004; McCutcheon and Elimelech, 2006; McCutcheon et al., 2006).

$$Sh = 1.85 \left(Re Sc \frac{d_h}{L} \right)^{0.33} \quad (\text{for laminar flow}) \quad (2.7)$$

$$Sh = 0.04 (Re)^{0.75} (Sc)^{0.33} \quad (\text{for turbulent flow}) \quad (2.8)$$

where Re is the Reynolds number, Sc the Schmidt number, d_h the hydraulic diameter and L the length of the channel. The mass transfer coefficient ' k ' is related to the Sherwood number ' Sh ' by the following equation (McCutcheon and Elimelech, 2006):

$$k = \frac{Sh D}{d_h} \quad (2.9)$$

where D is the diffusion coefficient of the feed solute. The concentrative ECP modulus is then calculated using the mass transfer coefficient as follows:

$$\frac{\pi_{F,m}}{\pi_{F,b}} = \exp \left(\frac{J_w}{k_F} \right) \quad (2.10)$$

Here, J_w represents the experimental water flux while $\pi_{F,m}$ and $\pi_{F,b}$ are the osmotic pressures of the FS at the membrane surface and the bulk solution, respectively. The exponential term in equation (2.10) is positive which indicates that $\pi_{F,m} > \pi_{F,b}$ and is concentrative in nature.

Dilutive ECP and concentrative ECP are similar phenomena except that in the case of the dilutive phenomenon, the convective permeate water flux across the membrane displaces and drags the draw solutes away from the membrane surface (McCutcheon

and Elimelech, 2006; McCutcheon and Elimelech, 2007). In other words, the DS concentration at the membrane surface ($C_{D,m}$) is lower than the bulk DS concentrations ($C_{D,b}$). This dilution effect reduces the net osmotic pressure or the effective driving force of the DS. Therefore, the dilutive ECP modulus can be defined in a similar way to the concentrative ECP modulus, except that the concentration at the membrane surface decreases (McCutcheon and Elimelech, 2006; McCutcheon et al., 2006):

$$\frac{\pi_{D,m}}{\pi_{D,b}} = \exp\left(-\frac{J_w}{k_D}\right) \quad (2.11)$$

The water flux model in the FO process in equation (2.6) does not consider the influence of the CP effects. By taking into consideration the modified boundary conditions due to CP effects (Figure 2.10(a)), the water flux can be represented by the following, which is a modified version of equation (2.6):

$$J_w = A \sigma [\pi_{D,m} - \pi_{F,m}] \quad (2.12)$$

Assuming that salt does not cross the membrane (an ideal membrane is a perfect barrier to solutes), the value of the reflection coefficient (σ) can be taken as unity. Substituting equations (2.10) and (2.11) in (2.12), the revised flux model for a symmetric membrane illustrated by Figure 2.10(b) is given as follows:

$$J_w = A \left[\pi_{D,b} \exp\left(\frac{J_w}{k_D}\right) - \pi_{F,b} \exp\left(\frac{J_w}{k_F}\right) \right] \quad (2.13)$$

Dense symmetric polymeric membranes are unavailable, however, and most pressure based dense membranes, including commercial FO membranes, are made of a thick and porous support layer with a thin rejection layer on the top. The presence of a support layer in the asymmetric membranes provides additional resistance to mass transfer within the support layer known as ICP, which must be considered for modelling flux in the FO process.

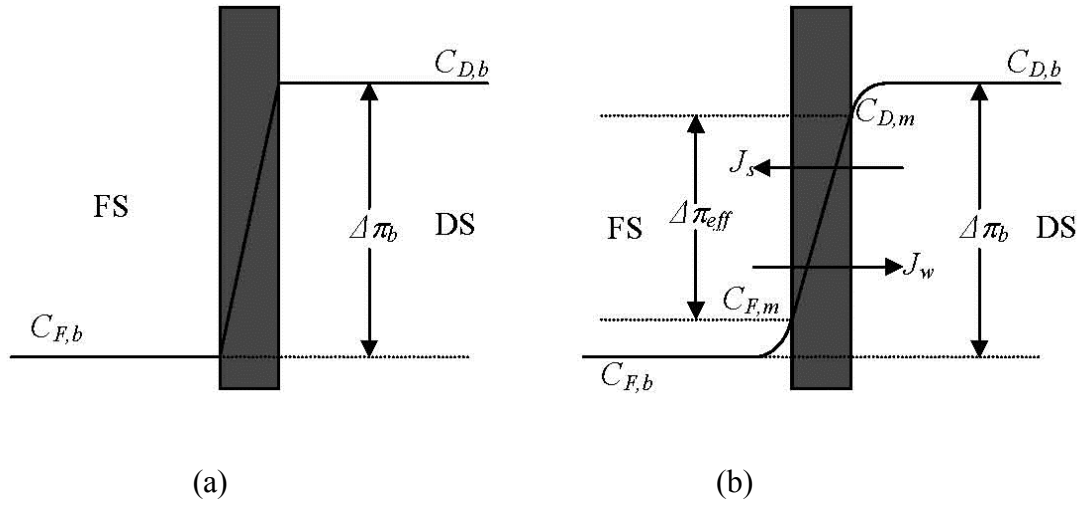


Figure 2.10: Concentration polarisation in a symmetric membrane, (a) before the osmotic process and (b) during the osmotic process. C : refers to the solute concentrations that generate osmotic pressure. Subscripts D , F , b and m refer to the DS, FS, bulk solution and membrane boundary layer respectively. $\Delta\pi_b$ Refers to the net bulk osmotic pressure and $\Delta\pi_{eff}$ refers to the effective osmotic pressure or the effective driving force.

2.8.3.2 Dilutive ICP coupled with concentrative ECP

When the active membrane layer faces the FS and the support layer faces the DS, as shown in Figure 2.11(a), the dilutive phenomenon on the DS side now occurs within the membrane support layer. This phenomenon is termed dilutive ICP, and this mode of membrane orientation is usually termed FO mode and used for any separation process, including the desalination process. Dilutive ICP is illustrated in Figure 2.11(a). The water flux in FO mode was described by Loeb et al. [19] as follows:

$$K = \left(\frac{1}{J_w} \right) \ln \frac{B + A\pi_{D,b}}{B + J_w + A\pi_{F,m}} \quad (2.14)$$

Rearranging Eq. (2.14) and, by assuming $B=0$ and incorporating Eq. (2.10) to account for the concentrative ECP on the FS side of the membrane, the flux model for dilutive ICP coupled with concentrative ECP is given as follows:

$$J_w = A \left[\pi_{D,b} \exp\left(-J_w K_D\right) - \pi_{F,b} \exp\left(\frac{J_w}{k_F}\right) \right] \quad (2.15)$$

The above equations indicate that both ECP and ICP phenomena contribute negatively to the net driving force in the osmotic process. The presence of the flux parameter J_w in the exponential terms in Eq. (2.13) and Eq. (2.15) also suggests that increasing the water flux will contribute to a further decrease in the net driving force, which creates a situation where flux itself acts as a self-limiting factor for the osmotic process (McCutcheon and Elimelech, 2006). The CP phenomena are the primary causes of the lower-than-expected water flux because they lead to a reduction in the net driving force across the membrane.

2.8.3.3 Concentrative ICP coupled with dilutive ECP

When asymmetric membranes are used in the FO process, the orientation of the membrane is significant and must accordingly take into account the influence of the internal concentration polarisation. When the membrane active layer of the asymmetric membrane faces the DS and the support layer faces the FS, as shown in figure Figure 2.11(b), this orientation is commonly termed a pressure retarded (PRO) mode and is used when the FO process is intended for energy generation (Gray et al., 2006; McCutcheon and Elimelech, 2006; Tang et al., 2010; Jung et al., 2011; Zhao et al., 2011). In this orientation, the water from the FS within the support layer crosses through the membrane towards the DS located on the other side (active layer) of the membrane. As the salt is rejected by the membrane rejection/active layer, the salt concentration in the support layer increases. Although this concentrative phenomenon is similar to the ECP described earlier, the difference with this membrane orientation is that the back diffusion of the concentrated salt on the membrane surface is restricted by the presence of the membrane support layer, which enhances the salt concentration. This phenomenon is known as concentrative ICP occurring in the PRO mode of operation (Gray et al., 2006; McCutcheon and Elimelech, 2006). The ICP phenomenon is unique to the FO process, and since ICP occurs within the protected confines of the porous layer in either membrane orientation, the ICP effects cannot simply be reduced by providing higher cross flow velocity, as in in ECP (McCutcheon and Elimelech, 2006; McCutcheon and Elimelech, 2007; Tan and Ng, 2008).

The expression for the PRO mode of membrane orientation was derived by Lee et al. (1981) and was later described for osmosis by Loeb et al. (Loeb et al., 1997). This

expression describes the ICP effects by relating water flux and other membrane constants as follows:

$$K = \left(\frac{1}{J_w} \right) \ln \frac{B + A\pi_{D,m} - J_w}{B + A\pi_{F,b}} \quad (2.16)$$

where B is the salt permeability coefficient of the active layer and K is the solute resistivity for diffusion within the porous support layer. K is defined as follows:

$$K = \frac{t\tau}{D\varepsilon} \quad (2.17)$$

where D is the solute diffusion coefficient, t , τ , and ε are the thickness, tortuosity, and porosity of the support layer and thus K is a measure of the severity of ICP (McCutcheon and Elimelech, 2006).

For high water flux and high salt rejecting membranes, the value of B is negligible compared to the other terms in Eq. (2.16). Ignoring the salt flux B in Eq. (2.16) and rearranging the equation by incorporating the dilutive ECP effect from Eq. (2.9), the flux model for concentrative ICP coupled with dilutive ECP is given by:

$$J_w = A \left[\pi_{D,m} \exp\left(\frac{J_w}{k_D}\right) - \pi_{F,b} \exp(J_w K) \right] \quad (2.18)$$

Therefore, K in Eq.(2.18) is a measure of how easily a solute can diffuse into and out of the membrane support layer, and thus is a measure of the severity of ICP. The exponential term in Eq.(2.18) is the factor that takes into account the concentrative ICP modulus. The positive exponent indicates that the ICP effect is concentrative in nature. All the terms in Eq. (2.18) can be readily determined through experiments or calculations.

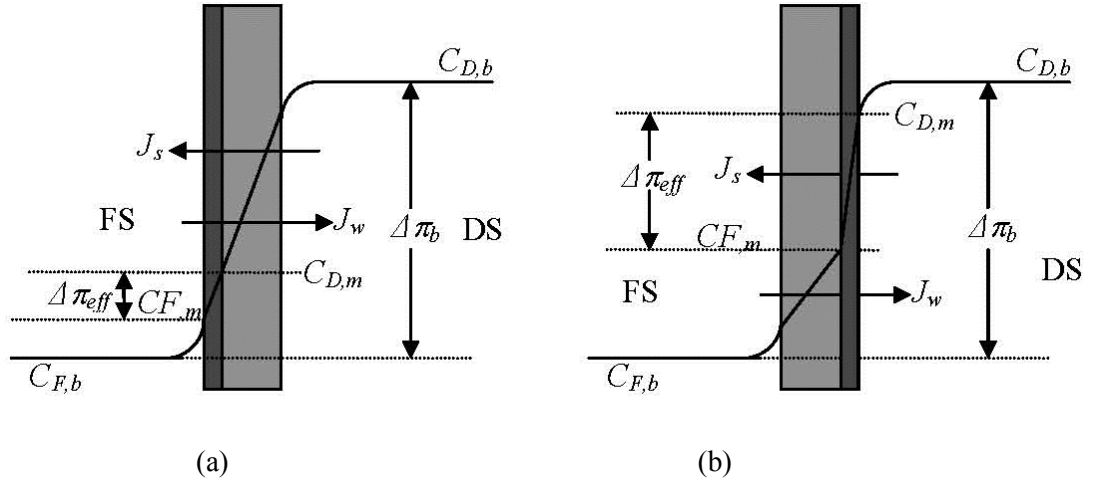


Figure 2.11: Concentration polarisation in an asymmetric membrane in: (a) Forward osmosis mode where an active layer faces FS and a support layer faces DS (concentrative ECP and dilutive ICP) and (b) pressure retarded osmosis mode where an active layer faces DS and a support layer faces FS (concentrative ICP and dilutive ECP). C : refers to the solute concentrations that generate osmotic pressure. Subscripts D , F , b and m refer to the DS, FS, bulk solution and membrane boundary layer respectively. $\Delta\pi_b$ refers to the net bulk osmotic pressure and $\Delta\pi_{eff}$ refers to the effective osmotic pressure or effective driving force.

2.8.4 Solute transfer in the FO process

In pressure driven membrane processes such as the RO process, the mass transfer across the membrane occurs only in one direction, i.e towards the permeate side of the membrane. Although it is assumed that the membrane acts as perfect barrier, no synthetic membranes are an ideal or perfect barrier and therefore permeation of salts due to diffusion is inevitable (Phillip et al., 2010). In the RO process, such a diffusion of solutes is measured in terms of salt rejection and or salt permeability coefficient.

In the FO process, the mass transfer occurs in both directions of the membrane depending on differences in concentration and the water chemical potential. The chemical potential of water is always higher for the feed solution than for the DS in the FO process and therefore the net transfer of water occurs only in one direction (from the FS to the DS). However, diffusion of solutes occurs in both directions: forward diffusion of feed solutes (from FS to the DS) and reverse diffusion of draw solutes (from the DS to the FS). The forward diffusion of feed solutes is similar to the RO process described earlier, while reverse diffusion is unique to the FO process because of the presence of two independent solutes on each side of the membrane and because the solute diffusion occurs in reverse direction to the water flux.

Reverse salt movement can be a significant disadvantage for FO because it can complicate feed water concentrate management and is also likely to decrease the net osmotic potential or driving force (Hancock and Cath, 2009; Phillip et al., 2010) and increases the fouling potential of the feed solution by forming complexes with the feed constituents (Hancock and Cath, 2009; Lay et al., 2010; Lee et al., 2010; Zou et al., 2011; She et al., 2012). Moreover, the reverse diffusion of draw solutes is also an economic loss because lost draw solutes cannot be recovered and fresh draw solutes need replenishment (Achilli et al., 2010). It is therefore important that the DS with low reverse solute flux are identified and selected for application. Most recent efforts have attempted to synthesise FO membranes that have high solute rejection and selectivity, and a number of high performing thin film composite FO membranes have been already reported (Wang et al., 2010b; Yip et al., 2010; Wei et al., 2011b).

2.8.4.1 Forward diffusion of feed solutes

The solute flux (J_s) of a particular solute through a semipermeable membrane is given by Fick's law (Mallevialle et al., 1996; Mulder, 1997; Hancock and Cath, 2009):

$$J_s = B \cdot \Delta c \quad (2.19)$$

where B is the salt permeability coefficient of the membrane and Δc is the concentration differential across the membrane. B can be determined from RO experiments (Lee et al., 1981; Achilli et al., 2009a) and is given by the following relationship (Achilli et al., 2009a):

$$B = \frac{A(1-R)(\Delta P - \Delta \pi)}{R} \quad (2.20)$$

where R is the membrane salt rejection, A is the pure water permeability coefficient of the membrane, ΔP is the applied pressure differential across the membrane and $\Delta \pi$ is the net osmotic pressure differential across the membrane. The membrane pure water permeability coefficient and salt rejection properties can be experimentally determined in RO mode while B can be calculated using Eq. (2.20). Normally, the forward diffusion of solutes in the RO process is measured in terms of salt rejection, which can then be used to calculate the solute permeability coefficient B of the membrane process using equation (2.20).

Eq. (2.19) suggests that the salt transport across the semi-permeable membrane is considered only for each individual solute, while the effect of cumulative concentrations of various solutes is not considered (Hancock and Cath, 2009). Besides, Eq. (2.19) is acceptable only for dilute solutions. The early theoretical studies on RO using irreversible thermodynamics deduced that the diffusion of solutes occurs through both diffusion and convective transport originating from coupled effects associated with solvent diffusion (Kedem and Katchalsky, 1958; Spiegler and Kedem, 1966). Therefore, the solute flux (J_s) through a semipermeable membrane occurring in the same direction as water flux in RO process is represented by the convective-diffusion equation as follows (Hancock and Cath, 2009):

$$J_s = \omega \Delta\pi + (1-\sigma) J_w \Delta c_m \quad (2.21)$$

where ω is the membrane's solute permeability coefficient, Δc_m is the solute concentration gradient at the membrane surface, J_w , σ and $\Delta\pi$ have been defined previously. The first product represents the diffusive mass transport through the membrane due to Donnan equilibrium effects, while the second term represents convective mass transport (Donnan, 1924; Hancock and Cath, 2009).

2.8.4.2 Reverse diffusion of draw solutes

Several recent publications have discussed models for the reverse diffusion of draw solutes in the FO process (Hancock and Cath, 2009; Phillip et al., 2010; Yong et al., 2012). In the FO process, reverse diffusion of the draw solutes from the DS through the membrane towards the FS is inevitable due to concentration differences between the two solutions, as presented by Eq. (2.19). The reverse movement of draw solutes in the FO process is measured in terms of reverse solute flux (RSF) (J_s) which indicates the rate of diffusion of draw solutes across the membrane in a reverse direction to the water flux. RSF is also a measure of the amount of DS lost per unit area of membrane per unit time.

Phillip et al. (2010) proposed the following model to predict the RSF in the FO process.

$$J_s = \frac{J_w C_D}{1 - \left(1 + \frac{J_w}{B}\right) \exp\left(\frac{J_w S}{D}\right)} \quad (2.22)$$

where C_D is the bulk concentration of the draw solute and

$$S = \frac{t \tau}{\varepsilon} \quad (2.23)$$

The membrane structural parameter S indicates the average distance a solute molecule must travel through the support layer when travelling from the bulk draw solution to the active layer. The value of S can be determined from FO and RO experiments as per the methods described by others (McCutcheon and Elimelech, 2006; Yip et al., 2010).

The absolute value of RSF is less significant because it has no relationship with the amount of water extracted during the FO process. From Eq. (2.19), it appears that the RSF (J_s) will be proportionately high when higher DS concentrations are used for the FO process. However, from Eq. (2.1), (2.2) and (2.6), it is clear that at higher DS concentrations, the net osmotic pressure will also be proportionately higher, indicating that the water flux will increase proportionately. Therefore, specific RSF (SRSF) has been proposed as the ratio of RSF to water flux, which indicates the amount of draw solutes lost by reverse diffusion per unit volume of water extracted from the FS (Hancock and Cath, 2009; Hancock et al., 2011). Assessing RSF is important in the FO process because it also increases replenishment costs, in addition to the disadvantages described above (Hancock and Cath, 2009; Achilli et al., 2010)[18]. SRSF refers to the ratio J_s/J_w and indicates the selectivity of the membrane to certain types of solutes (Hancock and Cath, 2009).

$$SRSF = \frac{J_s}{J_w} \quad (2.24)$$

Combining equation 2.22 and 2.24, the SRSF can be expressed as follows:

$$SRSF = \frac{C_D}{1 - \left(1 + \frac{J_w}{B}\right) \exp\left(\frac{J_w S}{D}\right)} \quad (2.25)$$

For the same solute, the SRSF is found to be similar for any osmotic potential/concentration, indicating that this ratio relates to the membrane's selectivity of the active layer and is independent of the DS concentration and membrane support structure (Hancock and Cath, 2009; Phillip et al., 2010). SRSF provides a third parameter for the evaluation of FO performance in addition to permeate flux and salt rejection. A higher ratio or SRSF indicates a lower membrane selectivity and lower FO efficiency (Zhao et al., 2012c).

2.8.5 Membranes for Forward Osmosis

Membranes are an integral part of the osmotic process because they allow only the solvent to pass through while retaining the solutes. Any dense membrane can be used for the osmotic process (Cath et al., 2006). During the early stages of osmotic studies, a variety of membranes including animal bladders, collodion (nitrocellulose), rubber and porcelain were used (Anderson, 1977; Baker, 2004; Cath et al., 2006). Following the development of the Loeb–Sourirajan membrane in the 1960s, RO membranes consisting of both flat sheet (Votta, 1974; Kravath and Davis, 1975; Goosens and Van Haute, 1978; Mehta and Loeb, 1978a; Loeb et al., 1997) and hollow-fibre membranes (Mehta and Loeb, 1978b) were mostly used to conduct FO studies (Cath et al., 2006).

Studies on the FO process using these salt-rejecting RO membranes experienced very low flux, however, even though the theoretical osmotic pressure gradient was very high when a DS containing very high concentration was used (Cath et al., 2006; Ng et al., 2006). This was, as explained earlier, due to the asymmetric design of the RO membranes that caused two different types of CP effects. While the presence of a support layer does not affect the performance of pressure based membrane processes, it has a significant influence on the FO process (Cath et al., 2006; Gray et al., 2006; McCutcheon and Elimelech, 2006; Ng et al., 2006).

In the 1990s, Osmotek Inc. and Hydration Technologies Inc. (now known as HTI, of Albany, Oregon), developed the first special membrane for FO applications which has since been used in a wide variety of applications by different research groups and in commercial applications, such as water purification for the military, emergency relief, and recreational purposes (Cath et al., 2006; Zhao et al., 2012c). This is a proprietary membrane which is made of cellulose triacetate (CTA) embedded on the neatly woven

polyester fabric with a total thickness of less than 50 μm (Cath et al., 2006; McCutcheon et al., 2006; Tang et al., 2010; Qin et al., 2012; Zhao et al., 2012c). A cross-sectional SEM image of the CTA FO membrane shown in Figure 2.12 is quite different from the standard RO membranes [22]. A typical RO membrane has a very thin active layer (less than 1 μm) with a thick porous fabric support layer, as shown in Figure 2.14(a). By contrast, the thick support layer is absent from the CTA FO membrane and instead, a polyester mesh is embedded that provides mechanical support to the CTA FO membrane with a total thickness of only about 50 μm Figure 2.14(b). Most of the recent studies on the FO process have used a CTA FO membrane, and all these studies indicate that the CTA FO membrane currently made by HTI offers superior performance to the RO membranes in the FO process (Cath et al., 2006). It has been demonstrated that membrane characteristics – particularly the membrane's structural properties – have a major impact on water flux in the FO process.

Many studies (Cath et al., 2006; Ng et al., 2006) have suggested that the ideal FO membrane should be symmetric, have hydrophilic properties, a dense active/rejection layer with high rejection but minimum thickness and tortuosity, and high water flux, and it should provide sufficient mechanical strength to withstand fluid flow. Given the practical difficulties in synthesising a thin and symmetric membrane with good mechanical strength from polymer materials, some form of support layer seems inevitable. Synthesising polymeric membranes that have all these characteristics is still a challenge, and it has been found that improving one characteristic often results in compromising another. For example, improving the membrane selectivity/rejection often results in lowering the water flux, indicating that there is always a trade-off when improving one aspect of the membrane's properties (Wei et al., 2011a; Yip and Elimelech, 2011; Lay et al., 2012). Synthesising a thin and dense rejecting membrane without a support layer is a big challenge and most recent attempts have therefore sought to improve the structural properties of the membrane support layer (such as porosity and thickness) to minimise ICP effects.

Several studies have recently focussed on the development of polyamide (PA) based thin film composites (TFC) FO membranes with significantly improved structural properties. The preparation methods for the TFC FO membranes are similar to the TFC polyamide RO membranes: phase inversion for the preparation of a porous substrate,

which is then followed by interfacial polymerisation for the formation of a thin film PA active layer on the top. Both flat sheet TFC FO membranes (Yip et al., 2010; Song et al., 2011; Tiraferri et al., 2011; Wei et al., 2011a; Wei et al., 2011b; Widjojo et al., 2011; Wang et al., 2012) and hollow fibre TFC membranes (Chou et al., 2010; Wang et al., 2010b) have been reported for FO applications.

Yip et al. (2010) synthesised the flat sheet PA based TFC FO membranes by the interfacial polymerisation of m-phenylenediamine (MPD) and trimesoyl chloride (TMC) on porous polysulfone (PSf) substrates that were cast on polyester nonwoven fabrics. Wei et al. (2011b) later also reported the synthesis of similar flat sheet PA based TFC FO membranes containing unique structures with straight finger-like pores under a thin sponge-like skin layer, using PSf as the substrate. Both studies reported that the substrate support layer formed by phase inversion played an important role in the formation of a thin spongelike layer sitting on top of highly porous macrovoids (Tiraferri et al., 2011). Widjojo et al. (2011) prepared TFO FO membranes containing sulfonated material using a similar method, and their study indicated that the content of the sulfonated material was responsible for more ready formation of a sponge-like membrane substructure, which could favour higher water permeability.

Several other flat sheet TFC FO membranes have been reported, some of which purportedly offer much better performance than the currently commercialised CTA FO membrane by HTI. These include PES/sulfonated PSf-alloyed membranes by Wang et al. (2012), a nonporous PES FO membrane by Yu et al. (2011), and a nanofibre TFC FO membrane formed by electrospinning followed by interfacial polymerisation (ES-IP) by Song et al. (2011). The nanocomposite FO membrane has been reported to have low tortuosity, high porosity and high salt rejection (Bui et al., 2011; Song et al., 2011).

Applying a similar TFC fabrication technique, a hollow fibre FO membrane was synthesised. In the course of its design, it was found that the desired FO membrane structure should have a very small portion of sponge-like layer in a thin and highly porous substrate (Chou et al., 2010; Wang et al., 2010b). Recently, a similar TFC hollow fibre membrane has been modified for application in power generation by pressure retarded osmosis with a power density of up to 10.6 W/m^2 , which is

comparable with the best flat sheet PRO membranes prepared in the laboratory (Yip et al., 2011; Chou et al., 2012).

Several other groups have attempted the fabrication of new FO membranes. One such attempt concerns the chemical modification of existing RO membranes to prepare a membrane for FO applications. A polydopamine (PDA) was used as a novel bio-inspired hydrophilic polymer membrane to modify the support layers of commercial TFC RO membranes for FO applications (Arena et al., 2011). This modification resulted in improved water flux and reduced ICP. Another group developed a hollow fibre FO membrane that is positively charged with a NF-like selective layer by the polyelectrolyte post-treatment of apolyamide-imide (PAI) microporous substrate using polyethyleneimine (PEI), which was found to be suitable for heavy metal removal (Shaffer et al., 2012). The same group developed a flat sheet FO membrane that has a positively charged NF-like selective layer prepared on a woven fabric embedded substrate, using a similar method (Qiu et al., 2012). Tang et al. fabricated an FO membrane using a layer-by-layer assembly method that has enhanced surface negative charge density and hydrophilicity using polycation and polyanion (Qiu et al., 2011; Saren et al., 2011). Wang et al. (2010a) introduced double-skinned FO membranes to remove ICP effects. This FO membrane comprises a highly porous sub-layer sandwiched between two selective skin layers prepared via the phase inversion method.

The development of suitable semi-permeable membranes is critical to the advancement of FO applications. Membranes that can achieve high flux and salt rejection, have minimal internal CP, and have high mechanical strength to support high hydraulic pressures could lead to improved performance in current applications as well as the development of new applications for FO (Cath et al., 2006). In the above studies, most of the efforts to fabricate a new FO membrane have focussed on lowering the ICP effects in the FO process by improving the structural properties of the FO membrane. Above all, the PA based TFC FO membrane seems to be a promising candidate for FO applications; however, it also has been realised that there is a strong trade-off between water permeability and salt rejection. Increasing permeability usually results in reduced salt rejection and increased reverse solute flux (Wei et al., 2011a). Therefore, the target of membrane synthesis should include a focus on the pore density of the TFC membrane, which could enhance water permeability without significantly affecting salt

rejection. Other properties that offer potential improvement in the overall performance of the FO process include hydrophilicity and the membrane charge, which plays a significant role in the FO process (McCutcheon and Elimelech, 2008; Widjojo et al., 2011). A review of recent advances in the development of the FO membrane is provided by Zhao et al. (2012c) and is shown in Table 2. 3, presented according to their fabrication methods.

Table 2. 3: Developments in FO membranes. Adapted from the table by Zhao et al. (2012c)

Year	Membranes	Materials	Preparation methods
2005	Capsule wall membrane	Cellulose acetate or ethyl cellulose	Dip-coating, phase inversion
2007	Hollow fibre NF	Polybenzimidazole (PBI)	Dry-jet wet phase inversion
2008	Flat sheet cellulose acetate membrane	Cellulose acetate	Phase inversion and annealing at 80–95 °C
2009	Dual-layer hollow fibre NF	PBI–PES/PVP	Dry-jet wet phase inversion (i.e. coextrusion technology)
2010	Hollow fibre	PES substrates, polyamide active layer	Dry-jet wet spinning and interfacial polymerisation (IP)
2010	Hollow fibre NF	Cellulose acetate	Dry-jet wet spinning
2010	Flat sheet double-skinned	Cellulose acetate	Phase inversion and annealing at 85 °C
2010	Flat sheet TFC membrane	Polysulfone (PSf) support, Polyamide active layer	Phase inversion and IP
2010	Double dense-layer membrane	Cellulose acetate	Phase inversion
2011	Modified RO	PSf support modified by polydopamine	Chemical coating
2011	Flat sheet composite	Cellulose acetate cast on a nylon fabric	Phase inversion
2011	Flat sheet composite	PAN substrate, multiple PAH/PSS polyelectrolyte layers	Layer-by-layer assembly
2011	Positively charged hollow fibre	PAI substrate treated by PEI	Chemical modification
2011	Positively charged flat sheet	PAI substrate treated by PEI	Chemical modification
2011	Flat sheet TFC polyamide	PES/SPSf substrate, Polyamide active layer	Phase inversion and IP
2011	Flat sheet TFC polyamide	PES/sulfonated polymer substrate, Polyamide active layer	Phase inversion and IP
2011	Flat sheet TFC	PSf support, polyamide active layer	Phase inversion and IP
2011	Nanoporous PES	PES cast on PET fabric	Phase inversion
2011	Cellulose ester membrane	Cellulose ester	Phase inversion
2011	Flat sheet TFC polyamide	PES nanofibre support, polyamide active layer	Electrospinning and IP
2011	Flat sheet TFC polyamide	PSf nanofibre support, polyamide active layer	Electrospinning and IP

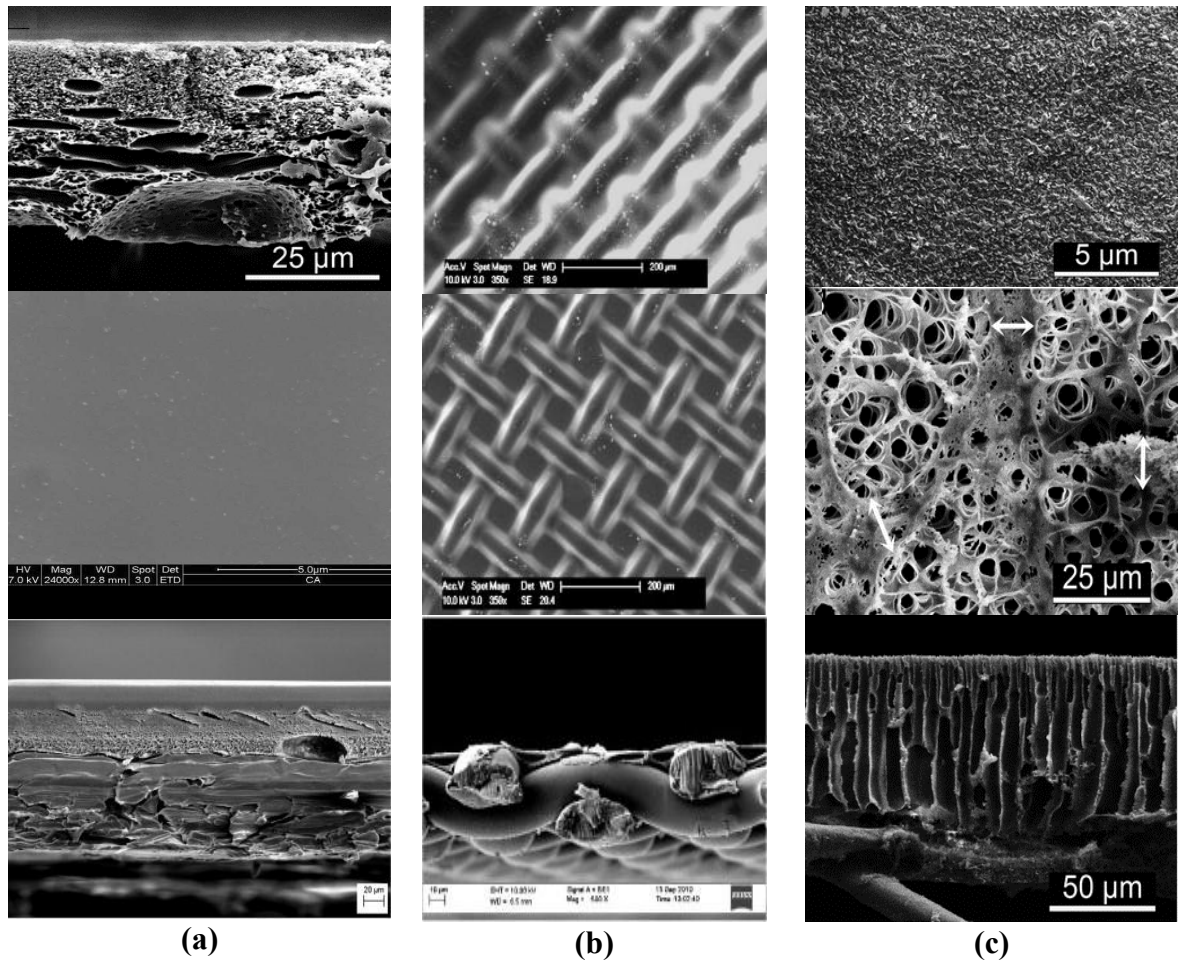


Figure 2.12: Comparative SEM images of polymeric membranes (a) RO membrane, (b) CTA FO membrane, and (c) thin film composite FO membrane. Images were compiled from several sources (Yip et al., 2010; Wei et al., 2011b; Zhao and Zou, 2011; Qiu et al., 2012).

2.8.6 Potential applications of the FO process

2.8.6.1 Desalination for potable water

The idea of natural osmotic pressure as a driving force in the FO process has motivated many researchers to investigate its potential application for desalination, including seawater desalination. Initially, desalination by the FO process using cellulose acetate flat sheet and hollow fibre membrane was investigated with glucose as the DS. The main objective was to apply this batch desalination process for emergency water supplies, such as for use on lifeboats or in relief situations during natural disasters, since the process need not involve the separation of draw solutes. The focus was on DS such as glucose (Kravath and Davis, 1975), glucose and fructose (Kessler and Moody, 1976) and fructose (Stache, 1989) because the diluted DS can be used directly for drinking.

HTI has already commercialised hydration bags for military, recreational and emergency relief situations to provide drinking water that contains a nutrient rich solution when potable water becomes inaccessible (Figure 2.13).



Figure 2.13: Commercial application of forward osmosis nutritious drinks. Hydration bags of different sizes commercialised by HTI Inc., USA. (Source: HTI Inc., USA)

Recent effort has been directed to the application of the FO desalination process for potable water. Generally, FO desalination involves two main steps: osmotic desalination and the separation of draw solutes and fresh water from the diluted draw solution. Any solutions that generate osmotic pressure higher than the osmotic pressure of the saline water source can be used to extract water by the osmotic process. For potable water desalination by the FO process, the DS must have special properties. Besides meeting the general selection criteria such as high solubility, high osmotic pressure (much higher than 26 atm for seawater feed), and pH compatibility with the FO membrane, the draw solutes for potable water should be easy to separate, recover and regenerate for reuse with minimum effort. Any trace concentration of the draw solutes in the final desalted water should meet the WHO Guidelines for drinking-water quality (WHO, 2011); therefore, one of the main challenges in the application of FO desalination for potable water is the post separation of draw solutes from the pure water and regeneration for further reuse. This post-treatment process requires energy, and the success of the FO process will ultimately depend on the post-treatment process. The concept of desalination by the FO process for potable water is shown by the schematic diagram in Figure 2.14.

McGinnis (McGinnis, 2002b) proposed a mixture of potassium nitrate (KNO_3) and sulfur dioxide (SO_2) as the DS for seawater desalination. In this two-stage FO process, water from aqueous solutions is recovered by taking advantage of the highly temperature dependent solubilities of KNO_3 and SO_2 , as well as the relatively temperature indifferent solubility of NaCl , the primary solute present in seawater. Subsequently, a $\text{CO}_2\text{-NH}_3$ solution was proposed for the draw solutes, formed by mixing ammonium carbonate and ammonium hydroxide in specific proportions to form three different salt species: ammonium bicarbonate, ammonium carbonate and ammonium carbamate (McCutcheon et al., 2005; McCutcheon et al., 2006; McGinnis and Elimelech, 2007). The $\text{CO}_2\text{-NH}_3$ solution can generate osmotic pressure of up to 238 bar which is more than adequate in generating water flux by the FO process. A schematic diagram of FO desalination using $\text{CO}_2\text{-NH}_3$ as the DS is presented in Figure 2.15(a). Once the DS is diluted, the $\text{CO}_2\text{-NH}_3$ mixture can be separated by moderate heating (near $60\text{ }^\circ\text{C}$) which decomposes to CO_2 and NH_3 . Separation of the fresh product water from the diluted draw solution can be achieved by several separation methods, such as the multi-stage distillation process or membrane distillation (MD) methods. Figure 2.17 (b) shows the separation and recovery of NH_3 and CO_2 gases by a multiple column distillation process heated at about 60°C . The degasified solution left behind in the column consists of pure product water and the distillate is a reconcentrated draw solution available for reuse in the FO desalination process (McGinnis and Elimelech, 2007). This concept has also been investigated by several other groups using NH_4HCO_3 as the DS for seawater desalination, although one of the issues observed with this DS is the low solubility of NH_4HCO_3 , the high reverse diffusion of solutes (Achilli et al., 2010), and the early decomposition of NH_4HCO_3 at about $30\text{ }^\circ\text{C}$ (Ng and Tang, 2006; Hancock and Cath, 2009).

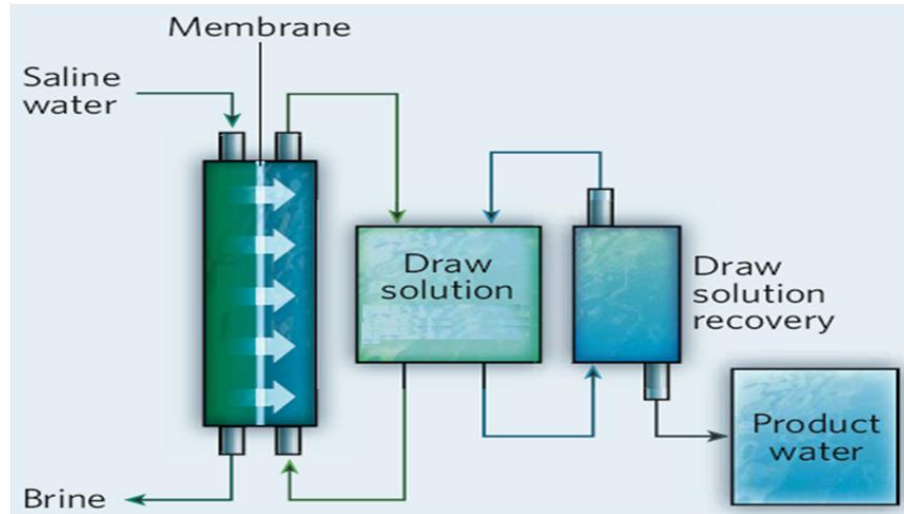


Figure 2.14: The concept of FO desalination for potable water (Dewolf, 2011).

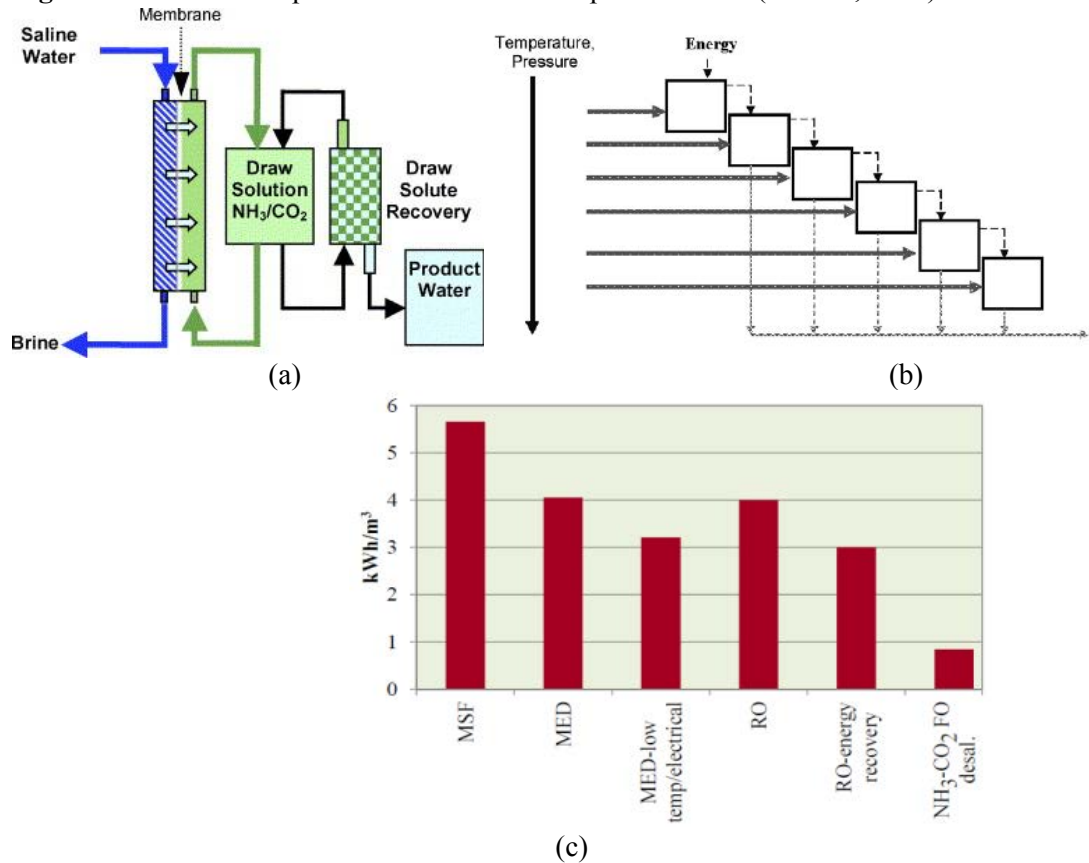


Figure 2.15: FO desalination for potable water (a) using $\text{NH}_3\text{-CO}_2$ solution as DS (Cath et al., 2006), (b) post-recovery of NH_3 and CO_2 by multiple column distillation process (McGinnis and Elimelech, 2007) and (c) energy comparison of the different desalination processes (McGinnis and Elimelech, 2007).

Other studies suggested using a hybrid FO–NF system for seawater (Tan and Ng, 2010) and brackish water desalination (Zhao and Zou, 2011; Zhao et al., 2012b). In this concept, DS containing inorganic multivalent ions were used as the DS for the FO process, and NF was used as the post-treatment to remove the draw solutes because NF

offers high rejection of multivalent ions and also requires much less energy than the RO process (Figure 2.16). In an extreme case, RO was applied as the post-treatment process for the separation and recovery of draw solutes from the diluted DS (Bamaga et al., 2009; Choi et al., 2009; Cath et al., 2010; Bamaga et al., 2011; Yangali-Quintanilla et al., 2011). In these combined FO–NF or FO–RO processes, FO offers several major benefits, including high quality drinking water due to the multi-barrier protection, reduced RO fouling because of the pre-treatment by FO, recovery of the osmotic energy of RO brine, low energy input, and no need for chemical pre-treatment. In fact, the FO process acts as a pre-treatment process (i.e. osmotic dilution) in the second type of FO desalination. To obtain fresh water, additional water recovery methods must be used to desalinate the diluted draw solution.

Other attempts include the use of hydrophilic nanoparticles as the draw solutes for FO desalination where UF was used as a post-treatment for the separation and recovery of nanoparticles from the diluted DS (Ling and Chung, 2011a; Ling and Chung, 2011b). The same researchers also proposed the use of magnetic nanoparticles (MNPs), since the separation and regeneration of MNPs draw solutes can be easily performed using magnetic fields (Ling et al., 2010). However, one of the issues with MNPs is the low osmotic pressure they can generate due to the agglomeration of MNPs. Although ultrasonication was suggested as a means to reduce this agglomeration of MNPs, it also weakened the magnetic properties of MNPs, thereby reducing its regeneration efficiency as well as adding energy to the sonification process.

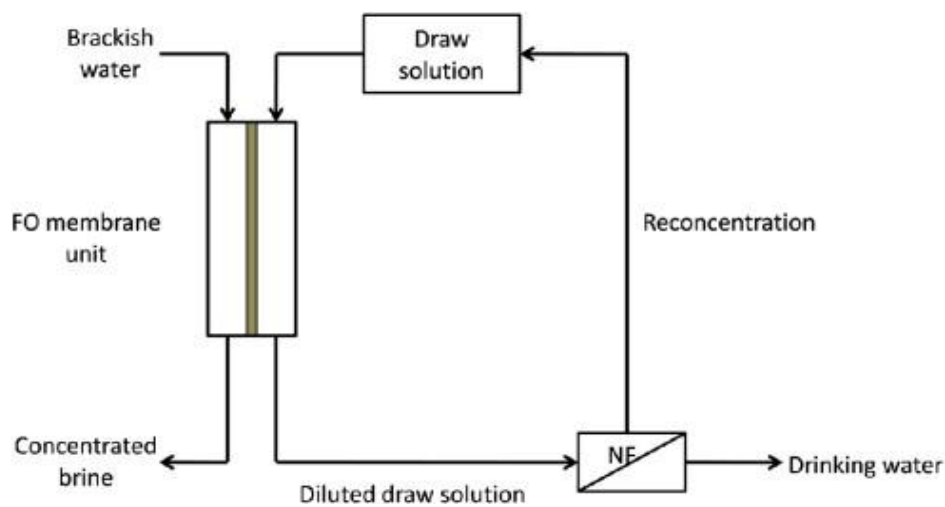


Figure 2.16: Schematic diagram of the hybrid FO–NF system configuration. Adapted from Zhao et al. ((2012b)

2.8.6.2 Other potential applications of the FO process

2.8.6.2.1 Pre-treatment to RO desalination for potable and non-potable purposes

The FO process is very efficient in removing suspended solids, microorganisms and a wide range of dissolved solids and organics that represent a potential fouling and scaling risk to the RO membranes. Therefore, FO has been investigated as a pre-treatment option for the seawater reverse osmosis (SWRO) process because it improves the quality of water and reduces the desalination cost due to lower energy requirements for pre-treatment and the RO process (Bamaga et al., 2009; Cath et al., 2009; Bamaga et al., 2011). It was observed that pre-treatment using FO could increase RO recovery by up to 80% of the feed water, thereby considerably decreasing the total cost of desalination. Usually, a two-stage FO process is used in integrated FO-RO desalination (Cath et al., 2009; Bamaga et al., 2011), as shown in Figure 2.17. In the first stage of the FO process, seawater is used as the DS to extract water from impaired water sources such as brackish water or secondary/tertiary wastewater effluent from a wastewater treatment plant, treating the impaired water in the process during the dilution of the seawater. This diluted seawater feed requires much less energy than the undiluted seawater feed and is also devoid of fouling species, most of which would already have been removed from the impaired water during the FO pre-treatment process. The impaired water undergoes processing through a multiple barrier system to ensure that the water quality is suitable for potable purposes.

The concentrated brine produced from the first stage RO process can be used as the DS for the second stage FO process, either to extract more water from impaired water sources, or from seawater, or from brackish water sources (Bamaga et al., 2009), before being used as feed for the next RO desalination process. In this way, the FO process helps to enhance the total recovery rate of the seawater and ultimately decreases the total cost of the desalinated water.

RO desalination for non-potable purpose such as irrigation is not only cost prohibitive due to the energy intensive nature of the process; the RO process alone is often not adequate to meet the stringent boron and chloride standards for agricultural irrigation water (Shaffer et al., 2012). Most often, an additional post-treatment or a second pass

can generate osmotic pressure equal to or higher than the solubility of the feed solution, it can theoretically achieve a 100% recovery rate, although this is practically impossible as a result of scaling and increased pumping costs due to increased feed viscosity.

The FO process has been evaluated for the treatment of RO concentrate because of its potential to achieve very high recovery rates without significant energy expenditure. Martinetti et al. (Martinetti et al., 2009) reported recoveries of up to 90% from RO brines, although water recoveries were limited by the precipitation of organic salts on the membrane surface. However, Na₂EDTA cleaning and simple osmotic backwash fully restored water fluxes.

2.8.6.2.3 Wastewater and leachate treatment

In the absence of applied hydraulic pressure, the FO process is characterised by low fouling problems and therefore a number of studies for its potential application in wastewater treatment have recently been reported. Applications of the FO process for wastewater treatment include the osmotic membrane bioreactor (OSMBR) (Achilli et al., 2009b; Lay et al., 2011; Xiao et al., 2011), anaerobic digester concentrate (Holloway, 2006), and the treatment of landfill leachate (York et al., 1999). Most investigations on OSMBR are limited to NaCl as the DS (Achilli et al., 2009b; Lay et al., 2011; Xiao et al., 2011), but this opens up the potential for using seawater and the concentrated brine from a nearby RO desalination plant as the DS for an OSMBR. The FO membrane in MBRs offers the advantage of having higher pollutant rejection with lower hydraulic pressure compared to a conventional MBR system. TOC and NH₄⁺-N removals were much higher than those obtained with conventional MBRs, with removals greater than 99% compared to 95% with traditional processes (Achilli et al., 2009b). Although reverse salt diffusion of the DS caused initial flux decline in the OSMBR process, salt concentration in the bioreactor stabilised after certain period of operation, after which flux decline was only caused by membrane fouling. The level of salinity observed in the bioreactor did not have a toxic effect on the biological process, indicating that NaCl is a suitable DS for this application.

Holloway et al. (2006) investigated the use of FO for the concentration of centrate (a liquid stream produced by the sludge dewatering process) using NaCl as the DS. Although membrane fouling affected the water flux with time, water flux was almost

completely restored after hydraulic cleaning. Colour and odour removal was almost 100%, phosphorus rejection exceeded 99%, and total Kjeldahl nitrogen and ammonia rejections were about 92% and 87% respectively.

Landfill leachate is a complex solution, generally composed of organic compounds, nitrogen, TDS and heavy metals, and it is usually treated at wastewater treatment facilities that mainly focus on the removal of organics, nutrients and heavy metals. York et al. (York et al., 1999) studied the possibility of using FO as a process to treat landfill leachates, especially TDS. A full-scale system was designed using a solution of 75g NaCl/L as the DS. In this system, the FO process was used to draw water from the leachate into the DS. The diluted DS was then treated by an RO process to produce freshwater and reconcentrate the DS. The combined FO/RO process proved to be more efficient than the RO process alone, because RO is less resistant to fouling than the FO process. This system was able to remove the vast majority of contaminants present in the feed solution. TDS rejection was almost 98% and most contaminants had more than 99% rejection.

2.8.6.2.4 Pharmaceutical industry

Proteins have a wide range of commercial applications, particularly in the pharmaceutical industry, but enriching and separating protein is technically and economically challenging because most proteins are chemically unstable and heat sensitive. The potential use of the FO process for enriching proteins has been reported using MgCl_2 as the DS (Yang et al. (2009) and hydrophilic magnetic nanoparticles (MNPs) as the DS (Ling et al., 2010; Ge et al., 2011; Ling and Chung, 2011b). These studies found that the FO process was able to enrich lysozyme product to high purity without changing the conformation or denaturing the protein, due to the low reverse solute flux of these draw solutes.

Osmotic pumps have been commercialised for the continuous, controlled and targeted release of drugs for the long-term treatment of patients with a chronic illness (Wright et al., 2003). An osmotic pump system is composed of a titanium cylindrical reservoir with a semi-permeable membrane that separates the DS (mixture of NaCl and pharmaceutical excipients) chamber from the drug compartment containing a tiny piston. An osmotic gradient between the tissue water and the DS induces water to flow

across the membrane, increasing the pressure inside the DS compartment. It then continuously pushes the piston, thereby delivering the drugs into the body through a small orifice located on the other side of the cylinder (Cath et al., 2006).

2.8.6.2.5 Food processing industry

The FO process operates at low temperatures and low pressures and these characteristics have significant advantages for food industry applications as the process does not cause sensory (i.e. taste, aroma and colour) or nutritional (i.e. vitamins) degradation. Popper et al. (1966) investigated the FO process for the concentration of fruit juices, using highly concentrated NaCl as the DS. Although they could produce a highly concentrated fruit juices by this method, they observed that the presence of NaCl in the concentrated juice due to the reverse diffusion of NaCl was an issue. Herron et al. (1994) evaluated and observed the FO process to be useful in concentrating juices, coffee and wines using sugar solution as the DS. This study was extended by Petrotos et al. (1998) to the concentration of tomato juice using six different compounds (i.e. calcium chloride, calcium nitrate, glucose, sucrose and polyethylene glycol 400 or PEG400) as the potential DS. Their study indicated that the choice of a suitable DS depends greatly on its mass transport characteristics. Garcia-Castello et al. (2009) evaluated the FO process for sucrose concentration, using NaCl as the DS, and concluded that much higher sucrose concentration factors can be obtained by FO compared to the RO process, although water fluxes were comparatively lower than they were in the RO process.

2.8.7 Current challenges of the FO process for desalination

Although the novel concept of FO was developed as early as 1968 (Popper et al., 1968), it has not been able to compete and advance because the process still faces several technological barriers. Two major barriers are the lack of an ideal FO membrane and the lack of ideal draw solutes, especially for desalination for potable water, and they are discussed separately below:

2.8.7.1 Lack of an ideal membranes for the FO process

A major technical barrier to the commercial application of the FO process has been the lack of an ideal FO membrane that could produce high water flux comparable to the RO

process (Wang et al., 2010b; Yip et al., 2010; Tiraferri et al., 2011). As discussed earlier, the current asymmetrical membranes used for pressure based filtration result in concentration polarisation (CP) effects that severely decrease the net osmotic pressure between the two solutions and hence lowers the water flux across the membrane (Cath et al., 2006; Gray et al., 2006; Tan and Ng, 2008; Tang et al., 2010). While the ECP that occurs on the membrane's surface can be mitigated using crossflow, similar to pressure based membrane filtration systems such as RO, ICP occurs within the porous support layer of the asymmetrical membranes and therefore cannot be mitigated easily (Cath et al., 2006). ICP is exclusive to the FO process and is said to be mainly responsible for the much lower water flux achieved in the FO process than the expected or theoretical water flux (Gray et al., 2006).

Although several high performing membranes tailored for FO applications have been reported recently, particularly thin film composite membranes, water flux still remains lower than in the RO process based on the bulk net osmotic gradient. Polymer membranes are the most affordable salt rejecting membranes, but they are also weak, meaning that they need to be strengthened by a supporting layer. Such a supporting layer provides resistance in the form of ICP, which severely reduces the effective osmotic gradient. Recent effort has been devoted to attempts to modify and improve the structural properties of the support layer, which has to some extent significantly improved the performance of the FO process.

Since the supporting layer is inevitable for a polymeric membrane, the other effort has been to synthesise a symmetric membrane and carbon nanotubes (CNT), and biomimetic membranes are potential membranes for future FO applications. Vertically aligned CNT are observed to have water flux of several orders of magnitude higher than current FO membranes, although there have been issues around the poor rejection properties of such membranes (Gethard et al., 2010; Schnorr and Swager, 2010; Wang et al., 2010b; Yip et al., 2010). Attempts are now being made to improve the salt rejection properties of the CNT by incorporating functional groups on the surface of the carbon nanotubes.

Since the FO process has comparatively lower water flux than the RO process using the currently available commercial FO membranes, it should be acknowledged that the

membrane surface area required will be significantly higher than for RO plant, depending on the capacity of the plant. Therefore, the capital cost of an FO desalination plant is likely to be comparatively higher than that of an RO plant, on the basis of current membrane performance and modular design. With further research, however, the performance of FO membranes and their modular designs are expected to improve in the future.

2.8.7.2 Lack of suitable draw solutions for desalinated potable water

Application of the FO process for potable water must accompany a post-treatment process to separate the draw solutes and the pure water from the diluted DS after desalination. Challenges remain related to separation and recovery of the draw solution from desalinated water, as this additional post-treatment process consumes energy. The success of FO desalination in the future, especially for drinking purposes, will rely mainly on how easily and efficiently the draw solution can be separated and recovered from the desalinated water (McCormick et al., 2008). Other than the $\text{NH}_3\text{-CO}_2$ solution and the hydrophilic magnetic nanoparticles, there are no other more effective draw solutes that can be easily separated from the pure water using minimum effort. However, where the fate of the draw solution after desalination is irrelevant, the FO process offers a significant advantage over RO desalination, and this potential must be exploited.

2.8.7.3 Process limitations

In the pressure-based membrane process, the phenomenon of CP effects increases the osmotic pressure of the feed water at the membrane surface, reducing the water flux, and this ECP phenomenon is well-understood and modelled (Elimelech and Bhattacharjee, 1998; Sablani et al., 2001). The CP effect, particularly ECP, is largely mitigated by providing horizontal crossflow shear and turbulence on the membrane surface instead of the dead end filtration process. The FO process is unique, because two independent solutions flow in contact with the membrane on each side of the membrane surface, which gives rise to two different types of CP effects and further reduces the effective osmotic gradient. CP effects are inevitable in membrane processes and the issue of CP effects in the FO process is compounded by the presence of the thick support layer in the asymmetric membrane (Babu et al., 2006; Gray et al., 2006).

ICP is intrinsic to the FO process and is found to be critical because it occurs within the membrane support layer; it therefore cannot be mitigated simply by altering the hydrodynamic conditions (as in the case of ECP).

2.9 Fertilisers and food production

2.9.1 Fertiliser usage in the World

Plants grow and reproduce by using water and nutrients from the soil, carbon dioxide from the air and solar energy from sunlight (FAO, 2003). When the nutrients are continuously used up by the plants, the soil must be replenished to maintain soil fertility and productivity (Roy, 2007). The quality of the plants and food depends on the soil and the climatic conditions. While climatic conditions cannot be regulated, soil deficiency can be overcome by the addition of fertilisers (Hunt, 1938), which provide the additional nutrients essential for plant growth and development. Fertiliser is composed of either organic or inorganic matter of both natural or synthetic origin which, when added to the soil, supplies one or more plant nutrients essential for plant growth.

The scientific contribution and foundation for the modern fertiliser industry was laid by von Liebig in 1840 through his guiding philosophy of perfect agriculture as the true foundation of all trade and industry of nations, which must be based on the scientific principles of chemistry (Kiiski, 2009; Paull, 2009). During the second half of the 19th century, naturally occurring potash salts were discovered and developed as fertilisers. Fritz Haber and Carl Bosch developed the Haber process to produce ammonia from the nitrogen in the air in 1909-10, which at the time was mainly used for explosives. After World War I, large stocks of the ammonium nitrate used as an explosives ingredient during the war were released for agricultural use in the early 1920s (IFA, 2002; Roy, 2007). In the 1930s, ammonia was found to be a useful and economical method of supplying nitrogen through the ammoniation of superphosphate that involved the conversion of ammonia to nitric acid using the Ostwald process.

Fertiliser has played a significant role in improving agricultural productivity and in meeting the increasing demand for food. Population growth is one of the major factors that drives increased demand for food production, as indicated by the proportionate growth in the population and fertiliser usage, illustrated in Figure 2.19. Other factors such as growing income level, dietary changes and the preferences of the populations of

developing countries also translate into increased food needs (FAO, 2003; Stewart et al., 2005; Roy, 2007). This rising demand for agricultural commodities is usually characterised by an increase in fertiliser usage. Since the land area is almost static, the increased food demand must be met by more enhanced productivity, which means intensive agriculture (FAO, 2003). The role of mineral fertilisers in improving agricultural output is well established (Colwell, 1968), with a positive correlation between cereal production and fertiliser usage, especially in developing countries where growth rates are higher than in developed countries (Orman and Hojjati, 1995; FAO, 2003; Fageria et al., 2008). The use of fertiliser in the world has increased about fivefold since 1960, with N fertiliser alone contributing to about 40% of the increase in per-capita food production in the past 50 years (Smil, 2002; FAO, 2006). To satisfy global food demand in the 21st century, agricultural productivity must increase; thus, fertiliser is likely to still play a dominant role in improving the productivity of existing cultivable lands, although other technological advances such as farm mechanisation and sustainable production must also be considered (FAO, 1981; Baligar et al., 2001; FAO, 2003). Due to already high application rates, environmental concerns, reduction in government subsidies and trade liberalisation policies, the increase in fertiliser usage in the developed countries will be modest in comparison to the developing countries where there will be maximum growth (FAO, 2003).

Although the global economic and financial crisis had a significant impact on agriculture and fertiliser demand, the world production of major crops was expected to increase in 2011 because world food prices had been rising strongly, surpassing the earlier peak in 2008 (FAO, 2011). Fertiliser consumption in the world increased significantly in 2010 and the demand is expected to grow at 2.0% per annum between 2011 and 2015 (1.7% for nitrogen, 1.9% for phosphate and 3.1% for potash) (FAO, 2011).

The total annual fertiliser nutrient ($N+P_2O_5+K_2O$) consumption in the world was 168.2 million tons in 2007, which increased to 170.7 million tonnes in 2010. In 2015, it is forecasted to reach 190.4 million tonnes, as shown in Figure 2.20.

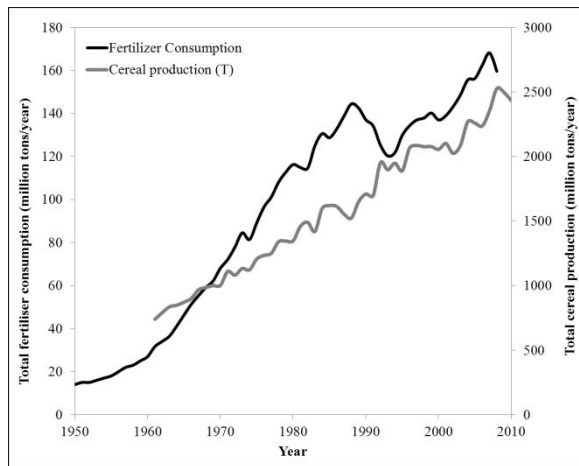


Figure 2.19: Figure: World's total cereal production and total fertiliser use between 1950 -2010. Adapted from World Bank Statistics (WB, 2012)

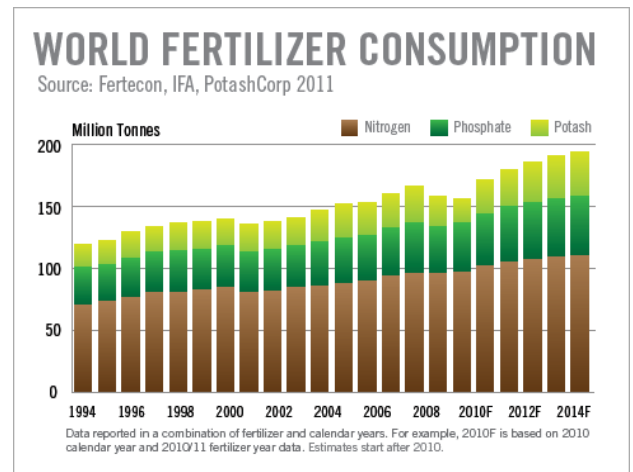


Figure 2.20: World NPK usage 1994-2014.

2.9.2 Fertiliser usage in Australia

Australia uses five to six million tonnes of fertilisers each year, providing around one million tonnes of nitrogen, half a million tonnes of phosphorus and two hundred thousand tonnes of potassium (FIFA, 2009). It has been estimated that fertilisers account for about 12% of the value of the material and service inputs used in Australian agriculture, with annual sales in excess of \$2 billion and the full economic effect on Australia's GDP in excess of \$8 billion a year (FIFA, 2009).

Table 2.4 is a list of major fertiliser products (imported and domestic) used in Australia alongside the amount of nutrient elements in those products. In 2008, Australia used some 4.6 million tonnes of fertilisers, with urea, single superphosphate, and ammonium phosphates (MAP and DAP) being the most dominant fertilisers used (FIFA, 2009).

Table 2.4: Major imported and domestic fertiliser products used in Australia 2008 (FIFA, 2009)

Major fertilisers	Tonnes	Approximate Tonnage of Principal Elements				
		N	P	K	S	Ca
Urea	1,042,980	479,771	-	-	-	-
Single superphosphate	1,031,937	-	92,874	-	113,513	206,387
Mono-ammonium phosphate (MAP)	646,956	64,696	142,330	-	9,704	-
Di-ammonium phosphate (DAP)	470,158	84,628	94,032	-	7,052	-
Potassium chloride (muriate of potash)	259,683	-	-	129,841	-	-
Ammonium sulphate (SOA)	263,616	55,359	-	-	63,268	-
Triple superphosphate	78,521	-	15,704	-	942	11,778
Anhydrous ammonia	75,112	39,711	-	-	-	-
TOTAL	4,634,369	785,757	360,043	177,336	240,663	226,495

Although the works of Fritz Haber and Carl Bosch on inventing synthetic fertiliser has significantly contributed to agricultural productivity, the use of this fertiliser has had unintended consequences. These fertilisers were used as explosive materials during World War II that resulted in prolonged war and the loss of 10 million lives (Paull, 2009). In addition, there are environmental risks associated with the increased and excessive or inappropriate use of fertilisers and other agrochemicals, including nitrogen imbalance, increase in soil salinity, sodicity, acidity, alkalinity and eutrophication of fresh and marine waters (Peryea and Burrows, 1999; FAO, 2003; FIFA, 2009). Leaching of fertiliser nutrients could also potentially contaminate groundwater resources. A recent study shows that nitrous oxide (N₂O) emissions from soils contribute around one-third of non-CO₂ agricultural greenhouse gas (GHG) emissions (FAO, 2003). Therefore, fertiliser nutrient management is the key issue in sustainable soil fertility. N, P, K fertilisation aims not only for a high economic return on investment through optimised yield and quality, but also for minimal environmental hazards (Hera, 1996).

2.9.3 Types of fertilisers used for food production

Sixteen elements have been identified as being essential for the normal growth and development of all plants (Glass, 1989; Kafkafi and Kant, 2005) and the list is provided in Table 2.5. Of all these essential elements, four elements (carbon, hydrogen, oxygen, and nitrogen) are derived directly or indirectly from the air and together constitute more

than 90% of plant material. The other six essential elements (calcium, magnesium, potassium, phosphorus, iron, and sulphur) are derived from the soil. Although all these elements are essential for healthy plant growth, demand varies according to factors such as crop type, cropping seasons, etc. (Oliver and Barber, 1966; Bates, 1971; Baldwin, 1975). The elements that need special consideration are nitrogen (N), phosphorus (P), potassium (K), calcium (Ca) and sulphur (S), and of these five elements, NPK are the primary nutrients under consideration for mineral or synthetic fertilisers. Based on the types of major elements required by plants, fertilisers are classified as nitrogen, phosphorous or potassium fertilisers (NPK). The number of major elements present in each fertiliser determines their classification as straight (single or basic fertilisers), compound or mixed/blended fertilisers.

2.9.3.1 Nitrogen fertilisers:

Nitrogen forms an important component of proteins and chlorophyll in plants and therefore N is essential for the healthy growth of the plant (IFA, 1998). Since N is usually responsible for increases in crop yield, N is taken up in large quantities amongst the major NPK nutrients, as is evident from the N usage data shown in Figure 2.20 and Table 2.4. A small but frequently regulated amount of N nutrient is preferable to large amounts with less frequency to maintain healthy plant growth and reduce nutrient leaching and runoff. Excessive N results in excessive leafy growth with low fruit yield.

Approximately 79% (by volume) of the Earth's atmosphere contains N (in the form of N_2 gas), but only a very limited number of plant varieties, chiefly legumes, can utilise this N directly from the air. This means that for most other plant crops, N must be made available to the soil in a dissolved solution for continuous cropping (FAO, 2003). Inorganic N in synthetic fertilisers, such as urea, is produced by fixing N from the atmosphere using natural gas as the energy source (Binford, 2006). Urea is the most widely used N fertiliser in the world (Fan et al., 1996). Table 2.6 shows some of the fertilisers that are used as a source of N for agricultural production.

2.9.3.2 Phosphorous fertilisers

Phosphorus is an essential component of every living cell, giving it an indispensable role in many physiological and biochemical processes because it cannot be replaced by

other elements (Syers et al., 2008). P plays a significant role plant energy, and it is responsible for stimulating cell division in plants, promoting plant growth and root development, accelerating ripening and improving the quality of grain. Usually, P is taken up by plants in the early stages of their life, such as during the seedling stage of annuals and the early regrowth of perennials. P, like N, is a nutrient that plants require in large quantities, as is evident from the NPK usage data in Figure 2.20 and Table 2.4. The mobility of P in the soil is low, and application is therefore required a few weeks before planting. Literature shows that depending on several factors, the application of P is about 80 kg/ha per crop of P for most vegetable crops. Efficient use of P is important because P is a finite and non-renewable resource and moreover wastage of P to the environment could cause eutrophication of the water bodies (Syers et al., 2008). Table 2.6 shows some of the fertilisers used as a source of P for agricultural production.

2.9.3.3 Potassium fertilisers

Potassium (K) is the third major nutrient required for plant growth. The term ‘potash’ comes from the colonial practice of burning wood in large pots and using the ashes as fertiliser, as well as for making soap, gunpowder and glass (Thompson). K provides several important functions for the plants, such as activating or catalysing enzyme actions for facilitating the transport of nutrients and their assimilation in the xylem and phloem; maintaining the structural integrity of plant cells; regulating turgor pressure; mediating the fixation of N in leguminous plant species; and in protecting plants to some degree from certain plant pests and diseases (FAO, 2003). K also helps to maintain electrical balance within plant cells. Potassium chloride (KCl), known as muriate of potash, is now the major source (95%) of K in the world (FAO, 2003). The various mineral fertilisers containing potassium are listed in Table 2.6.

2.9.3.4 Blending of fertilisers

Bulk blending is defined as the physical mixing of two or more granular fertiliser materials to produce mixtures containing nitrogen (N), phosphorus (P), potassium (K) and other essential plant nutrients (Beaton, 1997). Blending allows small batches of high analysis soil and crop-specific fertilisers to be mixed together and transported in an economical manner. Blending is not only convenient and effective for farmers; it also has a smaller environmental footprint, but at the same time it provides balanced

fertilisers according to the need of farmers and minimises waste (Beaton, 1997). The blending of fertilisers is usually done with dry or solid form ingredients at the factory, for easy transportation and handling; however, blending can also be performed in solution, especially in water, to create a blended fertiliser solution, as long as the mixture is compatible and does not form unintended products or precipitates. Such blending can be performed onsite at farms for fertigation purposes.

Blended fertilisers are created to meet the varying needs of crop, soil and climatic conditions, using a limited range of fertilisers to provide a wide range of blended products of mixed nutrient content. The ingredients of a blended fertiliser can be straight materials (a single or basic fertiliser contains only one essential plant nutrient), materials such as urea or potassium chloride or granulated compound fertiliser (containing more than one major nutrient) mixed together, or a combination of the two types of fertilisers mixed together. Blends have the advantage of allowing a very wide range of fertiliser grades which makes it possible to match a fertiliser exactly to a soil test recommendation. The relationships between and among the elements can have a significant effect on the plant, and therefore elemental levels of certain nutrients in the blends should not create plant toxicity (Kafkafi and Kant, 2005).

Table 2.5: The essential elements, their form for uptake, and functions in the plant. (Source: (Mengel and Kirkby, 1987). Adapted from (Kafkafi and Kant, 2005).

Essential elements	Form for uptake	Functions in the plant
C, H, O, N, S	Ions in solution (HCO_3^- , NO_3^- , NH_4^+ , SO_4^{2-}) or gases in the atmosphere (O_2 , N_2 , SO_2)	Major constituents of organic substances
P, B	Ions in solution (PO_4^{3-} , BO_3^{3-})	Energy transfer reactions and carbohydrate movement
K, Mg, Ca, Cl	Ions in solution (K^+ , Mg^{2+} , Ca^{2+} , Cl^-)	Nonspecific functions, or specific components of organic compounds or maintaining ionic balance
Cu, Fe, Mn, Mo, Zn	Ions or chelates in solution (Cu^{2+} , Fe^{2+} , Mn^{2+} , MoO^- , Zn^{2+})	Enable electron transport and catalysts for enzymes

Table 2.6: List of principal chemical fertilisers used worldwide

Name of fertilisers	Chemical formula	Nutrients
Ammonia	NH_3	N
Ammonium bicarbonate	NH_4HCO_3	N
Ammonium carbamate	$\text{NH}_4\text{CO}_2\text{NH}_2$	N
Ammonium chloride	NH_4Cl	N
Ammonium hydrate	NH_4OH	N
Ammonium nitrate	NH_4NO_3	N
Ammonium nitrate ammonium sulfate	$(\text{NH}_4)_3\text{NO}_3\text{SO}_4$	N-S
Ammonium nitrate sulfate/bisulfate	$\text{NH}_4\text{HNO}_3\text{SO}_4$	N-S
Ammonium phosphate	$(\text{NH}_4)_3\text{PO}_4$	N-P
Ammonium sulphate	$(\text{NH}_4)_2\text{SO}_4$	N-S
Calcium nitrate	$\text{Ca}(\text{NO}_3)_2$	N-Ca
Diammonium hydrogen phosphate	$(\text{NH}_4)_2\text{HPO}_4$	N-P
Mono calcium phosphate monohydrate	$\text{CaH}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	P-Ca
Mono-ammonium phosphate	$\text{NH}_4\text{H}_2\text{PO}_4$	N-P
Phosphoric acid	H_3PO_4	P
Potassium chloride	KCl	K
Potassium dihydrogen phosphate	KH_2PO_4	P-K
Potassium hydrogen phosphate	K_2HPO_4	P-K
Potassium nitrate	KNO_3	N-K
Potassium sulphate	K_2SO_4	K-S
Potassium thiosulphate	$\text{K}_2\text{S}_2\text{O}_3$	K-S
Single superphosphate	$\text{Ca}(\text{H}_2\text{PO}_4)_2$	P-Ca
Sodium nitrate	NaNO_3	N
Sodium tripolyphosphate	$\text{Na}_5\text{P}_3\text{O}_{10}$	P
Tri ammonium nitrate ammonium sulfate	$(\text{NH}_4)_5\text{NO}_3\text{SO}_4$	N-S
Tripotassium phosphate	K_3PO_4	P-K
Urea	$\text{CO}(\text{NH}_2)_2$	N

2.9.4 Water and irrigation

Plants require large quantities of water for healthy growth. An analysis of the plant mass indicates that water typically makes up 80 – 95% of the mass of growing plant tissues, while this may be in the range of 45-50% for woody plant tissue (Kramer and Boyer, 1995). About 95% of the water used by plants is lost through transpiration, while the rest is used during photosynthesis to produce the carbohydrates necessary for plant growth. The rate of transpiration depends on factors such as water availability and temperature. The water required for the plants is provided either through rain fed water (Campbell, 2005; Wang et al., 2006) or through an extensive network of irrigation systems, as can be seen in modern agricultural practice (Rosegrant et al., 2009).

2.9.4.1 Irrigation water use in the world

An adequate and secure supply of food for the world's increasing population and changing dietary habits as a result of higher income is important. Land for the expansion of agricultural farmland is not only limited but also has to compete with requirements for urban and industrial expansion. The only reasonable solution is to increase the productivity of the limited amount of existing land at an unprecedented rate (Plusquellec, 2002) which calls for intensive agriculture practices to meet the growing demand for agricultural produce.

Intensive agriculture depends on farm mechanisation, the supply of adequate plant nutrients (fertilisers) and a secured supply of irrigation water for crops that is not dependent on rainwater, which has become less reliable in the face of global warming and a changing climate. Irrigation is therefore expected to play a significant role in improving agricultural yield without expanding the land, especially in developing countries.

Since a large quantity of water is required for agriculture, water withdrawals for agriculture production currently account for 72% of the total global water withdrawn (surface water and groundwater), and even up to 90% in some developing countries (Cai and Rosegrant, 2002; Wisser et al., 2008; Rosegrant et al., 2009). Although irrigated agricultural land currently accounts for only some 20% of arable land, it contributes close to 40% of total crop production (FAO, 2003). Given that the percentage of irrigated agriculture is expected to increase to 50% by 2030, and to 70% by 2050, the percentage of water usage for agricultural production will definitely increase beyond the current 72% of total water consumption. The extensive use of water for irrigation will have both regional and global impacts by altering the normal hydrological cycle, which can be dramatic and can transform large, mainstream rivers into 'losing streams' with substantial reductions in flow (Wisser et al., 2008).

2.9.4.2 Irrigation in Australia and water trading

Large-scale irrigation in Australia started in the late 1880s. The total irrigated area grew steadily between 1920s and mid-1950s and then increased dramatically in the mid-1990s. Since then, the total irrigated area has fluctuated between 2.0 and 2.5 million ha

depending on seasonal water availability. In 1995, a ‘cap’ was introduced for diversions in the Murray-Darling Basin; however, MDB is now considered to be over-allocated and water is being re-allocated to the environment to strengthen the ecological functioning of the river system. The waters of northern Australia’s tropics are relatively untapped and therefore may come under pressure for exploitation as a potential source of water for irrigation and urban use, which will include urban stormwater and sewage water. Otherwise, there is no additional untapped water source available for irrigation or urban growth in Australia. Without new water sources, all water users must become more efficient and that will require more research, innovative solutions and the broad adoption of those solutions (NPSI, 2011).

Australia currently has an estimated 41,000 agricultural irrigation businesses with an annual production value of \$9–\$11.5 billion, which is about 30% of total agricultural production, and therefore irrigation forms a crucial part of the Australian economy (NPSI, 2011; Vlotman and Kulkarni, 2012). In 2010-2011, the water use for agriculture in Australia was 7,551 GL, of which 64% was concentrated in the Murray-Darling Basin, as shown in Table 2.7 (ABS, 2012b). New South Wales and Queensland were the states with the highest consumption of water for agriculture in Australia. The total agricultural land in Australia in 2010-2011 was 410 million hectares, but only 0.5% of this land is irrigated and yet it is responsible for 30% of the agricultural produce of the country (NPSI, 2011; ABS, 2012b). The MDB has 85 million hectares of agricultural land making up 21% of all the agricultural land in Australia. The water application rate in the MDB is currently 3.8 ML/ha, which is higher than non-MDB areas which have an application rate of 2.8ML/ha indicating that the MDB is the most intensive irrigation area in Australia (ABS, 2012b).

The agricultural industry typically uses the highest amount of Australia’s total water consumption at 65%-70%, although this percentage dropped recently to close to 50% due to scant rainfall and drought. The vast majority of irrigated water use is controlled by regulations and licences, making the water trading system in Australia unique in the world. Irrigators in Australia require an authorised water allocation to extract specified amounts of water from rivers or bores (groundwater) or from irrigation supply systems. The irrigated production of food and fibre is one of the strengths of regional economies in Australia and is the driver of the following features (NPSI, 2011):

- irrigated farms tend to have relatively high levels of labour per hectare
- engineering and technical support is needed for irrigation delivery and drainage systems
- local processing, packaging and transport generate more jobs and maintain communities
- local produce (fruit, nuts, wine and cheese) complements tourism and dining experiences.

The system of water markets in Australia was introduced during the mid-1980s and irrigators enjoy two types of water rights (Peterson et al., 2005; Wheeler et al., 2009; Wheeler et al., 2010). Water entitlement refers to the perpetual right to access water on a seasonal basis, depending on availability. Although the water entitlement right originally emanated from land ownership, currently it is a distinct property right that can be sold separately from the land. The second right is known as water allocation and is the right to extract a certain volume of water during the current irrigation season. Water allocations are announced by the designated authority and allocation percentages are fundamentally determined by the available water in storage and climatic conditions (Wheeler et al., 2009).

Water trading refers to the buying and selling of water allocations (temporary water trades) and water entitlements (permanent water trades). Water trading allows water rights to shift towards uses where the yields and marginal returns are higher (net of transfer costs). Other merits of water trading are that the revenue from water sales can be used to supplement farm income and provide finance for other on-farm or off-farm activities, or it can sometimes even facilitate exit from an industry (Peterson et al., 2005). Water trade can also lessen the impact of reductions in the availability of irrigation water during the seasons of drought.

Table 2.7: Australian agricultural water use by State and Territory in 2010–11. Source: (ABS, 2012b)

States	Agricultural businesses	Irrigation	Other agricultural uses	Total water use
	no.	ML	ML	ML
NSW	43,541	2,745,896	236,239	2,982,135
Vic.	32,407	1,134,701	165,648	1,300,349
Qld	28,435	1,693,994	265,908	1,959,903
SA	14,059	621,308	77,721	699,029
WA	12,529	253,759	93,349	347,109
Tas.	4,085	172,709	28,490	201,199
NT	522	22,713	37,587	60,300
ACT	75	293	285	578
Australia	135,654	6,645,375	905,227	7,550,601
MDB	53,588	4,507,454	307,481	4,814,935
Non-MDB	82,066	2,137,920	597,746	2,735,666

2.9.5 Fertigation

The method of applying fertilisers to crops is one of several factors that affect fertiliser use efficiency (Haynes, 1988; Mohammad et al., 1999; Hou et al., 2007). There are different methods for the application of fertilisers such as broadcast sprays and liquid injection. Liquid injection is one of the preferred options because it avoids crop damage caused by burning the leaves of young plants. Although liquid fertilisers provide no immunity against environmental hazards such as pest, frost or drought, it has been found that crops continually grown using liquid injection have become more resilient to such factors and that yields have increased compared to crops grown using the granular method of fertilisation (Dasberg et al., 1988; Haynes, 1988). The application of fertilisers in liquid form is therefore often seen as being more favourable than the use of granular fertilisers, although soil, crop and environment testing is nevertheless required to confirm its suitability for liquid fertiliser application.

Fertigation is the term used for the fertilised irrigation of plants or crops or the application of plant nutrients, mineral fertilisers, soil improvers and soluble fertilisers through a pressurised irrigation system (Papadopoulos and Eliades, 1987; Haynes, 1988; Magen, 1995; Hagin and Lowengart, 1996; Playán and Faci, 1997; Papadopoulos, 1999; NGIA and HA, 2002; Kafkafi and Kant, 2005; Alva et al., 2008). ‘Fertigation’ is a fusion of the two words: ‘fertiliser’ and ‘irrigation’ and this term was first used in the USA to describe the bubbling of anhydrous ammonia into irrigation water, although other fertilisers were also applied through a sprinkler and drip irrigation system (Kafkafi

and Kant, 2005; Eissa et al., 2010). Efficient use of fertiliser and water is critical to sustained agricultural production and fertigation can be used to improve fertiliser and water use efficiency more effectively than conventional methods of fertiliser application (De Kreij et al., 2007; Hou et al., 2007).

The application of plant nutrients through the irrigation system (fertigation) or the application of other chemicals by the same system (chemigation) became popular because of the efficiency and convenience to farmers of such a system (Papadopoulos and Eliades, 1987). In micro-irrigation systems, such as drip/trickle irrigation and sprinkler irrigation, fertigation can be used to apply fertilisers directly through the irrigation system to the region where most of the plant roots develop (Haynes, 1988; Magen, 1995; Hanson et al., 2006; Phocaides, 2007; Alva et al., 2008). Fertigation is now the accepted and most common method of applying the majority of crop nutrition, especially when liquid or soluble fertilisers are used rather than granular fertilisers, which are spread through broadcast and are reliant on rain or sprinklers to wash them into the root zone (Zhang et al., 1996; Playán and Faci, 1997; Treder, 2006; Alva et al., 2008). Fertigation is used extensively in commercial agriculture and horticulture, and its use is beginning in general landscape applications as dispenser units become more reliable and easy to use (Playán and Faci, 1997; Imas, 1999). Fertigation is especially popular for greenhouse growers, who employ constant fertigation (proportional) using irrigation controllers that control the quantity of fertiliser according to the flow rate of each irrigated zone (De Kreij et al., 2007; Sonneveld and Voogt, 2009).

There are several advantages of fertigation and they include the following (Papadopoulos and Eliades, 1987; Mohammad et al., 1999):

- Ease of handling fertilisers
- Fertiliser use efficiency due to optimisation and uniform distribution of nutrients at the required depth near the roots
- Uses customised nutrient blends based on requirements
- Agronomic effectiveness is equal to other types of fertilisers when equal amounts of plant food are compared
- Can be used with other chemicals such as insecticides, pesticides, fungicides, etc.

- Increased nutrient absorption by plants
- Reduction in fertiliser and chemicals needed
- Reduction in water usage due to the resultant increased root mass of the plant being able to trap and hold water
- Application of nutrients at the precise time they are needed and at the rate they are utilised

Another advantage of fertigation is in the application in mixture of other micronutrients and fungicides in a dust free environment, eliminating the separate application of those chemicals. In addition to fertigation and chemigation, fungigation and herbigation are similar but specific terms used for the application of fungicide and herbicide or pesticide chemicals with the irrigation water (Ogg Jr, 1986). Chemigation, including fungigation and herbigation, is considered to be a more restrictive and controlled process due to its potential to cause harm to humans, animals, and the environment, and it is therefore generally more regulated than fertigation.

The disadvantages of fertigation include the leaching of fertiliser nutrients when excessive fertiliser is used in the water, as this can cause unintended pollution of groundwater bodies (Hagin and Lowengart, 1996). Modern methods of orchard cultivation require more effective ways of irrigation and fertilisation, and fertigation offers the advantage of being able to regulate fertiliser doses and the frequency of water and nutrient applications according to specific requirements of plant age, growth cycle and weather conditions (Mearns et al., 1996).

CHAPTER 3



University of Technology Sydney

Faculty of Engineering & Information Technology

EXPERIMENTAL INVESTIGATIONS

3.1 Introduction

The chapters that follow this in the Thesis are the result of a study carried out through both simulation and bench-scale experimental investigations. The experimental investigation works are divided into two parts: one covering the forward osmosis (FO) process and the other covering the pressure based membrane process of nanofiltration (NF) or reverse osmosis (RO). The FO process was carried out using mainly fertilisers and draw solutions (DS) although a few other inorganic fertilisers were used for comparative studies. The NF process was investigated as a pre-treatment or post-treatment process to the fertiliser drawn FO (FDFO) desalination process. The RO process was used only to determine the basic membrane properties such as the pure water permeability coefficient and salt rejection of the FO and RO membranes used for the FO process.

This chapter describes in detail the general experimental procedures for all the bench-scale investigations carried out within the scope of this study, including the types of DS and feed solutions (FS) used for the experiments. Descriptions of the experimental procedures specific to certain work but not included in detail within this chapter can be found in their respective chapters.

3.2 Experimental Materials

3.2.1 Feed solutions for the forward osmosis and nanofiltration processes

3.2.1.1 Feed solutions for the forward osmosis process

Different types of feed solutions (FS) were used for the bench-scale investigation, depending of the type of study specified in each chapter. In most cases, deionised water or DI (Milli-Q, Millipore with EC 4.0 $\mu\text{S}/\text{cm}$ and TOC 4 ppb) was used as the FS, especially when the study involved the comparative performances of different DS. The FS also consisted of model brackish water (BW) of 5,000 mg/L NaCl and model seawater or SW of 35,000 mg/L NaCl.

Table 3.1 shows the composition of various FS used in the studies. In most chapters, the brackish water or BW refers to the simulated brackish water with total dissolved solids (TDS) of 5,000 mg/L of NaCl solution. However, in some chapters this nomenclature

may also include brackish water such as BW5, BW10, BW20 and BW35 representing the TDS of the FS as 5,000, 10,000, 20,000 and 35,000 mg/L of NaCl respectively.

A model brackish groundwater was also used in Chapter 10 to simulate the actual brackish groundwater (BGW) found in the Buronga salt interception scheme (SIS) at Mildura, NSW, within the Murray-Darling Basin (MDB). Saline groundwater is abundant within the MDB (ANRA, 2009) and it has contributed to increased river salinity, one of the major environmental issues in the MDB as described in Chapters 2 and 4. Buronga is one of the 18 different locations along the Murray Darling Rivers where SIS has been in operation for the past several years (some since 1960s), diverting 324,162 tonnes of salt a year from entering the Murray River (MDBA, 2011b). FDFO desalination has significant potential for application in the MDB and is particularly suitable for integrating with the existing SIS. The feed water used in this study therefore simulates the characteristics of the BGW found at the Buronga SIS location. The GW data provided by NSW State Water shows that the characteristics vary throughout the year; however, the average annual composition was considered in preparing a simulated BGW for this study. The detailed composition of the simulated BGW is shown in Table 3.2, while the detailed composition of the groundwater for one year is shown in Appendix A.

Since salinity varies throughout the year, it was appropriate to simulate the BGW of different TDS, and this study therefore used four different types of simulated BGW as the FS with its TDS varying from 3,912 to 27,382 mg/L. The TDS may appear to have a strange value here, but this happened because of calculation errors made during the initial preparation of the FS with hydrated salts. The TDS of the BGW originally proposed were 5,000, 10,000, 20,000 and 35,000 mg/L for BGW5, BGW10, BGW20 and BGW35 respectively, but their actual concentrations after subtracting the mass of the water from the hydrated mass were lower. Nevertheless, the same nomenclature has been adopted. All the chemicals used for the preparation of the FS were of reagent grade and obtained from Sigma-Aldrich Australia. The FS was prepared by dissolving the salts in DI water with the help of magnetic stirrer at 200-300 rpm for 10 to 20 minutes to ensure that all salts were fully dissolved and uniformly mixed before starting the experiments.

Table 3.1: Compositions of FS used for all FO studies. Osmotic pressure of the FS was determined by OLI Stream Analyser 3.2 (OLI Systems Inc., Morris Plains, NJ, US).

Type of FS	Total dissolved solids (TDS)	Osmotic pressure π (atm)	Measured pH
Deionised water (DI)	Pure water		7.0
Brackish water (BW5) or BW	5,000 mg/L NaCl	3.90	7.0
Brackish water (BW10)	10,000 mg/L NaCl		7.0
Brackish water (BW20)	20,000 mg/L NaCl		7.0
Seawater (BW35 or SW)	35,000 mg/L NaCl	28.00	7.0
Brackish groundwater (BGW)			
BGW5	3,912 mg/L	2.74	6.80
BGW10	7.824 mg/L	5.35	6.90
BGW20	15.647 mg/L	10.56	6.95
BGW35	27.382 mg/L	18.56	6.95

Table 3.2: Detailed composition of synthetic BGW feed for various TDS concentrations. This composition simulates the BGW usually found at Buronga SIS in the MDB. Osmotic pressure was calculated using OLI Stream Analyser 3.2 (OLI Systems Inc., Morris Plains, NJ, US).

TDS→ Compounds↓	BGW5	BGW10	BGW20	BGW 35
NaCl	1.857	3.713	7.426	13.000
Na ₂ SO ₄	0.897	1.794	3.588	6.280
KCl	0.067	0.134	0.268	0.470
CaCl ₂ .2H ₂ O	0.159	0.317	0.634	1.110
MgCl ₂ .6H ₂ O	1.974	3.947	7.895	13.820
NaHCO ₃	0.047	0.094	0.189	0.330
Total TDS (g/L)	3.912	7.824	15.647	27.382
π (atm)	2.74	5.35	10.56	18.56
pH	7.81	7.72	7.93	7.33

3.2.1.2 Feed solutions for the nanofiltration process

Nanofiltration (NF) has been used as an integrated process with FDFO desalination, discussed in Chapter 10. NF is evaluated either as a pre-treatment or post-treatment option to the FDFO desalination process. When NF was used for pre-treatment, the FS consisted of BG, the compositions of which are described in Table 3.2. When NF was used as a post-treatment, the FS consisted of diluted fertiliser solutions prepared to simulate product water from the FDFO desalination process using FS of various TDS (BGW5 to BGW35). More details on this can be found in Chapter 10.

3.2.2 Draw solutions for the forward osmosis experiments

3.2.2.1 Single or straight fertiliser solutions as DS

Eleven different types of fertiliser that are commonly used for agriculture were used as the DS and are listed in Table 3.3. All the FO experiments were conducted using pure grade fertilisers as the draw solutes. Draw solutions of specified molar concentrations were prepared by dissolving the salts in DI water. To obtain a homogeneous solution, the mixture was continuously stirred using a magnetic bar at 200–300 rpm for 10 to 20 minutes at room temperature before the start of the experiments.

It should be mentioned here that all the experiments for the study included in Chapter 8 were conducted at Korea University (Seoul, Korea), while the rest of the experiments were conducted at UTS. All the chemicals used were of reagent grade. The chemicals at Korea University were supplied by Samchun Chemicals Co. Ltd., Korea, while the chemicals used at UTS were mostly supplied by Sigma-Aldrich, Australia.

Table 3.3: List of chemicals used as draw solutes for the bench-scale crossflow FDFO desalination process.

Name of fertilisers	Chemical formula	MW	Remarks
Ammonium nitrate	NH_4NO_3	80.04	Fertiliser reagent grade
Ammonium sulphate (SOA)	$(\text{NH}_4)_2\text{SO}_4$	132.1	Fertiliser reagent grade
Ammonium chloride	NH_4Cl	53.5	Fertiliser reagent grade
Calcium nitrate	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	164.1	Fertiliser reagent grade
Sodium nitrate	NaNO_3	85.0	Fertiliser reagent grade
Potassium chloride	KCl	74.6	Fertiliser reagent grade
Mono-ammonium phosphate (MAP)	$\text{NH}_4\text{H}_2\text{PO}_4$	115.0	Fertiliser reagent grade
Diammonium phosphate (DAP)	$(\text{NH}_4)_2\text{HPO}_4$	132.1	Fertiliser reagent grade
Potassium nitrate	KNO_3	101.1	Fertiliser reagent grade
Potassium phosphate	KH_2PO_4	136.09	Fertiliser reagent grade
Urea	$\text{CO}(\text{NH}_2)_2$	60.06	Fertiliser reagent grade
Calcium chloride dihydrate	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	147.02	Reagent grade
Magnesium phosphate heptahydrate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	246.47	Reagent grade
Sodium sulphate	Na_2SO_4	142.04	Reagent grade

3.2.2.2 Blended fertiliser solutions as DS

Blended (mixed) fertilisers were also used as the draw solutes for the FDFO desalination process. Fertiliser blends were prepared by mixing two or more fertilisers together in the DI water in specific molar ratio to provide a suitable ratio of the major nutrients, mainly Nitrogen (N), Phosphorous (P) and Potassium (K) or NPK. Blended fertiliser solutions were prepared in a similar way to the procedures adopted in Section 3.2.2.1 but using mixtures of different straight fertilisers, listed in Table 3.3. More details of the preparation of the blended fertiliser DS are given in Chapters 9.

3.2.2.3 Other inorganic draw solutes

In addition to the fertiliser draw solutes, other draw solutes such as CaCl_2 , MgSO_4 and Na_2SO_4 were also used in the experiments in Chapter 6 for the purpose of making comparative studies. They were selected because of the presence of divalent ions that results in lower reverse diffusion through the membrane during the experiments. The procedures for the preparation of DS remained same as described in Section 3.2.2.1.

3.2.3 Membranes and their characteristics

3.2.3.1 Determination of basic membrane properties

Only those basic membrane properties relevant to this study were determined; namely, the pure water permeability coefficient (A) of the membranes and salt rejection. The experimental procedures are described under Section 3.3.2. The overall thickness of the membranes was determined using a digital micrometre (Model 293-330 Mitutoyo, Japan), shown in Figure 3.1.



Figure 3.1: Digital micrometer (Model 293-330 Mitutoyo, Japan) used for measuring the total thickness of the membrane

3.2.3.2 Forward osmosis membranes

Two different types of FO membranes were used in this study. The commercially available FO membranes used for all the FO experiments in this study were supplied by Hydration Technology Innovations (HTI), LLC, Albany, USA marked as cartridge membrane. According to the manufacturer, the cartridge membrane is made up of cellulose triacetate (CTA) with embedded polyester screen mesh. The characteristics of the membrane have been widely reported in many other publications (McCutcheon et al., 2005; Cath et al., 2006; Tang et al., 2010) and also discussed in Chapter 2.

The second FO membrane used was a polyamide based thin film composite (TFC) flat sheet membrane recently synthesised by Woongjin Chemicals Co. (Korea). This membrane was hand-casted and non-optimised membrane and therefore used only for comparative study in Chapter 6 and not. All other FO experiments in this study were conducted using CTA FO membrane unless stated otherwise.

The pure water permeability test was conducted at various applied pressures using a bench-scale RO unit as per the experimental procedures described in Section 3.3.2. The plots of the pure water flux at various applied pressures are presented in Figure 3.2 and the pure water permeability coefficient (A) of the membranes is summarised in Table 3.4. These results show that the cellulose triacetate (CTA) FO membranes have a PWP coefficient of $1.02 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ while the TFC FO membrane had a PWP of $5.215 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$.

Salt rejection tests of the FO membrane were conducted using similar experimental procedures but using 5,000 mg/L NaCl solution as the FS in RO mode. The salt rejection of the FO membrane was observed to be between 80% and 90%, as shown in Figure 3.3.

The overall physical thicknesses of the virgin FO membranes were measured using a digital micrometre (Model 293-330 Mitutoyo, Japan). The thickness of the CTA FO membrane was $93 \pm 3 \text{ }\mu\text{m}$.

The zeta potential of the thin FO membrane was measured by an electrophoresis method (SurPASS electrokinetic Analyzer, Anton Paar) using polylatex (520 nm) in 10 mM

NaCl solution as a standard particle, as described by Thanuttamavong et al. (2002). The solutions of 0.1 N HCl and 0.1 N NaOH were used to adjust the pH of the solution. Figure 3.4 shows the variation in zeta potential of a clean thin FO membrane as a function of pH. The zeta potential of the FO membrane was zero for pH less than 6 but became negative at pH higher than 6, reaching approximately 18 mV at pH 11.5.

3.2.3.3 Reverse osmosis membrane

A flat sheet Thin-film composite (TFC) polyamide (PA) RO membrane was used in the FO process for comparative study with the FO membranes in Chapter 6. The RO membrane was the SWRO membrane obtained from Woongjin Chemicals, Korea. The pure water permeability of the RO membrane was observed to be $1.87 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (Figure 3.2 and Table 3.4 and the NaCl rejection was 96.5%, as shown in Figure 3.2 and Table 3.4. The overall thickness of the RO membrane was 142 ± 2 measured by digital micrometer (Model 293-330 Mitutoyo, Japan). Table 3.4 shows the summary of the properties of the SWRO membrane used in this study.

3.2.3.4 Nanofiltration (NF) membrane

A flat sheet TFC NF membrane (NE90) was supplied by Woongjin Chemicals, Korea. The pure water permeability coefficient (A) of the NF membrane tested in this study was observed to be $10 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (Figure 3.2 and Table 3.4). The zeta potential of NE90 is reported by Nguyen et al. (2009) to be about -30 mV at neutral pH. The NaCl rejection of NE90 was observed to be about 85%, almost similar to the rejection data provided by the manufacturer between 85 and 95%. All NF experiments were conducted using this flat sheet NE90 membrane. According to the manufacturer's specifications, NE90 has a molecular weight cut-off (MWCO) of 220 Da.

Table 3.4: Basic properties of the four different types of membrane used in this study. PWP: Pure water permeability coefficient (A). The material composition is as provided by the manufacturer.

Basic properties	CTA FO	TFC FO	SWRO membrane	NF membrane
Manufacturer	Hydration Technology Innovations, Inc.	Woongjin Chemicals, Korea	Woongjin Chemicals, Korea	Woongjin Chemicals, Korea
Model	Cartridge membrane	Hand-casted	SWRO membrane	NE90
PWP ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$)	1.02±0.03	5.215±0.512	1.87±0.10	10.00±0.51
Rejection for 5,000 mg/L NaCl at 10 bar	93%	85.2%	99.5%	85.0%
Total membrane thickness (μm)	93±3	147±16	142±2	N/A
Material of rejection layer	Cellulose tri acetate	Polyamide	Polyamide	
Material support layer	Polyester mesh embedded	TFC poly sulfone	TFC poly sulfone	TFC poly sulfone

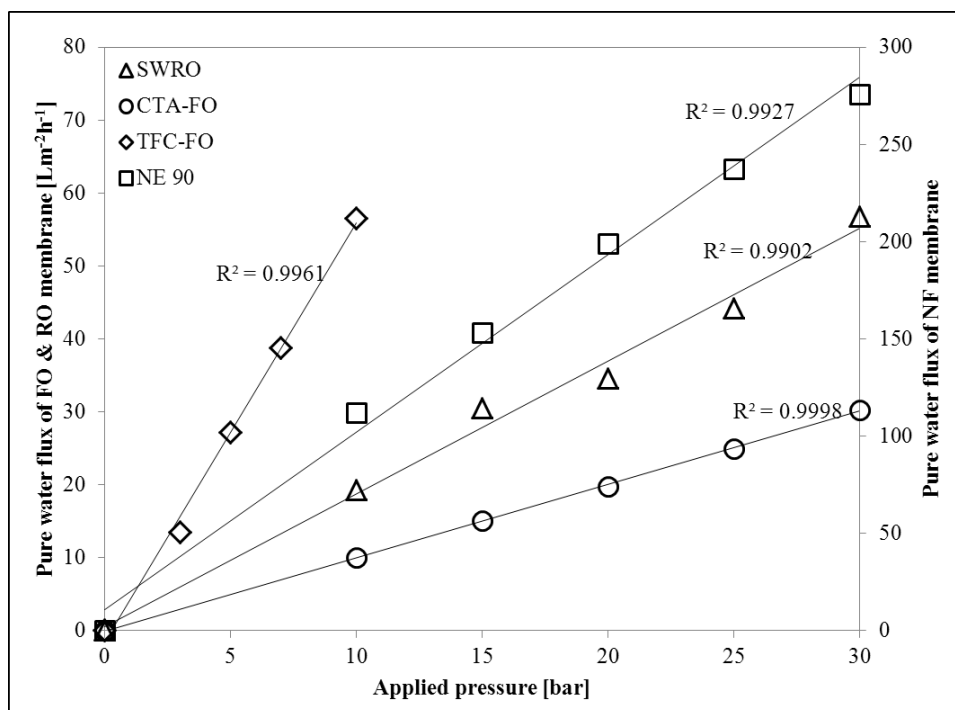


Figure 3.2: Pure water permeability tests of all the membranes used in this study. The PWP of the CTA FO, SWRO and NE 90 are 1.02, 1.87 and 10.00 $\text{Lm}^{-2}\text{h}^{-1}$ respectively

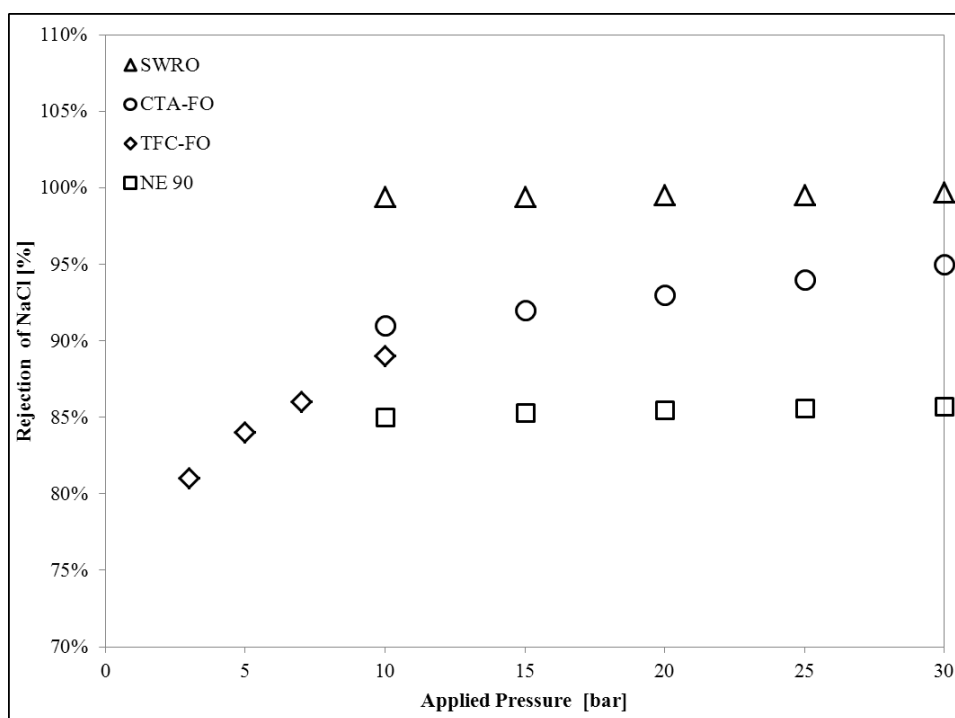


Figure 3.3: Salt rejection characteristics of all the membranes tested using 5,000 mg/L NaCl solution as feed water.

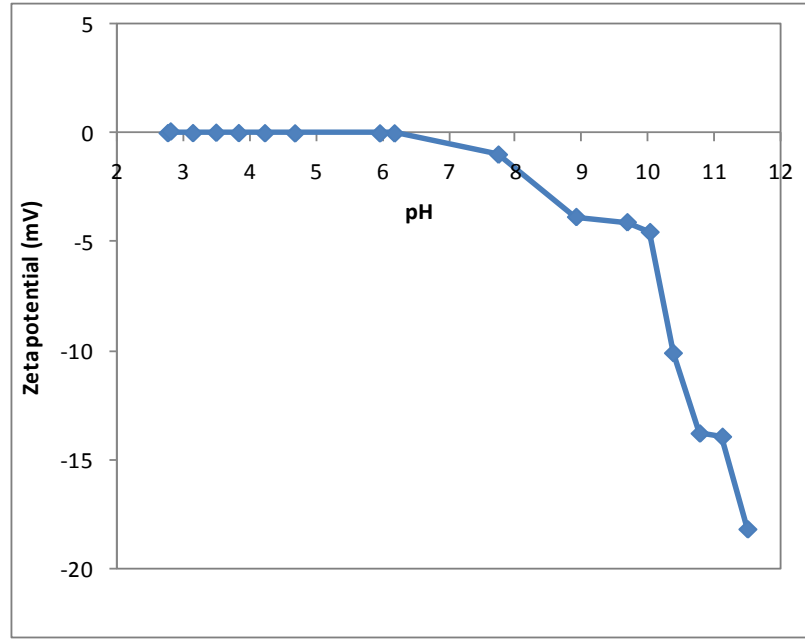


Figure 3.4: Zeta potential data of the thin CTA-FO membrane as determined using streaming potential and streaming current analyser (SurPASS electrokinetic Analyzer, Anton Paar), measured at Korea University, Seoul.

3.3 Bench-scale experimental performance testes

3.3.1 Bench scale crossflow forward osmosis experimental set-up

All the experimental investigations for the FO process in this study were performed using a bench-scale crossflow filtration unit. Figure 3.5 shows the bench scale crossflow FO unit used for the experimental studies. The FO unit consists of an FO cell with channel dimensions of 7.7 cm length x 2.6 cm width x 0.3 cm depth and an effective membrane area of $2.002 \times 10^{-3} \text{ m}^2$. Two channels are provided on both sides of the membrane to allow feed water to flow on one side of the membrane and draw solution on the side of the membrane.

Unless otherwise stated, all the FO performance experiments in this study were carried out at a crossflow rate of 400 ml/min which gives a turbulent flow with a crossflow velocity of 8.5 cm/s. The 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 temperature of all solutions was maintained at $25 \pm 1^\circ\text{C}$ using a temperature water bath controlled by a heater/chiller unless stated otherwise. Water flux across the membrane in the FO process was calculated from the change in the volume of the DS in the DS tank. The

change in the DS volume was recorded continuously by connecting the DS to a digital mass scale connected to a computer for online data logging at three-minute intervals. The water flux J_w (in $\text{Lm}^{-2}\text{h}^{-1}$) was calculated using the following relationship:

$$J_w = \frac{\text{Change in DS volume (L)}}{\text{Time (h)} \times \text{membrane area (m}^2\text{)}} \quad (3.1)$$

The initial volume of both the DS and FS was 2.0 L each. The solutions after passing through the membrane were returned to their respective tanks. This led to the continuous dilution of the DS and a continuous increase in the concentration of the FS, resulting in a decrease in water flux with time. However, the water flux (J_w) was selected from the point at which a stable flux was observed from the plot of flux (J_w) versus time, which usually happened within the first 30 minutes of operation. Each experiment was carried out for a duration of at least six hours for adequate diffusion of draw solutes and help effective monitoring of the reverse diffusion of draw solutes.

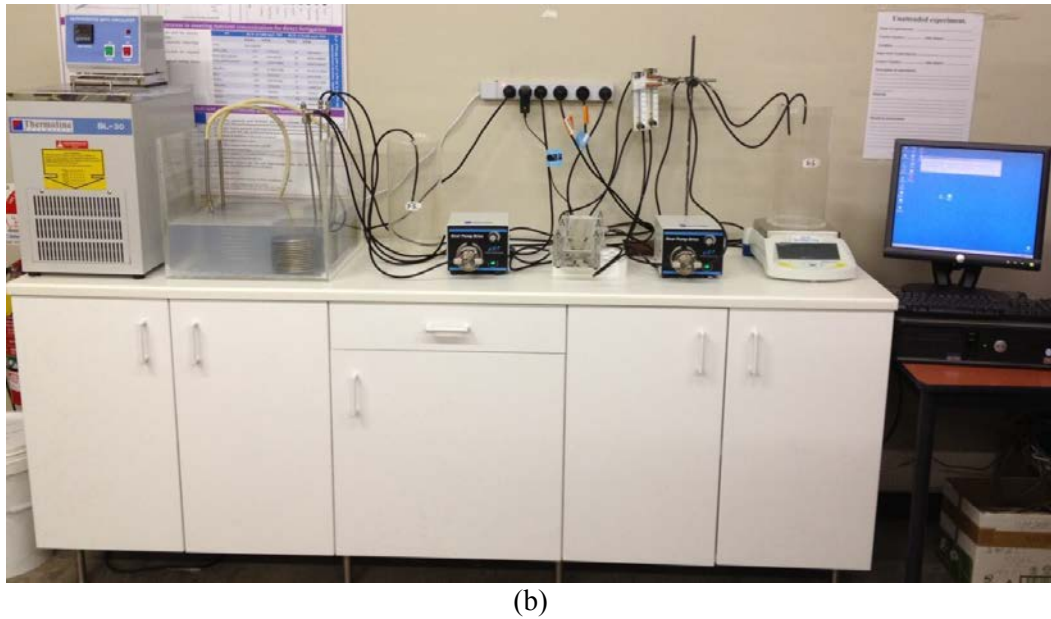
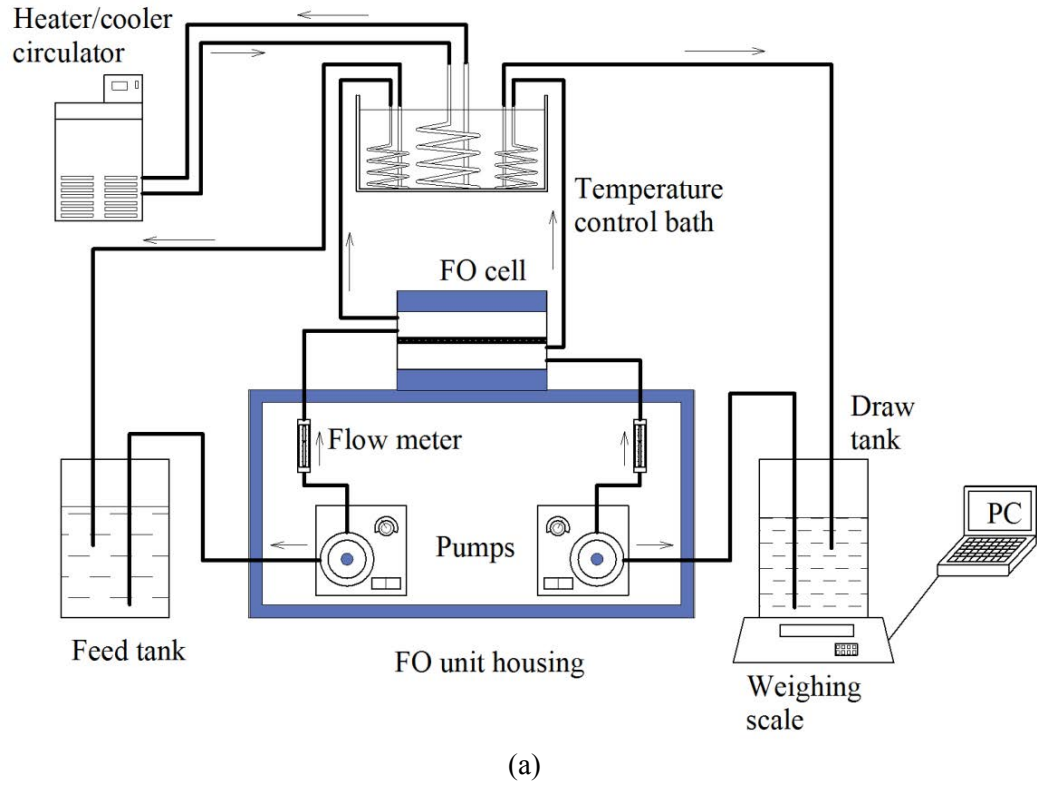


Figure 3.5: Bench-scale crossflow forward osmosis experimental setup. (a) Schematic of the bench-scale crossflow FO membrane unit and (b) the bench-scale FO unit used for all FO experiments

3.3.2 Crossflow bench-scale NF/RO experimental setup

A crossflow nanofiltration unit was used as pre-treatment or post-post-treatment to the FDFO desalination process. The same unit was also used in testing the pure water permeability and rejection properties of all the membranes. The bench scale crossflow

NF/RO experimental setup is shown in Figure 3.6. The membrane cell consisted of a rectangular crossflow channel with similar dimensions (membrane effective area of $2.002 \times 10^{-3} \text{ m}^2$) to the FO cell described in Section 3.3.1, except that the channel in this cell was only on one side of the membrane. The crossflow rates were maintained at 400 ml/min or (8.5 cm/s crossflow velocity). The initial volume of the FS was 3.0 L. Both the permeate and the retentate were recycled back to the feed tank except during the measurement of the permeate flux. The water flux J_w (in $\text{Lm}^{-2}\text{h}^{-1}$) in the NF/RO process was calculated using the following relationship:

$$J_w = \frac{\text{Volume of permeate water collected (L)}}{\text{Time of collection (h)} \times \text{membrane area (m}^2\text{)}} \quad (3.2)$$

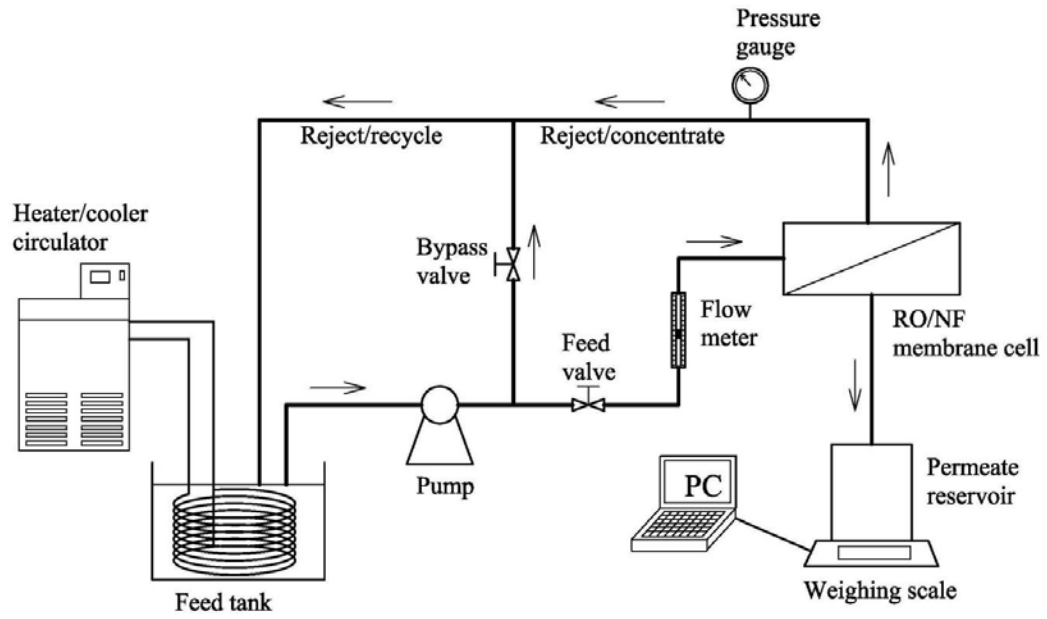
The water flux was determined at various operating pressures depending on the need of the experiment and the unit had a pressure rating of up to 80 bar controlled by a variable speed regulator.

The salt rejection R (in %) of the membranes in the NF/RO mode of operation was determined by measuring the electrical conductivity ($\mu\text{S/cm}$) of the FS and the permeate and using the following relationship:

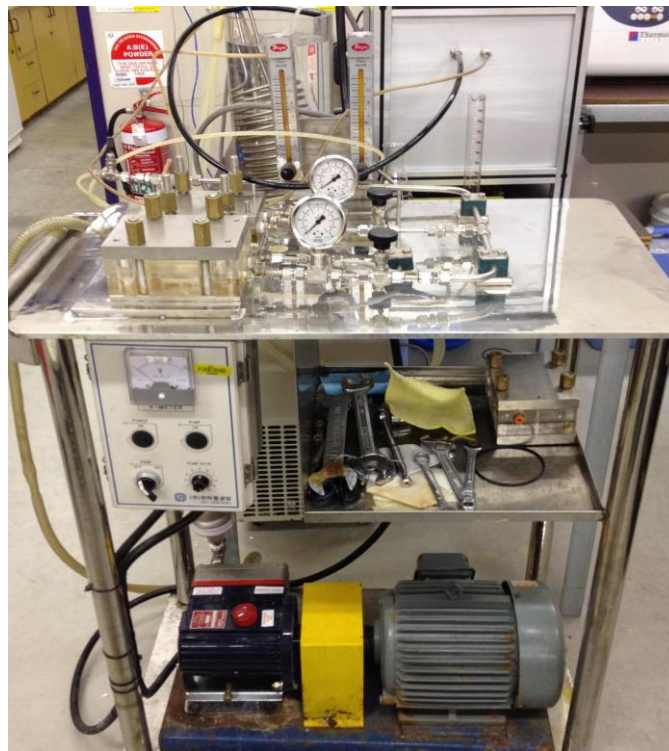
$$R(\%) = \left(1 - \frac{C_p}{C_0} \right) \times 100 \quad (3.3)$$

where C_p and C_0 are the permeate and initial FS concentrations respectively measured with the help of electrical conductivity.

When a mixture of salts was used as the FS, Eq. (3.3) provided only the total rejection or TDS rejection. The rejection of individual salts or elements was determined by analysing the permeate samples using inductively coupled plasma–mass spectrometry or ICP-MS (Perkin Elmer Elan DRC-e).



(a)



(b)

Figure 3.6: Bench scale pressure based membrane processes experimental setup. (a) Schematic drawing of the bench scale cross-flow NF/RO unit and (b) bench scale crossflow NF/RO unit

3.4 Analyses of the solution samples

3.4.1 Calculation of the osmotic pressure and speciation of the salt solutions

The speciation and the osmotic pressure of the fertiliser DS and the FS were predicted using an OLI Stream Analyser 3.2 (OLI Systems Inc., Morris Plains, NJ, US). This software uses thermodynamic modelling based on published experimental data to predict the properties of solutions over a wide range of concentrations and temperature (McCutcheon et al., 2006). Figure 3.7 shows a screenshot of the OLI Stream Analyser 3.2 modelling software interface.

In one of the experiments in Chapter 7, osmolality of the fertiliser draw solutions were used. The osmolal concentrations were measured using a cryoscopic osmometer (OSMOMAT 030-D, Genotec, Germany, shown in Figure 3.8), based on the freezing point depression method and had measurement range of 0-2.5 osmoles/kg. Osmometer calibration was performed using NaCl standards of 2.0 osmoles/kg, as received from the same supplier.

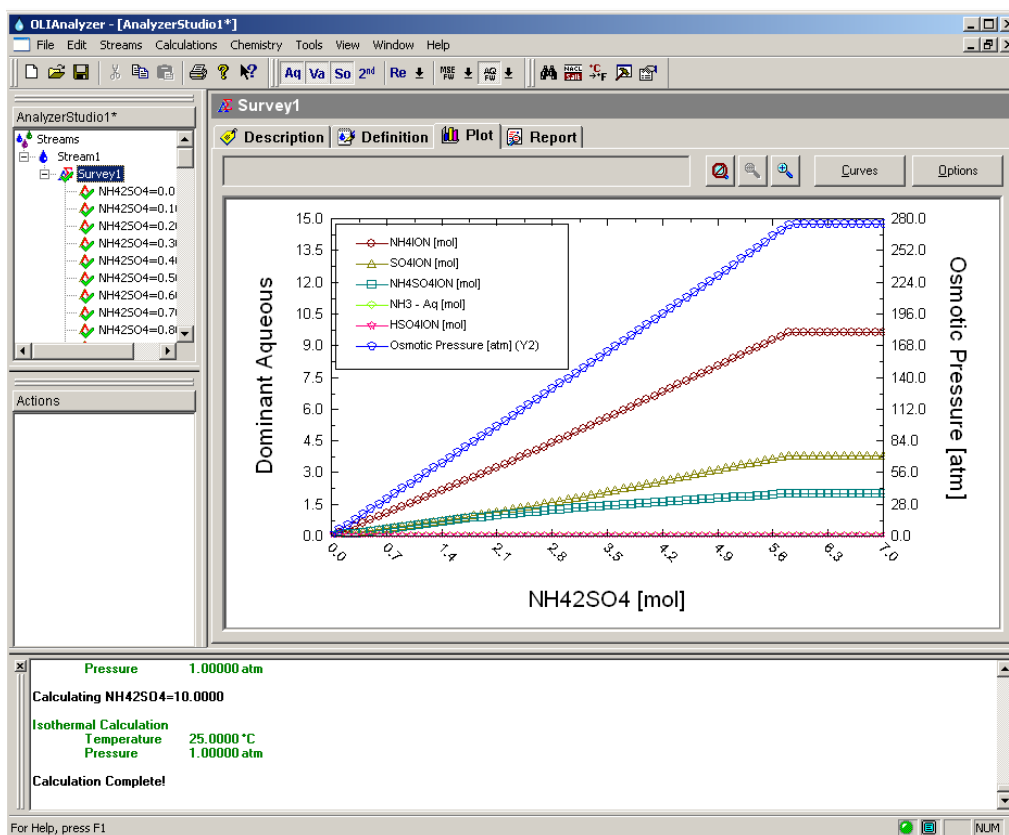


Figure 3.7: OLI Stream Analyser 3.2, a thermodynamic modelling software (OLI Systems Inc., Morris Plains, NJ, US)

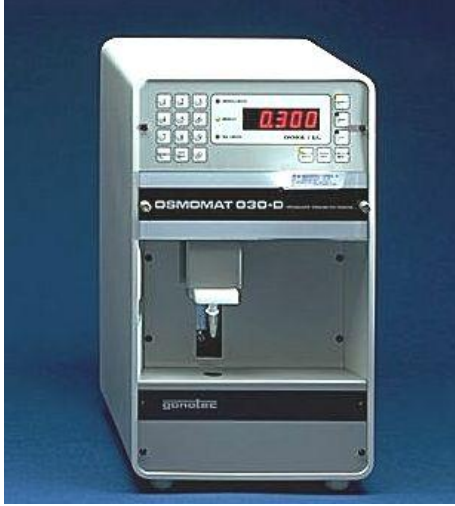


Figure 3.8: Osmometer used for measuring the osmolality of the solution cryoscopic osmometer (OSMOMAT 030-D, Genotek, Germany)

3.4.2 Calculation of performance ratio of the water flux in the FO process

The standard water flux in the FO process is represented by the following equations.

$$J_w = A[\pi_{D,b} - \pi_{F,b}] \quad (3.4)$$

where A is the pure water permeability coefficient of the membrane, $\pi_{D,b}$ and $\pi_{F,b}$ are the bulk osmotic pressures of the DS and FS respectively. It has been observed in all the FO studies that the experimental water flux is significantly lower than the water flux predicted using the above equations, indicating that the bulk osmotic pressure in the equation is not fully available for generating water flux during the FO process. Although a more complex model has been developed to account for concentration polarisation effects in the flux model, a more convenient method called performance ratio (PR) has been used to measure the performance of the FO process. PR is calculated as a percentage of actual or experimental water flux (J_w) to theoretical water flux (J_t), as shown below:

$$PR (\%) = \frac{J_w}{J_t} \times 100 \quad (3.5)$$

J_t is calculated using Eq. (3.4). The osmotic pressure of the DS and FS can be calculated using an OLI Stream Analyser or other standard osmotic pressure formula. PR is particularly useful for studies on the comparative performances of the different types of

DS. PR indicates the bulk osmotic pressure available for the effective generation of water flux across the membrane (McCutcheon et al., 2006).

3.4.3 Measurement of the reverse diffusion of draw solutes

The polymeric membrane is not an ideal membrane because it cannot completely reject the solutes, and solute transfer can therefore occur on both sides of the membrane (Hancock and Cath, 2009; Phillip et al., 2010; Hancock et al., 2011). The performance of the FO process was also measured in terms of reverse solute flux and forward salt rejection. The term ‘RSF’ has been commonly adopted because the diffusion of draw solutes occurs in reverse direction to the water flux. Assessing the RSF in the FO process is important because it not only indicates the loss of draw solutes and increases replenishment costs but, it may also complicate the management of feed concentrate (Hancock and Cath, 2009). The solute flux of an individual solute (J_s) through any semipermeable membrane is governed by concentration gradients between the two solutions and is commonly described using Fick’s law (Mallevialle et al., 1996).

Our initial investigation indicated that the reverse solute concentration at the feed side was significantly lower than the draw solution concentration used initially. For the dilute solution, the molar concentrations indicated a very good correlation with the electrical conductivity (EC) for all the selected draw solutions, and RSF was therefore monitored using EC as an indicator. When a single fertiliser compound was used, the RSF was monitored by recording the EC of the DI feed online using a multimeter (CP-500L, ISTEK) with separate probes attached and connected to a computer for data logging. When a BW or BGW was used as the FS, or blended salts were used as the DS, the RSF was measured by collecting and analysing the feed water samples at the end of each experiment. Samples were analysed using inductively coupled plasma–mass spectrometry or ICP-MS (Perkin Elmer Elan DRC-e at Southern Cross University, Australia).

The reverse diffusion of draw solutes towards the feed is measured in terms of reverse solute flux (RSF) and specific reverse solute flux (SRSF). The RSF J_s (in $\text{mmol.m}^{-2}.\text{h}^{-1}$) was measured using the following relationship:

$$J_s = \frac{(2.0 - \Delta V) \times C_s \times 1000}{M_w (\text{mol/kg}) \times \text{membrane area} (\text{m}^2) \times \text{time} (\text{h})} \quad (3.6)$$

where ΔV is the total volume of water that enters the DS from the FS during a certain operation time (h) of the FO process and C_s is the concentration of the draw solutes in the FS in the feed tank at the end of the experiment. The RSF in Eq. (3.6) is therefore a measure of the rate of draw solute lost through reverse diffusion or permeation per unit area of membrane per unit time. However, the absolute value of RSF is less significant as it has no relationship with the amount of water transferred across the membrane during the FO process. A term-specific reverse solute flux (SRSF), a ratio of water RSF to water flux has been proposed which indicates the amount of draw solutes lost by reverse diffusion per unit volume of water extracted from the FS (Hancock and Cath, 2009; Phillip et al., 2010) as follows:

$$SRSF = \frac{J_s (\text{gm}^{-2}\text{h}^{-1})}{J_w (\text{Lm}^{-2}\text{h}^{-1})} \quad (3.7)$$

While J_s is obtained from Eq. (3.6), J_w is obtained from Eq. (3.2).

When DI water was used as the FS, the RSF and SRSF was determined with the help of electrical conductivity using a standard curve of DS concentration versus electrical conductivity. However, when the FS consisted of BW or BGW, the draw solute concentration in the FS was measured using ICP-MS (Perkin Elmer Elan DRC-e).

3.4.4 Measurement of salt rejection of the FO process

In the FO experiments, the forward rejections of the feed solutes were measured by taking the DS sample at the end of each experiment and analysing it using ICP-MS (Perkin Elmer Elan DRC-e). Analysing the sample was a challenge, especially when high DS concentrations were used during the experiments because the concentration of feed solutes were significantly lower in comparison with the DS. Each sample was analysed using several dilution factors and the results were selected once the mass balance was satisfied.

CHAPTER 4



University of Technology Sydney

Faculty of Engineering & Information Technology

THE NOVEL FERTILISER DRAWN FORWARD OSMOSIS DESALINATION: CONCEPT AND ITS APPLICATION IN THE MURRAY-DARLING BASIN

4.1 Introduction

The performance of reverse osmosis (RO) desalination technologies using state of the art RO technology has improved manyfold in terms of energy consumption in the last decade or so, but it nevertheless remains energy intensive in nature (McGinnis and Elimelech, 2007; Greenlee et al., 2009). The law of thermodynamics sets a minimum limit on the work energy required to desalinate water which is equal to 0.75 kWh/m³ of desalted water at zero recovery and 1.06 kWh/m³ at 50% recovery for seawater (Semiat, 2008). Practically, however, the most efficient RO desalination plant with an energy recovery system has been reported to consume about 2.1 - 3.2 kWh/m³. The unit energy consumption for RO desalination increases with recovery rates (Elimelech and Phillip, 2011; Subramani et al., 2011). Fouling still proves to be a major challenge for membrane application (Greenlee et al., 2009; Phuntsho et al., 2011a) and any attempt to further reduce energy for desalination also proportionately increases the capital, total energy requirements and operational costs of the plant (Semiat, 2008). Since energy and climate change issues are inter-related (Semiat, 2008), addressing global water scarcity problems requires an extensive investment in research to identify robust and innovative methods of purifying water at lower energy consumption and cost (Shannon et al., 2008). Any low energy desalination technologies could have a significant impact for drought stricken countries such as Australia, where saline water is abundant in the form of seawater along coastal areas and brackish groundwater in inland areas.

This has led to renewed research interest in the forward osmosis (FO) process, which works on the principle of a natural osmotic process driven by the osmotic gradient between two solutions of different osmotic concentrations separated by a semi-permeable membrane. Until recently, FO technology suffered from major technological barriers, as a result of which its commercial application has been limited. The first such barrier was the lack of a membrane suitable for the FO process. As noted in Chapters 1 and 2, the existing pressure based salt rejecting membranes, such as RO or nanofiltration (NF) membranes, have limitations for the FO process due to their asymmetric design, that causes severe concentration effects, some of which are unique to the FO process. However, there have been several promising breakthroughs recently with the synthesis of thin film composite (TFC) FO membranes with higher water flux

and salt rejection than the existing lone FO membrane (Wang et al., 2010b; Yip et al., 2010; Wei et al., 2011b; Wang et al., 2012).

The second major technological challenge is in finding a suitable draw solute for universal application. An ideal draw solute should not only generate high osmotic pressure but, among other things, it should be able to easily separate, recover and regenerate so that the final product water is free from the draw solutes, and the recovered draw solute should be recycled again and again without deterioration. The separation and recycling of draw solutes are particularly important if the target of the FO desalination is to provide potable water. So far, only two candidates have been cited as potential draw solution (DS) candidates: a thermolyte solution containing carbonate compounds of ammonium (McCutcheon et al., 2005; McCutcheon et al., 2006; McGinnis and Elimelech, 2007; McGinnis et al., 2007) and magnetic nanoparticles (Ling et al., 2010; Ge et al., 2011; Ling and Chung, 2011a).

The separation and recovery of the DS require an additional processing unit, which consumes energy and therefore still remains a significant challenge for drinking water applications. The success of FO desalination for potable purposes will depend on how easily and efficiently the draw solute can be separated from the water (Phuntsho et al., 2011b). The limitations of this technology have been already discussed in Chapter 2.

The objective of this chapter is to describe in detail the concept of a fertiliser drawn forward osmosis (FDFO) desalination, where the diluted fertiliser DS after desalination can be directly used for fertilised irrigation or fertigation. The article begins with a brief explanation of the concept of FDFO desalination, followed by a discussion on the opportunities for applications within the context of MDB. This Chapter is an extension of the article published in the Reviews in Environmental Science and Bio/Technology (Phuntsho et al., 2012a)

4.2 The concept of the FDFO process for direct fertigation

Desalination using the natural osmotic process is a novel concept, although its application for potable water using seawater or brackish water still remains a significant challenge, as discussed earlier. The separation of diluted draw solutes from desalted water for recovery and regeneration is not an easy task, as it requires an additional

processing unit and therefore consumes extra energy. For FO desalination to be more competitive than conventional RO desalination processes for potable water production, it is essential that the post separation process for DS has low capital cost, low energy consumption, and very low operating cost. Finding an ideal DS to meet these requirements is still a big task; therefore, the commercial application of FO desalination for potable water still requires more research work.

The FO process is certainly an attractive option if the DS after dilution can be used directly as it is and does not require the separation and recovery of draw solutes. This is possible when a draw solute is used that adds value to the product water. In such cases, the diluted DS can be used directly, thereby avoiding the need for additional separation and recovery steps and making significant savings in energy costs for FO desalination technology (Hoover et al., 2011). One such case is desalinating or purifying water for emergency relief supplies during disasters, using nutrients such as concentrated sucrose (Kravath and Davis, 1975; Cath et al., 2006). The technology has also been used for emergency potable water supplies in situations where there is little available storage capacity, such as on lifeboats or small craft. Forward osmosis has also been investigated for other applications where the post-treatment for the separation and recovery of draw solutes is not necessary and especially where the potential exists for using a natural draw solute such as seawater or RO concentrate as the DS (Yangali-Quintanilla et al., 2011; Chung et al., 2012). The potential applications include concentration of industrial wastewater (Anderson, 1977), concentration of anaerobic digester concentrate (Holloway et al., 2007), sucrose concentration (Garcia-Castello et al., 2009), dewatering of press liquor derived from orange production (Garcia-Castello and McCutcheon, 2011), and drinking water augmentation with a hybrid FO system using impaired water (Cath et al., 2010; Yangali-Quintanilla et al., 2011).

Another promising area of application is desalination for irrigation using fertilisers as the DS (Moody, 1977). When fertilisers are used as the DS, the diluted DS after desalination can be directly used for fertigation, thereby avoiding the need for separation and recovery. Since fertilisers are extensively used in agricultural production, such a process would provide nutrient-rich water for direct fertigation from any saline water source.

The concept of using fertiliser as an osmotic extractor for agricultural water reclamation was first reported by Moody and Kessler (1976). Although the potential for such an application is immense, works on this particular concept did not receive attention until recently, mainly due to the lack of a suitable membrane for the FO process. Figure 4.1 provides the general process layout of the FDFO desalination for fertigation. In the FO process, two different solutions are used: saline water as the feed water on one side of the membrane, and highly concentrated fertiliser solution as the DS on the other side of the membrane. The two solutions are continuously kept in contact with the membrane through a modest crossflow system, to minimise the influence of concentration polarisation (CP) effects. Due to the osmotic gradient across the semi-permeable membrane, water flows from the feed solution with lower concentration towards the highly concentrated fertiliser DS, desalting the saline feed water in the process. After extracting the water by the FO process, the fertiliser DS becomes diluted, with the extent of dilution depending on the feed water salinity. The final fertiliser solution can be used directly for fertigation if it meets the water quality standards for irrigation in terms of salinity and fertiliser/nutrient concentration. If the final fertiliser concentration exceeds the nutrient limit, then further dilution may be necessary before it can be applied for fertigation.



Figure 4.1: The conceptual process layout diagram of fertiliser drawn forward osmosis desalination for direct fertigation

4.3 Advantages of FDFO desalination

4.3.1 Low energy and low cost desalination process

The FO process is solely based on the difference in concentration gradient between the two solutions, with no hydraulic pressure necessary for driving the water through the

membrane. The only energy required in the FO process is for maintaining a modest crossflow rate of the feed and DS in contact with the membrane surfaces and providing adequate shear force to minimise the CP effects that are intrinsic to any membrane filtration process. One of the potential candidates for use as a DS for potable water desalination by the FO process is a mixture of ammonia and carbon dioxide ($\text{NH}_3\text{-CO}_2$). A detailed analysis of the energy required for $\text{NH}_3\text{-CO}_2$ desalination by the FO process was reported by McGinnis and Elimelech (McGinnis and Elimelech, 2007) and this data has been used as a reference to compare the energy requirement for the FDFO desalination process.

Table 4.1 shows the comparative energy requirement for different desalination technologies (as available in the literature). Different figures have been reported on the total energy requirement for each desalination technology, and selected figures are shown in Table 4.1. It is clear from this table that the FO desalination process using $\text{NH}_3\text{-CO}_2$ as DS requires comparatively lower energy than any other existing desalination technology, even after considering the recovery process for the draw solutes from the diluted DS. The total energy required for $\text{NH}_3\text{-CO}_2$ has been estimated at 0.84 kWh/m^3 , which includes 0.5 kWh/m^3 of energy for $\text{NH}_3\text{-CO}_2$ recovery and 0.24 kWh/m^3 electrical energy for running the pumps (including the pumps for the distillation process). This total energy, when compared with other current desalination technologies on an equivalent work basis, can save between 72% and 85% of energy (McGinnis and Elimelech, 2007). Although the performance of $\text{NH}_3\text{-CO}_2$ as the DS could vary from the fertiliser DS, nevertheless the figures in Table 1 provide a fair indication that the energy required for FDFO will also be substantially lower given the fact that the recovery of draw solutes from the diluted DS is not necessary. The only energy required will be to keep the fluid in contact with the membrane, using pumps and the crossflow system, which has been estimated at about 0.24 kWh/m^3 . The energy required for FDFO desalination for direct fertigation will therefore be naturally lower than 0.24 kWh/m^3 which is in fact lower than the theoretical energy required, based on limiting energy in thermodynamics for separating salt and water from seawater. Energy consumption by the RO process increases with an increase in recovery rates, whereas in the FO process, recovery rates depend on the highest osmotic pressure a draw solute can generate in solution, and therefore has no significant relation to external energy input. More discussion on this can be found in Chapter 5.

Table 4.1: Comparison of energy requirements for seawater desalination with existing desalination technologies. Adapted from ^a(Semiati, 2008), ^b(McGinnis and Elimelech, 2007) and ^c(Elimelech and Phillip, 2011; Subramani et al., 2011). The figure for FO for direct fertigation has been adopted from McGinnis and Elimelech^b by removing the energy required for DS separation by the distillation process.

Desalination Technology	Total equivalent work energy (kWh/m ³)
Multi stage flash (MSF) distillation	10-58 ^a , 5.66 ^b
Multi effect distillation (MED)	6-58 ^a , 4.05 ^b
MED-low temp/electrical	5-6.5 ^a , 3.21 ^b
Reverse osmosis (RO)	4-6 ^b
RO with energy recovery	3-4 ^a , 3.02 ^b , 2.1-3.2 ^c
Ammonia-carbon dioxide FO desalination (low temp, 1.5 M feed) with draw solute recovery process.	0.84 ^b
FDFO desalination for direct fertigation without post separation and recovery process	<0.24

Existing desalination technologies are undoubtedly energy intensive in nature. This is the main reason why desalination is still limited to drinking water supplies and other commercial/industrial uses, rather than for irrigation purposes where the water requirement is comparatively large. However, if low energy desalination technologies are made available, it will have a significant impact on the agriculture sector, especially in those countries where drought is frequent but there is abundant saline water in the form of seawater in coastal areas and brackish groundwater in inland areas. Since FO desalination requires low energy, FDFO desalination technology has the potential to be applied to irrigation, where a large amount of water is required. Besides low energy consumption, the FO process has other merits in terms of lower capital costs from the lower pressure ratings of pumps, pipes and fittings compared to high-pressure, conventional RO desalination systems. Another advantage of this technology is that it could easily be powered by renewable energy, such as wind and solar energy, thereby giving this technology a zero carbon footprint. Renewable energy, especially solar energy, is abundant in most remote communities in Australia, and can therefore easily be tapped for such uses.

4.3.2 Direct use of FDFO product water for fertigation

Since freshwater sources are becoming scarcer every year, low energy desalination processes such as FDFO desalination technology could play a significant role in augmenting water for irrigation. Besides making irrigation water available at lower energy from saline water sources, FDFO desalination provides nutrient-rich water for

fertigation, creating opportunities for improving the efficiency of water use through greater innovation in water savings and irrigation infrastructures.

Fertigation is the application of irrigation water with fertilisers, either in dissolved solution or in suspended form. Fertigation has several advantages compared to the application of water and fertiliser separately, such as minimum loss due to leaching, optimisation of the nutrient balance by supplying the nutrients directly to the root zone, control of nutrient concentration in the soil solution, savings in labour and energy, and flexibility in the timing of fertiliser application relative to crop demand (Papadopoulos and Eliades, 1987). Such technology is also handy for those farms that have already adopted fertigation, because it can easily be integrated within their existing fertigation system.

Fertigation is more efficient and cost-effective for supplying water and nutrients to crops simultaneously than conventional broadcast application (Hanson et al., 2006). Fertigation can also be advantageous for application in mixtures with other micronutrients, chemical pesticides (as in chemigation), and/or fungicides (by fungigation), all in the correct or necessary proportions, thereby eliminating separate application modes for those chemicals (McBeath et al., 2007).

4.4 Potential application of FDFO desalination process in the context of the Murray-Darling Basin (MDB) in Australia

The FDFO desalination process has the potential for application in any part of the world where fresh water resources are unavailable for irrigation and where saline water is abundant. However, the discussion here is focussed on the application in the MDB in Australia, where the water debate has been in the public domain for some decades.

4.4.1 Water issues in the MDB and the proposed basin plan

As discussed in Chapter 2, the MDB is under enormous stress as a result of past water management decisions and a severe and prolonged drought, with these problems being compounded due to natural climate variability and climate change (MDBA, 2010b). The amount of surface water diverted for consumptive use has increased from 2,000 GL/y in 1920 to water entitlements of 11,000 GL/y in the 1990s (MDBA, 2010b). The combined

effect of drought and the over-allocation of water has significantly reduced river flows through the Murray mouth since 2002, seriously impacting the river ecosystem in the whole basin (MDBA, 2010b). Of the total 23 catchments within the basin, the health of the river ecosystem for 20 catchments is in a 'poor' to 'very poor' state. In the past decade, the basin has faced increasing water quality problems and frequent outbreaks of blue-green algae blooms (MDBA, 2010b). It is genuinely felt that there is an urgent need to lower the water allocation to maintain adequate environmental flow for a sustainable river ecosystem (MDBA, 2010b; Wentworth Group, 2010).

A guide to the proposed basin plan was released in Oct 2010 by the MDB authority (MDBA) (MDBA, 2010b) that proposed to make between 4,000 and 5,000 GL of water a year available for environmental flows. To achieve this target, a massive cut of 20% - 50% in water allocation through buybacks of the water allocation was initially proposed in the *Guide to the Basin Plan*, which led to strong protests from the farming community (MDBA, 2010b). The draft basin plan was released by the MDBA in May 2012 and proposed to return 2,750 GL of water to the rivers for environmental flows. This current draft plan has received criticism from both environmental scientists and the farming community. The scientists have alleged that the proposed water cut of 2,750 GL is inadequate for the full health of the river. Scientific studies have shown that the rivers must run at least two thirds full for the river system to be restored to full health, which means returning a minimum of 5000 GL of water to the environment. Farmers have voiced their concerns that such a massive cut could deprive farmers of their livelihood and would therefore have significant social and economic impacts. This draft plan has recently been revised after consultation with state environment ministers, and the current proposal as it stands is to vary the amount of water to be returned to the environment to between 2400 and 3200 GL.

The reduction in the existing water allocation is therefore imminent under the proposed basin plan, although there is still debate on the amount of water that needs to be returned to the environment to improve the ecological health of the river system. Nevertheless, the reduction will have a significant socio-economic impact in the basin since most of Australia's food and fibre comes from this basin. Alternative sources of water for agricultural irrigation are therefore essential to the continued production of

adequate food and fibre, not only for Australia but also for export to other nations that depend on foreign food imports.

4.4.2 Existing salt interception scheme

The MDB has a rich groundwater source, but this groundwater cannot be used directly for irrigation due to high salinity. The intrusion of brackish groundwater contributes to increased river salinity and is a major environmental issue facing the MDB (Ife and Skelt, 2004). The basin is a naturally saline environment as a result of the weathering of rocks and cyclic salts deposited over many years. The groundwater systems close to the Murray River hold more than 100,000 million tonnes of salt. Salinity in Australia has damaged natural resources and infrastructure, and is also impacting terrestrial biodiversity (Goss, 2003). The allocation of river water for extensive consumptive use has significantly reduced the river flow volume and exacerbated the river salinity problem.

Since 1988, the states of NSW, Vic and SA, together with the Australian Commonwealth, have funded and installed a number of salt interception schemes (SIS) to divert saline groundwater and drainage water before it enters rivers, thereby controlling increases in river water salinity. Currently, there are 18 SIS locations within the basin, as shown in Figure 4.2.

The SIS consists of large-scale groundwater pumping stations that intercept brackish groundwater flows and dispose of them at some distance from the river by using salt management basins, which basically consist of open evaporation ponds. The location of the wells or borefields is designed to create a zone of pressure in the aquifer which is equal to or slightly less than the pressure at the river, as shown in Figure 4.3. In this way, the groundwater flow is maintained towards the bore wells rather than towards the rivers, thereby causing the flattening or local reversal of the hydraulic gradient between the borefield and the river. The design is aimed to maximise the interception of brackish groundwater and prevent the salt getting into the river whilst continuing to minimise the induced flow from the river to the borefield. An efficient and effective scheme is one which minimises capital and operating (especially energy) costs whilst maximising the reduction in river salinity.

The intercepted saline groundwater is stored in evaporation and infiltration basins located further away from the rivers. A total of 17,358 mega litres of brackish groundwater was pumped out in 2010-2011 from the 18 SIS locations combined, preventing an estimated 324,162 tonnes of salt from reaching the Murray River, thereby significantly reducing salinity in the Murray River (MDBA, 2011b). Salt produced from the evaporation ponds has been commercialised by some companies. Figure 4.4 shows images of one of the SIS locations.

Although SIS has significantly helped to reduce river water salinity downstream of the MDB (Goss, 2003), the disposal and management of the intercepted saline groundwater is a major problem for these schemes. Records of the energy consumed in running the pumps at these SIS locations in 2010-2011 indicate that the average electrical energy required to pump brackish groundwater is about 0.3915 kWh/kL (MDBA, 2011b). Since the pumped-out groundwater is completely lost through evaporation, there is no other value to be gained from this brackish groundwater other than to prevent river salinity, although commercial salt harvesting is practised at certain locations. The groundwater is simply lost through evaporation and therefore does not lead to sustainable use of groundwater resources. The following section proposes the application of the FDFO desalination process to inland saline water resources for irrigation.

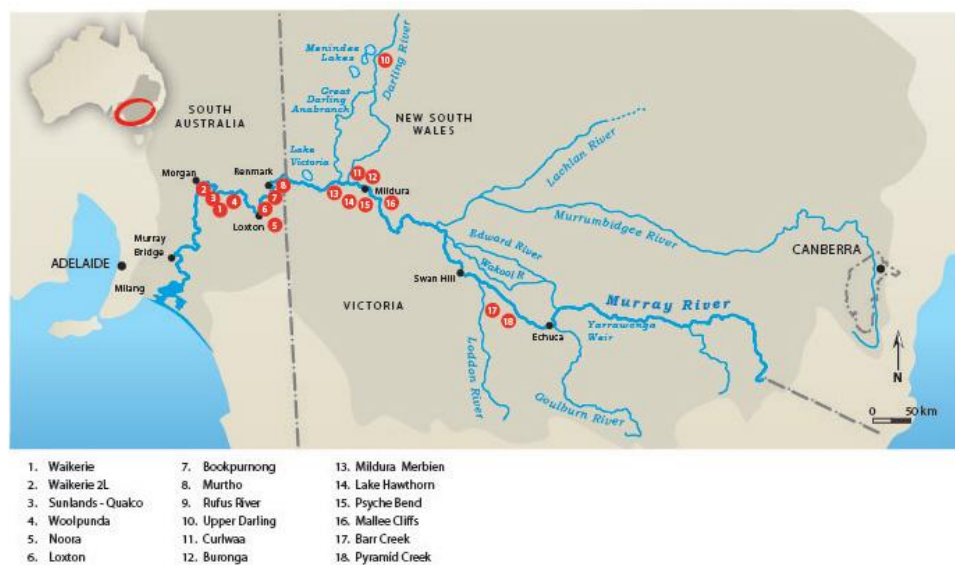


Figure 4.2: Locations of the salt interception schemes in the Murray-Darling Basin. (Source: (MDBA, 2010a))

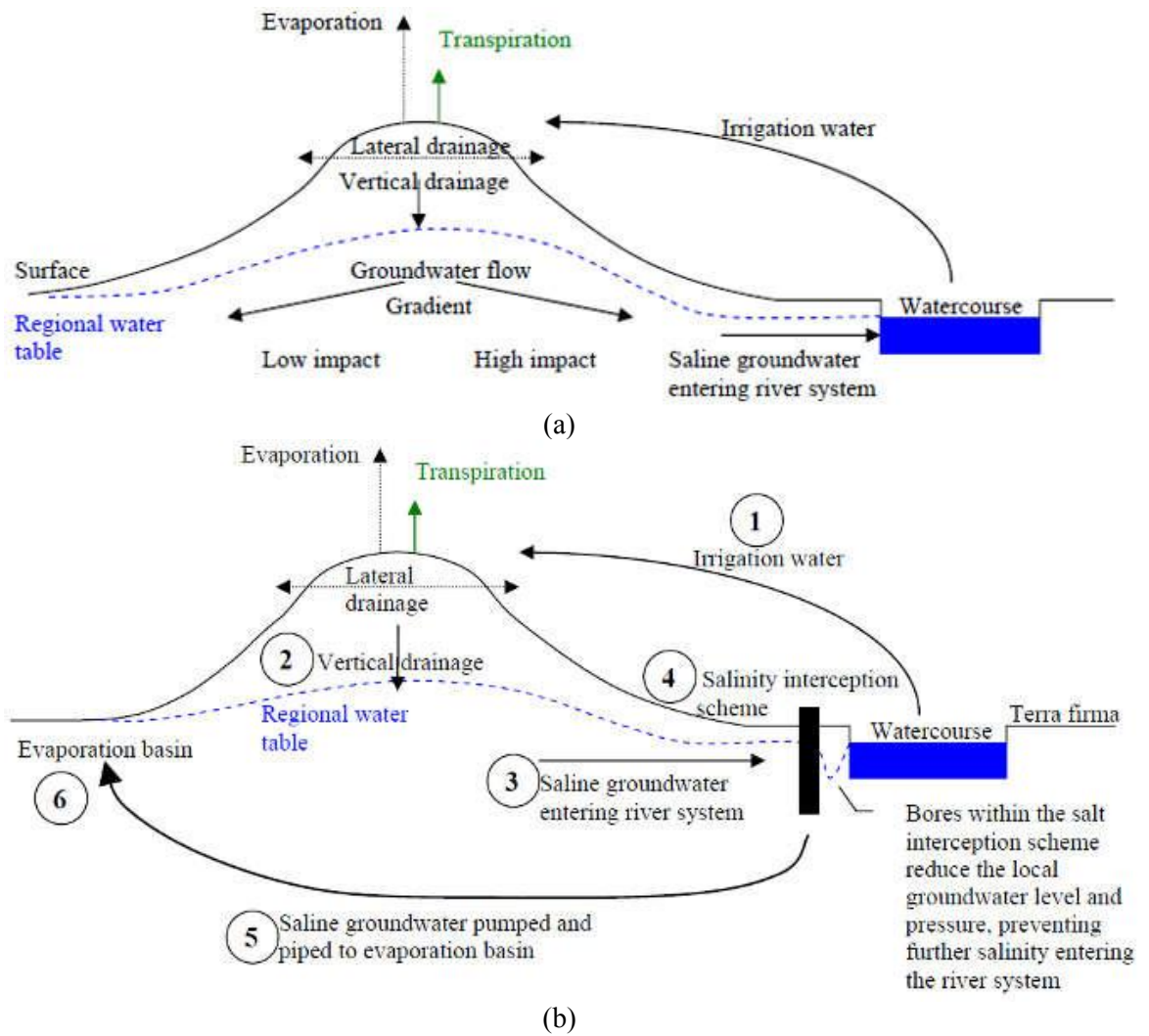


Figure 4.3: Design and operation of the salt interception scheme in the MDB (a) without SIS and (b) with SIS. (Source: MDBA).



(a)



(b)



(c)



(d)

Figure 4.4: Images of the salt interception scheme at Buronga in NSW: a) SIS borewell sites, (b) water outfalls, (c) evaporation ponds, and (d) salt harvesting

4.4.3 Alternative SIS using FDFO desalination process

A sustainable SIS in the MDB is therefore required that not only serves to prevent salts from reaching the river but also promotes the sustainable use of brackish groundwater. One way of achieving this is to use this brackish groundwater as an alternative source to river water for irrigation. The use of groundwater will reduce the pressure on the river water and make more water available for environmental flows in the river system. However, direct irrigation using groundwater is impractical due to the high salinity content, the salinity in some places being as high as seawater. This high salinity content in the water can have a deleterious effect on the productivity of agricultural crops (Cheeseman, 1988), and brackish groundwater therefore has to be desalted first, to make it fit for irrigation.

Desalination technologies are energy intensive, thus technology such as low energy FDFO desalination could play a significant role in providing a sustainable SIS in the MDB. Desalination by FDFO can be integrated with the current SIS and can make

sustainable use of brackish groundwater for irrigation. Figure 4.5 shows the proposed application of FDFO desalination at the current SIS locations. Although FDFO desalination can be applied to other areas, there are specific reasons why this particular case has merit. Due to process limitations, FDFO desalination alone is not likely to produce water of suitable quality for irrigation without requiring additional water to dilute the fertiliser concentration before application. This limitation is extensively discussed in Chapter 5. Therefore, FDFO desalination at this stage can be used as an option to augment the reduced water allocation resulting from the buybacks to maintain adequate environmental flows, as proposed in the current *Murray Darling Basin Plan* (MDBA, 2011c). Moreover, this technology is suitable for use during drought seasons when the available water for consumption is low. The existing water can be combined with the FDFO product water for fertigation, especially if the FDFO product water requires further dilution to make fertiliser concentration acceptable for irrigation. Such approaches offer multiple advantages, including: making water available for irrigation; the sustainable use of groundwater; and reducing dependence on river water for irrigation, thereby making adequate water available in the river for environmental flows and a healthy river ecosystem, while still serving the original purpose of salt interception. While the above potential application is specific to MDB, FDFO can also be applied to other areas and other countries where saline water is plentiful and where the existing fresh water source is inadequate for irrigation.

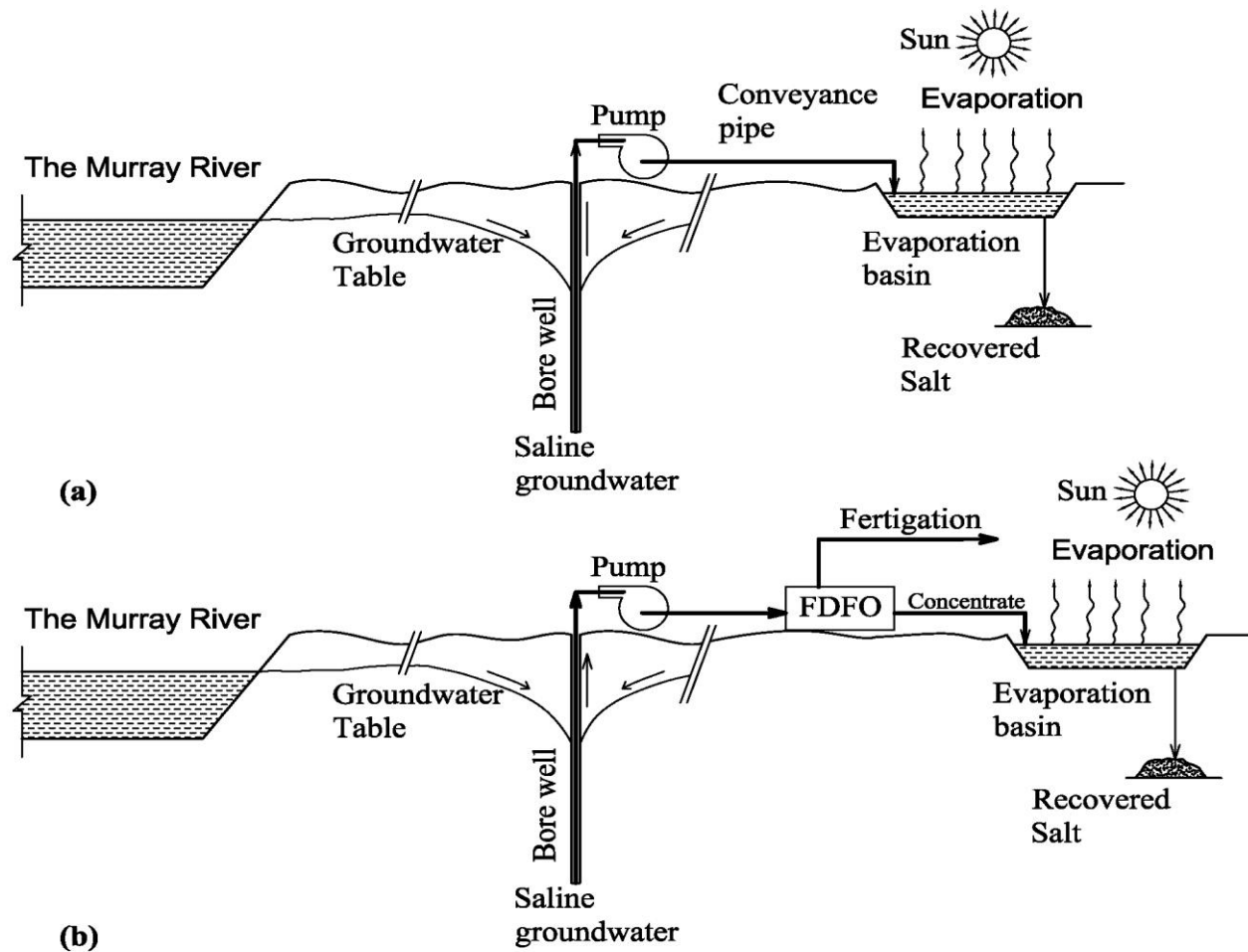


Figure 4.5: Cross sectional view of the (a) existing salt interception scheme (SIS) (18 in total) installed along the Murray and Darling Rivers and (b) the alternative SIS scheme which integrates FDFO desalination for the sustainable use of brackish groundwater for irrigation.

4.5 Concluding Remarks

The discussion in this chapter has noted that the application of FO desalination for potable water still suffers from the lack of an ideal draw solute. Since the water quality standard for drinking water is high, finding ideal draw solutes that can be easily separated from water and regenerated for reuse using minimum energy is yet to be achieved. This is the main reason why FDFO desalination offers novelty in applications where the complete separation and recovery of draw solutes are not necessary but can be used directly as it adds value to the end use for fertigation. The concept of FDFO desalination has been explained and the advantages of reduced energy requirement compared to conventional desalination processes have been discussed. When fertilisers are used as the draw solutes in the FDFO desalination process, the diluted fertiliser solution after desalination can be directly applied for fertigation, thereby avoiding the need for the separation and recovery of the DS. The energy required for fertiliser driven FO desalination is expected to be comparatively lower than current state of the art RO desalination technologies. Since FDFO is a low energy process, this particular technology can also be easily powered by renewable energy, such as solar and wind energy, which exists in abundance in many arid countries, including Australia. Since fertilisers are extensively used for agricultural production, FDFO desalination does not create additional environmental issues related to fertiliser usage. In fact, FDFO desalination could add more value to irrigation water, providing greater opportunities for improving the efficiencies of water and fertiliser use.

Fertiliser drawn forward osmosis desalination technology can be applied in any area of the world, but due to its process limitations in its current form, its potential application was discussed only in the context of the water issues in the Murray Darling Basin in Australia. The draft basin plan proposes to cut water allocations for consumptive use by 2,750 GL per year and under such circumstances, FDFO desalination technology is a suitable option for augmenting irrigation water by using brackish groundwater. FDFO desalination can easily be integrated with existing salt interception schemes where brackish water is currently pumped out every day and simply allowed to evaporate, losing precious water.

CHAPTER 5



University of Technology Sydney

Faculty of Engineering & Information Technology

SCREENING OF FERTILISERDRAWSOLUTES AND ESTIMATING WATER EXTRACTION CAPACITIES

5.1 Introduction

Different types of fertilisers are used for agricultural production, and it is therefore important to understand which types of fertilisers are more useful for fertiliser drawn forward osmosis (FDFO) desalination. It is therefore important to screen and assess suitable fertiliser candidates for use as draw solutes in the FDFO desalination process. Before the preliminary assessments are conducted, this chapter introduces some of the theoretical considerations and simple models used for the calculations of parameters such as the volume of water a unit mass of fertiliser can extract from a saline water source, and the water quality in the form of nutrient concentrations that can be achieved by the FDFO process in the final product water.

Understanding the volume of water a unit mass (in kg) of fertiliser can extract from a feed water of particular salinity is essential in understanding the final nutrient concentration; a particular type of fertiliser draw solution (DS) can result in the final FDFO product water using feed water of a certain salinity. The water extraction capacity of the fertiliser is also essential from the point of view of farming economics, because fertiliser that can extract a large volume of water is naturally desirable so that the cost of desalinated water remains lower.

The objective of this chapter is therefore to assess the volume of water that each fertiliser can extract from feed water of different salinity, and the final nutrient concentrations (N/P/K in g/L) that each fertiliser can achieve when used as the DS for the FDFO desalination. Assessment was conducted for eleven selected fertilisers and estimation was also made on the amount of additional potable water required for further dilution to meet the water quality standard for direct fertigation.

5.2 Fertiliser candidates for draw solutes

5.2.1 Screening of fertilisers as draw solutes

The choice of fertiliser DS for FDFO desalination for fertigation will be guided by many factors, including fertiliser economics and the performance of a particular fertiliser as the draw solute for the FDFO process. Fertiliser economics relate to the availability and cost of fertilisers. Each fertiliser must also have suitable physicochemical properties for use as a draw solute in the FO process, such as

solubility, pH compatibility with the FO membrane used, types of species formed in the solution, and water extraction capacity, which depends on the molecular weight and osmotic pressure of the fertiliser DS. The final selection will also be guided by the nutrient requirements for the particular target crop (Moody and Kessler, 1976). The existing commercial CTA FO membrane has a limited pH range between 4.0 and 8.0, while the recently reported thin-film composite membrane has been reported to have a significantly higher pH range (Yip et al., 2010; Wang et al., 2012).

A comprehensive list of chemical fertilisers (synthetic and mineral) used for agriculture in many parts of the world is provided in Chapter 2. However, only those fertilisers commonly used in Australia were considered for assessment as draw solutes for the FDFO desalination process. Australia uses between five and six million tonnes of fertiliser each year, which includes around one million tonnes of nitrogen (N), half a million tonnes of phosphorus (P) and two hundred thousand tonnes of potassium (K) (FIFA, 2009). The most-used single nutrient fertilisers in Australia are single super phosphate and urea, followed by monoammonium phosphate (MAP) or $\text{NH}_4\text{H}_2\text{PO}_4$, diammonium phosphate (DAP) or $(\text{NH}_4)_2\text{HPO}_4$ and others, as shown in Table 5.1.

Before running bench scale experiments, an initial screening of fertiliser for the DS is conducted to determine basic properties, such as water solubility, pH, speciation and osmotic pressure. OLI Stream Analyser software was found to be useful for this purpose. It is important to ensure that the DS is usable within the tolerable pH range for the membrane used in the FO process. Regardless of the final application, any draw solute should ideally be inert, neutral or near neutral pH and non-toxic (Miller and Evans, 2006). It should also have high osmotic potential, much higher than the osmotic potential of the target saline water. For example, seawater has an osmotic pressure of 26 atm, while the osmotic pressure for brackish water is usually lower depending on the salinity of the water. The DS should not react chemically with the feed solutes to form undesirable products that could hamper either the osmotic process or the ultimate use of the product water. Consideration was given to the fact that the current commercial CTA FO membrane has a pH range between pH 4.0 and 8.0 (Vos et al., 1966; Baker, 2004). However, pH may not be a limiting factor in the future when a new generation of thin film composite FO membranes are made available (Wang et al., 2010b; Yip et al., 2010).

Based on the preliminary screening, eleven different fertilisers were selected for study (Table 5.1). They are the most commonly used fertilisers around the world as crop nutrients, and they are not perceived as causing any potential problems when used as the DS for FO desalination. The list contains both single/straight and double/complex fertilisers. Although complete fertilisers (Nitrogen Phosphorous Potassium or NPK) are also available commercially, they are usually mixed or blended fertilisers; their chemical compositions remain proprietary and they are therefore excluded in our assessment. The selected list does not include ammonia solution, ammonium carbamate and ammonium bicarbonate fertilisers because they have been widely used as the DS in other studies (McCutcheon et al., 2005; Cath et al., 2006; McCutcheon et al., 2006; McGinnis, 2009). Moreover, ammonia carbamate and ammonia bicarbonate solutions are volatile and therefore a potential problem when handling the DS. All the selected fertilisers had pH within the range (4.0 to 8.0) acceptable for use with the commercially available CTA FO membrane.

Table 5.1: List of selected fertilisers for FO DS testing with their physical and chemical properties. *pH values as measured at 2.0 M. Solubility and speciation data were adapted from OLI Stream Analyser speciation results. HS: Highly soluble

Name of fertilisers	Chemical formula	MW	pH* @ 2M	Max. Solubility
Urea	CO(NH ₂) ₂	60.05	7.00	19.65 M
Ammonium nitrate	NH ₄ NO ₃	80.04	4.87	H.S
Ammonium sulfate (SOA)	(NH ₄) ₂ SO ₄	132.1	5.46	5.7 M
Ammonium chloride	NH ₄ Cl	53.5	4.76	7.4 M
Calcium nitrate	Ca(NO ₃) ₂	164.1	4.68	7.9 M
Sodium nitrate	NaNO ₃	85.0	5.98	10.5 M
Mono-ammonium phosphate	NH ₄ H ₂ PO ₄	115.0	3.93	3.7 M
Diammonium hydrogen phosphate	(NH ₄) ₂ HPO ₄	132.1	8.00	6.5 M
Potassium dihydrogen phosphate	KH ₂ PO ₄	136.1		
Potassium nitrate	KNO ₃	101.1	5.99	3.3 M
Potassium chloride	KCl	74.6	6.80	4.6 M

5.2.2 Thermodynamic properties of the fertiliser draw solutions

Table 5.2 shows the types of species formed for each fertiliser and the osmotic pressure at 2.0 M solution based on the OLI Stream Analyser 3.2. The number of species formed refers to the colligative properties of the solution, which is important because they contribute directly to the osmotic pressure of the solution. In addition, the types of

species formed in the solution are important because they affect the performance of the FO process, especially in terms of mass transfer across the membrane.

Most of the selected fertilisers generate charged species, with the exception of NH_4NO_3 , NaNO_3 , KCl , KH_2PO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$ and urea where very small quantities of uncharged species are expected to be formed at higher concentrations. The osmotic pressure is a colligative property of the solution and therefore depends on the number of species formed and not on the type and nature of species. Figure 5.1 shows the osmotic pressure of eleven selected fertiliser solutions at different concentrations at 25 °C. $\text{Ca}(\text{NO}_3)_2$ generates the highest osmotic pressure of about 600 atm at its maximum solubility. This is because the $\text{Ca}(\text{NO}_3)_2$ in solution forms the highest number of species compared to other fertilisers in solution. When a comparison is made at equal molar concentrations (say at 2.0 M in Table 5.2), the next highest osmotic pressure observed is for DAP (95.0 atm), followed by SOA (92.1 atm). The lowest osmotic pressure is observed for urea (46.1 atm at 2.0 M); however, because of its very high solubility, it generates osmotic pressure in excess of 200 atm at concentrations higher than 10 M. These results indicate that all the selected fertilisers generate osmotic pressure that is much higher than seawater (~28 atm) or brackish water, indicating their suitability for use as an osmotic DS.

Table 5.2: List of chemical fertilisers screened for investigation as draw solutes for the FDFO desalination process

Fertilisers	MW	$\pi@2.0\text{M}$ (atm)	*Max π (atm)	Species formed in 2.0 M solution at 25 °C and 1.0 atm pressure.
Ca(NO ₃) ₂	164.1	108.5	601.0	NO ₃ ⁻ : 3.47 M, Ca ²⁺ : 1.47M, CaNO ₃ ⁻ : 0.53 M, total = 5.47 M
(NH ₄) ₂ HPO ₄	132.1	95.0	293.0	NH ₄ ⁺ : 3.94M, HPO ₄ (ion): 1.79M, P ₂ O ₇ (ion): 0.07M, H ₂ PO ₄ (ion): 0.02M, HP ₂ O ₇ (ion): 0.02M.
(NH ₄) ₂ SO ₄	132.1	92.1	274.8	NH ₄ ⁺ : 3.07M, SO ₄ ²⁻ : 1.07M, NH ₄ SO ₄ ⁻ : 0.93M
NH ₄ Cl	53.5	87.7	356.0	NH ₄ ⁺ : 2M Cl ⁻ : 2M
NH ₄ H ₂ PO ₄	115.0	86.3	181.3	NH ₄ ⁺ : 2.0M, H ₂ PO ₄ ⁻ : 1.76M, H ₂ P ₂ O ₇ (ion): 0.10M, H ₃ PO ₄ (aq): 0.02M, HP ₂ O ₇ (ion): 0.004M,
NaNO ₃	85.0	81.1	417.9	Na ⁺ : 1.92M, NO ₃ ⁻ : 1.92M, NaNO ₃ (aq 0.08M@2M)
KCl	74.6	80.1	226.5	K ⁺ : 1.99M, Cl ⁻ : 1.99M, KCl (aq.): 0.01M @2M,
NH ₄ NO ₃	80.04	64.9	3346.1	NH ₄ ⁺ : 0.85M, NO ₃ ⁻ : 0.85M, NH ₄ NO ₃ : aq 1.15M
KNO ₃	101.1	59.9	101.4	K ⁺ : 2.0M, NO ₃ ⁻ : 2.0M
**KH ₂ PO ₄	136.09	58.0	58.0	1.8 M K ⁺ , 1.735 M H ₂ PO ₄ (ion), 0.026 H ₂ P ₂ O ₇ (ion), H ₃ PO ₄ (aq 0.0064 M), HPO ₄ (ion)
Urea	60.06	46.1	338.4	Urea

*Osmotic pressure at maximum solubility. **Data refers to maximum solubility at 1.8 M concentration.

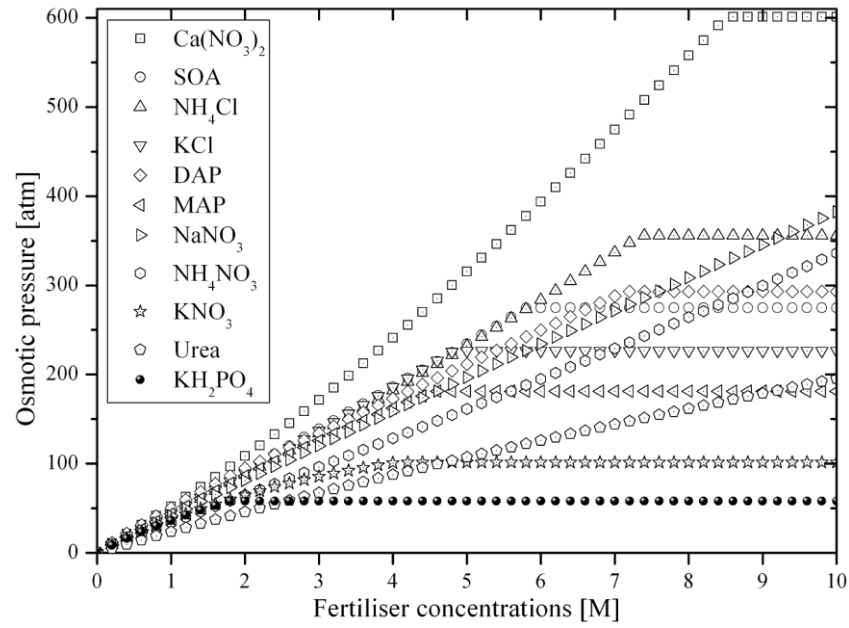


Figure 5.1: Variation of osmotic pressures of the 11 selected fertiliser DS at 25 °C analysed using OLI Stream Analyser 3.2

5.3 Water extraction capacity of selected fertilisers

5.3.1 Osmotic equilibrium in the forward osmosis process

Before calculating the expected nutrient concentrations in the final FDFO product water, it is important to understand the fundamentals of the FO process based on which the expected final nutrient concentrations are calculated. In the FO desalination process, water from the saline feed water moves towards the highly concentrated DS (when separated by a semipermeable membrane) as a result of the osmotic gradient. The standard water flux (J_w) in the FO process is given by the following equation.

$$J_w = A[\pi_{D,b} - \pi_{F,b}] \quad (5.1)$$

where A is the pure water permeability coefficient of the membrane, $\pi_{D,b}$ and $\pi_{F,b}$ are the bulk osmotic pressures of the DS and FS respectively. However, as discussed in Chapter 2, Eq. (5.1) is valid only when the solutions are very dilute. At higher DS and FS concentrations, concentration polarisation (CP) effects influence the water flux in the FO process. The presence of two independent solutions on each side of the membrane results in two different types of CP effects: concentrative CP on the membrane surface facing the FS and dilutive CP on the membrane surface facing the DS; the latter is unique to the FO process.

For a process operated in FO mode (FS facing the membrane active layer and DS facing the porous support layer), concentrative external CP (ECP) occurs on the membrane active layer facing the FS and dilutive internal CP (ICP) inside the membrane support layer facing the DS. The modified flux equation is shown below and takes into account ICP and ECP in the FO mode of operation (McCutcheon and Elimelech, 2007):

$$J_w = A[\pi_{D,m} - \pi_{F,m}] \quad (5.2)$$

$$J_w = A[\pi_{D,b} e^{(-J_w K)} - \pi_{F,b} e^{(J_w/k_F)}] \quad (5.3)$$

where $\pi_{D,m}$ and $\pi_{F,m}$ are the osmotic pressures of the DS and FS at the membrane surfaces respectively, k_F is the mass transfer coefficient of the feed and K the solute resistance to diffusion within the membrane support layer defined by:

$$K = \frac{t\tau}{D\varepsilon} \quad (5.4)$$

where D is the diffusion coefficient of the draw solute, t , τ and ε are the thickness, tortuosity and porosity of the support layer respectively.

Figure 5.2 shows the FO process operated with crossflows in two different directions. The FS and DS concentrations at their respective inlet points are represented by $C_{F,i}$ and $C_{D,i}$. As the solutions travel along the channel length, the water from the FS permeates through the semi-permeable membrane driven by the osmotic/concentration gradient between the two solutions. In this process, the concentration of the FS and DS gradually changes along the length of the channels. For example, the initial concentration of the FS ($C_{F,i}$) gradually increases along the length of the channel reaching maximum at the outlet point ($C_{F,o}$). By contrast, the initial concentration of the DS ($C_{D,i}$) gradually decreases because of the dilution from the incoming water from the feed side, reaching a minimum concentration ($C_{D,o}$) at the outlet ends. The variations of the solution concentrations are indicated by colour gradient, with dark blue indicating higher concentrations and light blue indicating lower concentrations.

To arrive at osmotic equilibrium, the following assumptions have been made:

- The membrane is perfectly semi-permeable allowing only water to pass through the membrane while completely rejecting the solutes
- There are no CP effects on either side of the membrane at osmotic equilibrium because of the zero flux
- The same solutes are used on both sides of the membrane. NaCl solutions have been used as solutes on both sides of the membrane to illustrate the osmotic equilibrium.
- The length and width of the membrane in consideration or the total membrane area is sufficient to achieve osmotic equilibrium within the given length of the membrane modules
- The concentration of DS existing at the end of the FO membrane module determines the extent of the osmotic process that has taken place within the membrane module

Consider 3.0 M NaCl ($\pi_{D,i} = 234$ atm) as DS and 0.6 M NaCl ($\pi_{F,i} = 27$ atm) as FS for the purpose of illustration. The assumption is that the FO process is operated at a feed recovery rate of 80%, which means that the final concentration of the FS will be 3.0 M NaCl from its initial 0.6 M concentration.

If the FO process is operated in the counter-current crossflow mode (Figure 5.2(a)), the initial DS concentration $C_{D,i}$ decreases from 234 atm to 27 atm ($C_{D,o}$), reaching osmotic equilibrium with the incoming FS at its outlet. On the other side of the membrane, the incoming FS from the opposite direction increases its initial concentration as it travels along the channel, reaching approximately 162 atm (assuming an 80% recovery rate). The variation in the bulk osmotic pressures of the DS and FS and the net bulk osmotic pressures along the length of the channel (described by arbitrary sections 0 to 10) are shown in Figure 5.2 (b) for the FO process operated in counter-current mode. This plot shows that initially the bulk osmotic gradient is about 207 atm and reaches zero at the end of the channel due to osmotic equilibrium.

The following inference can be drawn from Figure 5.1(a) and 5.1(b):

- The final FS concentration at the outlet ($C_{F,o}$) cannot exceed the initial DS concentration ($C_{D,i}$) at the inlet, i.e ($C_{F,o} \leq C_{D,i}$)

- The final DS concentration at the outlet ($C_{D,o}$) cannot be lower than the initial FS concentration ($C_{F,i}$) at the inlet, i.e ($C_{D,o} \geq C_{F,i}$)
- The movement of water from FS to DS will occur until the net osmotic pressure of the two solutions becomes zero ($\Delta\pi = 0$) and the osmotic pressure of the DS is equal to the osmotic pressure of the FS (osmotic equilibrium).
- Since the same solutes are used for both DS and FS, osmotic equilibrium occurs at similar concentrations, meaning that at osmotic equilibrium $C_{D,o} = C_{F,i}$ or $C_{D,o} - C_{F,i} = 0$.
- The highest FS concentration at the outlet ($C_{F,o}$) that can be achieved in the FO process using the counter-current mode is the maximum solubility of the feed solutes, and is never higher than the initial DS concentration ($C_{D,i}$). The recovery rate of the FS will therefore depend on the initial DS concentration ($C_{D,i}$) used.
- The net osmotic pressure remains almost constant along the channel length

The above inference indicates that the extent of the osmotic process will be limited to $C_{D,o} = C_{F,i}$ when the FO process is operated in counter-current mode.

A different inference can be made if the FO process is carried out in co-current mode, as shown in Figure 5.2(c) and 5.2(d). Since the FS flows in the same direction as the DS, the osmotic pressure of the FS increases along the length of the channel, reaching maximum at the exit point (161 atm at 80% recovery rate). Because of the increased osmotic pressure of the FS at the exit of the DS, it is not possible for the DS to dilute beyond the concentration of the FS. The concentration of the DS ($C_{D,o}$) at the exit in this case will be equal to but not less than 162 atm or ($C_{F,o} = 3.0$ M at 80% recovery rate) and it is impossible to achieve DS concentration lower than this. The plot of the variations in the bulk osmotic pressures in Figure 5.2(d) indicates that the initial net bulk osmotic pressure in the co-current mode of application is lower than in the counter-current mode; nevertheless, the final concentrations of the DS remain significantly higher than the initial concentration of the FS. Therefore, it is clear from the co-current mode of application that the final DS concentration ($C_{D,o}$) cannot be lower than the final FS ($C_{F,o}$) concentration, i.e $C_{D,o} = C_{F,o} \gg C_{F,i}$. If the FS is operated at high recovery rates, the final DS concentration will also be correspondingly high.

The results from Figure 5.2 indicate that crossflow directions play a significant role in determining the recovery rates of the FO process and the final concentration of the diluted DS from the FO desalination process. Details of recovery rates are discussed in Section 5.5.

The osmotic equilibrium can also be explained from Eq. (5.3). When the FO process occurs in counter-current mode, as discussed above, the following observations are made:




As $J_w \rightarrow 0$,

$$\pi_{D,m} \text{ or } \pi_{D,b} e^{(-J_w K)} \rightarrow \pi_{D,b} \text{ and } \pi_{F,m} \text{ or } \pi_{F,b} e^{(J_w / k_F)} \rightarrow \pi_{F,b}$$

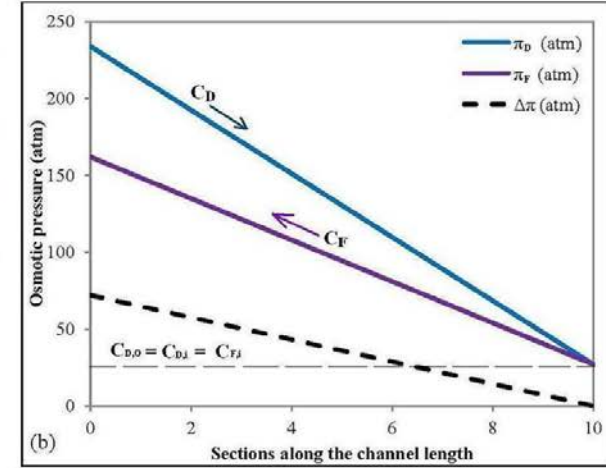
hence,


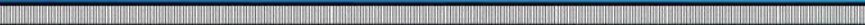

$$\left[\pi_{D,b} e^{(-J_w K)} - \pi_{F,b} e^{(J_w / k_F)} \right] \rightarrow \left[\pi_{D,b} - \pi_{F,b} \right] \quad (5.5)$$

The significance of this is that, as the water flux decreases due to continuous dilution of the DS, the degree of ICP and ECP effects in the FO process also becomes negligible indicating that, at very dilute DS concentrations, the water flux in the FO process can be shown by Eq. (5.1). This indicates that, at lower DS concentrations or lower net osmotic pressure, the water flux in the FO process given in Eq. (5.2) or Eq. (5.3) can be represented by Eq. (5.1). In other words, the net movement of water from the FS to the DS will occur until the bulk osmotic pressure of the DS reaches osmotic equilibrium with the bulk osmotic pressure of the initial FS when the FO process is operated in counter-current mode. This has been experimentally verified and is explained in the next paragraph. Eq. (5.5) cannot hold true if the FO process is operated in co-current mode, indicating that crossflow directions play a significant role in the FO process.

Channel length	0	1	2	3	4	5	6	7	8	9	10
π_D (atm)	234	213	193	172	151	131	110	89	68	48	27
DS→											$C_{D,o}$
Membrane											
←FS											$C_{F,i}$
π_F (atm)	162	149	135	122	108	95	81	68	54	41	27
$\Delta\pi$ (atm)	72	64.8	57.6	50.4	43.2	36	28.8	21.6	14.4	7.2	0

(a)



Channel length	0	1	2	3	4	5	6	7	8	9	10
π_D (atm)	234	227	220	212	205	198	191	184	176	169	162
DS→	 $C_{D,o}$										
Membrane											
FS→	 $C_{F,o}$										
π_F (atm)	27	41	54	68	81	95	108	122	135	149	162
$\Delta\pi$ (atm)	207	186.3	165.6	144.9	124.2	103.5	82.8	62.1	41.4	20.7	0

(c)

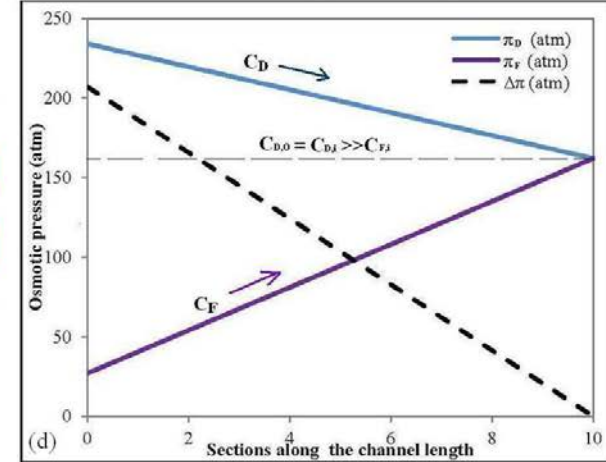


Figure 5.2: Model explaining the influence of crossflow directions on the solution concentrations and the osmotic pressure during the FO desalination process. $C_{F,i}$ and $C_{F,o}$ represent the FS concentrations at inlet and outlet points respectively, while $C_{D,i}$ and $C_{D,o}$ represent the DS concentrations at inlet and outlet points respectively.

To determine the DS concentrations (or the bulk osmotic pressure) at which the water flux reaches zero or near zero, experiments were conducted at different low DS concentrations using brackish water (BW) (5,000 mg/L NaCl) as feed. Two types of DS were selected for the experiments: KCl (containing only monovalent ions) and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (containing both mono and divalent ions). The water fluxes are plotted against the bulk osmotic pressure of the DS, as shown in Figure 5.3. From this figure, it is clear that, at low DS concentrations, the water flux in the FO process becomes zero when the bulk osmotic pressure of the DS reaches osmotic equilibrium with the bulk osmotic pressure of the BW feed (i.e. $\pi_{D,b} = \pi_{F,b} = 3.9 \text{ atm}$), irrespective of the type of draw solute used. This shows that as the DS becomes more and more diluted due to the influx of water from the feed water, the bulk osmotic pressure of the DS decreases, thereby reducing the net driving force and ultimately the water flux across the membrane. At low water flux, the CP effects are also comparatively low and if the process is allowed to continue, the osmotic process will persist until the bulk osmotic pressures of the DS and the FS become equal (osmotic equilibrium).

In reality, it may not be economically viable for the osmotic process to continue using a DS concentration below a certain level because the cost of energy for pumping the DS and FS will far outweigh the amount of water it can extract within a specific time. An optimum initial DS concentration could be determined based on the total membrane area in a single membrane module array and feed salinity concentrations.

Although it is possible to achieve osmotic equilibrium, the water flux will be very low at lower DS concentration, and it will be economically impractical to continue the process to the extent of osmotic equilibrium. An optimum DS concentration (lower limit) for the FO process is therefore necessary. From the above findings, it is clear that, it is theoretically not possible to achieve a diluted DS concentration that is lower than the FS concentration without external influence, and this is perhaps one of the major limitations of the FO process.

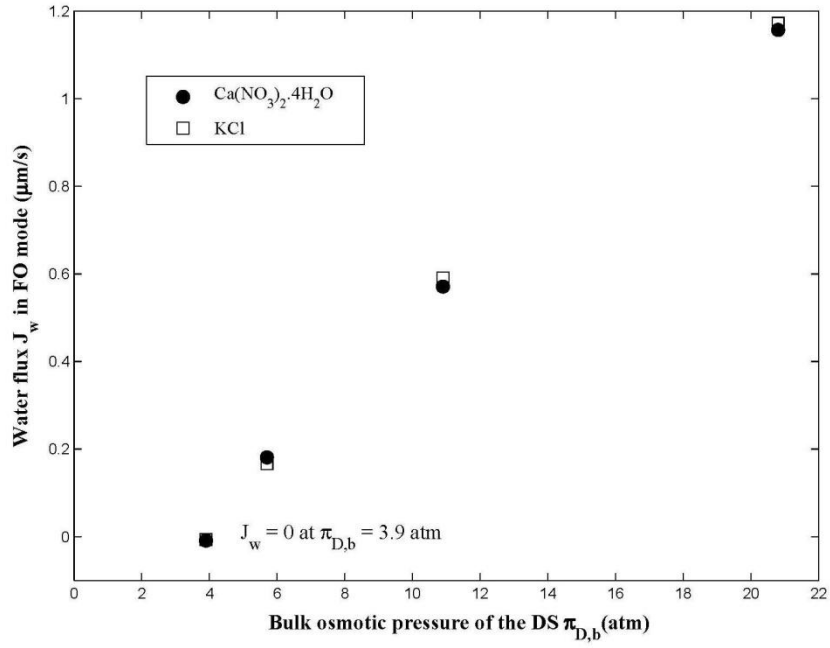


Figure 5.3: Variation of water flux in the FO process at low DS concentrations or bulk osmotic pressure. The water flux at $\pi_{D,b}=3.9$ atm was zero.

5.3.2 Water extraction capacities

Eq. (5.5) indicates that DS can extract water from the FS until the osmotic pressure of the DS reaches equilibrium with the osmotic pressure of the FS when the FO process is operated in counter-current crossflow directions. Consider 1.0 L of initial DS prepared using 1.0 kg of draw solute with molecular weight (MW). The initial DS concentration can be represented as follows:

$$C_{D,i} = \frac{1000}{MW} \quad (5.6)$$

Consider an FS with an initial concentration of $C_{F,i}$. Under the counter-current crossflow conditions in the FO process, the osmotic process will occur until the final DS concentration reaches osmotic equilibrium with the initial FS concentration as follows:

$$C_{D,0} = C_{F,i} \quad (5.7)$$

Based on the mass balance, the total volume of water (in L) that a kilogram of fertiliser can extract from saline water can be estimated from the following equation:

$$V = \left(\frac{1000}{MW C_{D,0}} \right) - 1 \quad (5.8)$$

$C_{D,0}$ is the molar concentration of the DS that generates equal bulk osmotic pressure (osmotic equilibrium condition) with the osmotic pressure of the FS with a concentration of $C_{F,i}$. Eq. (5.8) indicates the volume of water a kilogram of fertiliser as draw solute can extract depending on the MW of the draw solute used and the molar concentration of the DS at which it generates equal osmotic pressure with the FS.

It must be clarified here that $C_{D,0} = C_{F,i}$ is valid only when the same draw solutes are used for both the DS and FS. When different draw solutes are used, for example, NaCl salt for FS and an inorganic fertiliser salt for DS, $C_{D,0}$ and $C_{F,i}$ are not equal, although their osmotic pressures are equal. The $C_{D,0}$ will therefore vary depending on the types of draw solute used and the osmotic pressure of the FS.

The volume of water that a kilogram of fertiliser can extract, based on Eq. 5.8, is presented in Table 5.3 for the eleven selected fertilisers, using different types of feed sources. Fertilisers with a low molecular weight (MW) all contain a higher number of moles of draw solute per unit mass and therefore can generate higher osmotic pressure and extract more water. NH_4Cl , having the lowest molecular weight of all the selected fertilisers in this study, can extract the highest volume of water: 28–1090 L/kg from brackish water (BW) sources of different total dissolved solids (TDS). KCl extracts the next highest amount of water, between 20 and 780 L/kg, followed by NaNO_3 and NH_4NO_3 . Other fertilisers, such as KH_2PO_4 and $\text{Ca}(\text{NO}_3)_2$ with the largest MW amongst the selected fertilisers, extract the lowest volume of water per kg of fertiliser from any source.

Table 5.3: Final concentration of fertiliser DS at osmotic equilibrium with feed water after desalination. BW1, BW2, BW5, BW10, BW20 and BW35 all represent simulated brackish water with a TDS of 1000, 2000, 5000, 10,000 20,000 and 35,000 mg/L of NaCl respectively.

TDS (mg/L NaCl)	1,000	2,000	5,000	10,000	20,000	35,000						
Feed π (atm)	0.802	1.59	3.91	7.76	15.52	28.0						
Feed ID	BW1	BW2	BW5	BW10	BW20	BW35	BW1	BW2	BW5	BW10	BW20	BW35
Fertilisers	Equivalent concentrations of fertiliser DS (M)						Volume of water per kg of fertiliser (L/kg)					
NH ₄ Cl	0.0171	0.0344	0.0861	0.174	0.353	0.643	1089	542	216	107	52	28
KCl	0.0171	0.0344	0.0860	0.173	0.351	0.638	782	389	155	76	37	20
NH ₄ NO ₃	0.0177	0.0364	0.0955	0.202	0.431	0.820	704	342	130	61	28	14
NaNO ₃	0.0172	0.0345	0.0867	0.176	0.360	0.665	684	340	135	66	32	17
DAP	0.0123	0.0252	0.0649	0.134	0.279	0.526	614	299	116	56	26	13
SOA	0.0130	0.0272	0.0723	0.152	0.320	0.598	583	277	104	49	23	12
KNO ₃	0.0172	0.0347	0.0877	0.180	0.377	0.722	574	284	112	54	25	13
MAP	0.0172	0.0344	0.0859	0.173	0.350	0.636	506	252	100	49	24	13
Urea	0.0329	0.0653	0.1607	0.321	0.649	1.189	505	254	103	51	25	13
Ca(NO ₃) ₂	0.0125	0.0257	0.0668	0.139	0.292	0.530	488	236	90	43	20	10
KH ₂ PO ₄	0.0172	0.0348	0.0879	0.181	0.380	0.733	425	210	83	40	18	9

5.3.3 Expected nutrient concentrations in the final FDFO product water

The final nutrient concentration in FDFO is estimated based on the total volume of water extracted by a unit mass of fertiliser DS, as shown in Table 5.3. Eq. (5.1) indicates that the FO process will continue to occur until the osmotic pressure of the diluted DS reaches equilibrium with the FS, irrespective of which initial DS concentration is used. Based on this premise that osmotic equilibrium is attained when the diluted DS reaches its concentration equivalent to the osmotic pressure of the feed solution, the molar concentrations of each fertiliser DS can be determined based on the osmotic pressure of the particular feed solution. The feed waters of six different TDS are considered to assess the expected fertiliser nutrient concentrations in the final FDFO product water after desalination. The nutrient concentrations are assessed in terms of N/P/K and presented in Table 5.4.

It has been shown in Table 5.3 that, depending on the types of fertilisers used as DS, each fertiliser will reach osmotic equilibrium at different concentrations. At this diluted DS concentration, the nutrient concentration must meet the water quality standards for irrigation if the final product water from the FDFO desalination plant is to be used directly for fertigation. Therefore, it is important that the final FDFO product water meets the nutrient concentration, otherwise further dilution is required before applying for fertigation. A very high fertiliser nutrient concentration can be detrimental to plants because it increases salinity and toxicity.

Table 5.4 shows the nutrient (NPK) concentrations (in mg/L) in the final FDFO product water for each fertiliser DS using six different types of feed water. It is clear from the data that the nutrient concentrations in the final FDFO desalination depend on the types of fertilisers used and the TDS of the feed water used. When higher TDS water is used as feed, the nutrient concentrations in the final FDFO product water increase proportionately.

The lowest N concentration was observed for MAP, NaNO_3 , NH_4Cl and KNO_3 with 240 mg/L with feed TDS of 1,000 mg/L (BW1); however this increases to 480, 1200, 2400, 4900 and 8900 mg/L of N with BW2, BW5, BW10, BW20 and BW35 respectively. Urea will result in very high N concentration of 920 mg/L with BW1 in the final FDFO product water, and NH_4NO_3 will also result in N concentration of 490

mg/L with BW1 and much higher with higher TDS feed. These results indicate that when high N containing fertilisers such as urea and NH_4NO_3 are used as DS, the N concentration in the final FDFO product water will be significantly higher than in the other fertilisers containing low nitrogen. Another reason for high N concentration with urea is that although urea has high solubility, it generates one of the lowest osmotic pressures amongst all the fertilisers at equimolar concentration.

Diammonium phosphate, MAP and KH_2PO_4 will result in P concentrations of 381, 531 and 534 mg/L with BW1 feed and proportionately higher at higher TDS feed. All three potassium fertilisers result in K concentrations of about 670 mg/L using BW1 and proportionately higher at higher TDS feed.

Table 5.5 provides the highest recommended NPK nutrient concentrations for different types of plant crops. The required nutrient concentration for fertigation varies depending on many factors, such as types of crops to be irrigated, cropping seasons, soil nutrient conditions, etc. (Oliver and Barber, 1966). In general, the required NPK nutrient concentrations vary from 50 to 200 mg/L for N, 12 to 60 mg/L for P, and 15 to 250 mg/L for K, depending on the types of crops and growing seasons (Phocaides, 2007). Comparing the data in Table 5.4 and Table 5.5, it is clear that it will not be possible to achieve the required water quality standards by the FDFO desalination process, especially if the feed water salinity is higher than BGW1. The nutrient concentrations are significantly higher, especially for feed with higher TDS, indicating that a high dilution factor is needed to achieve recommended concentrations. This means that the additional dilution required is of several orders of magnitude before it can be used for direct fertigation. For example, if the target crop is a cucumber, it is necessary for the N/P/K nutrient concentration to be 200/50/200 mg/L. Only four fertilisers (MAP, NaNO_3 , NH_4Cl and KNO_3) achieve a close to acceptable N concentration for the cucumber with BW1, and any feed with TDS higher than 1,000 mg/L will require a substantial amount of dilution before the fertiliser solution can be used for fertigation. Using MAP, NaNO_3 , NH_4Cl and KNO_3 as the DS, for example, will require a dilution factor of more than 2 to make the N concentration acceptable for the cucumber at 200 mg/L using feed with TDS of 2,000 mg/L (BW2). The dilution factor increases to 6.05, 12.3, 25 and 46.5 for the DS for these same fertilisers when used with feed water of

BW5, BW10, BW20 and BW35 respectively. The dilution factor required with other fertilisers is even higher than KNO_3 .

The other issue to be noted with the results in Table 5.4 is that of the variable dilution required when fertilisers containing more than one nutrient are used as the DS. For example, MAP requires a dilution factor of 2.5 for N concentration, while the dilution factor for P is 10. Similar issues exist with other fertilisers such as DAP, KNO_3 and KH_2PO_4 . These issues can, however, be solved by using blended or mixed fertilisers as DS. Details on the blended fertiliser DS has been covered separately in Chapter 9.

Table 5.4: Estimated nutrient concentrations (in mg/L) in the final FDFO desalination product water evaluated in terms of the three major nutrients.

	BW1	BW2	BW5	BW10	BW20	BW35
DS	N/P/K (mg/L)	N/P/K (mg/L)	N/P/K (mg/L)	N/P/K (mg/L)	N/P/K (mg/L)	N/P/K (mg/L)
MAP	240/531/0	482/1,066/0	1,200/2,660/0	2,420/5,360/0	4,900/10,800/0	8,900/19,700/0
NaNO ₃	240/0/0	483/0/0	1,210	2,460/0/0	5,000	9,300
NH ₄ Cl	240/0/0	482/0/0	1,210	2,430/0/0	4,900	9,000
KNO ₃	241/0/673	486/0/1,356	1,230/0/3,430	2,52/0/7,04	5,300/0/14,700	10,100/0/28,200
DAP	345/381/0	706/781/0	1,820/2,010/0	3,75/4,15/0	7,800/8,600/0	14,700/16,300/0
Ca(NO ₃) ₂	349/0/0	720/0/0	1,870	3,89/0/0	8,200	14,800
SOA	363/0/0	761/0/0	2,020	4,27/0/0	9,000	16,700
NH ₄ NO ₃	496/0/0	1,020/0/0	2,670	5,66/0/0	12,100	23,000
Urea	921/0/0	1,829/0/0	4,500	8,99/0/0	18,200	33,300
KCl	0/0/670	0/0/1,345	0/0/3,360	0/0/6,78/	0/0/13,700	0/0/24,900
KH ₂ PO ₄	0/534/674	0/1,077/1,359	0/2,720/3,440	0/5,60/7,07	0/11,800/14,800	0/22,700/28,700

Table 5.5: Recommended maximum nutrient concentrations (in ppm) in the fertigation water for various types of crops. (Source: (Phocaides, 2007)).

Types of crops	N	P	K
Citrus	50	12	15
Bananas	50	15	40
Tomatoes	180	50	250
Cucumbers	200	50	200
Bell peppers	170	60	200
Cabbages	100	60	200
Onion	100	50	150
Squashes	200	50	200
Potatoes	150	50	180
Groundnuts	120	50	200
Watermelons	150	50	150

5.4 Options for lowering nutrient concentrations in the final FDFO product water

It was observed in Section 5.3 that the final FDFO product water contains a nutrient concentration much in excess of the recommended nutrient concentration for the direct fertigation of crops. If the nutrient concentration does not meet the fertigation standard, the DS must be further diluted to make the desalted water fit for fertigation. The nutrient concentration in the final fertiliser DS also depends on the type of fertiliser used as the DS and the salinity of the feed water. Based on the results in Table 5.4, it is apparent that achieving nutrient concentration for direct fertigation will be a significant challenge in the FDFO desalination process, especially with high salinity water such as seawater. Achieving acceptable nutrient concentration therefore forms the major task of this study. Dilution is one easy way to make the nutrient concentration acceptable for fertigation; however, it is clear from Table 5.4 that the dilution factor is very high. When the dilution factor is too high, FDFO desalination can serve only as an alternative source of water to augment fresh water resources and not as a main source of water for irrigation. This option is not acceptable if the site has no access to any sort of potable water for irrigation. Since maintaining the required nutrient concentration is essential for fertigation, several techniques to lower the nutrient concentrations in the final FDFO product water were evaluated in this study. The efforts of most of the succeeding

chapters therefore focus on investigating the performance of these options in achieving acceptable nutrient concentrations.

One option, covered in Chapter 9, was to use a DS prepared by blending different types of fertilisers so that the final FDFO product water contained all the essential nutrients, thereby decreasing the concentration of one particular nutrient. Using blended fertiliser as a DS was observed to significantly reduce the concentration of particular nutrients in the final FDFO product water compared to using single fertilisers as the DS.

Another option evaluated in this study is the integration of an additional process that helps to reduce the nutrient concentrations in the final FDFO product water, but such an additional process must have a low energy consumption so that the total energy cost of the irrigation water remains comparatively lower than conventional desalination processes, making the desalination more competitive and feasible for irrigation purposes. One proposal is to integrate nanofiltration (NF) as an additional process with the FDFO desalination process, since NF requires much less energy than the RO process. A recent study has reported that an integrated FO/RO desalination process is much more energy efficient than RO alone for drinking water and, integrated FO-NF is therefore certainly expected to have a comparatively lower energy requirement (Shaffer et al., 2012). Chapter 11 of the thesis is entirely focussed on the performance of the integrated FDFO-NF desalination process, in which NF was evaluated as either a pre-treatment option or a post-treatment option.

Although not included in this study, other options include integrating the FDFO desalination process with wastewater treatment, in which case wastewater effluent is used as an additional impaired water source for indirect dilution (Cath et al., 2009; Cath et al., 2010). This option is useful only when wastewater effluent is plentiful. The fouling issue of the FO process using wastewater effluent will be much less significant than the pressure based RO process.

5.5 Theoretical recovery rates in the FDFO process

The unit energy consumption for RO desalination increases with recovery rates (Elimelech and Phillip, 2011; Subramani et al., 2011) and for practical purposes, RO desalination plants are usually operated between 50-75% recovery for seawater (Semiat,

2008) and more using brackish water. However, depending on the osmotic pressure of the initial concentrated DS, it is possible to achieve high feed water recovery rates (McCutcheon et al., 2005; Martinetti et al., 2009) without requiring significant additional energy. Only a slight increase in energy consumption is expected due to the increase in viscosity of the DS when used at higher concentrations. Unlike the RO process, recovery rates in the FO process depend on the highest osmotic pressure that a draw solute can generate in solution, and therefore they have no significant relation to the external energy input.

The maximum possible theoretical recovery rates of each fertiliser DS using saline water of different TDS are estimated and presented in Table 5.6. The estimations were made based on the maximum osmotic pressure that a particular fertiliser can generate in solution, which was in turn based on its maximum solubility, as shown in Figure 5.1. The following assumptions were made for the estimation of the recovery rates of each fertiliser in the FO desalination process:

- The highest recovery rate is the rate at which the feed is concentrated to its maximum solubility. In this particular study, the solubility of NaCl salt (6.15 M with osmotic pressure of 404 atm) at 25 °C has been used, since the majority of salt in brackish water or seawater is composed of NaCl.
- The highest theoretical solubility of each fertiliser has been considered as the initial DS concentration.
- The FO process is operated in counter-current mode according to the assumptions made in Section 5.3.1 in which the movement of water across the membrane towards the DS will occur until the osmotic pressure of the DS reaches equilibrium with the osmotic pressure of the FS, irrespective of the rate of water transport across the membrane.

Theoretically, 100% recovery is possible if the fertiliser DS can generate osmotic pressure higher than the maximum solubility of the sodium chloride solution (6.15 M) with an osmotic pressure of 404 atm. For example, ammonium nitrate (being highly soluble in water) can easily generate osmotic pressure in excess of 404 atm. Similarly, calcium nitrate and sodium nitrate can also generate osmotic pressure in excess of 404 atm; therefore, the use of these fertilisers as DS for FO desalination can theoretically

achieve a 100% recovery rate. Depending on the TDS or the osmotic pressure of the feed water used, the recovery rates of other fertilisers vary. All fertilisers achieve recovery rates higher than 99% using feed water of TDS 1,000 mg/L NaCl (BGW1), although the recovery rates decrease when higher feed TDS is used. The solubilities of KNO_3 and KH_2PO_4 are low and therefore their recovery rates are also proportionately lower with only 70% and 51% respectively using TDS of seawater quality (BW35). All other fertilisers achieve recovery rates with seawater higher than 80%.

It must be noted that 100% recovery is not practical, because at higher concentration, the FS could precipitate and cause scaling on the feed side, impacting the water flux. Precipitation may occur earlier because in practice, the saline water from natural sources can include many other dissolved elements such as Ca, Mg, etc., which have lower solubility rates. The energy required to keep the fluid flowing will also rise because of the increase in viscosity of the feed water at higher concentration.

Table 5.6: Theoretical recovery rates of the FDFO process using selected fertilisers as the DS. Calculations were made based on the maximum osmotic pressure a fertiliser DS can generate at its highest solubility. The solubility and the osmotic pressure was predicted using OLI Stream Analyser 3.2.

Fertilisers	Max. solubility of DS	π at max solubility (atm)	NaCl at OE (M)	BGW1 (%)	BGW2 (%)	BGW5 (%)	BGW10 (%)	BGW20 (%)	BGW35 (%)
NH ₄ NO ₃	101.9 M	3346.1	6.15	100	100	100	100	100	100
Ca(NO ₃) ₂	22.04 M	601.0	6.15	100	100	100	100	100	100
NaNO ₃	10.95 M	417.9	6.15	100	100	100	100	100	100
NH ₄ Cl	7.35 M	356.0	5.59	99.7	99.4	98.5	96.9	93.9	89.3
Urea	19.65 M	338.4	5.38	99.7	99.4	98.4	96.8	93.6	88.8
DAP	7.13 M	293.0	4.82	99.6	99.3	98.2	96.4	92.9	87.6
SOA	5.8 M	274.8	4.58	99.6	99.3	98.1	96.3	92.5	86.9
KCl	4.82 M	226.5	3.94	99.6	99.1	97.8	95.7	91.3	84.8
MAP	4.56 M	181.3	3.29	99.5	99.0	97.4	94.8	89.6	81.8
KNO ₃	4.03 M	101.4	2.02	99.2	98.3	95.7	91.5	83.1	70.3
KH ₂ PO ₄	1.80 M	58.0	1.22	98.6	97.2	93.0	86.0	72.0	50.9

5.6 Concluding remarks

In this chapter, eleven different fertilisers that are commonly used worldwide were selected for investigation as draw solutes for the FDFO desalination process. While most soluble fertilisers can be used as DS, only those fertilisers that were compatible with the commercially available CTA FO membrane were used. The thermodynamic properties of the fertiliser solutions were also discussed.

A model was presented to explain the osmotic equilibrium that can be achieved in the FDFO desalination process; this osmotic equilibrium is one of the factors that limits the amount of water that a unit mass of fertiliser can extract from a feed of particular TDS. Based on this osmotic equilibrium, the water extraction capacities of each fertiliser DS was calculated for a range of feed water containing different TDS. The water extraction capacity of the fertiliser DS depends on factors such as the molecular weight of the fertiliser compound and the concentrations of the FS. Based on the water extraction capacity of each fertiliser, the expected fertiliser nutrient concentrations in the final FDFO product water were estimated in terms of N/P/K concentrations. By comparing the expected nutrient concentrations with the acceptable nutrient concentrations for different crops, it is clear that achieving acceptable nutrient concentrations for direct fertigation will be a challenge for the FDFO desalination process.

Several options to reduce the nutrient concentration were identified, including dilution using fresh water sources, integrating nanofiltration as either a pre-treatment or post-treatment process, blending of fertilisers to provide multiple nutrient species, and using a hybrid system of desalination and wastewater treatment by dual stage FO process. It was also observed that the FDFO desalination process could be operated at very high recovery rates without significant additional energy, unlike the RO process in which energy consumption is directly proportional to recovery rates. Depending on the fertilisers and the feed TDS, the recovery rates vary, with most fertilisers achieving recovery rates higher than 80% except with KNO_3 and KH_2PO_4 when a high TDS feed such as seawater is used.

CHAPTER 6



University of Technology Sydney

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ASSESSING THE FACTORS AFFECTING THE PERFORMANCES OF THE FORWARD OSMOSIS AND ITS IMPLICATIONS ON THE DESALINATION PROCESS

6.1 Introduction

Forward osmosis (FO) has recently become widely studied as a low energy process for desalination and other niche applications. Although the process is based on a simple, natural osmotic process, nevertheless the operation of the engineered osmotic process is not as simple as the already established pressure based membrane process (Lay et al., 2012). The process works well only with a special membrane and involves two unique solutions on both sides of the membrane. The fundamental understanding of the engineered osmotic process is still being gained, and there are several unanswered questions, such as which factors affect the performance of an FO system, especially the membrane. Such questions are significant, because flux determines the productivity of the membrane process and ultimately the viability of the technology (Lay et al., 2012). The flux of a membrane system is influenced by both the membrane's intrinsic properties and fouling, which is a complex issue (Belfort, 1984; Bellona et al., 2004; Al-Amoudi and Lovitt, 2007).

The osmotic pressure (π) of the ideal dilute solution is given by Van't Hoff's (1887) equation shown below.

$$\pi = n C R T \quad (6.1)$$

where n is the number of moles of solute in the solution, C is the solute molar concentration, R is the gas constant ($R=0.0821$) and T is the absolute temperature of the solution. The standard water flux in the FO process is given by the following equation (McCutcheon and Elimelech, 2006).

$$J_w = A \sigma \Delta\pi = A \sigma [\pi_D - \pi_F] \quad (6.2)$$

where A is the pure water permeability coefficient of the membrane, σ is the reflection coefficient (usually considered to be unity for calculations assuming a perfect barrier to solutes), π_D and π_F are the bulk osmotic pressures of the DS and the FS respectively and $\Delta\pi$ is the net osmotic pressure or net osmotic gradient. Eq. (6.2) therefore shows that the properties of the DS and the FS, especially the osmotic pressure, are major factors controlling water flux in the FO process.

Eq. (6.2) is valid only when the semi-permeable membrane used is symmetric (McCutcheon and Elimelech, 2006). All commercially available polymeric membranes are asymmetric in design and have different structural properties, a fact that has a significant influence on the performance of the FO process (Cath et al., 2006; Gray et al., 2006; McCutcheon and Elimelech, 2006; Ng et al., 2006). Details of the various types of CP effects have already been discussed in Chapter 2. Eq. (6.2) is modified to take into account various concentration polarisation effects. For the forward osmotic process operated with support layer facing DS and active layer facing FS (FO mode), the water flux is given by the following model (McCutcheon and Elimelech, 2007):

$$J_w = A \left[\pi_{D,b} e^{(-J_w K)} - \pi_{F,b} e^{(J_w / k_F)} \right] \quad (6.3)$$

where K is the solute resistance to diffusion within the membrane support layer and k_F is the mass transfer coefficient of the FS defined by the following equations:

$$K = \frac{t\tau}{D\varepsilon} = \frac{S}{D_D} \quad (6.4)$$

$$k_F = \frac{ShD_F}{d_h} \quad (6.5)$$

where t , τ and ε are the thickness, tortuosity and porosity of the membrane support layer respectively, D is the diffusion coefficient of the feed/draw solute, S is the structural parameter of the membrane support layer, d_h is the hydraulic diameter and Sh is the Sherwood number. The first term in Eq. (3) refers to dilutive internal concentration polarisation (ICP) as it occurs in the membrane support structure facing the DS and the negative term indicates that the phenomenon is dilutive in nature. The second term in Eq. (3) refers to concentrative external concentration polarisation (ECP) as it occurs on the membrane rejection layer facing FS.

For an FO process operated with a support layer facing the FS and active layer facing the DS (pressure retarded or PRO mode), the water flux is given by:

$$J_w = A \left[\pi_{D,b} e^{(-J_w / k_D)} - \pi_{F,b} e^{(J_w K)} \right] \quad (6.6)$$

From the above discussions, it is clear that the main parameters involved in the forward osmosis process are the semi-permeable membrane, draw solution, feed solutions and the operating environment. Any variation in the properties of these four major parameters could influence the performance of the forward osmosis process. The objective of this study is to evaluate how these four parameters influence the performance of the FO process for desalination. The performance is assessed in terms of the water flux and reverse solute flux (RSF). Water flux has direct implications for the energy requirement of the FO process, while RSF represents economic loss from replenishment cost and concentrate management. Understanding the roles of these factors is important not only for optimising the FO process but also for engineering the process to improve the performance of the FO desalination process. It should be mentioned here that temperature is one of these important FO operating parameters, but this is covered separately in Chapter 7.

6.2 Experimental

6.2.1 Draw solution and feed solutions

Five different types of solutes were used in this study: urea, KCl, CaCl₂, MgSO₄ and Na₂SO₄ all supplied as pure reagent grade (Sigma Aldrich, Australia). The FS consisted of either DI water or NaCl (Sigma Aldrich, Australia) solution prepared in DI water. NaCl solution of different concentrations was used as model brackish water (BW) representing FS of different total dissolved solids (TDS). Unless otherwise specified, the term BW refers to an NaCl FS of TDS 5,000 mg/L. The thermodynamic properties of the solutions such as osmotic pressure, viscosity and diffusion coefficient were analyzed using OLI Stream Analyzer 3.2 (OLI Systems Inc., Morris Plains, NJ, US). This software uses thermodynamic modeling based on published experimental data to predict properties of solutions over a wide range of concentrations and temperatures (McCutcheon et al., 2006). The method for the preparation of the DS and FS has already been described in Chapter 3.

6.2.2 Performance experiments using bench-scale FO unit

Performance of FO process was conducted using a bench-scale FO unit set up and the details can be found under Chapter 3. Three different types of membranes were used in this study. They include commercial CTA-FO membrane (HTI Inc., USA), commercial

polyamide based TFC RO membrane or TFC-RO (SWRO, Woongjin Chemicals, Korea) and newly synthesized TFC-FO membranes (Woongjin Chemicals, Korea). The characteristics of the CTA FO membrane have been widely reported (McCutcheon et al., 2005; Cath et al., 2006; Tang et al., 2010) and so are the properties of the TFC-RO membranes (Prakash Rao et al., 1997; Li and Wang, 2010; Zou et al., 2010). Polyamide based TFC-RO membrane was recently synthesized membrane by Woongjin Chemicals. Since the membrane is a proprietary of Woongjin Chemicals, the detail methods for the synthesis of the membrane have been excluded from publication except some basic properties for its performance data. This TFC-FO membrane is hand-casted membrane and is still in the process of optimization and development before commercialization.

6.3 Influence of membrane properties on the performance of the FO desalination process

Any selectively permeable membrane material can be used for the FO process (Cath et al., 2006) however, membrane properties play a crucial role in the efficiency of the FO process (Lay et al., 2012). To assess the influence of membrane properties on the FO desalination process, three different membranes were used and their performances compared in terms of the type of membrane and membrane orientation. The performances of these two membranes in FO process are presented in Table 6.1. The influence of membrane orientations in the performance of FO process and its implications are also discussed.

6.3.1 Basic properties of the membranes tested

The PWP of the three membranes determined in RO mode of operation were 1.015, 2.951 and 5.215 $\text{Lm}^{-2}\text{h}^{-1}\text{atm}^{-1}$ for CTA-FO, TFC-RO and TFC-FO membranes, respectively. Although, the water flux of the TFC-FO membrane was higher than the other two membranes, its NaCl rejection was the lowest with only about 85%. The very high PWP for TFC-FO membrane is probably because of damage to the membrane when subjected to hydraulic pressure which is also indicated by the lower NaCl rejection. TFC-RO membrane showed the highest NaCl rejection of 99.5%. The overall physical thicknesses of the three virgin membranes were measured using a digital

micrometer (Model 293-330 Mitutoyo, Japan) which confirmed that the two TFC (RO and FO) membranes are thicker than the CTA FO membrane ($93 \pm 3 \mu\text{m}$).

6.3.2 Comparative performance of membranes in the FO process

Although the PWP coefficient of the CTA FO membrane ($1.015 \text{ Lm}^{-2}\text{h}^{-1}\text{atm}^{-1}$) is much lower than the RO membrane ($2.951 \text{ Lm}^{-2}\text{h}^{-1}\text{atm}^{-1}$), the water flux of the CTA FO membrane was consistently more than 20 times higher than the RO membrane in the FO process under all the conditions reported in Table 6.1. These confirm earlier studies (Gray et al., 2006; McCutcheon and Elimelech, 2006; Ng et al., 2006) that, the commercial RO membranes are not suitable for FO process. Earlier studies on the FO process using traditional salt-rejecting RO membranes showed that there was very low flux, even with a DS containing that contained very high osmotic pressure (Cath et al., 2006; Ng et al., 2006). This was later explained by the asymmetric design of the membranes that caused two different types of CP effect as explained under Section 1. The TFC-RO membrane used in this study has asymmetric structure and is hence prone to ICP effects within the support layer in addition to the ECP that usually occurs on the active layer side of the membrane. The TFC-RO membrane is about 1.5 times thicker than the thin CTA-FO membrane due to the thick support layer. The presence of the thick support structure increases the structural parameters of the membrane (S in equation (6.4)) thereby increasing the resistance to the diffusivity of the draw solutes within the membrane support layer (K in equation (6.4)) and increasing the dilutive CP phenomenon. When the FO process was tested using the RO membrane with its support layer removed, water flux was found to be significantly higher, even higher than the CTA FO membrane (Tang and Ng, 2008).

Recently many groups have been attempting to synthesize high performance membranes for the FO applications by modifying the structural properties of the TFC membrane support layer (Wei et al., 2005; Yip et al., 2010; Tiraferri et al., 2011; Wei et al., 2011b). The modification includes decreasing the support layer thickness and increasing the porosity of the membrane. The performance of the TFC-FO membrane was compared with the CTA-FO and the TFC-RO membranes. Although the thickness of the TFC-FO membrane was comparable to its own TFC-RO membrane, TFC-FO membrane showed very high water flux both in terms of PWP and FO flux. The water

flux using 1 M KCl as DS and DI as FS was three times higher than that of the CTA-FO membrane and about 64 times higher than TFC-RO membrane although this order of magnitude was slightly lower when NaCl solution was used as feed water. This significant difference in water flux in FO process for TFC-FO membrane is due to the modifications of the membrane support layer that helped in reducing the structural parameter of the membrane. Figure 6.1 shows the comparative cross sectional SEM images of the three membranes. The cross sectional image of the CTA membrane in Figure 6.1(a) indicates that the support layer is highly porous with a many finger-like macro-voids ranging in some cases as large as 15 μm . The SEM images in Figures 6.1(b) and 6.1(c) do not show the presence of such support structure that hinders easy diffusion of draw solutes and therefore results in lower water flux in FO process than the TFC-FO membrane. It must also be however mentioned here that, because of the highly porous nature of the membrane support layer, the membrane showed poor mechanical strength. The TFC-FO membrane was susceptible to damage when operated at applied pressures higher than 4 bar.

The results in Table 6.1 also include the comparative performances of the three membranes in the rejection of solutes in both the directions. The results indicate that, the RSF of the two FO membranes (CTA-FO and TFC-FO) was significantly higher, in fact several orders higher than the RO membrane. For example, the RSF of the CTA-FO and TFC-FO membranes using DI water as the feed were 12.0 and 9.4 $\text{g m}^{-2}\text{h}^{-1}$ respectively, against that of RO membrane which was less than 1.0 $\text{g m}^{-2}\text{h}^{-1}$. The low RSF of the RO membrane is because of the high rejection property of the RO membrane as presented in the same Table. Although the NaCl rejection of CTA-FO membrane was higher than the TFC-FO membrane, its performance in terms of RSF was not better than TFC-FO membrane.

The absolute value of the RSF is however less significant because it bears no relationship to the amount of water extracted during the FO process. Therefore, specific RSF (SRSF) or the ratio of RSF to the water flux has been proposed which indicates the amount of draw solutes lost by reverse diffusion per unit volume of water extracted from the FS (Hancock and Cath, 2009; Phillip et al., 2010). In contrast to the RSF value, the results on SRSF in Table 6.1 show that, the RO membrane has the highest SRSF while the TFC-FO membrane showed the lowest SRSF. This is because the RO

membrane has very low water flux in the FO process than the TFC-FO membrane or the CTA-FO membrane which indicates that, although the RO membrane has higher rejection properties, its performance in the FO process is very poor in terms of reverse SRSF and water flux. Despite poor rejection properties in the RO mode of operation, the lowest SRSF for the TFC-FO membrane is unusual because according to equation (6), the RSF (J_s) is a function of only concentration gradient and the solute permeability. This indicates that, the structural properties of the membrane support layer could probably influence the RSF because of the increased diffusivity of the solutes within the membrane support layer.

It may be noted that, when the BW is used as feed, the RSF and SRSF were observed slightly lower for all the membranes while the forward feed salt rejection was slightly higher than the DI as feed. This is likely due to the presence of solutes on both sides of the membrane that interferes and influences the rate of diffusion across the membrane and more discussion on this effect can be observed later under section 3.3.

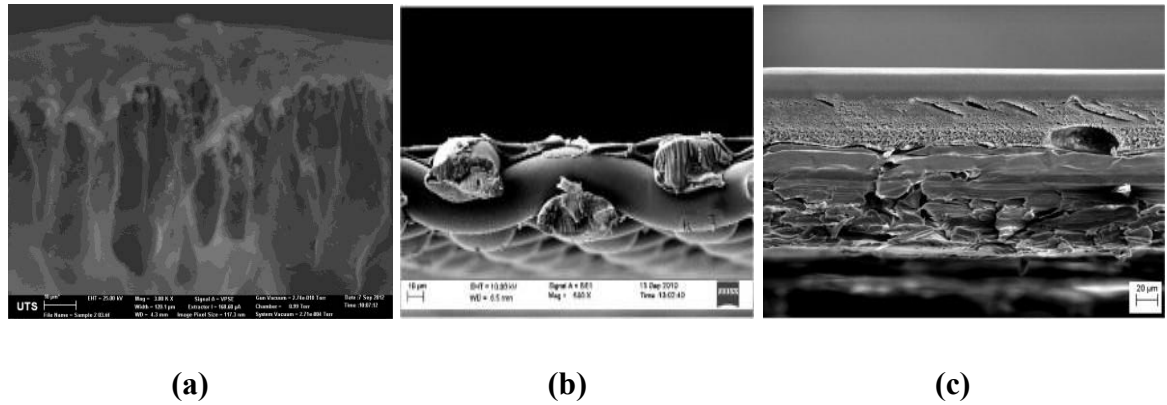


Figure 6. 1: Comparative SEM images of the cross section of the three membranes (a) Woongjin TFC-FO membrane, (b) CTA-FO membrane (Qiu et al., 2012) and (c) TFC-RO membrane (Wei et al., 2011b)

6.3.3 Influence of membrane orientation on the performance of the FO process

The results on the water flux with the three types of membrane indicate that the structural properties of the membrane support layer play a significant role in the performance of the FO process. For an FO process to be effective, the ideal membrane should be thin and symmetric but highly selective, with high water permeability (Cath et al., 2006; McCutcheon and Elimelech, 2006; Tang and Ng, 2008; Yip et al., 2010).

However, it is not practical to use a thin and symmetric membrane, especially when polymeric membranes are used, and therefore some form of support layer is necessary to provide mechanical strength (Yip et al., 2010; Zhang et al., 2010). To understand how the membrane's asymmetric design influences FO performance, experiments were conducted with different membrane orientations using both the CTA-FO membrane and the TFC-RO membrane with various DS concentrations. Both were compared in FO mode and in PRO mode. FO mode of operation refers to the membrane orientation in which the support layer faces the DS and the active layer faces the FS. The other orientation to FO mode is the PRO mode of membrane orientation.

Table 6.1 also shows the influences of membrane orientation on the performance of the FO process using the three membranes. The water flux in PRO mode of operation was observed to be comparatively higher than the FO mode of operation for all three membranes both with DI and BW as the FS. Higher water flux is always been obtained in PRO mode than in FO mode of operation (Gray et al., 2006; Jung et al., 2011; Lay et al., 2012). The difference in water fluxes in the FO mode and PRO mode is because of the difference in the membrane structural resistance depending on which sides of the solutions the support layer of the membrane is oriented. In the FO mode of operation, the DS faces the porous support layer of the membrane, while the feed faces the active layer. The incoming water flux from the feed side dilutes the DS at the membrane's surface and within the membrane's porous support layer, reducing the net osmotic pressure at the membrane's surface and lowering the water flux. Since the osmotic pressure of the DS at the membrane boundary layer is crucial to FO process, dilutive ICP severely affects water flux in the FO process. When BW is used as the feed, a concentrative ECP occurs on the active layer side further reducing the effective driving force and therefore the water flux which explains why water flux with BW as feed is slightly lower than DI water as feed. When DI is used as the FS in FO mode, concentrative ECP is absent on the active layer side of the membrane.

When the process is operated in PRO mode, the CP phenomenon reverses. Since the DS in PRO mode faces the membrane active layer, the phenomenon is dilutive ECP, which can be mitigated by the crossflow shear provided on the membrane surface. Although concentrative ICP occurs on the feed side of the membrane, its effect is less severe than dilutive ICP and this is the reason why water flux in PRO mode is higher than in FO

mode. Although the performance of the TFC-RO membrane in PRO mode was higher than in FO mode, its flux is still lower than $1.0 \text{ Lm}^{-2}\text{h}^{-1}$, which is significantly lower than in the CTA-FO and TFC-FO membranes. Even though PRO mode results in higher water flux in the laboratory scale studies under controlled conditions, in a practical situation, PRO mode is not suitable for desalination because the membrane is prone to severe membrane fouling as the porous support layer is directly exposed to the feed water containing scaling and fouling species (Tang et al., 2010; Zou et al., 2011; Zhao et al., 2012a).

In the PRO mode of operation, the draw solute concentration at the membrane surface is higher than it is in FO mode operation, which generates higher driving force and consequently higher water flux. However, the presence of higher draw solute concentration at the membrane surface in PRO mode also leads to higher RSF and SRSF as evident from Table 6.1, with both the CTA-FO membranes. The RSF and SRSF for the TFC-RO membrane in PRO mode was, however, lower than in FO mode, probably because the percentage water flux increase in PRO mode (~45% with DI) for the RO membrane was much higher than the CTA FO membrane (25% with DI).

Comparing the water fluxes in the FO mode and the PRO mode, the water flux in PRO mode for CTA-FO, TFC-RO and TFC-FO membranes were about 25%, 45% and 35% higher than the fluxes in FO mode respectively. The lower percentage of water flux in the PRO mode than the FO mode for CTA-FO membranes in comparison to the TFC-RO and TFC-FO membranes is probably an indication that, the CTA-FO membrane is more symmetric than the other two membranes.

The comparative studies on water and reverse solute flux for the three membranes indicate that, the performances of the FO membrane can be enhanced by improving the structural properties of the membrane support layer such as by increasing the porosity and reducing the thickness of the membrane support layer. A high flux membrane is the ultimate goal of many researchers as this will help increase the overall process efficiency and ultimately reduce the capital and operational cost of the FO desalination plant. However, it is also important that the mechanical strength of the membrane must also be considered while designing the high performance membrane. Although, synthesizing high performance FO membrane is still a trade-off amongst the water flux,

salt rejection and the membrane mechanical strength nevertheless, further effort must be focused on improving the mechanical strength of the support layer such as using alternate support materials.

Table 6. 1: Influence of the types of membranes and their orientation on the performance of FO process compared in terms of water flux and reverse solute fluxes. Solutions temperature: 25°C, crossflow: 8.5 cm/s, Mode: FO and PRO mode and in counter-current crossflow direction

Membrane properties	CTA FO	RO	TFC FO
Materials	Cellulose triacetate	Polyamide	Polyamide on PSF
Supplier	HTI Inc., USA	Woongjin Chemicals, Korea	WJ (TFC2)
PWP or A ($\text{Lm}^{-2}\text{h}^{-1}\text{atm}^{-1}$)	1.015 ± 0.029	2.951 ± 0.312	5.215
Salt rejection in RO mode using 5 g/L NaCl (%)	93	99.5	85.2
FO mode water flux 1 M KCl: DI FS ($\text{Lm}^{-2}\text{h}^{-1}$)	9.832	0.439	27.976
Reverse solute flux ($\text{g m}^{-2}\text{h}^{-1}$)	11.968	0.816	9.382
Specific reverse solute flux (g/L)	1.217	1.857	0.351
FO water flux 1 M KCl: 5 g/L NaCl FS ($\text{Lm}^{-2}\text{h}^{-1}$)	8.734	0.385	18.948
Reverse solute flux ($\text{g m}^{-2}\text{h}^{-1}$)	10.10	0.480	5.874
Specific reverse solute flux (g/L)	1.156	1.247	0.310
PRO mode water flux 1 M KCl: DI FS ($\text{Lm}^{-2}\text{h}^{-1}$)	12.195	0.636	37.729
Reverse solute flux ($\text{g m}^{-2}\text{h}^{-1}$)	23.890	0.534	96.381
Specific reverse solute flux (g/L)	1.959	0.840	2.555
PRO mode water flux 1 M KCl: 5 g/L NaCl FS ($\text{Lm}^{-2}\text{h}^{-1}$)	10.227	0.474	25.102
Reverse solute flux ($\text{g m}^{-2}\text{h}^{-1}$)	19.21	0.250	53.091
Specific reverse solute flux (g/L)	1.878	0.527	2.115
Membrane thickness (μm)	93 ± 3	142 ± 2	147 ± 16

6.3.4 Comparison of the Woongjin's new TFC-FO membrane with other recently reported TFC-FO membranes

Recently, several groups have reported the synthesis of high performance flat-sheet and hollow fiber membranes for FO and osmotic power applications. So far, the best performing polyamide based flat-sheet TFC FO membrane was reported by Tiraferri et al. (Tiraferri et al., 2011) with a water flux of $25 \text{ Lm}^{-2}\text{h}^{-1}$ (using 1.0 M NaCl as DS and

DI water as FS in FO mode) and hollow fiber TFC FO membrane with $33 \text{ Lm}^{-2}\text{h}^{-1}$ (Chou et al., 2010) (using 0.5 M NaCl as DS and DI water as FS in PRO mode). The water flux for TFC-FO membrane used in this study were 27.98 and $37.73 \text{ Lm}^{-2}\text{h}^{-1}$ in FO mode and PRO mode respectively using 1 M KCl as DS and DI as FS Table 6.1). These results indicate that, this TFC-FO membrane performs significantly much better than the recently reported TFC-FO membranes in FO process. This is probably because of the lower total thickness of this TFC-FO membrane compared to other recently reported TFC-FO membranes. Moreover, the support structure of this TFC-FO membrane appears to have larger finger-like macro-voids and therefore is comparatively more porous than the recently reported TFC-FO membranes (Wei et al., 2005; Yip et al., 2010; Tiraferri et al., 2011; Wei et al., 2011b). These larger macro-voids also explain why this non-optimized TFC-FO membrane shows weak mechanical strength.

It must be therefore mentioned that, the currently synthesized TFC-FO membrane still needs further optimization to improve the mechanical strength of the membrane to withstand a slight hydraulic pressure that may be developed while providing adequate crossflow velocity. It is important to note here that, KCl was used as a draw solute for assessing the performance of the TFC-FO membrane in this study where as NaCl was used in other studies. Based on the available literature, the performances of KCl and NaCl as draw solutes are comparable with KCl performing only slightly better than the NaCl (Achilli et al., 2010).

6.4 Influence of draw solution properties on the performance of the FO desalination process

In this section, the influences of the DS properties were investigated on the performance of FO desalination process using CTA FO membrane. The DS properties mainly included different types of DS and the influence of DS concentration on the FO performance. Five different types of draw solutes were investigated and they include KCl (monovalent ions), CaCl_2 (divalent cation and monovalent anion), Na_2SO_4 (monovalent cation and divalent anion), MgSO_4 (divalent ions) and urea (neutral compound).

6.4.1 Influence of the types of draw solution on the performance of the FO process

The osmotic pressure of each DS is shown in Figure 6.2. Of the five selected DS, CaCl_2 shows the highest osmotic pressure of 750 atm at 5.0 M concentration, while KCl with the next highest osmotic pressure was far behind with 310 atm at 5.0 M concentration. Although Na_2SO_4 showed the third highest osmotic pressure, its solubility was limited to about 2 M concentration and it therefore cannot generate osmotic pressure higher than 95 atm. Urea and MgSO_4 showed similar results but the lowest osmotic pressure was 107 atm at 5.0 M concentration.

Figures 6.3 and 6.4 show the influence of the types of DS, their osmotic pressure on the water flux and the performance ratio (PR) using DI and BW as the FS. PR is defined as the ratio of the experimental flux to the theoretical flux (determined based on the net bulk osmotic pressure using equation 6.2). PR represents the percentage of the bulk osmotic pressure effectively available for generating water flux in the FO process (McCutcheon et al., 2006; Phuntsho et al., 2011b). From the osmotic pressure in Figure 6.2, it appears that CaCl_2 should generate the highest water flux of the five DS because it has comparatively higher osmotic pressure; however, the results in Figures 6.3 and 6.4 show otherwise. The ranking of the five DS in terms of water flux at equal bulk osmotic pressures was $\text{KCl} > \text{Na}_2\text{SO}_4 > \text{CaCl}_2 > \text{MgSO}_4 > \text{urea}$ (Figure 6.3.a).

Although CaCl_2 has the highest osmotic pressure, its water flux was observed to be lower than KCl and Na_2SO_4 and even lower than MgSO_4 , which has one of the lowest osmotic pressures. The lower water flux with CaCl_2 is probably due to lower diffusivity of CaCl_2 within the membrane support layer thereby enhancing the ICP and reducing the effective driving forces. Urea has the lowest water flux since it has very low osmotic pressure at similar molar concentration. The low water flux for urea has also been explained in our earlier studies due to hydrophobic properties that may limit the contact of urea solution within the membrane support layer (Phuntsho et al., 2012b). These results show that the type of draw solute plays a significant role in the performance of the FO process besides its osmotic pressure. The modified flux model in equation (6.3) takes into account the properties of the draw solutes and feed solutes in predicting the water flux across the membrane.

6.4.2 Influence of the draw solution concentrations on the performance of the FO process and its implications

Although the water flux increased with the increase in the osmotic pressure of the DS, nevertheless; the increase was non-linear but logarithmic, as shown in Figure 6.3(a). This shows that increasing the DS concentration will not lead to proportionate increase in the water flux, as reported in other studies (Xu et al., 2010). When the DS concentration is increased, the net osmotic pressure increases, generating higher water fluxes temporarily but, the increased incoming water flux causes enhanced dilutive ICP within the membrane support layer, thereby keeping the overall gain in water lower. At higher DS concentrations, the water flux itself acts as a limiting factor and reduces the performance of the DS, as shown by the performance ratio (PR) of the water flux presented in Figure 6.3(b). The ranking of the PR of the DS was $\text{KCl} > \text{Na}_2\text{SO}_4 > \text{MgSO}_4 > \text{CaCl}_2 > \text{urea}$. The performance ratio or PR decreased rapidly with the increase in the osmotic pressure of the DS before finally reaching flat at higher osmotic pressure. This indicates that no matter how high the osmotic pressure a DS can generate, it will not be able to produce proportionate water flux by the FO process.

To illustrate further, CaCl_2 at 350 atm (~ 3.0 M) has a water flux of $12 \text{ Lm}^{-2}\text{h}^{-1}$; however, if CaCl_2 of 750 atm (5.0 M) is used as the DS, the water flux would increase to only $14 \text{ Lm}^{-2}\text{h}^{-1}$ (estimated based on the logarithmic correlation for CaCl_2). This is a meager 17% increase in water flux compared to the 114% increase in the osmotic pressure of the CaCl_2 DS. In fact the PR of CaCl_2 at 350 atm was only about 4% and may further decrease at higher concentration. These results indicate that, beyond a certain level of concentration for a particular DS, further increase in DS concentration will increase the pumping energy because the viscosity of the DS will increase. For example, the viscosity of CaCl_2 at 5 M (3.748 cP) is twice as high as the viscosity at 3.0 M concentration (1.960 cP) and therefore the pumping energy required at 5.0 M concentration will be significantly higher because pumping energy depends on fluid viscosity. There could be also other implications for the membrane process when a highly concentrated DS is used, such as membrane stability due to chemical exposure to increased ionic concentrations.

Figure 6.4 shows the performance of the five DS in terms of water flux and PR using BW as feed. The ranking of the water flux was similar to the results obtained in Figure 6.3(a) with DI as feed; however, the PR varied slightly when BW was used as feed (Figure 6.4(b)). The PR was higher at lower DS osmotic pressure, while at higher osmotic pressure, the PR was lower than the DI water. This difference in PR is due to the coupled influences of dilutive ICP on the DS and concentrative ECP on the FS. In addition, the dilutive and concentrative CP modulus are lower when low DS concentrations are used because of the comparatively lower flux attained (McCutcheon and Elimelech, 2006; Phuntsho et al., 2012b).

The above results indicate that, the selection of suitable draw solutes is important for several reasons. Draw solutes that generate higher water flux at lower concentrations are preferable as this could contribute to significant cost savings in terms of both capital and operation costs. However, other important issue that determines the choice of the draw solutes and not mentioned in this study is the end use of the product water after FO desalination. For potable purpose, the water and the draw solutes must be separated which will require post-treatment process and therefore additional cost.

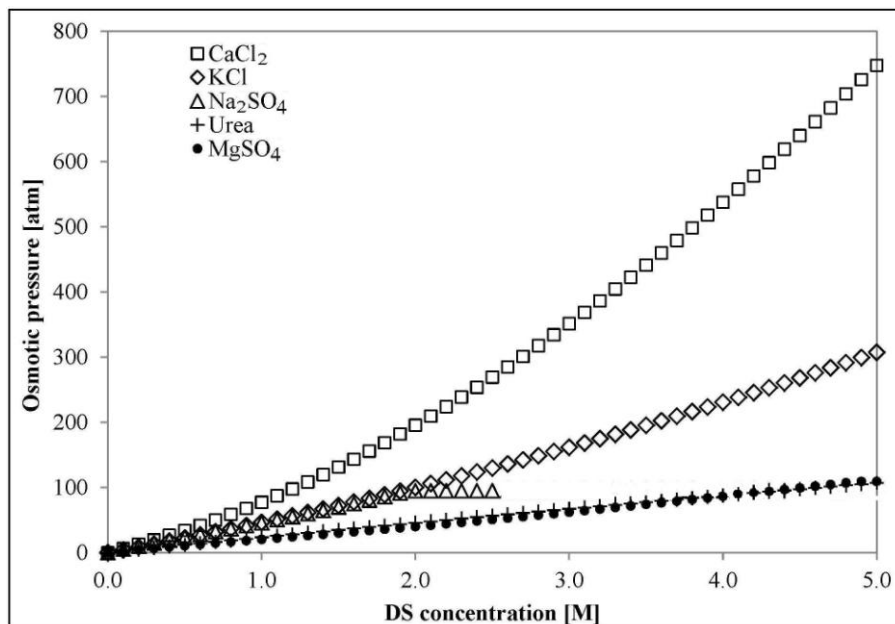
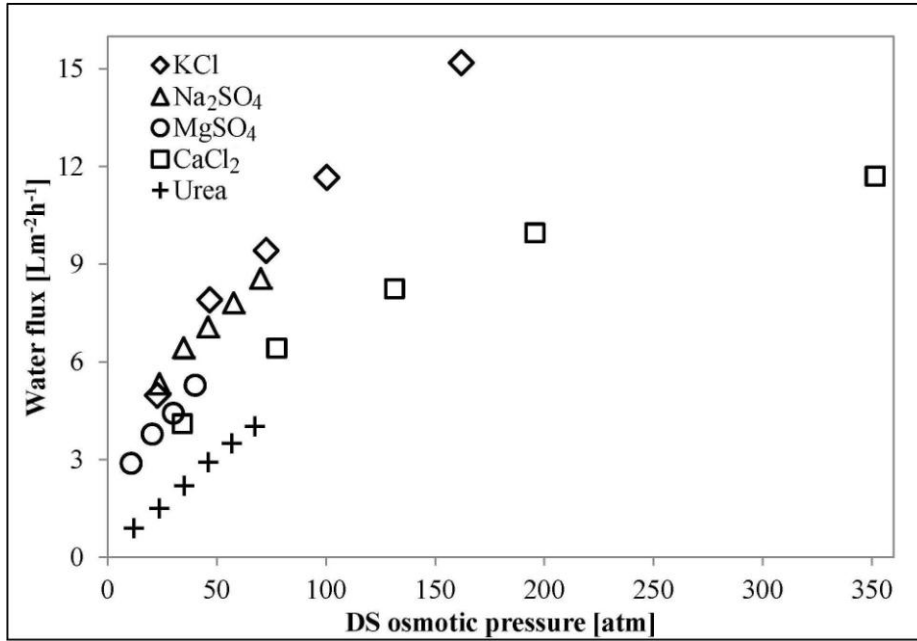
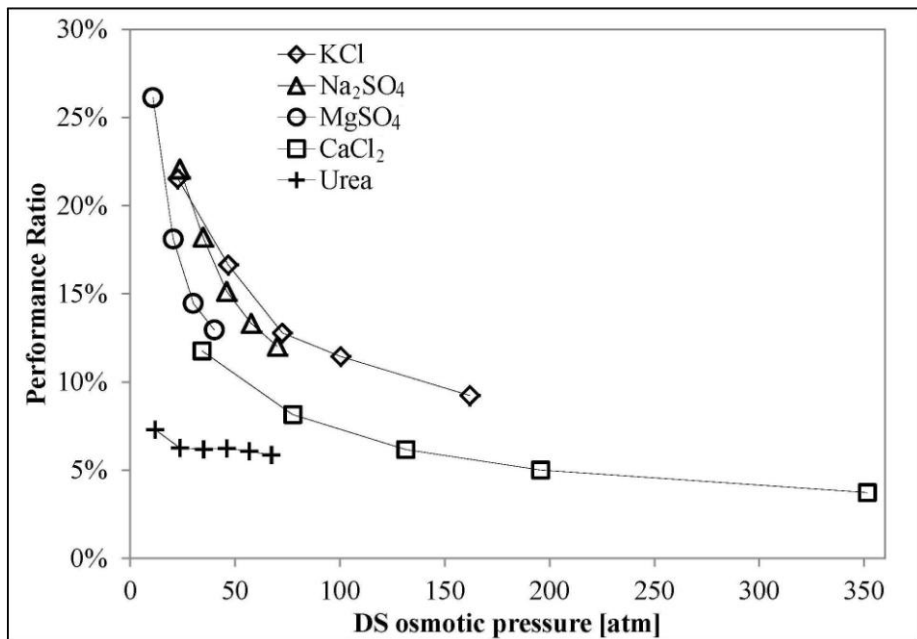


Figure 6. 2: Variation of osmotic pressure of the five different types of DS at various concentrations. Prediction made using OLI Stream Analyzer 3.2 at 25°C.

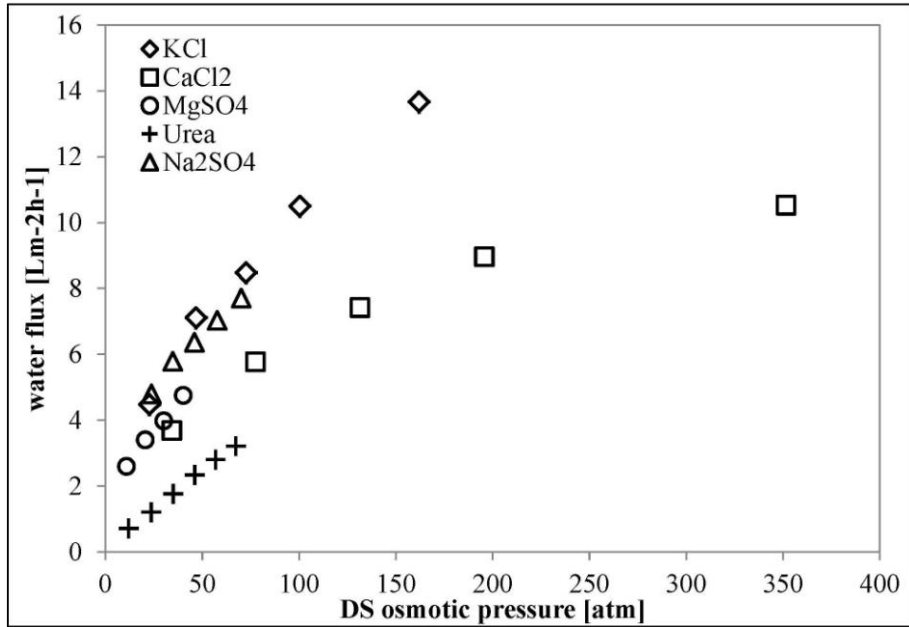


(a)

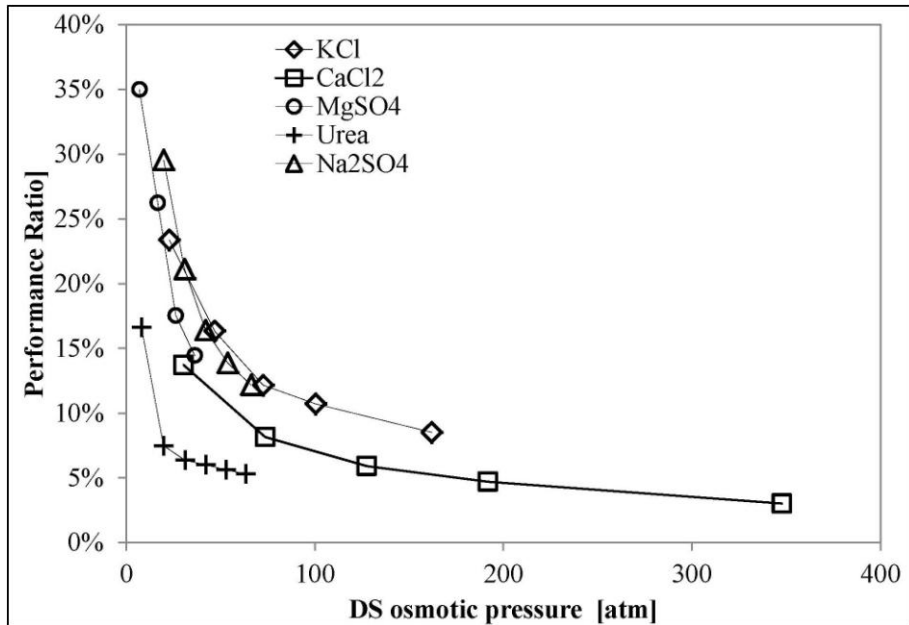


(b)

Figure 6. 3: Influence of the type of DS and their concentration on the performances of FO process in terms of water flux and the PR using DI as FS. (a) Water flux and (b) performance ratio. Feed: DI water, solutions temperature: 25°C, crossflow: 8.5 cm/s, Mode: FO and counter-current, Membrane: CTA FO



(a)

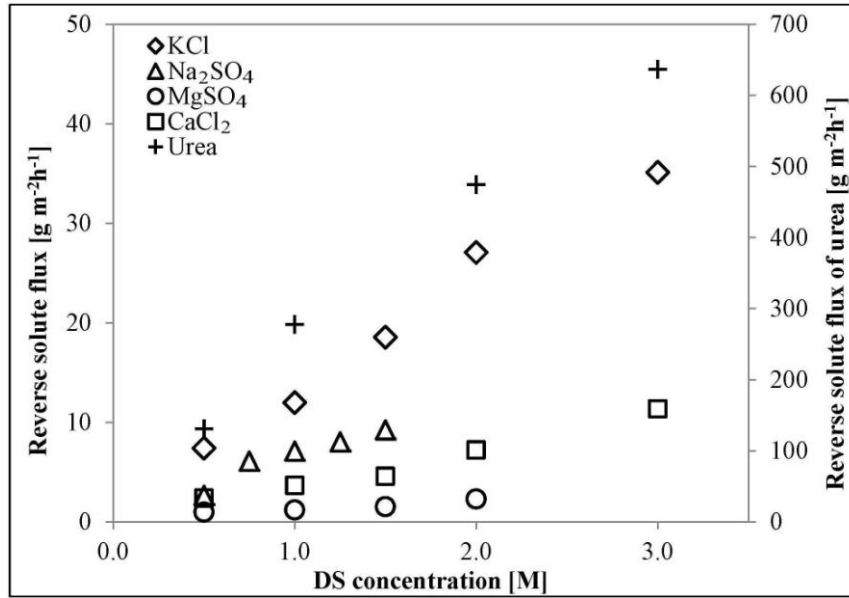


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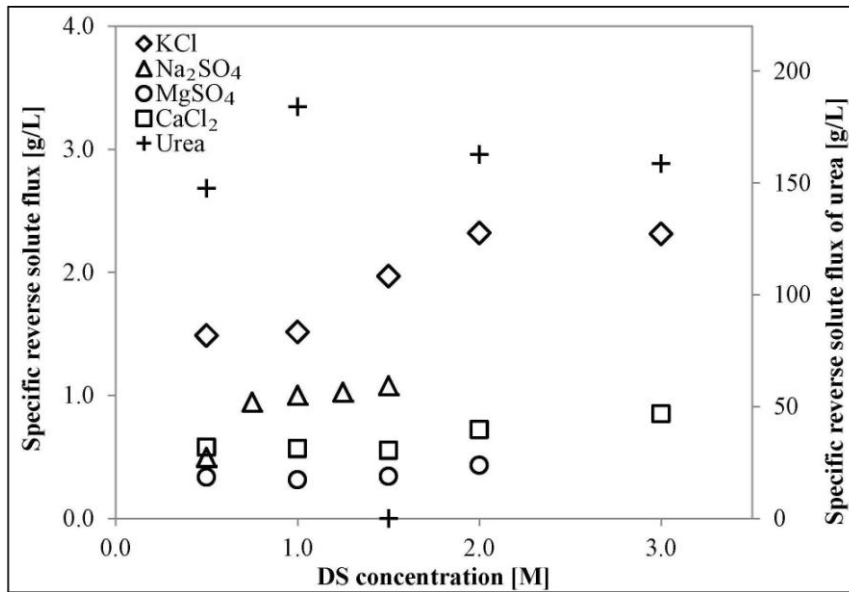
Figure 6. 4 : Influence of the type of DS and their concentration on the performances of FO process in terms of water flux and the PR using BW as FS. (a) Water flux and (b) performance ratio. Feed: BW water, solutions temperature: 25°C, crossflow: 8.5 cm/s, Mode: FO and counter-current, Membrane: CTA FO. Note that the RSF of urea is plotted in a different axis since the values were too high to be plotted in the same axis with the other DS.

Although, higher water flux can be generated using higher DS concentrations, the other implication of using higher DS concentration could be in terms of higher loss of draw solutes due to reverse diffusion and complications on the FS (Xiao et al., 2011; Ge et al., 2012). Figure 6.5 shows the comparative performances of the five different types of DS in terms of RSF and SRSF at various DS concentrations.

Figure 6.5 indicates that, urea as DS results in the highest loss of solutes by reverse diffusion of draw solutes as indicated by the highest RSF and SRSF amongst the five DS followed by KCl. The high RSF/SRSF of urea can be attributed to its low rejection by the membrane as urea is a neutral solute with the smallest molecular size in comparison to other DS (Phuntsho et al., 2012b). KCl is a monovalent compound and therefore its rejection by the membrane is expected to be comparatively lower than the divalent compounds (Achilli et al., 2010; Phuntsho et al., 2011b; Phuntsho et al., 2012b). The lowest RSF was observed for MgSO_4 and this is because it has both divalent anion and cation, which limit the diffusion of the solutes through the membrane active or rejection layer. The RSF increases with the increase in the DS concentration for all the DS tested however, this value is of less significance given that water flux increases at higher DS concentration. Figure 6.5(b) shows that the SRSF will be similar to each DS even if the RSF increases at higher DS concentration. SRSF should be constant irrespective of DS concentration for the same draw solute (Phillip et al., 2010).



(a)



(b)

Figure 6. 5: Variation of the loss of solutes due to reverse diffusion of draw solutes in terms of (a) reverse solute flux (RSF) and (b) specific reverse solute flux for different types DS and their concentrations using DI water as feed. Solutions temperature: 25°C, crossflow: 8.5 cm/s, Mode: FO and counter-current, Membrane: CTA FO. Note that the SRSF of urea is plotted in a different axis since the values were too high to be plotted in the same axis with the other DS.

The DS concentration would gradually decrease along the length of the FO module in real applications, or with time as water is extracted from the FS, but there must nevertheless be a critical or optimum initial DS concentration to begin the FO process.

It was shown in Figure 6.4(a) that, the water flux can be increased by using higher DS concentrations although this increase is non-linear at very high concentrations due to the water flux itself acting as a limiting factor by increasing the dilutive ICP phenomenon. After certain DS concentration, the PR of the DS becomes flat as shown in Figure 6.4(b) indicating that operating at concentrations higher than this will not be beneficial in terms of water flux, as the PR appears flat.

However operating the plant at higher water flux is naturally preferable because, this will require less membrane area for a desalination plant of particular capacity and hence lowers the capital cost of the plant. Alternatively, if the plant has a fixed membrane area, operating the membrane at higher flux will reduce the amount of time required to desalinate a fixed volume of water. However, using very high DS concentration could have other negative implications on the design and operation of the desalination plant.

The first implication of using highly concentrated DS is the increase of the pumping cost because of the increased specific weight and viscosity of the DS. The performance of the pump which requires are influenced by the characteristics of the fluid such as density or specific weight, viscosity, particulate content, and vapor pressure (Hydraulic Institute, 2006). The energy rating of the pump is given by the following equation:

$$P = Q \rho g H \quad (6.7)$$

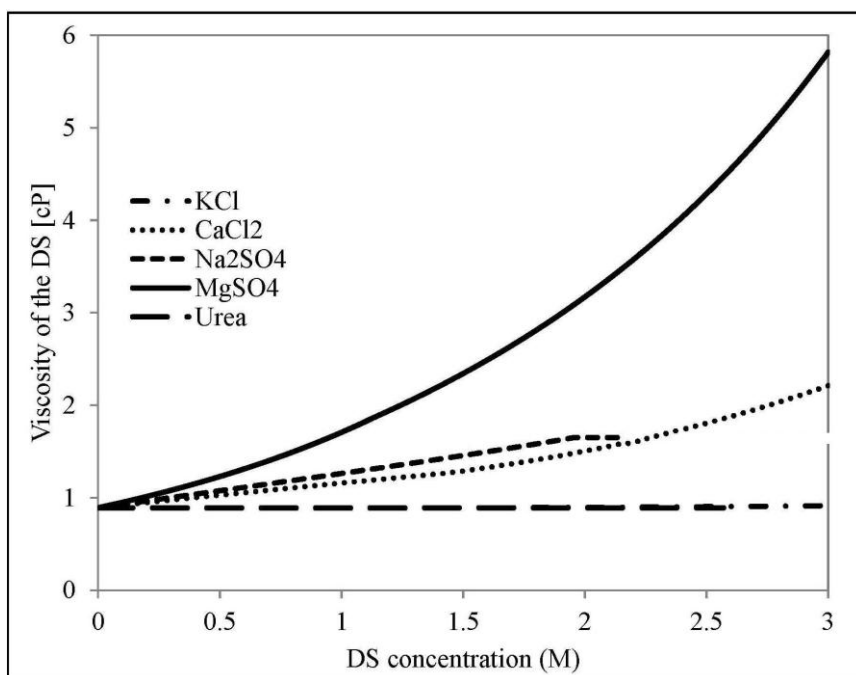
Where P is the power (W), Q is the flow discharge (m^3/s), ρ is the fluid mass density (kg/m^3), g is the acceleration due to gravity ($9.81 \text{ m}/\text{s}^2$) and H is the pressure head (m). Equation (6.7) indicates that the water required for the pump will increase with the increase in specific weight (ρg) assuming that the other parameters such as Q and H remain same irrespective of the DS concentration. Although, equation (6.7) does not include viscosity, the viscosity of the fluid affects all the operational parameters of the pump: total head, flow and efficiency (Li, 2000; Hydraulic Institute, 2006). A more viscous liquid consumes more energy during the pumping because its increased shear resistance creates frictional drag and heat on the pumps thereby requiring additional power to overcome this drag that reduces the pump's efficiency (Hydraulic Institute, 2006).

Figure 6.6 shows variation of the viscosity (Figure 6.6(a)) and specific weight (Figure 6.6(b)) of the five selected DS with its concentration. Specific weight of the DS increases with the increase in its concentration and therefore this is expected to increase the weight of the fluid that the pump has to displace, thereby enhancing the energy requirements for the pumps. Similarly, the viscosity of the DS increases at higher DS concentrations which also increase the energy required for pumping the DS. The other potential implications of using highly concentrated DS are the enhanced exposure of the pumps, piping and the fittings to high ionic strength solution, which could affect the life of the plant.

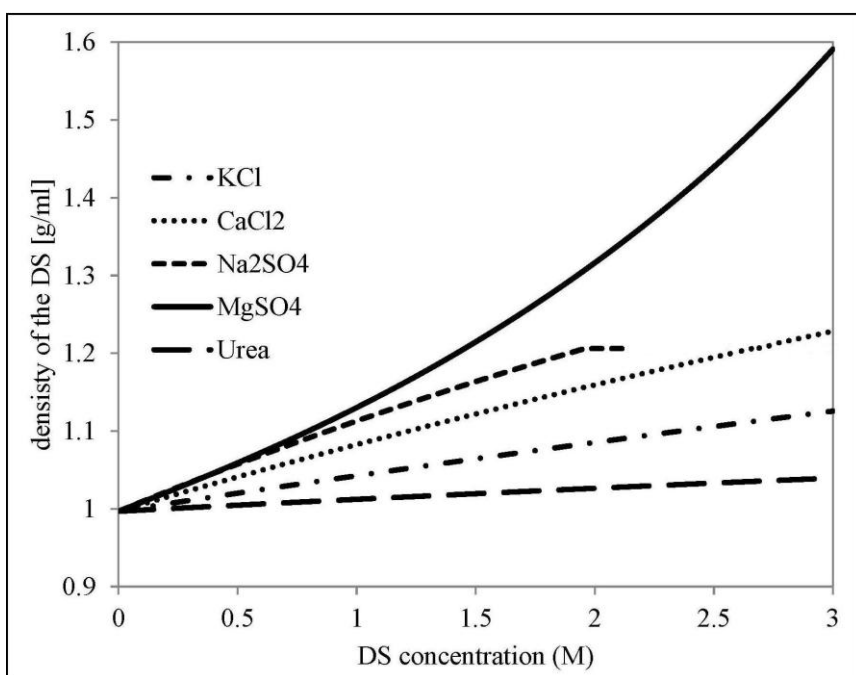
The other implication of using high concentrated DS is the recovery at which the plant can be operated. In an FO module with certain membrane area, the DS concentration decreases along the length of the FO module due to dilution by the incoming water from the feed and reaching minimum concentration at the DS outlet. On the other hand, the FS concentration increases along the length of the FO module reaching maximum at its outlet. If the DS and the FS are operated in counter current crossflow directions, the final diluted DS meets incoming feed and therefore the final DS concentration can reach a minimum of equivalent to the incoming feed concentration. Assuming that the membrane area is adequate within the membrane module, the concentration of the DS at its inlet (initial DS concentration) could determine the final feed concentrate and ultimately the feed recovery rates. If a very high initial DS concentration is used, the feed recovery rates will be proportionately higher. However, at very high recovery rates, the potential for scaling on the feed side will also increase because, it has been documented that scaling starts even before the feed concentrate reaches solubility limit (Meijer and Van Rosmalen, 1984; Zhao and Zou, 2011). If the recovery rate is high enough to reach the solubility limit of some of the salts present in the feed, scaling may have a detrimental impact on the water flux although this scaling is mainly expected to occur near the feed outlet (or DS inlet) region of the FO membrane module. Therefore, the initial DS concentration must be selected so that it does not promote scaling of the membrane that could have a negative impact on the overall performance of the FO desalination plant. The scaling would also be influenced by the type of ions present in the feed and their concentration.

What is therefore the best DS concentration to start with for the FO desalination? Figure 6.7 shows a hypothetical plot of the average water flux, pumping energy, feed recovery rates, membrane area required (for a fixed plant capacity) and pumping duration (for a fixed membrane area) of the FO desalination process as a function of DS concentration.

The water flux shows a logarithmic increase with the DS concentration. If a feed contains solutes that do not form precipitates or form scales, the water flux would be almost flat after reaching a certain concentration. However, if scaling precursors are present in the feed, the increased feed recovery rate at higher DS concentration would promote scaling and therefore reduction in the water flux. This fall in water flux is shown by dashed line in Figure 6.7. This DS concentration at which the feed starts to form scales and contribute towards flux reduction is assumed as the critical initial DS concentration for FO desalination to start with. If the initial DS concentration is higher than the critical concentration, the higher recovery rates would accelerate scaling. When this initial critical DS concentration is used, the membrane area must also be adequate so that the DS becomes diluted up to the point of osmotic equilibrium with the feed water so that the DS need not undergo further pumping for more dilution.



(a)



(b)

Figure 6. 6: Variation of the properties of the DS with its concentration (a) viscosity at different concentrations and (b) mass density at different DS concentrations.

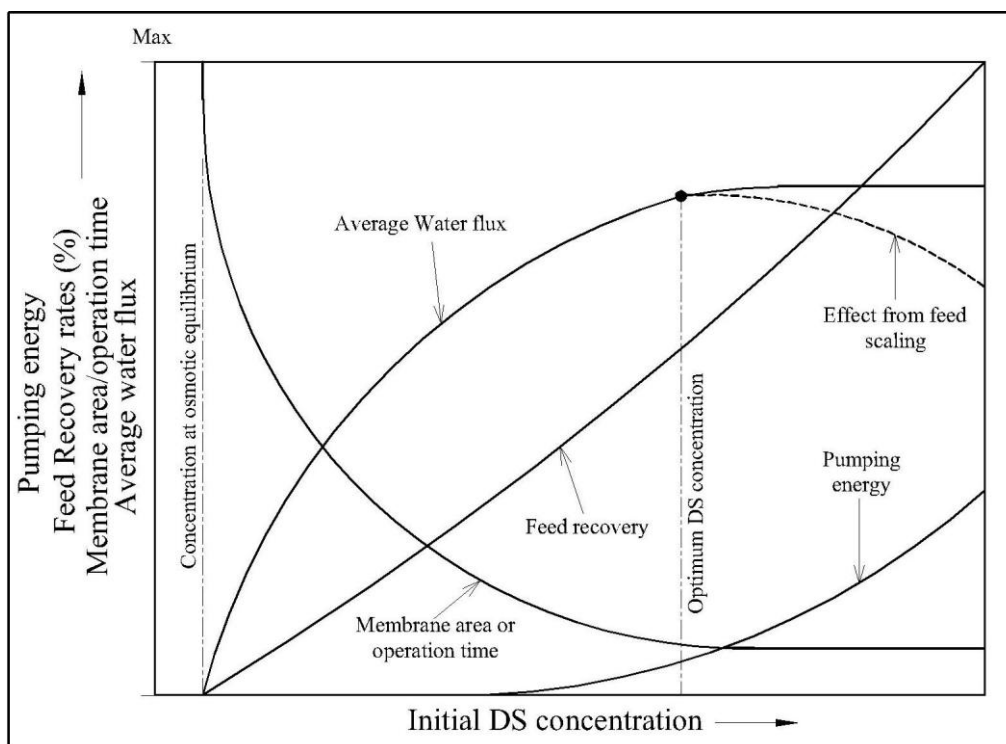


Figure 6. 7: Hypothetical correlation of water flux, feed recovery rates, membrane area and pumping duration with the initial DS concentration used in the FO desalination process.

6.5 Influence of feed solution concentration in the performance of the FO desalination process

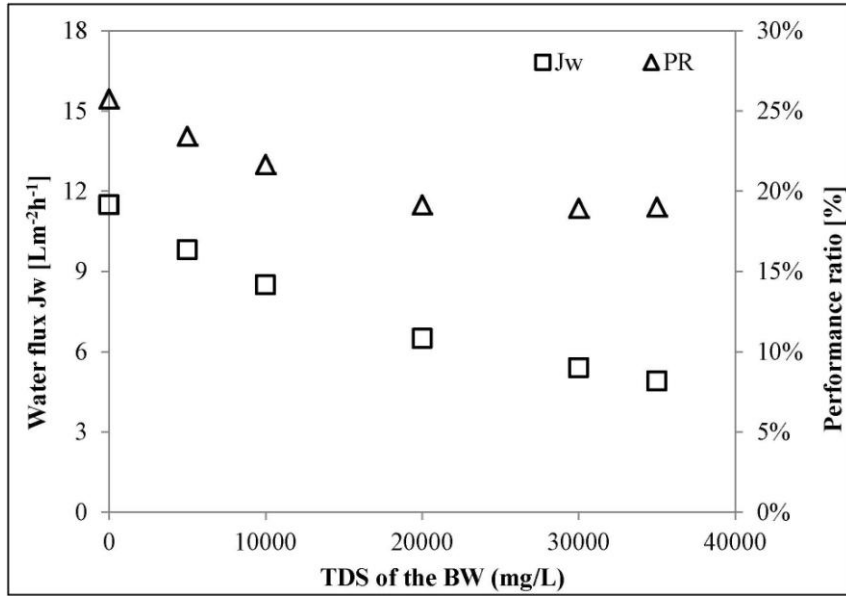
Feed solution (FS) properties play a significant role in the performance of the FO process just as they do in the RO process. While salinity concentration or the osmotic pressure of the FS directly influences the net osmotic pressure or the driving force, the presence of other solutes either in dissolved form or in suspended form could directly affect the performance of the FO process. In this particular study, however, only the influence of feed TDS has been considered. Four types of FS conditions were used that simulate brackish water to seawater quality (BW5, BW10, BW20 and BW35 corresponding to TDS of 5, 10, 20 and 35 g/L of NaCl respectively). FS TDS concentration can directly influence the net osmotic pressure or the driving force in the FO process (McCutcheon et al., 2006).

The influence of feed TDS on the performance of the FO process was studied using 1.0 M KCl as the DS with the CTA FO membrane and the results are presented in Figure 6.8. The water flux in the FO process shown in Figure 6.8(a), decreased with the

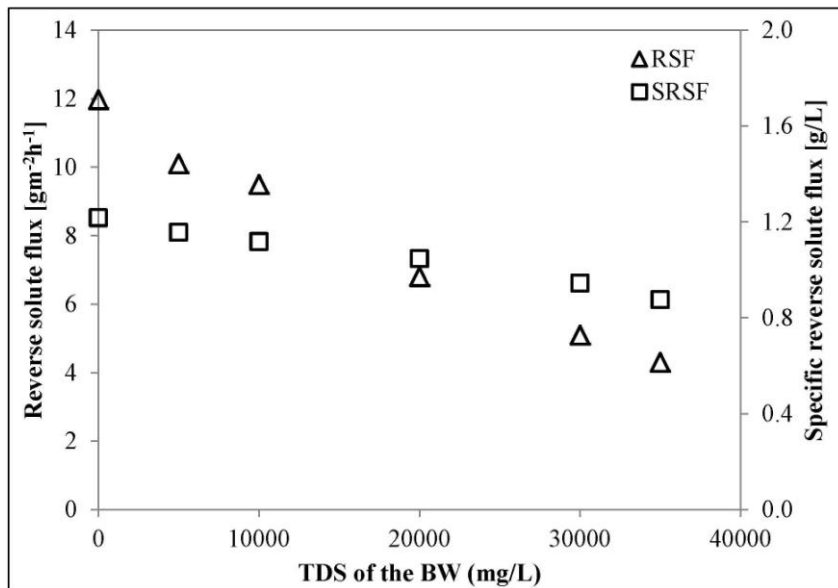
increase in feed TDS and this is expected because of the decrease in the net osmotic pressure. The DS concentration (osmotic pressure) was kept constant while the feed osmotic pressure increased at higher TDS concentration, thereby reducing the net driving force.

Although lower water flux is expected at higher feed TDS, the decrease in the PR with the increase in feed TDS up to about 20,000 mg/L is interesting. The PR of the FO flux by its definition does not depend on the net osmotic gradient but rather on the effective net osmotic gradient available for generating the water flux in the FO process. The decrease in the effective driving force in this particular situation is the sole function of the feed properties as the same DS condition is used for all the experiments. This in fact indicates that, the degree of concentrative ECP effects on the feed side is higher when higher TDS FS is used. This is probably because of the increase in the viscosity of the FS at higher TDS, which reduces the mass transfer coefficient for concentrative ECP but the influence of viscosity is not evident at higher feed as indicated by flattening of the PR plot in Figure 6.8(a). When a higher feed TDS, higher than 20,000 mg/L was used, the water flux does not decrease proportionately with the increase in feed TDS, which is also further supported by the flat PR plot. This shows that, the osmotic pressure of FS at higher TDS plays a less significant role in the performance of the FO process. This is probably because, at higher feed TDS, the water flux is lower and this lower flux in turn also reduces the severity of dilutive ICP which helps maintains similar water flux or PR when higher TDS feed is used. This finding has significant implication because it indicates that FO has a promising application for feed water containing high TDS or salt concentrations such as RO concentrate.

The influence of feed TDS on the reverse solute flux is shown in Figure 6.8(b). The RSF and SRSF decrease with the increase in feed TDS, indicating that the presence of different concentrations of feed solutes could influence the reverse diffusion of draw solutes. Eq. (6.6) indicates that the RSF is a function of the concentration gradient between the DS and the FS. Since the feed solute concentration increases at higher TDS, ΔC decreases and it is logical that the RSF and the SRSF decrease when higher TDS feed is used in FO process.



(a)



(b)

Figure 6. 8: Influence of FS TDS on the performances of the FO process using 1.0 M KCl as DS (a) in terms of water flux and the performance ratio and (b) in terms of reverse solute flux. Solutions temperature: 25°C, crossflow: 8.5 cm/s, Mode: FO and counter-current, Membrane: CTA FO.

6.6 Influence of operating parameters on the performance of the FO desalination process

Process parameters investigated include the influence of crossflow directions and crossflow velocity using KCl as DS and both DI and BW as feed with CTA FO

membrane. The results on the influence of crossflow rates are presented in Figure 6.9 while the influence of crossflow direction is presented in Figure 6.10.

6.6.1 Influence of crossflow rates on the performance of the FO process

Four different crossflows 100, 400, 800 and 1200 ml/min corresponding to crossflow velocities of 2.1, 8.5, 17.1 and 25.6 cm/s respectively (Reynolds number less than 2300 and therefore laminar flow), were used to study the influence of the crossflow rates on the water flux. The results in Figure 6.9 indicate that water flux increases when FO is operated at higher crossflow rates although the increase is logarithmic with optimum crossflow rate between 400 and 800 ml/min. Beyond this optimum crossflow rates, the influence of crossflow is insignificant and this was observed in other studies as well (Xu et al., 2010). This increase in water flux at higher crossflow rate is due to reduced concentrative ECP on the FS of the membrane since ICP is hardly affected by crossflows (FO operated under FO mode). This is evident from the fact that when DI is used as FS, there was no significant influence on the water flux as shown in the same Figure 6.9. In fact, the water flux with BW feed reaches almost close to water flux with DI water flux because of the significant reduction in ECP and also because the FO process was operated at very low recovery rates where influence of ECP is further reduced.

According to film theory, altering the solution flow rate changes the thickness of the mass transfer boundary layer at the surface of the membrane. At higher flow rates, the boundary layer is thinner, which results in higher rate of mass transfer and, consequently, reduced concentrative ECP (Wong et al., 2012). The permeate flux can be enhanced at higher crossflow rates however, the recovery rate has been observed to decrease at higher FS crossflow rates (Jung et al., 2011).

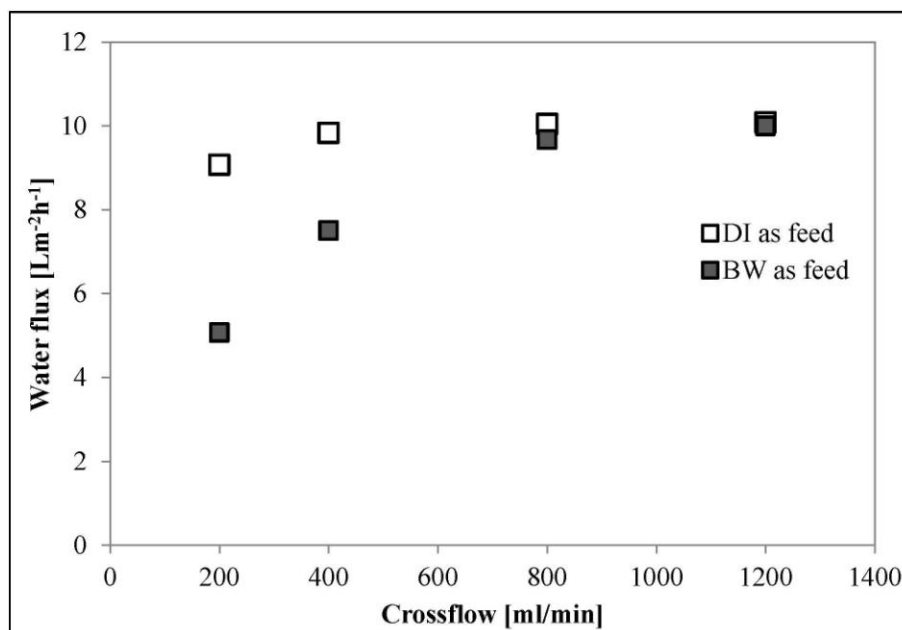


Figure 6. 9: Influence of crossflow rates on the performance of the FO process in terms of water flux using 1.0 M KCl as DS and BW5 and DI as FS. Solutions temperature: 25°C, Mode: FO and counter-current, Membrane: CTA FO

6.6.2 Influence of crossflow directions in the performance of the FO process

Since two independent solutions flow on either side of the membrane in FO process, the direction of crossflows can be maintained either in counter-current mode or in co-current mode. In counter-current mode, the DS and FS flow in opposite directions while in co-current mode, the DS and FS flow in the same direction. The influence of crossflow directions on the performance of FO process has been measured in terms of water flux and the experimental results are presented in Figure 6.10. No significant influence of crossflow directions was observed either using DI or BW as feed. Although, the water flux in co-current mode seemed consistent however, the flux is only slightly higher, less than 3% (except at 0.5 M KCl) which can be attributed to experimental errors. Other study have indicated no clear effect on the influence of crossflow direction in FO process (Jung et al., 2011) and this could perhaps be because most of the studies were conducted using smaller membrane cell.

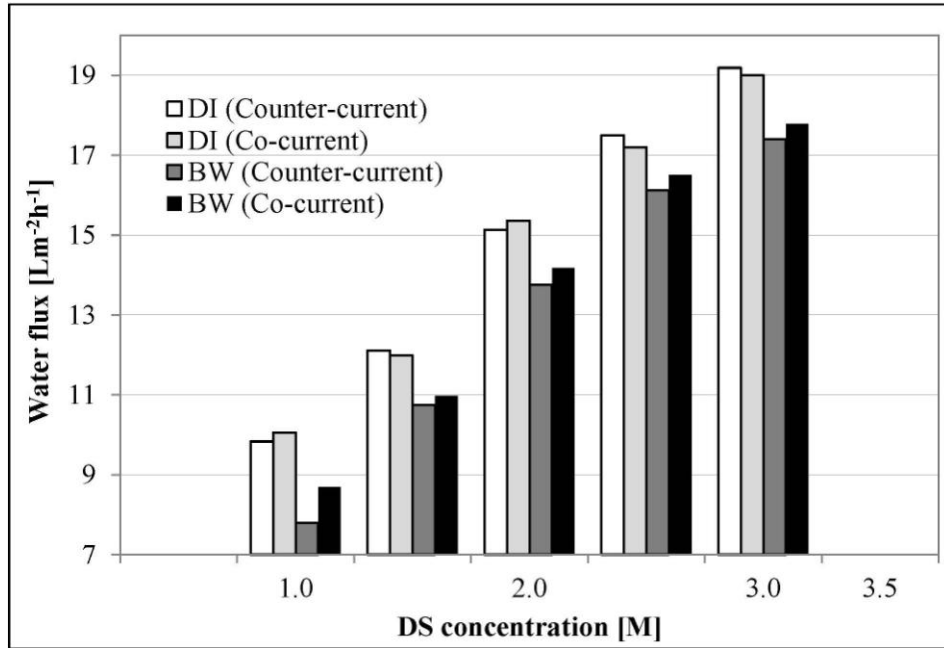


Figure 6. 10: Influence of crossflow directions on the performance of the FO process using KCl as DS. Solutions temperature: 25°C, crossflow: 8.5 cm/s, Mode: FO and counter-current, Membrane: CTA FO

6.7 Concluding remarks

In this study, the four major factors responsible for the performance of FO desalination process have been thoroughly investigated and their implications to the overall process discussed. The major factors assessed include membrane properties, DS properties, FS properties and finally the operating conditions. The influences of all these factors were measured in terms of water fluxes and the reverse diffusion of draw solutes. The following conclusions have been drawn from this particular study:

- A new and proprietary polyamide based TFC-FO membrane was introduced in this study and its performance compared with two commercial CTA-FO membrane and TFC-RO membrane. The performance of new TFC-FO membrane in terms of water flux and SRSF was significantly higher than CTA-FO membrane and TFC-RO membrane indicating that water flux can be significantly improved by modifying the structural properties of the membrane support layer. High performing membrane will have significant implications on the capital and operation cost of the desalination plant.
- Types of DS have more significant influence on the FO process than the osmotic pressure of the DS. Although adequate osmotic pressure of DS is desirable for FO

process, the influence of DS osmotic pressure was observed less significant at higher osmotic pressure and therefore selecting an optimum initial osmotic pressure may be essential for FO process to reduce pumping energy as pumping energy is affected by fluid density and viscosity. A critical DS concentration has been hypothesized based on the implications of DS concentrations on the capital and operational cost of the FO desalination plant. The initial DS concentration must be selected so that feed recovery is not too high that can accelerate scaling of membrane. At this point the total membrane area in the module must also be adequate so that the final diluted DS at the outlet reaches osmotic equilibrium with the incoming feed concentration.

- TDS of the feed plays a significant role in the performance of FO process however the influence of feed TDS was less significant for feed TDS higher than 20,000 mg/L indicating that FO has a promising potential for use with high TDS feed water. Although, water flux decreased at higher feed TDS, the RSF and SRSF is also lower at higher feed TDS. This is significant, as it would help reduce the loss of draw solutes and replenishment costs when high TDS feed such as seawater is used. However, this study did not account the influences of other feed properties such as the presence of fouling and scaling species and other physicochemical parameters.
- For operating parameters, the influence of crossflow velocity and the crossflow direction on the performance of FO process was investigated. The influence of crossflow velocity was effective only to certain extent beyond which the influence was not significant. The influence of crossflow direction on the FO water flux could not be clearly established in this study probably because of the limitation offered by the small cell dimension.
- This study indicates that, by optimizing the various parameters that relates to the membrane, FS and DS properties and the operating conditions, it is possible to improve the performance of FO desalination process.

CHAPTER 7



University of Technology Sydney

Faculty of Engineering & Information Technology

INFLUENCE OF TEMPERATURE ON THE PERFORMANCE OF THE FORWARD OSMOSIS DESALINATION PROCESS

7.1 Introduction

Several factors influence the performance of forward osmosis (FO) process and these factors relate to membrane properties, solution properties, the operating parameters, and all these factors have been covered in Chapter 6. Temperature plays a significant role in the performance of the pressure based membrane process such as reverse osmosis process (Traxler, 1928; Goosen et al., 2002; Agashichev and Lootahb, 2003). Likewise, temperature could play a significant role in the performance of the FO process as temperature has direct influence on the thermodynamic properties of the both the draw solution (DS) and the feed solution (FS). The influence of temperature on the rate of osmosis and dialysis has been recognised where increase in temperature increases the osmotic pressure of the solution (Traxler, 1928). RO permeate flux has been observed to enhance by up to 60% when feed temperature is increased from 20°C to 40°C. Temperature increase enhances permeate flux and recovery rates, and therefore reduces overall energy consumption in RO process (Goosen et al., 2002; Agashichev and Lootahb, 2003). Temperature influences the membrane permeability, osmotic pressure and the degree of concentration polarisation (CP) effects (Agashichev and Lootahb, 2003). Although energy is required to increase the temperature, it becomes handy especially where waste heat is readily available and can be suitably used to increase the water flux and recovery rates ultimately providing cost savings up to 15% of the RO desalination process (Agashichev and Lootahb, 2003).

This aim of this chapter is to evaluate the influence of temperature and the temperature difference between the DS and the FS in the performance of FO desalination process. Although a few studies have been reported on the influence of temperature in general FO process (Babu et al., 2006; Ng et al., 2006; Zhao and Zou, 2011), only the study by Cath et al. (2005) briefly covered on the influence of temperature difference and that too for osmotic distillation process. Therefore, to the best of the authors' knowledge, this study is the first one to observe the influence of temperature using temperature difference between the two solutions on the performance of the FO process. This is one reason why this study has been included as a separate chapter from Chapter 6. In addition to the performance of FO process, the study on the temperature difference is expected to provide additional information on the type of parameter and the extent of their influence on the performance of FO process. Although, operating the FO process

at higher temperature requires additional heat energy, operating FO desalination using temperature difference has advantages to elevate the temperature of only one of the solutions (e.g., only DS or FS) instead of heating both the solutions that require large amount of energy. This is because, the volume of concentrated DS is expected to be comparatively lower than feed volume in FO desalination process and therefore, it may be an effective way of enhancing FO performances with minimum energy input.

This chapter is an extension of the research article published by the author in the Journal of Membrane Science (Phuntsho et al., 2012c).

7.2 Theoretical

In order to understand the effect of temperature on the FO process performance, it is important to discuss briefly some of the underlying principles that govern the FO desalination process although some of them have already been included in the earlier chapters. When two solutions of different concentrations are separated by a semi-permeable membrane (that allows solvent to pass through and solutes to be retained), there is a thermodynamic tendency of the two solutions to become equal in concentrations. The solvent from the lower concentrated solution has a tendency to move through the membrane towards the higher concentrated solution, a phenomenon we know as osmosis. The following equations are worth mentioning again to show how the temperature could influence the performance of the FO desalination process.

The osmotic pressure (π) of the ideal dilute solution is given by Van't Hoff's (1887) equation shown below.

$$\pi = n C R T \quad (7.1)$$

Where n is the number of moles of solutes in the solution, C is the solute molar concentration, R is the gas constant ($R=0.0821$) and T is the absolute temperature of the solution. The standard water flux in FO process is given by the following equation (McCutcheon and Elimelech, 2006).

$$J_w = A \sigma [\pi_D - \pi_F] = A \sigma \Delta\pi \quad (7.2)$$

Where A is the pure water permeability coefficient of the membrane, σ is the reflection coefficient (usually considered unity for calculations assuming perfect barrier to solutes), π_D and π_F are the osmotic pressures of the DS and the FS respectively and the $\Delta\pi$ the net osmotic pressure (or net osmotic gradient). However, equation (7.2) is valid only for symmetric membrane. Equation (7.2) is modified below to take into account the influence of the asymmetric nature of the membrane and the phenomenon of dilutive internal concentration polarisation (ICP) and concentrative external concentration polarisation (ECP) for FO process operated in the FO mode (McCutcheon and Elimelech, 2006; McCutcheon and Elimelech, 2007; Tan and Ng, 2008).

$$J_w = A \left[\pi_{D,b} e^{(-J_w K)} - \pi_{F,b} e^{(J_w / k_F)} \right] \quad (7.3)$$

Where K is the solute resistance to diffusion within the membrane support layer and k_F is the mass transfer coefficient of the FS defined by the following equations:

$$K = \frac{t\tau}{D\varepsilon} = \frac{S}{D_D} \quad (7.4)$$

$$k_F = \frac{Sh D_F}{d_h} \quad (7.5)$$

Where t , τ and ε are the thickness, tortuosity and porosity of the membrane support layer respectively, D the diffusion coefficient of the feed/draw solute, S is the structural parameter of the membrane support layer, d_h the hydraulic diameter and Sh the Sherwood number given by the following relations:

$$Sh = 1.85 \left(\text{Re} \frac{\eta_F}{\rho_F D_F} \frac{d_h}{L} \right)^{0.33} \quad (\text{for laminar flow}) \quad (7.6)$$

$$Sh = 0.04 \text{Re} \left(\frac{\eta_F}{\rho_F D_F} \right)^{0.33} \quad (\text{for turbulent flow}) \quad (7.7)$$

Where Re is the Reynold's number, η_F the absolute viscosity of the FS, ρ_F the density of the FS and L the channel length.

Combining all the above equations, the flux in FO process can be presented as below:

$$J_w = AR \left[C_D T_D \exp\left(\frac{-J_w S}{D_D}\right) - C_F T_F \exp\left(\frac{J_w d_h}{Sh D_F}\right) \right] \quad (7.8)$$

The first term in equation (7.8) refers to the dilutive ICP that occurs within the membrane support layer facing the DS and the negative term indicates that the phenomenon is dilutive. The second term refers to the concentrative ECP that occurs on the external surface of the membrane active layer facing the FS. Dilutive CP phenomenon always occurs on the DS side of the membrane while concentrative CP always occurs on the FS side of the membrane. Whether the phenomenon is ICP or ECP will however depend on the membrane orientation as already discussed earlier in Chapter 6. For FO process with membrane support layer facing support layer (in FO mode of membrane orientation), the phenomenon is always dilutive ICP and concentrative ECP. Both ICP and ECP contribute towards reduced net driving force in FO process. It is apparent from the above equations that, the change in the temperature of the solutions could influence the water flux in FO process. Equation (7.8) also shows that, change in temperature of the FS may have minimal impact on the water flux because of the fact that $C_D \gg C_F$ even for a modest ECP modulus. This has led to our hypothesis in this study that, by simply elevating the DS temperature, the FO process should be able to achieve significantly improved performance.

7.3 Experimental

KCl solution of different concentrations were used as DS in all the experiments while FS consisted of either DI water or NaCl solution (5,000 g/L NaCl) representing model brackish BW. KCl was chosen as draw solute because its thermodynamic properties are well established (Harned and Cook, 1937; Hornibrook et al., 1942; Partanen and Covington, 2009) besides being used as fertiliser later in the other chapters. Detail method on the preparation of DS and FS can be found in Chapter 3.

The performances of the FO desalination process were measured in terms of water fluxes, reverse solute fluxes and the feed salt rejection rates. The experimental performance was carried out as per the procedures described in Chapter 3 thin FO membrane (HTI Inc. USA). The temperatures of the DS and FS were adjusted

separately using two separate temperature water bath controlled by separate heater/chiller as shown in Figure 7.1.

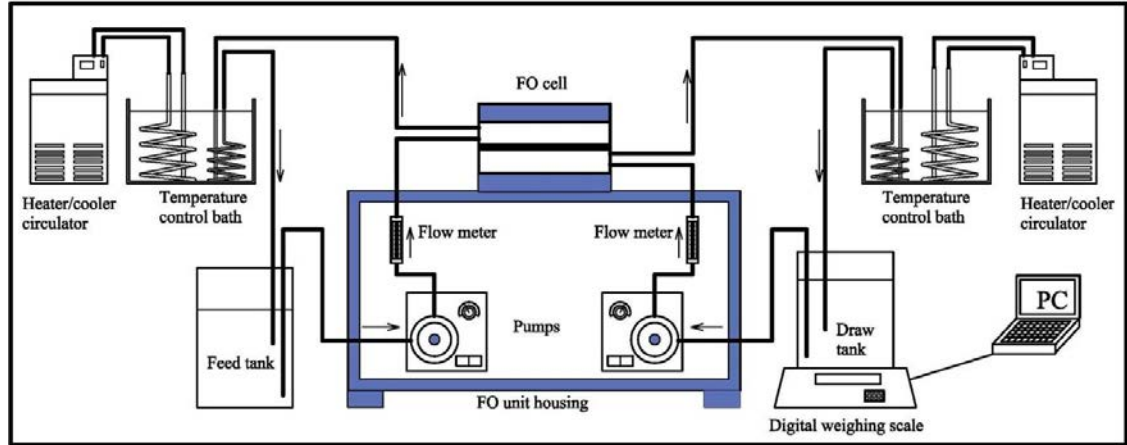


Figure 7.1: Schematic layout of the lab scale FO desalination unit for performance test. FO cell had an effective membrane area of $2.002 \times 10^{-3} \text{ m}^2$ (channel dimensions of 2.6 cm x 7.7 cm x 0.3 cm). All experiments were carried out at crossflow rate of 400 ml/min (8.5 cm/s) in counter-current mode for a minimum duration of six hours. Initial volume of DS and FS used were 2 litres in all the cases studied. Temperature of each solution was controlled independently using two different temperature control units.

7.4 Influence of temperature on the solution properties

As indicated by equations (7.1) to (7.7), temperature has a direct influence on the osmotic pressure of the solution and other thermodynamic properties such as diffusion coefficient, viscosity, etc ultimately affecting the FO water flux. Since FO process involves two independent feed streams on each side of the membrane, the influence of temperature on each solution may affect the FO process differently. The influence of temperature on the properties of DS and FS is discussed separately below.

7.4.1 Influence on DS properties and its potential implications

The influence of temperature on the thermodynamic properties such as osmotic pressure, diffusion coefficient and viscosity of KCl is first discussed. These properties were determined using OLI Stream Analyser 3.2. Figure 7.2 shows the osmotic pressure of KCl DS at 25°C, 35°C and 45°C and the percentage increases in osmotic pressure when the DS temperature is increased from 25°C to 35°C and 45°C. The increase in

osmotic pressure due to rise in temperature above 25°C varies from 2.9% to 3.1% at 35°C and 5.7 to 6.1% at 45°C indicating a just modest increase in osmotic pressure. The solubility of the KCl however increases substantially at higher temperature. An increase in osmotic pressure of the DS is expected to increase the net driving force and hence enhance the water flux during FO process.

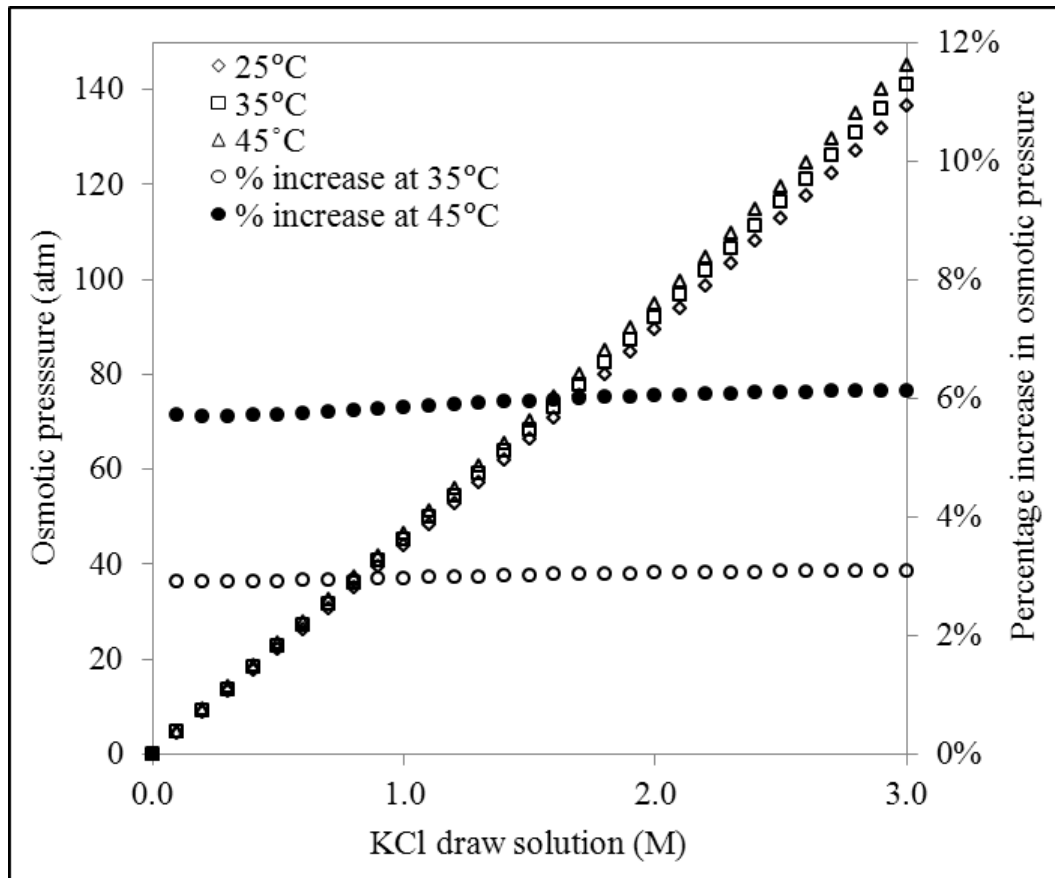


Figure 7.2: Osmotic pressure of KCl DS at different solution temperatures and the percentage increase in osmotic pressure when the DS temperature is raised from 25°C to 35°C and 45°C.

Figure 7.3 shows the variation of the viscosity of KCl DS with concentration at different temperatures and the percentage decrease in viscosity when the DS temperature is increased to 35°C and 45°C from 25°C. This figure shows that, the DS viscosity decreases between 19.2 and 15.6% when the DS temperature is increased from 25°C to 35°C and between 33.0% and 27.6% when increased from 25°C to 45°C, which indicates a substantial variation in comparison to the osmotic pressure in Figure 7.2. The viscosity indicated a non-linear relation with KCl concentration. It is hypothesised that lower viscosity of the DS may increase the rate of solution transport through the membrane support layer thereby reducing the ICP effects. A more viscous solute is

expected to have higher transport resistance within the membrane support layer thereby increasing the ICP effects.

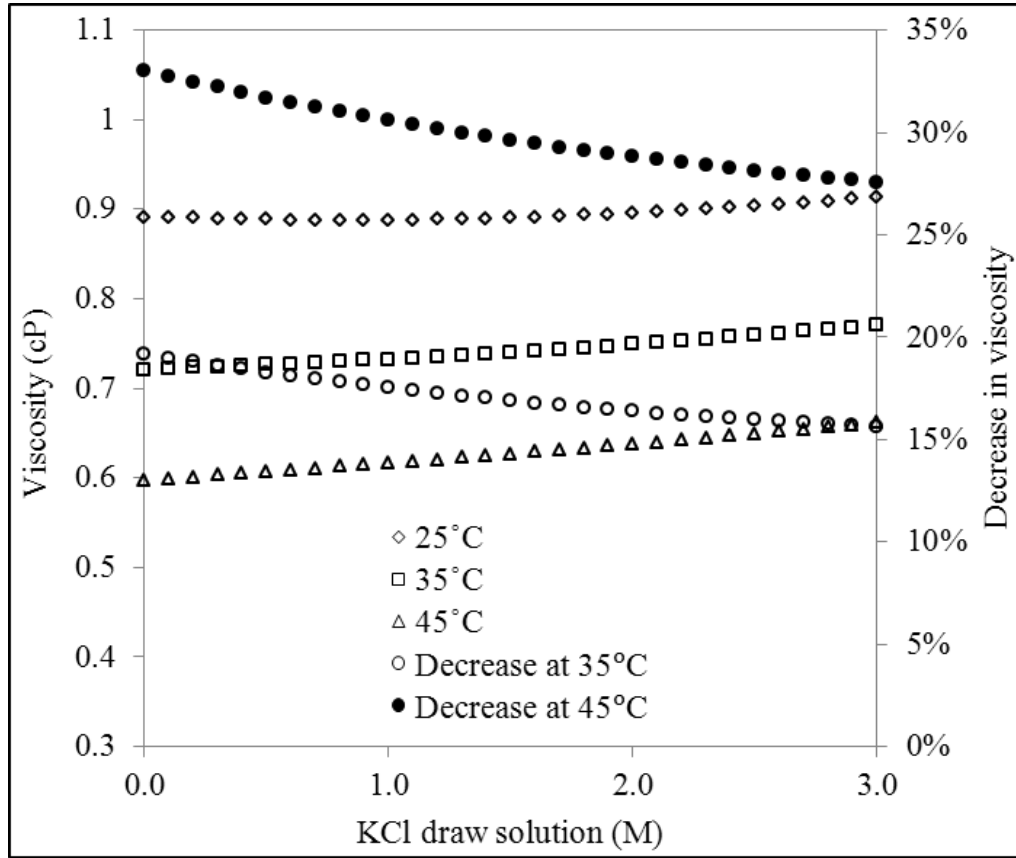


Figure 7.3: Viscosity of the KCl DS at different temperatures and the percentage decrease in viscosity when the DS temperature is raised from 25°C to 35°C and 45°C.

Figure 7.4 shows the variation of diffusion coefficient of KCl DS at different solution temperatures and the percentage increase in diffusion coefficients at elevated DS temperatures. The average diffusion coefficient (D_{ave}) of the KCl was calculated taking the individual diffusion coefficients of K^+ and Cl^- ions (from OLI Stream Analyser 3.2) using the following equation (Cussler, 2007; Tan and Ng, 2008).

$$D_{avg} = \frac{|Z_1| + |Z_2|}{(|Z_2|/D_1) + (|Z_1|/D_2)} \quad (7.9)$$

Where Z_i is the cation/anion charge of the ionic species and D_i is the individual diffusion coefficient of the cation/anion species in the water. The diffusion coefficient of KCl significantly increased at higher temperature varying from 24.4% to 25.6% when the DS temperature is increased from 25 at 35°C and from 51.6% to 54.0% when increased

to 45°C, an increase significantly higher than osmotic pressure (Figure 7.2) and viscosity (Figure 7.3) change. This increase in diffusion coefficient is expected to lower the solute resistivity within the membrane support layer ultimately reducing the ICP effects as indicated by equation (7.7). The diffusion coefficient of KCl is observed to be slightly non-linear with its concentration, gradually decreasing at lower concentration and then increasing gradually above 3.0 M concentration.

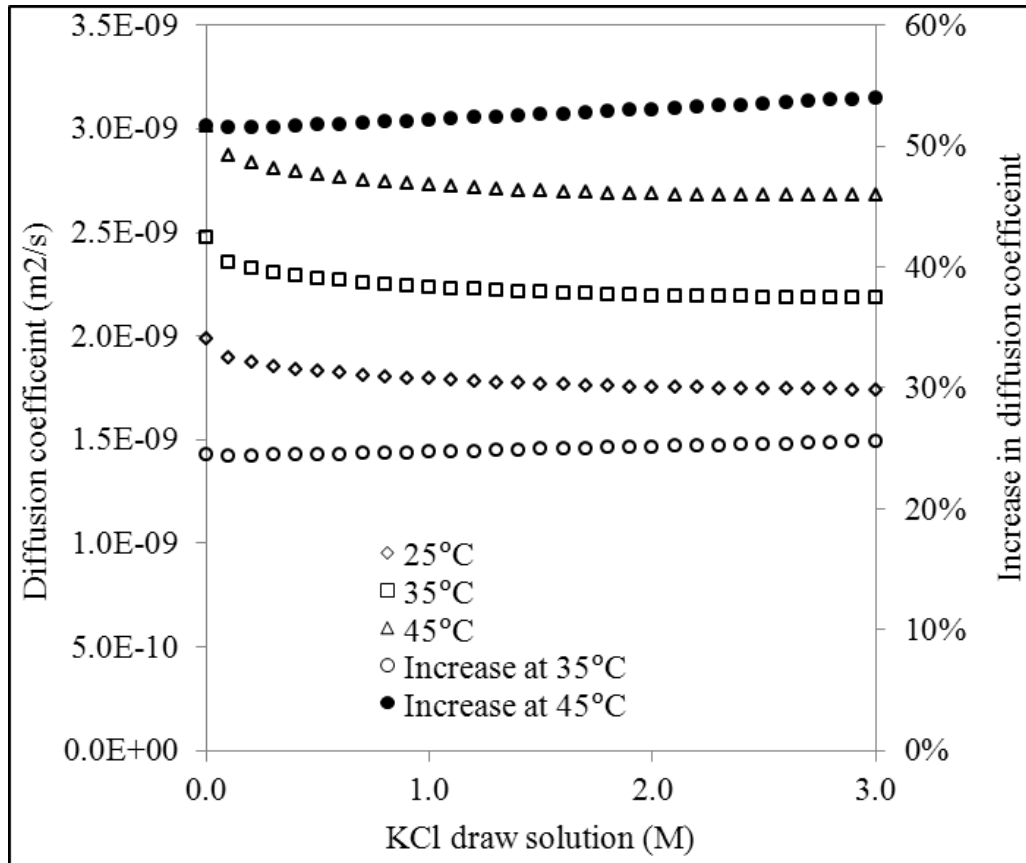


Figure 7.4: Diffusion coefficient of KCl DS at different solution temperature and the percentage increase in diffusion coefficient of KCl draw solute when the DS temperature is raised from 25°C to 35°C and 45°C.

7.4.2 Influence on FS properties and its potential implications

It is expected that, the temperature will have similar influence on the properties of the BW FS (5 g/L NaCl) like KCl DS. Table 7.1 shows some of the essential FS properties at three different temperatures. The osmotic pressure of the saline FS increased from 3.91 atm at 25°C to 4.02 and 4.13 atm at 35 °C and 45°C respectively, which is not a significant increase. The increase in osmotic pressure of the FS is of course undesirable since this will reduce the net osmotic pressure for driving the water in FO process.

However, the absolute viscosity (η) and the kinematic viscosity (ν) of the FS decrease with the increase in the temperature and this is likely to enhance the diffusivity of the water through the membrane thereby positively influencing the water flux. The diffusion coefficient (D) of the NaCl solute in the FS also increases with the increase in temperature. This in turn increases the mass transfer coefficient (k_F) of the feed reducing the ECP modulus of the feed (McCutcheon and Elimelech, 2006) as shown in Table 7.1.

Table 7.1: Thermodynamic properties of BW FS at various temperatures. The average diffusion coefficient of NaCl was calculated using equation 7.9 by taking the individual diffusion coefficients of Na^+ and Cl^- ions (from OLI Stream Analyser 3.2). All parameters determined using OLI Stream Analyser 3.2 except for *(Korson et al., 1969). Mass transfer coefficient was calculated using equation (7.5).

Properties of the 5 g/L NaCl FS	25°C	35°C	45°C
Osmotic pressure π atm	3.91	4.02	4.13
Absolute viscosity η cP	0.8982	0.7268	0.6026
Feed solution density kg/m^3	1000.39	997.27	993.50
Kinematic viscosity $\nu \times 10^{-7} \text{ m}^2/\text{s}$	8.9780	7.2875	6.0656
NaCl diffusion coefficient $D \times 10^{-9} \text{ m}^2/\text{s}$	1.5345	1.9306	2.3723
Mass transfer coefficient $k \times 10^{-5} \text{ m/s}$	1.4070	1.6410	1.8839
Absolute viscosity of pure water η_o cP	0.8903*	0.7195*	0.5963*

7.4.3 Influence of the temperature difference on the net bulk osmotic pressure

Instead of increasing the temperature of both the DS and FS, the effects of the temperature difference (heat only one of the solutions instead of both) were investigated. It is well established that the viscosity of the solution decreases with the increase in temperature while the diffusion coefficient of the solutes and the water molecules increases with the increase in temperature. While the temperature decreases the solution viscosity and increases the diffusion coefficients of both the DS and FS, the increase in osmotic pressure of the FS at higher temperature also contributes to decreased net osmotic pressure across the membrane, which is not desirable. However, this increase is not significant given the high osmotic pressure of the DS in comparison to FS. The mass transfer coefficient of the FS increases and this might likely offset the slight reduction in the net osmotic pressure due to increased osmotic pressure of the FS.

Figure 7.5 shows the net bulk osmotic pressure at various temperatures of the DS and FS. When the temperature of both the DS and the FS is increased from 25°C to 35°C and 45°C, the net osmotic pressure also increases as expected from 85.4 atm to 88.1 and 90.6 atm, respectively. This increased net osmotic pressure indicates that, higher driving force is available which can enhance the water flux through the FO membrane.

However, if a temperature difference is generated by heating only one of the solutions say DS to 35°C or 45°C, and keeping the FS temperature unchanged at 25°C, similar net bulk osmotic pressure was observed to heating both the DS and FS. In fact, a slightly higher net osmotic pressure was observed when only DS was heated rather than heating both or only FS. These show that, similar net osmotic pressure can be achieved by simply increasing the temperature of the DS or FS only instead of increasing the temperature of both FS and DS. This is important because, the total volume of DS to be heated is significantly lower than the total volume of the FS and therefore will require less amount of heat energy to enhance water flux in FO process.

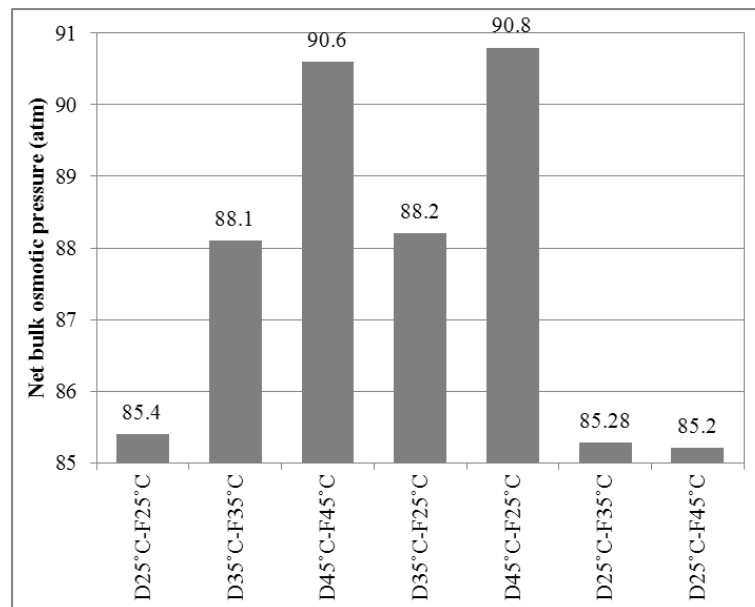


Figure 7.5: Net bulk osmotic pressure between the DS and FS at different temperatures of DS and FS. D refers to DS and F refers to FS. The data refers for DS of 2 M KCl and BW FS 5 g/L NaCl

7.5 Influence of temperature on the performance of FO process

FO experiments were conducted under isothermal conditions for DS and FS at 25°C, 35°C and 45°C. Figure 7.6 shows the influence of temperature on the pure water flux

(using DI water as feed) and water flux (using BW or 5 g/L NaCl as FS) of the FO process at various DS concentrations. It is clear from the figures that, the temperature has a significant influence on the water flux. Water flux improved significantly when the temperature of both the solutions was increased from 25°C to 35°C and 45°C. The increase of water flux is evident at all the DS concentrations tested. When the operating temperature of both the solutions was increased to 35°C from 25°C, the water flux increased between 6% and 17% (average 10.9%) using DI FS and between 3% and 23% (average 12.3%) using BW FS. The increase was observed between 37% and 42% (average 40.1%) using DI FS and between 26% and 63% (average 45.4%) using BW FS when the operating temperature is increased to 45°C. This is a substantial increase in water flux when the FO process is operated at higher temperatures. This enhanced flux at higher temperature could be a result of alteration of the thermodynamic properties of the solutions (assuming that the membrane properties are not affected significantly) such as osmotic pressure, viscosity and the diffusivity. Enhanced water fluxes have been reported in many other studies both for FO process (Ng et al., 2006; Zhao and Zou, 2011) and the reverse osmosis process (Agashichev and Lootahb, 2003; Babu et al., 2006). In many studies, enhanced water flux at higher temperature has been mainly thought to be caused due to decreased water viscosity which enhances the self-diffusivity of water and therefore mass transfer coefficient of the FS and also due to decreased CP effects (McCutcheon and Elimelech, 2006; Jawor and Hoek, 2009; Zhao and Zou, 2011). The results in Figure 7.6 however do not indicate which parameters are more or less responsible for increased flux at higher temperature.

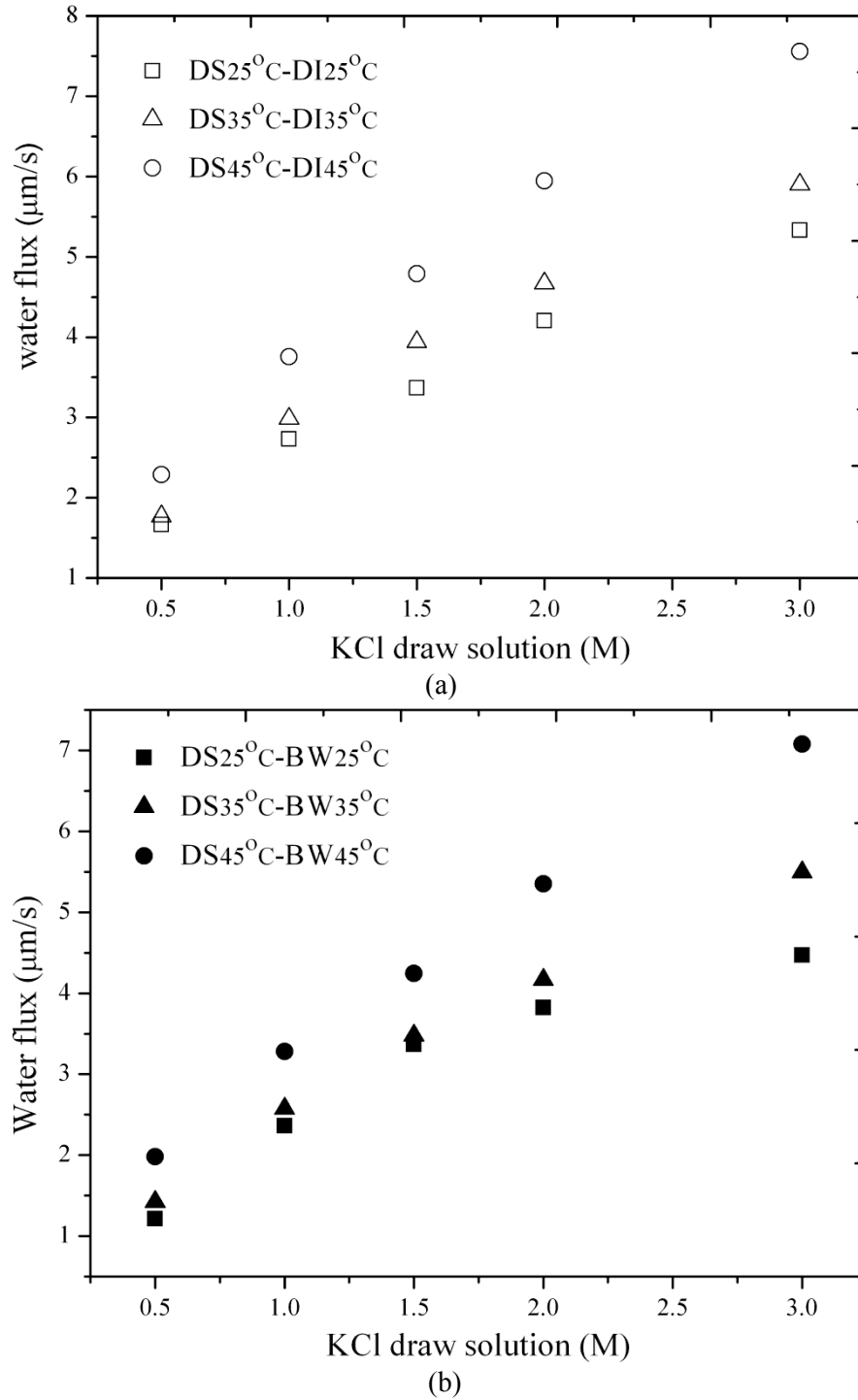


Figure 7.6: Variation of FO water fluxes with temperature using (a) DI water as FS and (b) BW as FS. In order to check the reliability of the data, each experiment was repeated and found that the flux data was within an experimental error of 1-5% only.

One of the interesting observations from Figure 7.6 is that, the slopes of the flux versus concentration curves varied for FO process operated at different temperatures using both DI and NaCl solution. This indicates that, the increase in water flux at higher temperature varies with DS concentrations. In order to determine the exact trend on how the temperature increase influences the water flux at different concentrations, the

percentage increase in water flux due to unit temperature rise was calculated and presented in Figure 7.7 for both DI FS and BW FS.

The first observation from Figure 7.7 is that, for every degree rise in temperature above 25°C, the average percentage gain in water flux is significantly higher at 45°C than at 35°C and this was true with both DI water and NaCl solution as FS. For example, for DI water as FS (Figure 7.7a), the water flux increased on average 1.1% for every degree rise in temperature from 25°C to 35°C. However, when the temperature was raised from 25°C to 45°C, the water flux increased on average 2.0% for every degree rise in temperature from 25°C to 45°C, which is twice as high as the flux increase at 35°C. A similar observation was made when BW FS was used (Figure 7.7b) although this increase was slightly higher. The water flux increased on average 2.3% for every degree rise in temperature from 25°C to 45°C while this average increase was only 1.2% for every degree rise in temperature from 25°C to 35°C.

These results indicate that, FO process conducted at 45°C will be able to gain much higher water flux per unit heat energy input than FO process operated at 35°C. However, higher water flux could also be a result of change in membrane properties besides solution properties. Goosen et al. (2002) observed up to 100% difference in pure water flux for polymeric membranes operated at 30°C and 40°C due to changes in the physical properties of the membrane such as pore sizes. No adverse change in membrane properties was observed in this study as discussed later under the section on reverse solute flux and salt rejection.

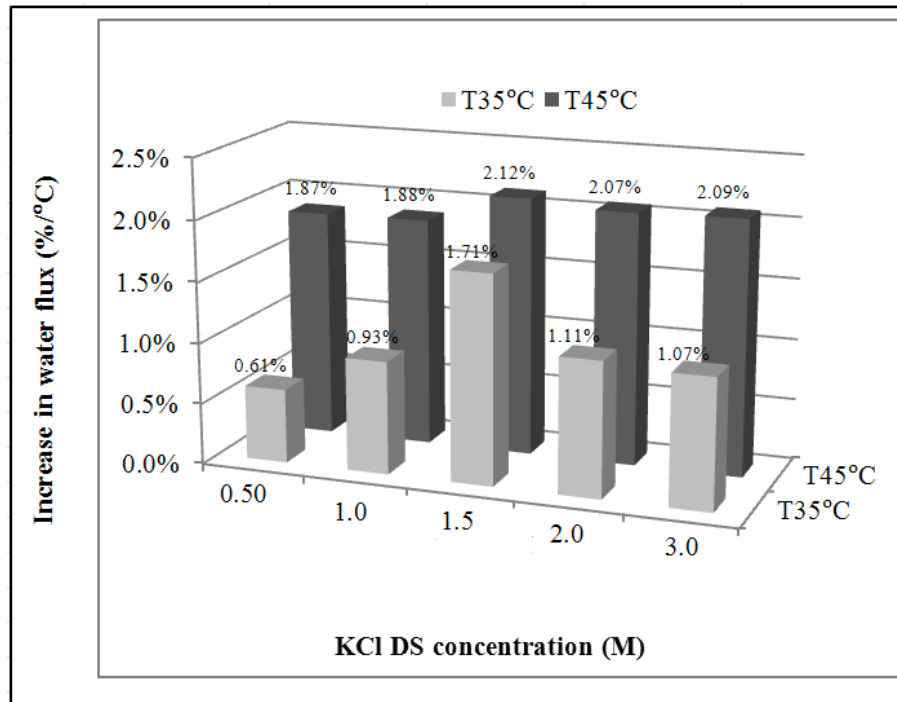
The next observation from Figure 7.7 is the influence of temperature on the percentage of water flux increase per unit rise in temperature that varies with DS concentration. The results indicate a modal distribution depicting upper critical points with DI water as feed and lower critical points with BW as FS. When DI is used as FS (Figure 7.7a), the percentage increase in water flux per unit rise in temperature gradually increases at lower concentration peaking at about 1.5 M DS concentration (upper critical point). However, when BW was used as FS, the percentage increase in water flux per unit rise in temperature showed an opposite trend than DI water as FS (Figure 7.7b). The percentage increase in water flux decreases initially with DS concentration up to 1.5 M and, gradually increasing above 1.5 M concentration (lower critical point). Combining

Figure 7.7a and Figure 7.7b reveals a hysteresis effect, a similar observations made by McCutcheon and Elimelech (2006). These results indicate that temperature plays a positive role in reducing the coupled effects of ICP and ECP at higher DS concentration.

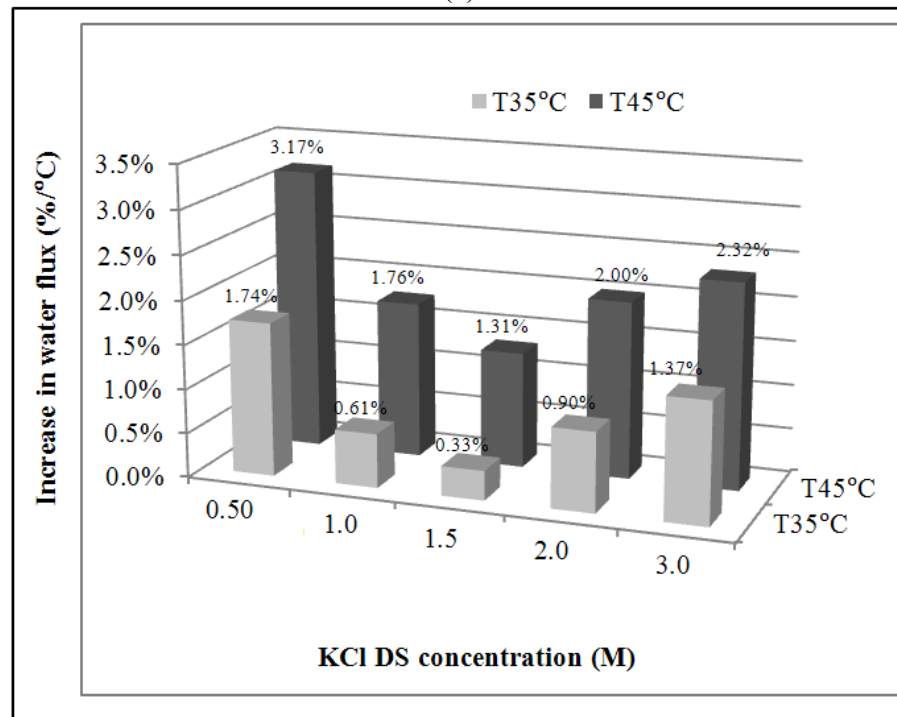
The difference in trend between the DI water and BW as FS that shows hysteresis effect can be explained as follows. When DI is used as FS, the flux in FO process is affected by only dilutive ICP (support layer DS) but when BW is used, the water flux is affected by both dilutive ICP and concentrative ECP (active layer facing FS). The results in Figure 7.7(b) may appear that, concentrative ECP plays an important role in lowering the water flux at lower DS concentrations but this effect is noticeable only up to DS concentration of 1.5 M. When BW is used, a concentrative ECP occurs on the FS side of the membrane in addition to dilutive ICP on the DS side and this is the reason why a decrease in water flux is observed at lower concentration up to 1.5 M. In addition, the decrease could also be partly contributed (although comparatively lower) by the slightly enhanced osmotic pressure of the FS at higher temperature. However, at higher DS concentrations, beyond 1.5 M, percentage gain in water flux increases when the solution temperature is increased. This indicates that, temperature reduces the severity of concentrative ECP on the water flux. This is supported by the fact that, at higher temperatures, the mass transfer coefficient k of the FS increases by 17% at 35°C and 34% at 45°C (Table 7.1) and this contributes to significant reduction in concentrative ECP and ultimately enhanced water flux.

The difference between the average total percentage gain in water fluxes for DI FS and BW FS was only 1.5% at 35°C and 5.3% at 45°C and this further supports that, concentrative ECP plays a much lower role in reducing flux for FO process operated at higher temperatures. It is accurate to assume that the effect of temperature on the DS properties using both DI as FS (Figure 7.7a) and BW as FS (Figure 7.7b) are similar. However, the slightly higher average percentage gain in water flux observed using BW FS than DI FS can be attributed to reduction in ECP (enhanced mass transfer coefficient) and increased diffusivity of water at lower viscosity at higher temperature. When DI water is used as feed, the increase in water flux is contributed only by the reduced viscosity and not by increased transfer coefficient due to absence of solutes in DI feed. These results have significant implications in the performance of the FO

process at elevated temperature in the real applications where the DS concentration decreases and feed concentration increases along the length of the membrane module.



(a)



(a)

Figure 7.7: Percentage increase in pure water flux per unit temperature rise for each range of KCl DS concentrations using (a) DI water as FS and, (b) BW as FS. Baseline temperature at 25°C. In order to check the reliability of the data, each experiment was repeated and found that the flux data was within an experimental error of 1-5% only

Operating the membranes at high pressure and temperature conditions can increase the flux rates however, such conditions also accelerate membrane deterioration and therefore must choose appropriate conditions (Dale and Okos, 1983). The FO membrane must be thermally stable while operating up to 45°C. The change in solute rejection properties of a polymeric membrane is one way of studying the thermal stability of the membrane (Wei et al., 2005). Two types of solute rejections occur in FO process and that includes rejection of draw solutes measured in terms of reverse diffusion of draw solutes or reverse solute flux (RSF) and forward rejection of feed (NaCl) solutes. The RSF, specific reverse solute flux (SRSF) and the feed solute rejection are presented in Figure 7.8 using both DI water and BW as FS for FO process operated at different temperatures. RSF is the measure of the amount of draw solute that diffuses through the membrane towards the FS per unit area of membrane in a unit time. Specific reverse solute flux (SRSF) is the ratio of the reverse solute flux to the water flux (J_s/J_w) and it indicates the amount of draw solute lost by reverse diffusion or permeation through the membrane towards the feed water during the FO process.

The RSF in Figure 7.8a and 7.8b increases with the increase in DS concentration. The model for RSF is discussed in Chapter 2. RSF is a function of the DS concentration, and the membrane structural and solute rejection properties. The results in Figure 7.8a and Figure 7.8b show that the RSF decreases when the solution temperature is increased from 25°C to 35°C however, it increases slightly when the temperature is further increased to 45°C. The decrease in RSF at 35°C is little surprising but can be explained as follows. When the temperature is increased to 35°C, the DS viscosity decreases (Figure 7.3) and the diffusion coefficient of KCl increases (Figure 7.4). This will likely decrease the resistivity to solute diffusion within the support layer thereby enhancing the back diffusivity of the draw solutes from the membrane rejection surface and likely causing a decreased permeation of the draw solute towards the feed. However, further increase in solute diffusivity of KCl at 45°C causes a slightly enhanced reverse diffusion of draw solutes towards the feed although the RSF at 45°C still remain lower than the RSF at 25°C. This increase in SRSF could also be due to slight change in the permeability of the polymer membrane at 45°C as evident from the high percentage of increase in water flux per unit rise in temperature observed at 45°C in Figure 7.7 earlier. However, further investigation is required to identify the relevant transport phenomena

in terms of membrane characteristics, which was not included within the scope of this study and hence recommended for future studies.

Figure 7.8c and Figure 7.8d shows that, the average SRSF of 20.4 g/L at 25°C decreases to 11.0 g/L at 35°C and 14.7 g/L at 45°C using DI FS. Similarly, the average SRSF of 18.6 g/L at 25°C decreases to 7.7 g/L at 35°C and 11.9 at 45°C using BW FS. This decrease is due to enhanced water flux at higher temperature. This is similar to the dilution phenomenon in the pressure-based filtration processes where higher salt rejection is observed when operated at higher water fluxes or operating pressures (McCutcheon et al., 2006). The SRSF at 45°C is slightly higher because of the increased permeability of the draw solutes at higher temperature. Although, a similar trend is expected from the forward rejection of the feed solute (NaCl) at 35°C and 45°C in Figure 7.9 due to slightly enhanced solute permeability however, the NaCl rejection marginally increased at higher temperature. The average rejection increased from 92.5% at 25°C to 93.6% at 35°C and 94.7% at 45°C. Besides the dilution effect from the enhanced water flux at higher temperature, the increase feed NaCl rejection could also be because of the ionic interactions in the ternary system due to the presence of common anion (Cl⁻) on both sides of the membranes. The presence of concentrated ions in the DS affects the flux of feed ions with the effect higher at higher DS concentrations (Hancock et al., 2011). This ionic interaction effects probably overshadows the decrease in NaCl rejection that is expected due to slight change in the membrane solute permeability as observed with draw solute flux. Other studies have noted a decrease in the solute rejection in RO process at higher temperature (Agashichev and Lootahb, 2003; Jin et al., 2009).

Another important observation from the study on the reverse draw solute flux is the different between the RSF and SRSF using DI water FS and BW FS. The RSF and the average SRSF shown in Figure 7.8 is consistently lower when the BW is used as feed than DI as FS. This also results in lower SRSF for FO process operated at 45°C. This indicates that the presence of solutes in the feed could reduce the RSF in the FO process. This is significant especially if high salinity water is used as a source of feed for FO desalination process. These results indicate that, operating FO process at elevated temperature of up to 45°C, does not lead to increased transport of solutes

indicating that this CTA FO membrane is thermally stable up to the temperature tested in this study.

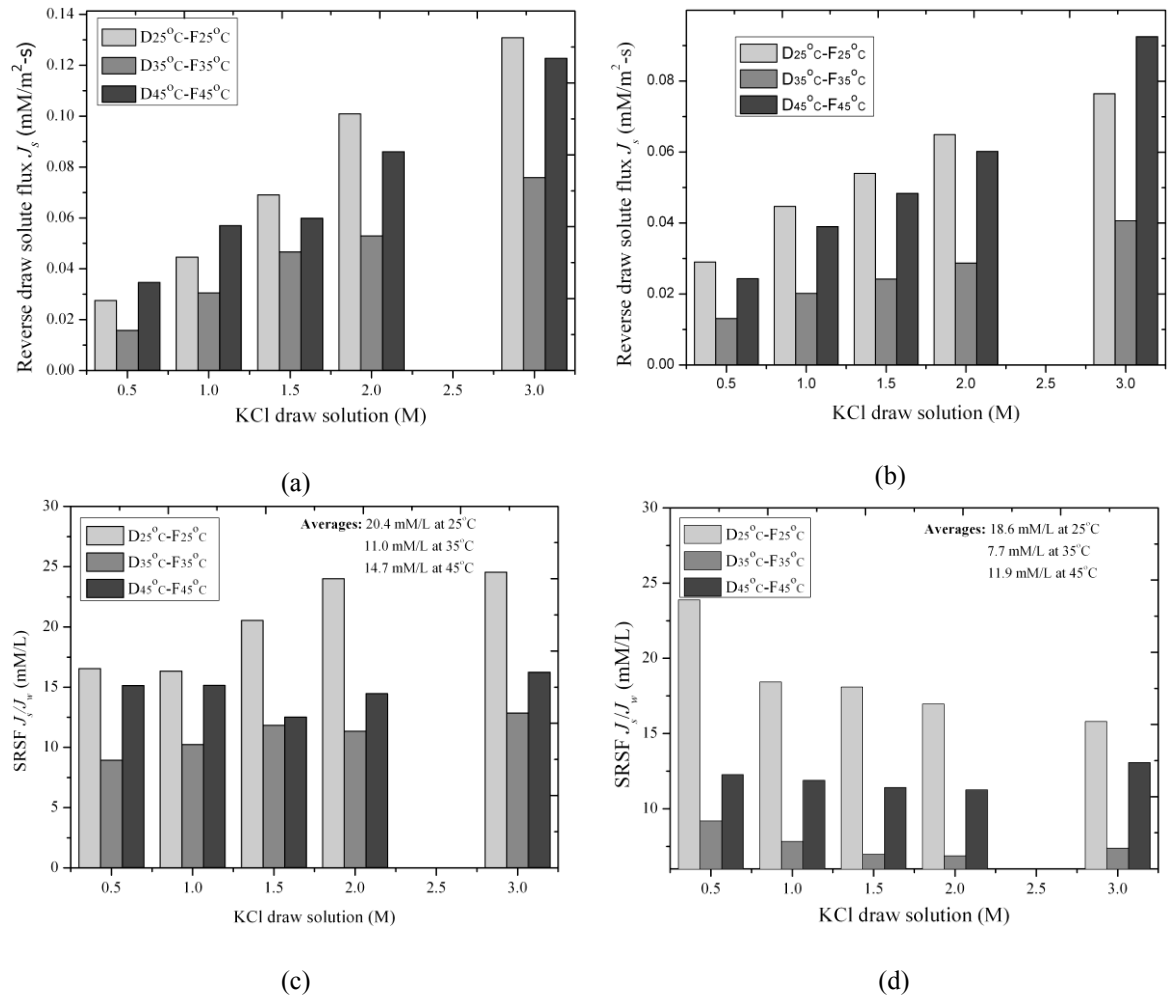


Figure 7.8: Solute rejections of the membrane (a) RSF using DI as FS, (b) RSF with BW as FS, (c) SRSF with DI as FS and (d) SRSF with BW as FS.

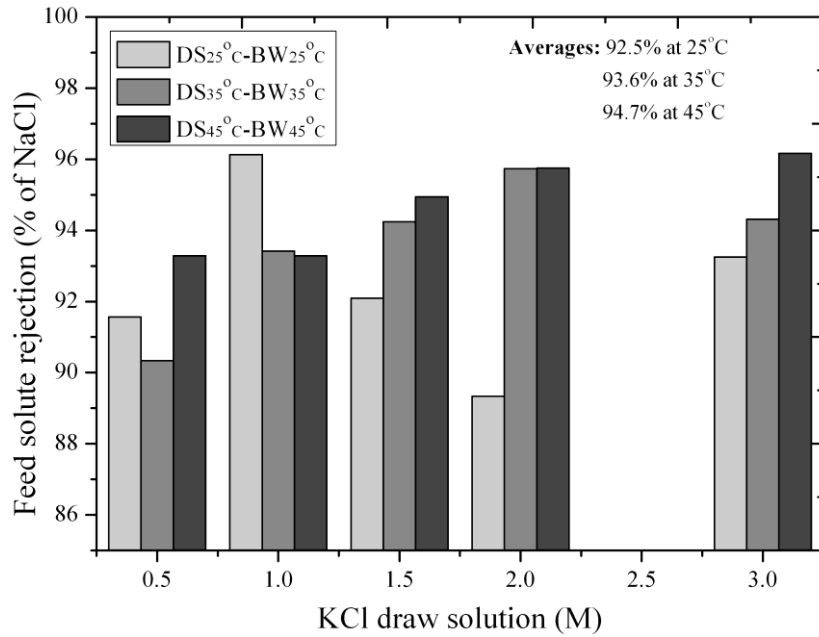


Figure 7.9: Forward rejection of BW feed solutes (NaCl) for FO process operated at different concentrations and temperatures. The initial feed concentration used is 5,000 mg/L.

7.6 Influence of temperature difference on the performance of FO process

Temperature difference was created between the DS and FS by elevating the temperature of one of the solutions while keeping the temperature of the other solution at baseline (25°C). Temperature difference is applied in the membrane distillation process (Schofield et al., 1990; Lawson and Lloyd, 1996) and also in forward osmosis/osmotic distillation process to enhance the water flux (Cath et al., 2005).

Figure 7.10 shows the water flux when the FO is operated at different temperature conditions. These results indicate that, maintaining temperature difference between DS and FS can also significantly influence the performance of FO process. The performances of FO process improved when the temperature of one of the solutions was heated by creating a temperature difference. The results in Figure 7.10 have been converted into total percentage gain in water flux when the temperature of the solution/solutions is increased and presented in Figure 7.11 while the average gain in water flux is summarised in Table 7.2 for all temperature combinations. Unlike the results in Figure 7.7, the flux gain in Figure 7.11 in this case is shown in total percentage gain instead of percentage flux gain per unit temperature since the increase with temperature difference pertains to temperature increase for only one of the solutions.

When the temperature difference is maintained by elevating the temperature of the DS to 35°C and keeping the FS temperature at 25°C, the average total increase in water flux was 4.1% with DI FS and 6.6% with BW FS. Likewise, when only the DS temperature is elevated to 45°C, the average total flux gain was 14.8% with DI FS and 21.4% with BWFS. This average gain in water flux is no doubt, lower than the total gain achieved when the FO process was operated at elevated isothermal conditions of 35°C or 45°C.

When the temperature of DS is only elevated to say 45°C, the average total water flux increase of 14.8% with DI FS and 21.4% with BW FS is solely due to change in the thermodynamic properties of the DS since the thermodynamic property of the FS remains same. Given only the slight increase in osmotic pressure at elevated temperatures (Figure 7.2), the change in DS viscosity (Figure 7.3) and diffusion coefficient of KCl (Figure 7.4) must be primarily responsible for enhancing the water flux by reducing ICP effects as indicated by equation (7.7). However, this percentage increase in water flux is far lower than the average total water flux increase of 40.1% with DI FS and 45.4% with BW FS achieved when both the solutions are operated at 45°C. This appears to indicate that, an additional increase in water fluxes of up to 25.3% and 24.4% must therefore come from the change in the thermodynamic properties of the DI FS and BW FS alone respectively, at elevated temperature of 45°C. This expected contribution from the change in the thermodynamic properties of FS is significantly high, even higher than the actual contribution from the thermodynamic properties of the DS alone.

If the influence of temperature on the thermodynamic properties of the FS is equally or even more important than DS, a proportionate gain in water flux must therefore be achieved when the temperature of the FS is only elevated but the results in Table 7.2 indicate otherwise. The average total gain in water flux when FS temperature is elevated to 45°C is only about 11.8% with DI FS and 14.6% with BW FS, which is comparatively lower than the required increase of 25.3% and 24.4% respectively. In fact, this average total percentage gain in water flux is even lower than the average total water flux gain when the FO is operated at elevated DS temperature only or elevated isothermal conditions at 45°C. Several interesting observations are made from the study.

A change in thermodynamic properties of DS alone contributes on average 21.4% of flux increase, while change in the thermodynamic properties of the BW FS alone contributes on average 14.6% with an expected combined average contribution of 36%. This indicates that, by elevating the temperature of the DS only (instead of FS only), FO process can gain water flux about half of what it can gain by increasing the temperature of both the FS and DS and substantially reduce heat energy required to raise the temperature of both the solutions. These results also indicate that, the thermodynamic properties of the DS play a more influential role on the water flux in FO process than the thermodynamic properties of the FS at higher temperature. The higher water fluxes gained while elevating the DS temperature (facing support layer) instead of FS (facing active layer) is also an indication that, dilutive ICP plays a more significant role than concentrative ECP in inhibiting the FO process performance. ICP is reduced when the DS temperature is increased while the concentrative ECP does not affect significantly as observed earlier. The combined contributions of DS alone and BW FS alone of 36% is still lower than 45.4% for FO process operated at 45°C isothermal conditions, indicating that an average increase of additional 9.4% is probably due to synergetic effects of raising the temperature of both the DS and FS.

When the temperature of DI FS is only elevated to 45°C, the average flux gain of 11.8% can be considered as solely due to decrease in the viscosity of the DI FS in the absence of ECP effects. This same average flux gain is 14.6% when BW is used as FS, which is a gain due to reduced ECP in addition to the change in the DS viscosity. Subtracting the lone effect of viscosity (11.8%), only 2.8% of the average flux increase appears to be caused due to increased mass transfer coefficient of the BW FS indicating that, for the BW FS, viscosity plays a significant role in enhancing water flux at higher temperature. This also indicates that, the influence on water flux due to slight increase in osmotic pressure of BW FS at higher temperature is overshadowed effects due to viscosity change. However, these results cannot clearly identify which thermodynamic parameter of the DS is more influential in increasing the water flux.

Also, notice the difference between the average flux gain at 35°C and 45°C per unit temperature rise (Table 7.2) in presence of temperature difference. The average flux gain per unit rise in DS temperature is twice or more as high as the average flux gain per unit rise in FS temperature. Combining plots in Figure 7.11a and Figure 7.11b also

exhibited a hysteric effect, similar to the one observed earlier in Figure 7.7. This indicates the gradual effect of concentrative ECP on the water flux in the presence dilutive ICP effects. However, by observing the average gain in water flux at different DS concentrations (Table 7.2), the influence on concentrative ECP in Figure 7.11 should not be significant. When FO was operated at temperature difference, it was often found difficult to stabilise the flux and this is perhaps the reason for negative flux gain observed in Figure 7.11.

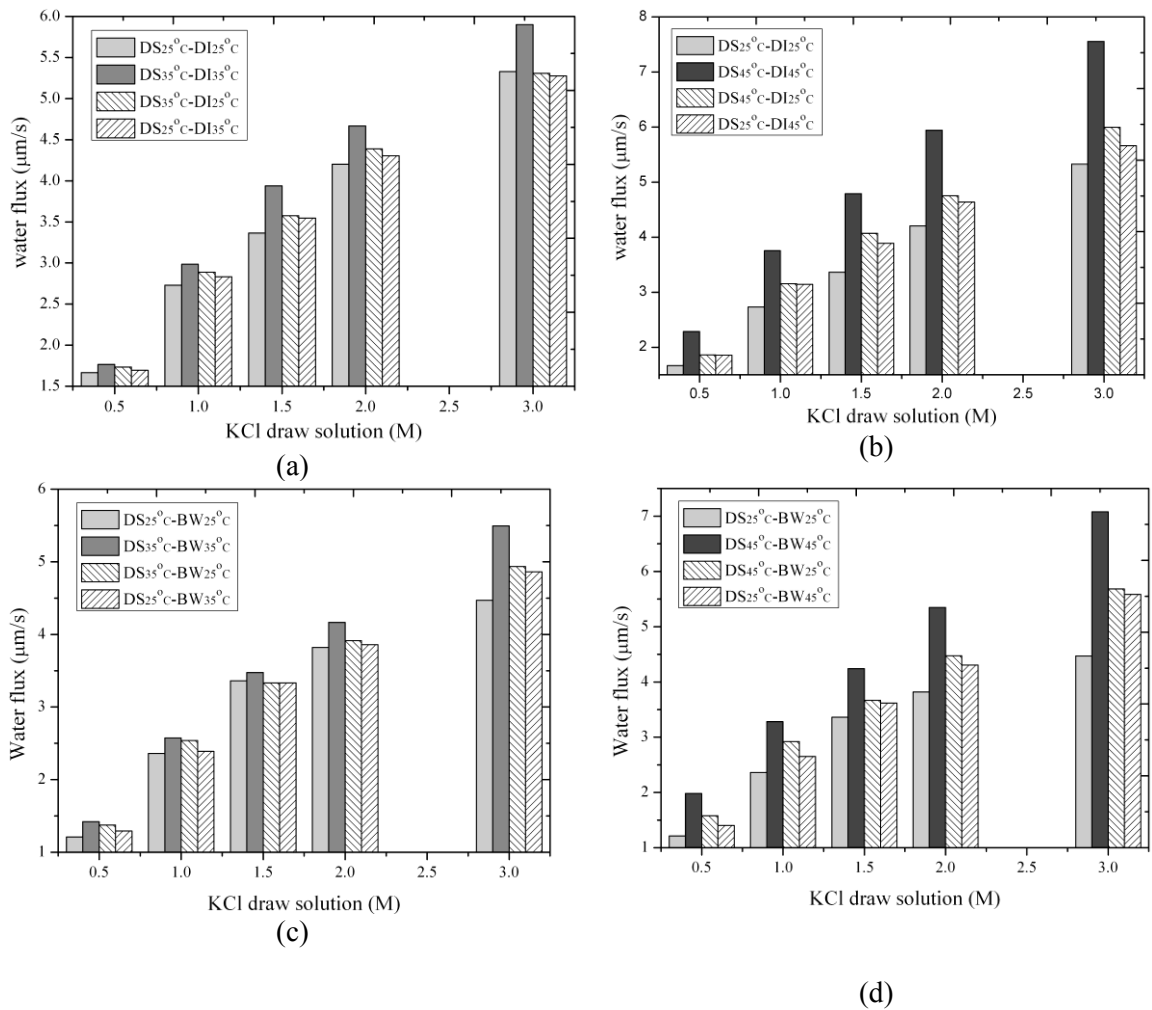


Figure 7.10: Influence of water fluxes in FO process operated at different temperature differences between the DS and the FS at temperature using DI water as FS (a and b) and using BW as FS (c and d). In order to check the reliability of the data, each experiment was repeated and found that the flux data was within an experimental error of 1-5% only.

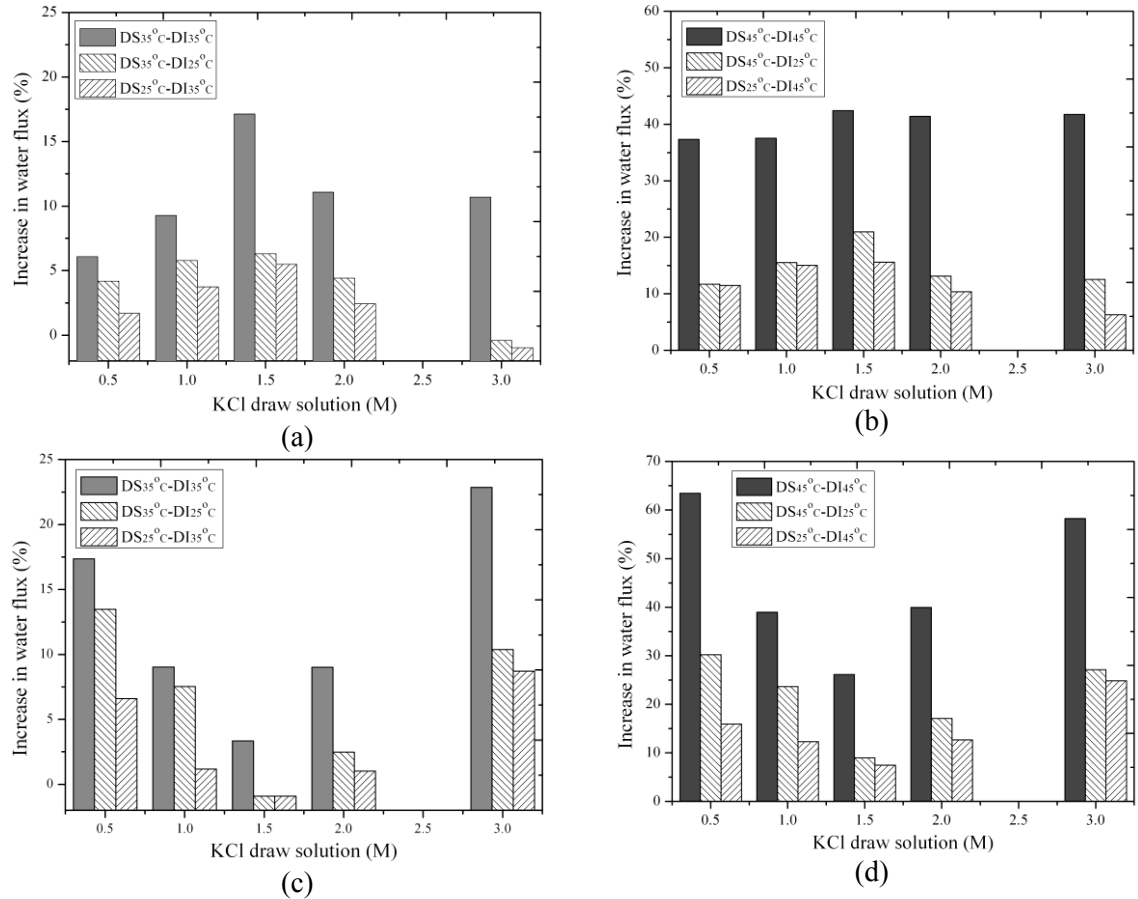


Figure 7.11: percentage increase in water flux when the solutions are heated at different temperatures using DI as feed water (a and b) and using BW as FS (c and d). The based temperature is 25°C for all the above four cases.

Table 7.2: Average increase in water flux due to rise to increase temperature from 25 to 35°C and 45°C for DS or FS or both.

Temperature conditions→		DS-FS 35°C-35°C	DS-FS 35°C-25°C	DS-FS 25°C-35°C	DS-FS 45°C-F45°C	DS-FS 45°C-25°C	DS-FS 25°C-45°C
DI	Total	10.86%	4.05%	2.5%	40.1%	14.8%	11.76%
	Per °C	1.1% per °C	0.4%	0.2%	2.0%	0.7%	0.6%
BW	Total	12.32%	6.59%	3.32%	45.4%	21.4%	14.6%
	Per °C	1.2%	0.7%	0.3%	2.3%	1.1%	0.7%

7.7 Concluding remarks

The influence of temperature and temperature difference on the performance of FO desalination process has been studied using the commercial CTA membrane using KCl as DS and NaCl as model BW FS. The following conclusions have been drawn from this particular study:

- Temperature plays a significant role in enhancing the performance of the FO desalination process.
- The water flux increased 12.3% and 45.4% when the temperatures of the DS and the BW FS were increased from 25°C to 35°C and 45°C, respectively. For every degree rise in temperature of the DS and FS above 25°C, water flux with BW increased on average 1.2% at 35°C and 2.3% at 45°C. Therefore, FO desalination process operated at 45°C will be able to gain water flux per unit heat energy input twice as high as for FO process operated at 35°C.
- The percentage gain in water flux per unit rise in temperature varied with DS concentration showing a modal distribution. Operating FO process at higher temperature reduces the concentrative ECP effects especially at higher DS concentrations.
- Operating FO desalination process at higher temperature can reduce the reverse draw solute flux and increase the feed salt rejection rates. The CTA FO membrane used in this study was found to be thermally stable at 45°C.
- Creating a temperature difference between the DS and the FS also significantly improved the performances of the FO desalination process. Increasing the temperature of the DS only from 25°C to 45°C improved water flux on average by more than 21% while this increase was only about 15% when the temperature of BW FS was elevated to 45°C. This has significant implication in FO process since heating only DS can substantially reduce the large amount of heat energy required if the temperature of the FS solution has to be increased.
- The study on the performance of FO process using temperature difference indicates that, the thermodynamic properties of the DS play a more influential role on the water flux in FO process than the thermodynamic properties of the FS at higher temperature. Increasing the DS temperature significantly reduced the ICP effects although this study could not establish which thermodynamic property of the DS in particular was more influential in the FO process at elevated temperature. For the BW FS, the increase in water flux is mainly contributed due to the reduction in viscosity and only very little due to decreased concentrative ECP effects.

CHAPTER 8



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PERFORMANCES OF SELECTED FERTILISERS AS DRAW SOLUTES IN THE FORWARD OSMOSIS DESALINATION PROCESS

8.1 Introduction

In Chapter 5, eleven different fertilisers were screened as potential candidates for use as draw solutes for the fertiliser drawn forward osmosis (FDFO) desalination process. In this chapter, the performances of the selected draw solutes are tested using a bench-scale forward osmosis (FO) process and their performances measured in terms of water flux and reverse draw solute flux. The performances are also compared based on the bulk theoretical and experimental water fluxes and how it varies based on their predicted bulk osmotic pressure.

It must be mentioned here that, this particular study was conducted at Korea University, Seoul the result of which was published in the Journal of Membrane Science (Phuntsho et al., 2011b). Only nine fertilisers then could be included in this study. Urea was not included during that time and therefore excluded in this chapter however; it is included in Chapters 9 and 10. Although the experimental conditions are similar with other chapters, the membrane used during this particular study was obtained from the Hydro well filter modules (Hydration Technologies Innovations, LLC, Albany, OR) and not as membrane samples usually provided by the company for research purpose. Although, this FO membrane is considered to be made up of cellulose triacetate (CTA) membrane embedded in a polyester woven mesh, similar to the membranes used for all the experiments in the other chapters, the pure water permeability for this batch of membrane was found to be higher than those membranes supplied by HTI for those experiments performed later at UTS. In order to avoid these discrepancies, the membrane transport properties determined at Korea University is used exclusively in this chapter. The water flux data obtained in this study is not used for comparison later with the data obtained in other chapters, as the pure water permeability of this batch of FO membrane was slightly higher than the FO membranes used for experimental investigations in other chapters.

This Chapter is based on the article published by the author in the Journal of membrane science (Phuntsho et al., 2011b).

8.2 Experimental

The membrane used was the membrane used during this particular study was obtained from the Hydro well filter modules (Hydration Technologies Innovations, LLC, Albany, OR). The membrane was peeled off from the spiral wound Hydro well filter modules, and soaked in the DI water for several days at 5°C before using for experiments. All chemicals used for the preparation of draw solutions (DS) and feed solutions (FS) were reagent grade supplied by Samchun Chemicals Co. Ltd., South Korea and they were used as received without any further treatment. Table 8.1 provides detail of the chemicals used. The details for the preparation of DS and FS are described under Chapter 5.

Table 8.1: Details of the chemical fertilisers used for the draw solution assessment

Name of fertilisers	Chemical formula	MW	Purity (%)	Supplier
Ammonium nitrate	NH_4NO_3	80.0	98.5	All chemicals supplied by Samchun Chemicals Co. Ltd., South Korea
Ammonium sulphate	$(\text{NH}_4)_2\text{SO}_4$	132.1	99.0	
Ammonium chloride	NH_4Cl	53.5	98.5	
Calcium nitrate	$\text{Ca}(\text{NO}_3)_2$	164.1	98.5	
Sodium nitrate	NaNO_3	85.0	98.0	
Potassium chloride	KCl	74.6	99.0	
Mono-ammonium phosphate (MAP)	$\text{NH}_4\text{H}_2\text{PO}_4$	115.0	98.0	
Diammonium hydrogen phosphate (DAP)	$(\text{NH}_4)_2\text{HPO}_4$	132.1	98.5	
Potassium nitrate	KNO_3	101.1	99.0	

8.3 Water flux generated by fertiliser draw solutions

The experimental pure water flux of each fertiliser draw solution as a function of its molar concentration is presented in Figure 8.1. The water flux increased at higher molar concentrations of the fertiliser concentrations however, the correlation between molar concentration and water fluxes was non-linear unlike osmotic pressure where the correlation was observed fairly linear correlation with the DS concentrations (See Chapter 5). In fact, a logarithmic correlation was observed between DS concentration

and the water flux for most fertilisers tested and presented in Figure 8.1 and similar observation was reported in other studies (Seppälä and Lampinen, 2004; Hancock and Cath, 2009). This means that, although the water flux increased with the increase in DS concentrations, the increase in water flux at higher DS concentrations were not proportional to the increased osmotic pressure at some point almost flattening at high concentration. As discussed in Chapter 6, this flattening of the water flux at higher DS concentration is a result of the more severity of dilutive ICP effects at higher osmotic pressure.

At the same molar concentrations, KCl DS generally showed the highest pure water flux at all concentrations except at the lowest concentration of 0.3 M where KNO_3 somehow showed the highest water flux. At 2 M concentrations, the next highest water flux was observed for NaNO_3 followed by $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl . KCl is also reported to have much higher flux than other inorganic draw solutions (Achilli et al., 2010). $(\text{NH}_4)_2\text{HPO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$ and NH_4NO_3 all resulted in the lowest water flux amongst all the selected fertiliser DS.

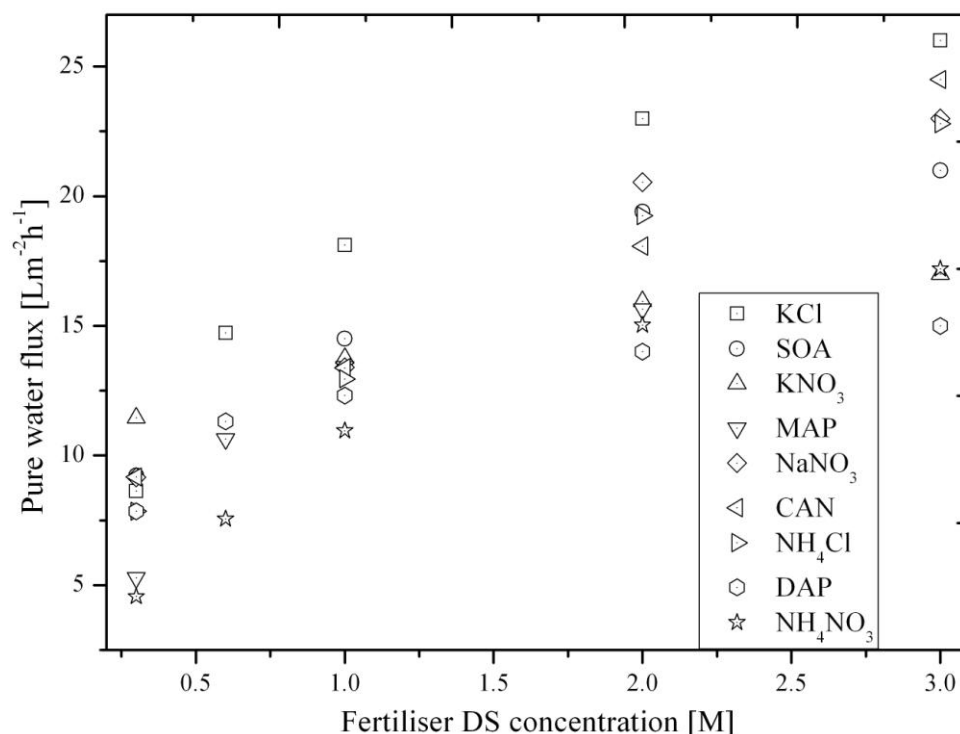


Figure 8.1: Pure water flux of the fertiliser DS as a function of molar concentrations. FS: DI water, Crossflow: 8.5 cm/s in counter-current mode, Temperature: 25°C. MAP: monoammonium phosphate, DAP: diammonium phosphate, SOA: ammonium sulphate.

8.4 Comparison of measured and predicted water fluxes based on bulk osmotic pressure

Tables 8.2 and 8.3 show the actual water flux, theoretical water flux and the performance ratio of the selected fertiliser DS (2 M concentration) using DI water and BW (0.3 M NaCl) as FS, respectively. As expected, the water flux using BW as FS (0.3 M NaCl) is considerably lower than the pure water flux because of the need to overcome the additional osmotic pressure of the FS during the FO process. It is evident from both the tables that, the experimental water fluxes are much lower than the theoretical or estimated fluxes mainly attributed to CP effects especially dilutive ICP (since $ECP = 0$ when DI water is used as FS) as reported by many earlier studies (Gray et al., 2006; McCutcheon and Elimelech, 2006; Achilli et al., 2010; Tang et al., 2010; Xu et al., 2010; Zou et al., 2011). The theoretical flux was calculated based on the bulk osmotic pressure (predicted using OLI Stream Analyser) at 2.0 M concentrations using the following equation.

$$J_w = A \sigma \Delta\pi = A \sigma [\pi_D - \pi_F] \quad (8.1)$$

Where A is the pure water permeability coefficient of the membrane, σ is the reflection coefficient (considered $\sigma = 1$), π_D and π_F are the bulk osmotic pressures of the DS and the FS respectively and the $\Delta\pi$ the net osmotic pressure (or net osmotic gradient). When DI water was used as FS as in Table 8.2, $\pi_F = 0$. The pure water permeability coefficient of this batch of thin FO membrane was found to be $A = 1.48 \pm 0.108 \text{ Lm}^{-2}\text{h}^{-1}\text{atm}^{-1}$ at 25 °C. The performance ratio (PR) of each fertiliser solution was calculated as a percentage ratio of actual or experimental flux (J_w) to the estimated theoretical flux (J_t) and the results are shown in the same table. These ratios indicate the percentage of the effective bulk osmotic pressure difference that is effectively generating water flux across FO membrane (McCutcheon et al., 2006).

It is clear from Tables 8.2 and 8.3 that, because of the comparatively lower water fluxes obtained in FO process in comparison to the theoretical water fluxes, the PR of the DS is quite low ranging a meagre 9.5% to 16.5% with DI water as FS and 6.4% to 12.9% with BW as FS. The PR of the DS varied widely depending on the types of fertilisers used, similar observations made in Chapter 6 with other types of DS. KCl and KNO_3

consistently showed one of the highest PR both using DI and BW as FS. The lowest PR amongst the 9 selected fertilisers were observed for $\text{Ca}(\text{NO}_3)_2$, $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ all of which contain multivalent ions.

Comparing Tables 8.2 and 8.3, the PR of fertiliser DS using BW as FS is lower than the DI water as FS. While dilutive ICP is present irrespective of the types of FS used in FO process, a coupled effects of dilutive (on the membrane support layer facing DS) ICP and concentrative ECP (on the membrane active layer facing FS) occurs when BW is used FS. The lower PR of the fertiliser DS using BW as FS is therefore due to the influence of concentrative ECP on the membrane active layer. This ECP phenomenon is similar to the pressure based membrane process such as reverse osmosis process.

Table 8.2: Performance ratio calculated using estimated theoretical flux and experimental flux using 1 M fertiliser DS and DI as feed water. Membrane permeability coefficient $A = 1.48 \pm 0.108 \text{ Lm}^{-2}\text{h}^{-1}\text{atm}^{-1}$. SOA: $(\text{NH}_4)_2\text{SO}_4$, MAP: $\text{NH}_4\text{H}_2\text{PO}_4$, DAP: $(\text{NH}_4)_2\text{HPO}_4$. PR: performance ration (J_w/J_t)

Fertilizers	π 2.0 M (atm)	Actual J_w ($\text{Lm}^{-2}\text{h}^{-1}$)	Estimated J_w ($\text{Lm}^{-2}\text{h}^{-1}$)	PR (J_w/J_t) (%)
KCl	89.3	22.81	138.40	16.48
NaNO_3	81.1	20.54	125.69	16.34
KNO_3	64.9	15.94	100.58	15.85
NH_4NO_3	64.9	15.04	100.58	14.95
NH_4Cl	87.7	19.25	135.92	14.16
SOA	92.1	19.41	142.74	13.60
MAP	86.3	15.66	133.75	11.71
$\text{Ca}(\text{NO}_3)_2$	108.5	18.08	168.16	10.75
DAP	95.0	14.01	147.24	9.52

Table 8. 3: Water fluxes and the performance ratio of fertiliser draw solutions (2 M) using 0.3 M NaCl as feed water. Membrane permeability coefficient $A = 1.48 \pm 0.108 \text{ Lm}^{-2}\text{h}^{-1}\text{atm}^{-1}$.

Fertiliser	J_w	π_{DS}	π_{FS}	$\Delta\pi=(\pi_{DS}-\pi_{DS})$	J_t	PR (J_w/J_t)
DS	($\text{Lm}^{-2}\text{h}^{-1}$)	(atm)	(atm)	(atm)	($\text{Lm}^{-2}\text{h}^{-1}$)	(%)
KNO ₃	10.19	64.9	14	50.9	78.8	12.9
KCl	14.86	89.3	14	75.3	116.6	12.7
NH ₄ Cl	14.52	87.7	14	73.7	114.1	12.7
SOA	12.20	92.1	14	78.1	120.9	10.1
NH ₄ NO ₃	7.79	64.9	14	50.9	78.8	9.9
NaNO ₃	8.57	81.1	14	67.1	103.9	8.2
Ca(NO ₃) ₂	11.76	108.5	14	94.5	146.3	8.0
MAP	7.63	86.3	14	72.3	111.9	6.8
DAP	8.07	95.0	14	81.0	125.4	6.4

8.5 Comparing experimental water flux and bulk osmotic pressure of different fertilisers

The results in Tables 8.2 and 8.3 indicate that, some of the fertiliser draw solutions with higher bulk osmotic pressure have much lower experimental flux than the expected flux. For example, Ca(NO₃)₂ has the highest bulk osmotic pressure amongst all the selected fertilisers however, its actual flux is lower than draw solution such as KCl, NaNO₃, NH₄Cl and (NH₄)₂SO₄. In addition to water flux and performance ratio, we have tried to observe the correlation between the experimental flux and the theoretical osmotic pressure of different fertiliser DS comparatively. The osmotic pressure and the experimental water flux of the DS were taken from Table 8.2 and their correlation plotted in Figure 8.2. The experimental flux of the five fertiliser DS (NH₄Cl, NaNO₃, KNO₃, KCl and NH₄NO₃) has a fairly linear correlation with the predicted osmotic pressure, while the other four fertilisers (NH₄H₂PO₄, (NH₄)₂HPO₄, Ca(NO₃)₂ and (NH₄)₂SO₄) showed very poor correlation. Several explanations were explored for this anomaly.

Firstly, the osmotic pressure is calculated using proprietary software (OLI Stream Analyser) and we lacked the understanding on the actual osmotic pressure prediction models used by this software. Calculation of theoretical osmotic pressure is not easy although data for few commonly used compounds are available and determination of

actual osmotic pressure is even more difficult because of the lack of ideal membrane (Robinson and Stokes, 1959a). Since osmotic pressure is a colligative property, the osmolality of a solution is directly related to the osmotic coefficient and therefore osmolality is the practical way of measuring the contribution of the various active solutes present in solution (Streng et al., 1978; Sklupalova and Zatloukal, 2009). We used the osmolality as an indicator to study the osmotic trend comparatively since, comparative method has some advantage as it enables sets of osmotic coefficients to be compared directly and it can examine consistencies between various sets of values. Since the osmometer used had measurement range only up to 2.5 osmoles/kg, we could not determine the osmolality of the draw solutions at 2 M concentration. However, the osmolality at 1.0 M concentrations was measured and their corresponding water flux and osmotic pressure used for comparison. The osmolality of the fertiliser draw solutions indicated linear correlation with the molar concentrations up to 1.0 M and the results are shown in Figure 8.3.

First, we compared the measured osmolality of the draw solution with the osmotic pressure predicted by OLI Stream Analyser for 1.0 M concentrations as shown in Figure 8.4. The osmolality of the selected fertiliser draw solutions indicated a fairly linear correlation with the osmotic pressure data from OLI software except for $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$ and NH_4NO_3 draw solutions. However, the results in Figure 8.5 still show poor correlation between the measured osmolality and the experimental flux similar to results in Figures 8.2 and 8.5. Although osmolality is a measure of the active solute that contributes to osmotic pressure, the non-linearity with the actual flux and the measured osmolality indicates that, the actual flux is influenced by factors other than the bulk osmotic pressure differences as explained in the next paragraph.

The anomaly between the bulk osmotic pressure of fertiliser draw solutions and the actual water flux indicates that, the nature of the species has significant influence on the severity of CP in the FO process. Since, experiments were conducted in FO mode (draw solution on the porous support layer side of FO membrane), ICP might be the main factor responsible for lowering pure water flux. ICP reduces the effective osmotic pressure difference across the membrane layer thereby lowering the water flux (McCutcheon and Elimelech, 2006; McCutcheon and Elimelech, 2007; Tan and Ng, 2008; Achilli et al., 2010; Tang et al., 2010). The results in Figure 8.2 also indicate that

the severity of ICP depends on the type of draw solution. ICP is modelled by considering the resistance to diffusion of solute molecules within the porous support layer (McCutcheon and Elimelech, 2007; Tan and Ng, 2008). $\text{Ca}(\text{NO}_3)_2$ with the highest molecular weight amongst the selected fertiliser draw solution is probably affected more severely by ICP. The rate of diffusion is inversely proportional to molecular mass (Polson and Van Der Reyden, 1950; Valencia and González, 2010). For the same osmotic pressure, draw solution with higher diffusion coefficient results in higher water flux (Achilli et al., 2010; Qin et al., 2010).

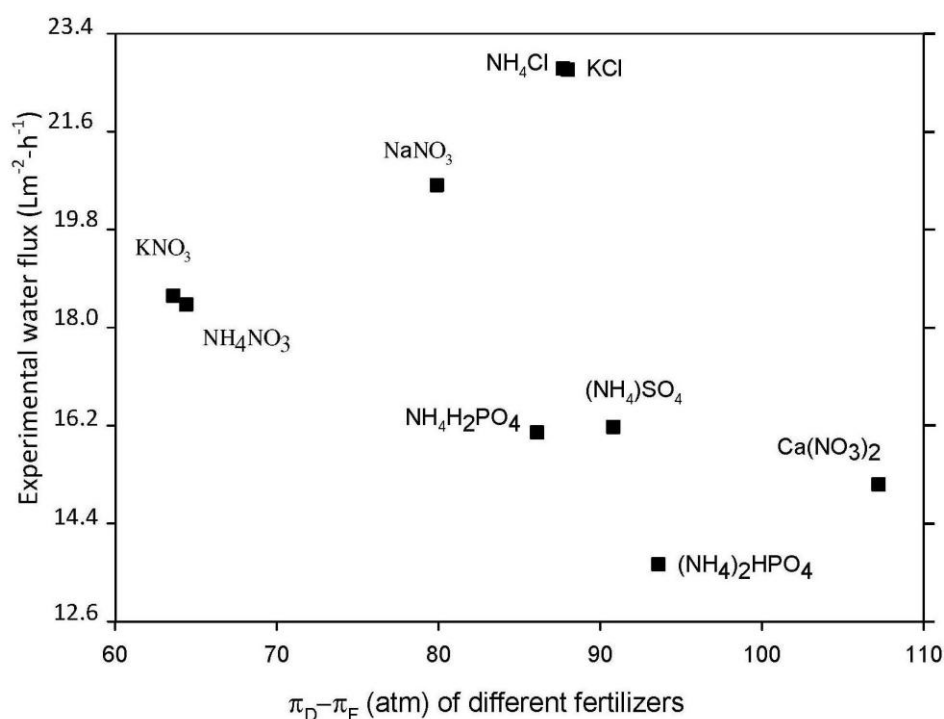


Figure 8.2: Experimental water flux of each fertiliser draw solutions as a function of predicted osmotic potential at 2.0 M

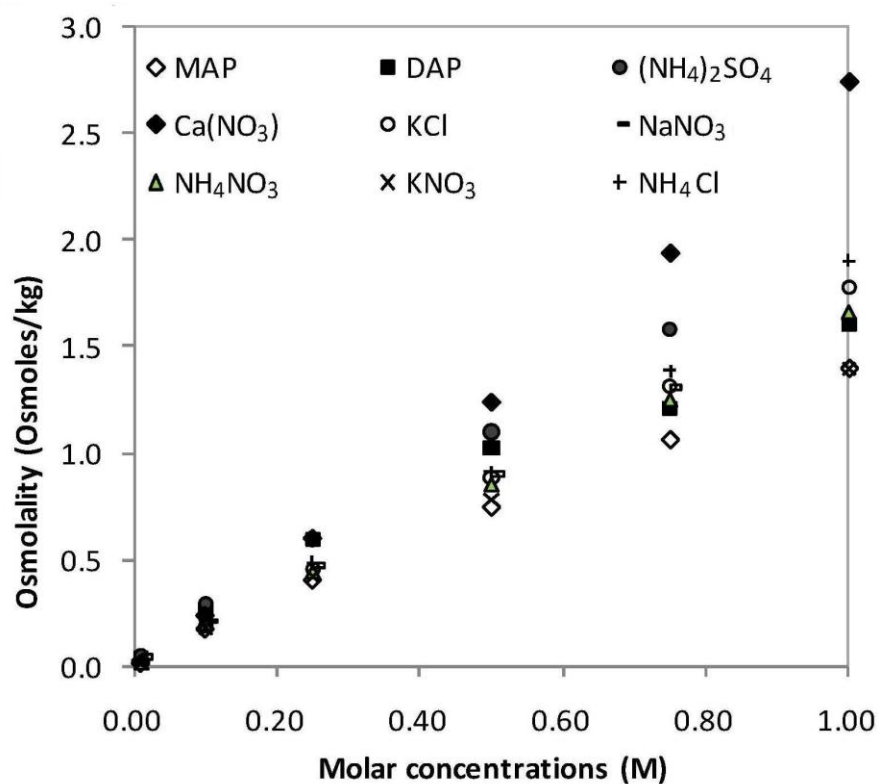


Figure 8.3: Osmolality of the draw fertiliser solutions at various molar concentrations determined using OSMOAT

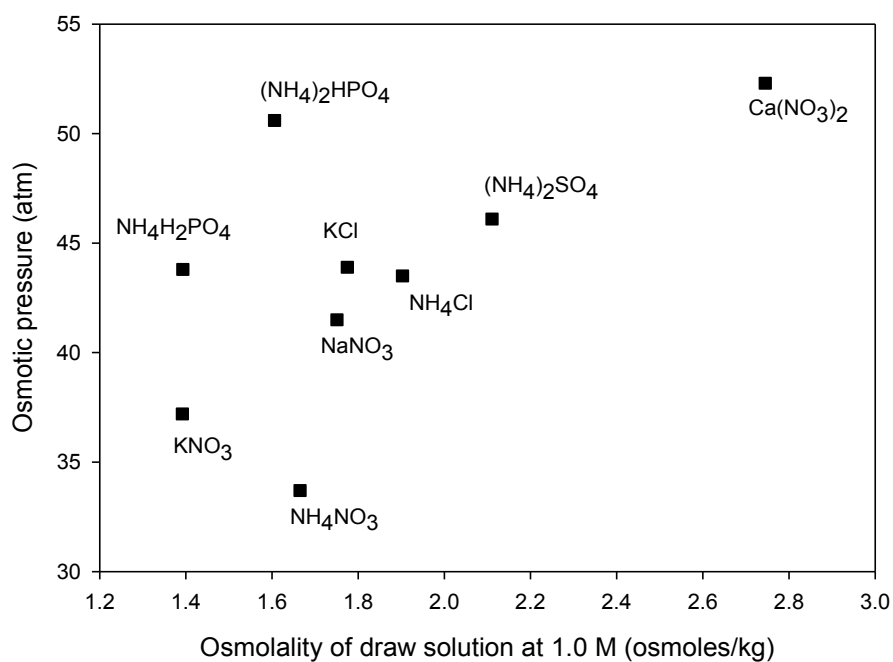


Figure 8.4: Theoretical osmotic pressure of the fertiliser draw solutions as determined by OLI Stream Analyser as a function of measured osmolality at 1.0 M concentration.

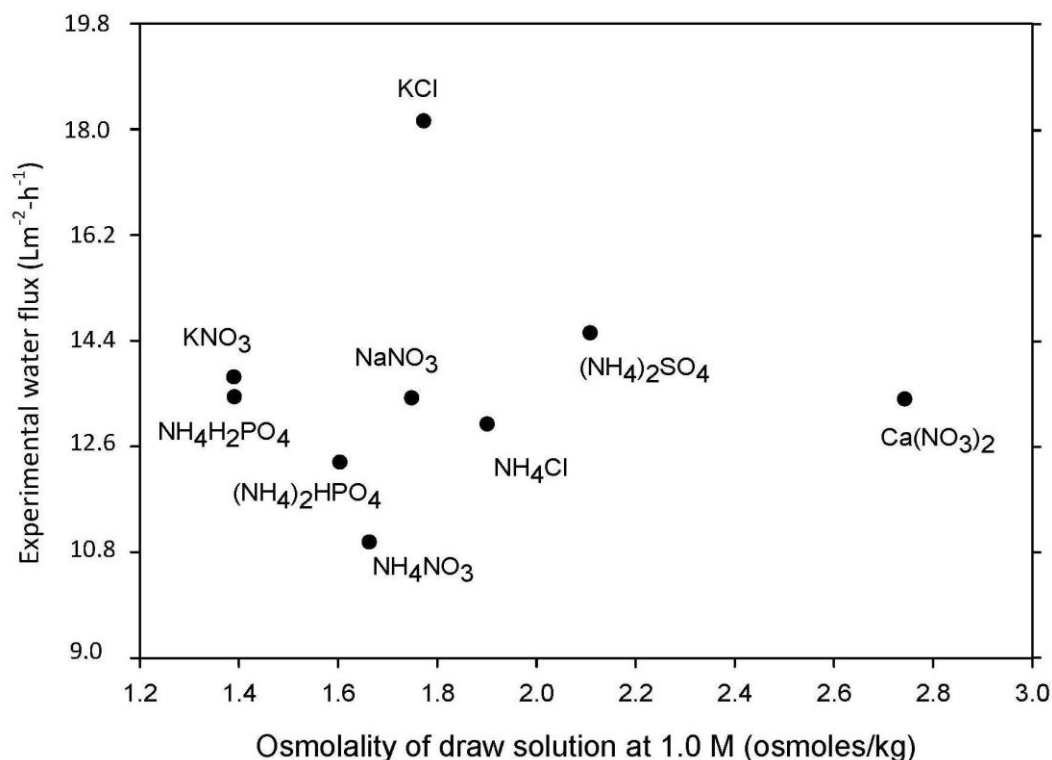


Figure 8.5: Experimental water flux of each fertiliser draw solutions as a function of osmolality of the 1.0 M fertiliser draw solution measured by osmometer.

8.6 Reverse fertiliser draw solute flux

No semi-permeable membranes are ideal or perfect barrier and therefore reverse salt permeation is inevitable (Phillip et al., 2010). Reverse salt movement can be a significant disadvantage for FO because it is not only an economic loss as it cannot be recovered but its presence in the feed concentrate could complicate the feed water concentrate management and also likely to decrease the net osmotic potential or driving force (Hancock and Cath, 2009; Phillip et al., 2010) and fouling potential of the feed solution (Hancock and Cath, 2009; Lee et al., 2010). Reverse solute flux (RSF) could be particularly significant especially when nitrogen and phosphorus containing draw solutions are used as these compounds are known to cause eutrophication in the receiving water environment. Therefore, it is essential to assess the performance of fertiliser draw solution in terms of RSF.

The performance of fertiliser draw solutions in terms of RSF varied widely depending on the type of fertilisers used as shown in Table 8.4. (NH₄)₂SO₄ showed the lowest RSF

amongst the selected fertilisers while NH_4NO_3 draw solution had the highest RSF value. In general, the ammonium compounds of sulfate and phosphate, and $\text{Ca}(\text{NO}_3)_2$ containing multivalent ions performed well in terms of RSF since lower RSF is preferred for FO any process. Table 8.4 also includes specific RSF, which is defined as the ratio between RSF and water flux (Hancock and Cath, 2009; Yen et al., 2010). Specific RSF actually indicates the amount of draw solute lost through diffusion or permeation through the membrane towards the feed water during the FO process. For example, 0.00103 M of NH_4SO_4 DS diffuses towards the feed water for every litre of water extracted while for NH_4NO_3 DS, it amounts to 0.189 M.

$(\text{NH}_4)_2\text{SO}_4$, $\text{Ca}(\text{NO}_3)_2$, $(\text{NH}_4)_2\text{HPO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$ have ionic species with hydrated diameter of SO_4^{2-} , PO_4^{2-} and Ca^{2+} comparatively much higher than the hydrated diameter of other fertiliser species (NH_4^+ , Cl^- , NO_3^- , K^+ and Na^+) (Achilli et al., 2010) and therefore could be one of the reasons for lower RSF. Ca^{2+} as divalent ions, also has much lower reverse permeation rate than monovalent ions (Hancock and Cath, 2009). In addition, $(\text{NH}_4)_2\text{HPO}_4$ draw solution has a weakly alkaline pH at 2 M concentration and at this pH, FO membrane remains slightly negative charged (data not shown). This negative charge could repel phosphate containing anions, which are usually made up of higher hydrated diameter with greater force. Achilli *et al.* (Achilli et al., 2010) also reported lower RSF for draw solutions containing SO_4^{2-} and Ca^{2+} species.

The other possible explanation is due to ion-pairing. Association of ions occurs as a result of purely electrostatic attraction between oppositely charged ions, a common behavior for divalent metal sulphates (Robinson and Stokes, 1959a) and calcium nitrate (Stokes and Robinson, 1948) in aqueous solution. KCl and NH_4Cl electrolytes are of the non-associated type, therefore do not form ion pair (Wishaw and Stokes, 1954). Although, $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ contain NH_4^+ with much smaller hydrated ion which can easily diffuse through the membrane, nevertheless their net diffusion will be low since these compounds have anions made up of much larger hydrated diameter (PO_4^{2-} , HPO_4^-) which cannot pass through the membrane and, in order to maintain electrical neutrality across the membrane, the smaller cations will naturally diffuse back to the draw solution.

NH_4NO_3 has obviously the highest RSF firstly because NH_4^+ and NO_3^- have much lower hydrated diameter. Secondly, ammonium nitrate does not dissociate fully in water. OLI speciation indicates that, at 2 M NH_4NO_3 concentration in water, about 1.15 M of NH_4NO_3 remains in non-dissociated form. Uncharged species have higher RSF than the charged species (Hancock and Cath, 2009).

The pH of the DI feed water changed significantly during the course of the FO process. For the $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, $\text{Ca}(\text{NO}_3)_2$, NH_4NO_3 , and NH_4Cl draw solutions, the pH of the DI feed water initially increased, and then decreased showing a peak, finally reaching almost a constant pH after certain time. Figure 8.6 shows variation of DI feed water pH. It is not explained at this time however, one interesting point to be noted is that, although the pH of these five draw solutions are acidic except for $(\text{NH}_4)_2\text{HPO}_4$, the pH of their corresponding DI feed water remained at around neutral pH throughout the experiment.

Ammonium phosphate fertilisers are the important group of the most concentrated soluble fertiliser materials containing both N and P, essential fertiliser elements needed by the plants (Ross et al., 1929) and can be either alone as fertiliser or is compatible to be used as mixed fertiliser with a number of other fertilisers (Thompson et al., 1949; IEC, 1961). Although, their water flux is lower than the other draw solutions, their low RSF makes them a promising candidate for FO desalination for fertigation.

Table 8.4: Reverse diffusion of fertiliser draw solutes during the FDFO process. RSF: reverse solute flux and SRSF: specific reverse solute flux is the ratio of the RSF to water flux or J_s/J_w . Operating conditions: DS: 2 M, FS: DI water. Cross flows: 400 ml/min in counter current FO mode.

Fertilisers	Actual J_w ($\text{Lm}^{-2}\text{h}^{-1}$)	RSF J_s ($\text{mmoles/m}^2\text{-s}$)*	SRSF or J_s/J_w (mmoles/L)
NH_4NO_3	15.04	0.790876	189.34
KNO_3	15.94	0.485625	109.65
NH_4Cl	19.25	0.333000	62.27
NaNO_3	20.54	0.277500	48.63
KCl	22.81	0.222000	35.03
$\text{NH}_4\text{H}_2\text{PO}_4$	15.66	0.069375	15.95
$(\text{NH}_4)_2\text{HPO}_4$	14.01	0.009713	2.50
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	18.08	0.009019	1.80
$(\text{NH}_4)_2\text{SO}_4$	19.41	0.005550	1.03

*RSF calculated for a minimum of 10 hours of FO operation for all cases.

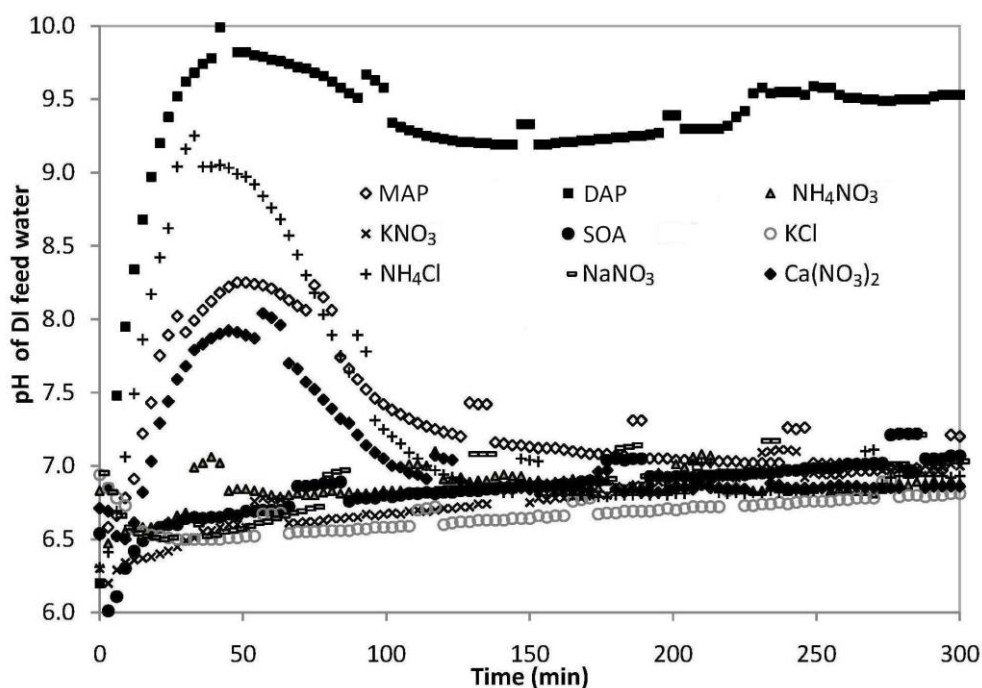


Figure 8. 6: Variation of pH of a DI feed during the FO process using different fertiliser draw solutions. Operating conditions: DS: 2 M, FS: DI water. Cross flows: 400 ml/min in counter current FO mode.

8.7 Concluding remarks

A novel low energy desalination concept using fertiliser drawn FO has been developed wherein desalinated water can be directly used for fertigation. This process avoids the need for an additional process for separating desalinated water and draw solution, which is one of the major challenges of FO technology. Based on this concept, about nine chemical fertilisers have been selected and tested and their properties thoroughly assessed for their application as FO draw solution. Following conclusions have been drawn from this particular study:

- All soluble fertilisers can generate osmotic pressure however, based on the currently available FO membrane technology, about nine different fertilisers were found most suitable candidates for draw solution and their performance assessed in more detail
- Different fertilisers resulted into different solution properties and therefore showed different osmotic potential. $\text{Ca}(\text{NO}_3)_2$ showed the highest osmotic

pressure while KNO_3 had the lowest osmotic pressure amongst the selected fertilisers.

- Although the experimental pure water flux increased with the increase in fertiliser concentrations however, their correlation was observed non-linear. KCl showed the highest pure water flux while $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ showed the lowest pure water flux amongst the selected fertilisers.
- The experimental pure water flux was much lower than the predicted flux which is mainly attributed to CP effects. In terms of performance ratio, KCl and NaNO_3 performed much better than all the other selected fertilisers
- A poor correlation between experimental pure water flux and the bulk osmotic pressure of all the selected fertiliser draw solutions was observed. This anomaly indicates that, the nature of the species has significant influence on the CP in the FO process although it does not affect the osmotic potential of the solution
- The performance of fertiliser draw solutions in terms of RSF varied widely depending on the type of fertilizers used. The ammonium compounds of sulfate and phosphate, and $\text{Ca}(\text{NO}_3)_2$ containing divalent anions had very low RSF which is very significant for any FO process as it prevents the loss of fertiliser nutrients.

CHAPTER 9



University of Technology Sydney

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BLENDED FERTILISERS AS DRAW SOLUTES FOR FORWARD OSMOSIS DESALINATION PROCESS

9.1 Introduction

In Chapter 8, it was observed that most of the soluble fertilisers could be used as draw solutes for FO desalination however; one of the limitations identified in Chapter 5 was the fertiliser nutrient concentration in the final fertiliser drawn forward osmosis desalination (FDFO) product water, which exceeds the required nutrient limit for direct fertigation. The minimum final nutrient concentration in the final FDFO product water is restricted by the osmotic equilibrium between the feed solution (FS) and draw solution (DS) in the FO process. This limit is in fact offered by the concentration of the FS which limits the extent of the osmotic process as described in Chapter 5. Even though the minimum concentration of nutrient required for fertigation of crops could vary considerably depending on many factors, such as type of crops, type of nutrients, , soil conditions and composition, cropping season, plant growth stage, etc. (Bates, 1971; Baldwin, 1975; Hornick, 1992; Glendinning, 2000), high fertiliser concentration would increase soil salinity and cause plant toxicity. If the final fertiliser nutrient concentration is higher than required, the final DS must be further diluted using additional fresh water to make the FDFO product water suitable for fertigation, but such situations are not desirable especially when other fresh water sources are unavailable. The dilution required is of several factors high especially when feed water with high total dissolved solids (TDS) is used. Other possible alternative include nanofiltration (NF) as either pre-treatment to reduce the feed TDS or as post-treatment to recover DS in the process reducing the final nutrient concentrations although this may require additional energy (Phuntsho et al., 2012a).

This chapter investigates the suitability of blending two or more single/straight fertilisers as DS for FDFO desalination, with the objective of achieving lower final nutrient concentrations in the final FDFO product water that could meet the water quality requirement for direct fertigation. The hypothesis is that, if the DS is composed of multiple nutrients, the final concentration of each nutrient could be much lower than using a single fertiliser. It is shown in this study that, nutrients in the final FDFO product water can be significantly lowered by using blended fertilisers as DS rather than using single or straight fertiliser as DS. This chapter is an extension of the research article published in the *Environmental Science and Technology* (Phuntsho et al., 2012b).

Bulk blending of fertilisers is very popular in the agriculture industry because it allows prescription mixtures based on specific soil and crop requirements and reduces the transportation costs for farmers (Beaton, 1997). The paper also compares the performances of the single fertiliser and the blended fertilisers in terms of water flux and reverse solute flux during FO process.

9.2 Experimental

All the experiments were carried out according to the procedures described in chapter 3. Eleven different fertilisers were used. Blended fertiliser DS consisted of mixtures of one or more than one single fertilisers in solution. The influence of blending was first investigated by blending two single fertilisers in equimolar ratio. Later the concept of customised blending was investigated where more than two different fertilisers were blended together to prepare a specific ratio for nitrogen, phosphorous and potassium (N:P:K). The performance of each fertiliser and blended fertiliser as DS for FO process was assessed using DI water and model brackish water or BW (5,000 mg/L NaCl) as FS.

9.3 Performance of single/straight fertilisers as draw solutions for FDFO desalination process

The osmotic pressure, pH and water flux of single or straight fertilisers as DS for FDFO desalination process is shown in Table 9.1 while shows the reverse draw solute flux is shown in Figure 9.1. The final concentration of the fertiliser (NPK or Nitrogen Phosphorous Potassium) DS after FDFO desalination with BW as FS is shown in Figure 9.2.

9.3.1 Properties of single fertiliser solutions

Table 9.1 shows the basic properties of the fertiliser DS such as pH and the osmotic pressure at 1.0 M concentration. All the 11 selected fertilisers have pH between 4.8 and 7.8, suitable for use with the currently commercially available FO membrane supplied by HTI Inc. Most of fertilisers tested in this study had solubility higher than 5.0 M except for $\text{NH}_4\text{H}_2\text{PO}_4$, KNO_3 and KH_2PO_4 with solubility less than 4.0 M, 3.5 M and 2.0 M concentrations respectively.

At 1.0 molar concentration, urea has an osmotic pressure of only 23.7 atm which is comparatively much lower than any other fertilisers. Although highly soluble in water, urea is considered a weak electrolyte and therefore does not dissociate to form any charged species in water (Venkatesan and Suryanarayana, 1956). The osmotic pressure is therefore significantly lower than many other soluble fertiliser solutions. A speciation result by OLI Stream Analyser also indicates that, urea does not dissociate to form charged ions unlike other fertilisers and this was evident from the very low electrical conductivity of urea as measured. Another reason for low osmotic pressure is due to its unique property of urea in solution where in urea has a tendency to self aggregation due to hydrophobic effect (Lee and van der Vegt, 2006; Stumpe and Grubmmuller, 2007) with urea-urea association increasing at higher concentration (Chitra and Smith, 2000) further reducing the osmotic pressure.

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ show the highest osmotic pressures amongst the fertilisers with 52.3 and 50.6 atm respectively at 1.0 M concentration. The variation of osmotic pressure with the fertiliser DS concentrations is provided in Figure 5.1 under Chapter 5.

9.3.2 Water flux of single fertiliser as draw solution

The performance test was carried out using DI water and BW as feed water under similar operating conditions and at 1 M fertiliser DS concentration and the results are presented in Table 9.1. Consistent with our earlier study in Chapter 8, amongst the 11 selected fertilisers, KCl showed the highest water flux both with DI water feed ($9.25 \text{ Lm}^{-2}\text{h}^{-1}$) and BW feed ($8.32 \text{ Lm}^{-2}\text{h}^{-1}$). NH_4Cl had the next highest water flux at $8.93 \text{ Lm}^{-2}\text{h}^{-1}$ with DI water feed and $8.17 \text{ Lm}^{-2}\text{h}^{-1}$ with BW feed. Urea showed the lowest water flux of only $2.05 \text{ Lm}^{-2}\text{h}^{-1}$ with DI water feed and $0.90 \text{ Lm}^{-2}\text{h}^{-1}$ with BW feed, which is significantly lower than any other fertiliser examined in this study.

Table 9.1 also presents the performance ratio (PR), calculated as a percentage ratio of actual water flux J_w , to theoretical water flux J_{wt} . PR indicates the bulk osmotic pressure available for effective generation of water flux across the membrane (McCutcheon et al., 2006; Phuntsho et al., 2011b). NH_4NO_3 showed the highest PR of more than 22% both with DI water and BW as feed. NH_4NO_3 is followed by KCl and NH_4Cl with more than 20% with both DI water and BW feed. Urea had the lowest PR of only about 8.5%

with DI water and even lower (4.5%) with BW feed. The poor performance of urea in terms of water flux is probably attributed to the unique property of urea solution. Urea has a tendency to self-aggregation due to the hydrophobic effect (Lee and van der Vegt, 2006; Stumpe and Grubmmuller, 2007), with urea-urea association increasing at higher concentration (Chitra and Smith, 2000). All fertilisers showed a PR higher than 10%, except urea. The PR of DI water and BW feed are observed quite similar probably because of the low salt concentration used in the BW feed except for urea and KNO₃ where the PR with BW was slightly lower than the BW feed.

Table 9.1: Performances of single fertilisers as DS in the FO process using DI water and BW as feed. J_{wt} : theoretical water flux calculated using equation (1); experimental water flux; Performance ratio or PR (J_w/J_{wt}). A: pure water permeability coefficient of the FO membrane ($A = 0.28194 \pm 0.008 \mu\text{m s}^{-1}\text{atm}^{-1}$). Bulk osmotic pressure of the BW feed (5,000 mg/L NaCl) taken is 3.9 atm. RSF data is obtained from the DI water as feed. FO Membrane: CTA.

Draw Solution	$\Delta\pi@1\text{M}$ (atm)	DI as feed water			BW as feed water		
		J_w $\text{Lm}^{-2}\text{h}^{-1}$	J_{wt} $\text{Lm}^{-2}\text{h}^{-1}$	PR (%)	J_w $\text{Lm}^{-2}\text{h}^{-1}$	J_{wt} $\text{Lm}^{-2}\text{h}^{-1}$	PR (%)
KCl	44.0	9.25	44.68	20.7	8.32	40.72	20.40%
NH ₄ Cl	43.5	8.93	44.14	20.2	8.17	40.18	20.30%
Ca(NO ₃) ₂	48.8	7.74	49.54	15.6	7.34	49.14	14.90%
NH ₄ NO ₃	33.7	7.67	34.20	22.4	6.91	30.24	22.90%
(NH ₄) ₂ SO ₄	46.1	7.16	46.80	15.3	6.16	42.84	14.40%
KNO ₃	37.2	6.73	37.76	17.8	4.21	33.80	12.50%
DAP	50.6	6.44	51.37	12.5	5.33	47.41	11.20%
KH ₂ PO ₄	36.5	6.23	37.04	16.8	5.80	33.08	17.50%
NaNO ₃	41.5	5.54	42.12	13.1	4.50	38.20	11.80%
MAP	43.8	5.29	44.46	11.9	4.75	40.50	11.70%
Urea	23.7	2.05	24.05	8.5	0.90	20.09	4.50%

9.3.3 Loss of nutrient by reverse movement of draw solutes using single fertilisers

In FDFO desalination, reverse movement of draw solutes is not only an economic loss, but also the presence of nutrients in the feed concentrate could make the concentrate management more complex as nitrogen (N) and phosphorous (P) can cause eutrophication and algal blooms in the receiving water (Hails, 2002; Jickells, 2005). Therefore, it is important that the DS with low reverse solute flux are identified and selected for application. Most recent efforts have been to synthesize FO membrane that has high solute rejection and selectivity and, a number of high performing thin film composite FO membranes have been already reported (Wang et al., 2010b; Yip et al.,

2010; Wei et al., 2011b). However, FO process can achieve very high recovery rates without additional energy (Martinetti et al., 2009) and therefore concentrate could be managed using simple method such as evaporation ponds for salt recovery especially for inland FDFO desalination.

In other studies (Achilli et al., 2010; Phuntsho et al., 2011b), the assessment of DS performance is usually done in terms of reverse solute flux or specific reverse solute flux (J_s/J_w or draw solute flux/water flux); however, a slightly different approach of assessment is adopted here. For fertilisation, the amount of essential nutrients present in the fertiliser is more important than the other non-essential elements or species present. Therefore, the reverse solute flux in FDFO has been measured in terms of the loss of macronutrients (NPK) per unit volume of water extracted from the feed instead of the whole fertiliser compound.

The results in Table 9.1 indicate that, urea as a DS results in a very high loss of nutrient (29.2 g/L of N). High reverse solute flux of urea is due to its low molecular size, and also because urea remains neutral or uncharged in water solution. Uncharged species or low molecular weight compounds more readily diffuse through the membrane by diffusion (Hancock and Cath, 2009). Besides high loss of nutrient by reverse diffusion, urea also has significantly lower water flux and, therefore, urea alone is not an ideal draw solute for the FDFO desalination process.

Calcium nitrate showed the lowest loss of nutrient by reverse diffusion (0.122 g/L of N). Consistent with other findings (Achilli et al., 2010; Phuntsho et al., 2011b), fertilisers containing divalent ions such as Ca^{2+} , HPO_4^{3-} , and SO_4^{2-} have significantly lower loss due to less reverse movement of draw solutes attributed to their relatively larger hydrated ions.

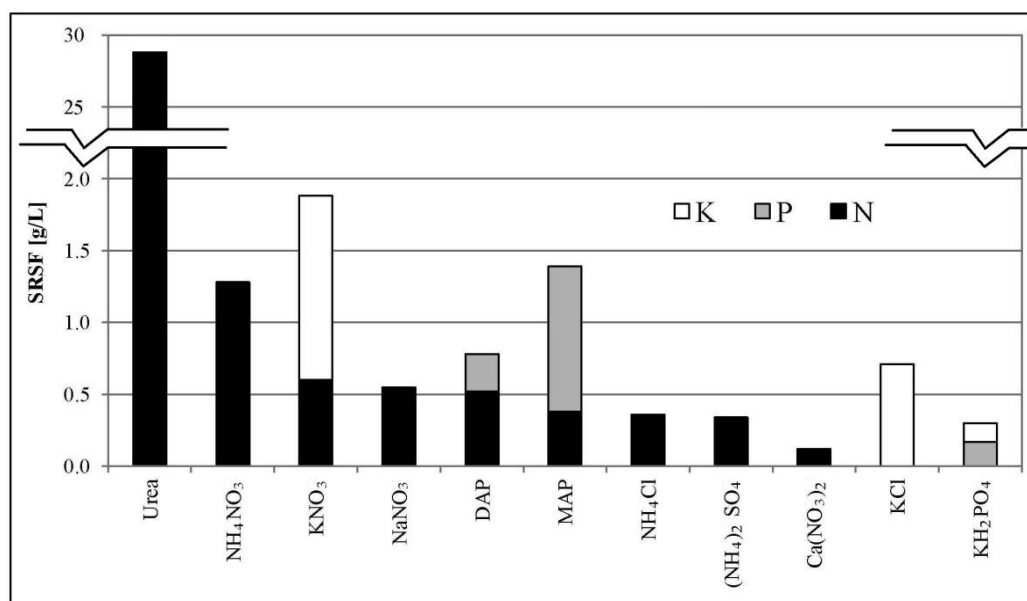


Figure 9.1: Reverse diffusion of draw solutes measured in terms of specific reverse solute flux (J_s/J_w) which is the ratio of reverse solute flux to the water flux of the eleven selected fertilisers.

9.3.4 Final nutrient concentration in the FDFO product water using single fertilisers as draw solute

The method to determine the nutrient concentrations in the final FDFO product water based on the osmotic equilibrium was discussed in detail in Chapter 5. Considering the bulk osmotic equilibrium between the DS and FS in the FO process, the expected NPK nutrient concentrations in the final FDFO product water for the 11 selected single fertilisers using BW (5,000 mg/L NaCl) as FS is presented again in Figure 9.2. It is clear from the figures that the nutrient concentrations in the final FDFO product water depends on the types of fertiliser used as DS.

For example, when urea and NH₄NO₃ is used as the DS, the final FDFO product water would contain 4.5 and 2.7 g/L of N in the final FDFO product water, respectively. The lowest N concentration is observed for MAP, NaNO₃ and NH₄Cl, with only about 1.2 g/L. The concentration of P is 2.7 and 2.0 g/L for MAP and DAP while the concentration of K is about 3.4 g/L with all K fertilisers. These concentrations will be proportionately higher if a FS with higher TDS is used as already discussed in Chapter 5.

Depending on the types of crops and growing seasons, the required nutrient concentration varies from 15 to 200 mg/L of N, 5 to 60 mg/L of P, and 8 to 250 mg/L of

K (Papadopoulos, 1999; Phocaides, 2007). For example, if the target crop is tomato, the nutritional requirement by fertigation would vary 120-200 mg/L N, 40-50 mg/L P, 180-300 mg/L K, 10-120 mg/L Ca, 40 to 80 mg/L Mg, etc. for a drip irrigation system, depending on the various plant growth stages (Imas, 1999). Phosphate (H_2PO_4^-) concentration above 2 moles/ m^3 or 62 mg/L of P can be toxic to some plants (Termaat and Munns, 1986). Therefore, the results in Figure 9.2 indicate that the final nutrient concentration of each nutrient using BW as FS is still high for direct fertigation. The final FDFO product water needs to be diluted several times to lower the nutrient concentrations to desired level. Although, further dilution can be achieved by using fresh water, it could be a significant impediment where fresh water for irrigation is unavailable. Options such as nanofiltration can also be suitably used as post-treatment for partial recovery of the nutrients (Tan and Ng, 2010; Zhao et al., 2012b) for further recycling and reuse by FDFO process while the permeate containing significantly lower nutrient concentrations can be used for direct fertigation (Phuntsho et al., 2012a). However, it is essential that FDFO desalination produce product water that either meets irrigation water quality or requires less dilution water.

One of the important observations noted from the final nutrient concentrations in Table 9.1 is that, those fertilisers containing a lower percentage of a particular nutrient element due to the presence of other elements in the compound result in lower final nutrient concentrations. Figure 9.3 presents a plot of the final nutrient N concentrations of different fertiliser DS with the percentage composition of N in each fertiliser. This plot shows a fairly good correlation between the percentage of N in different fertilisers and their N concentration in the final FDFO product water. This indicates that if the percentage of each fertiliser nutrient is reduced in the DS, the nutrient concentration in the final FDFO product water is also expected to be lower. One of the methods to reduce the percentage composition of the particular nutrient is by blending several nutrients in the single DS using different essential elements. This is the main motivation behind using blended fertilisers as DS for FDFO desalination process.

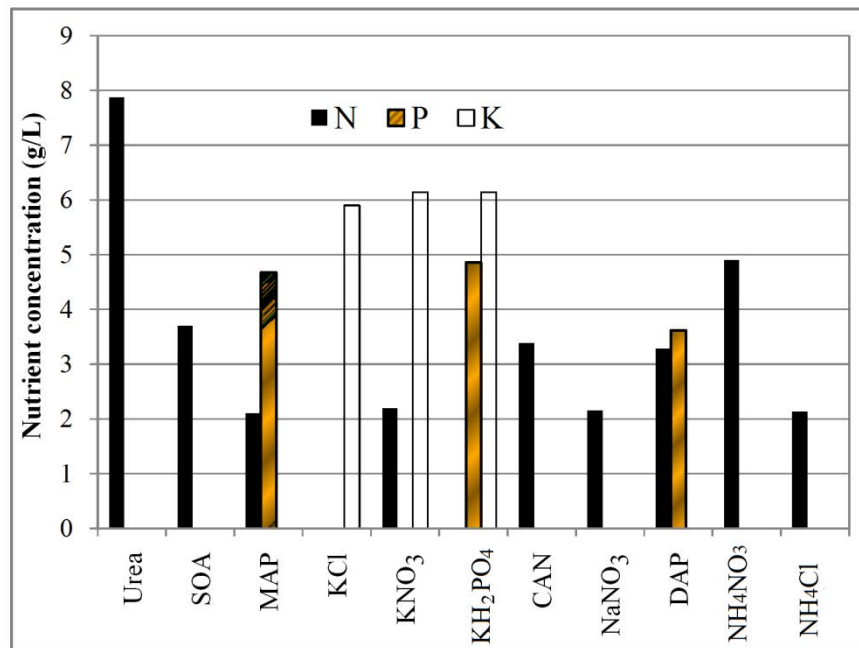


Figure 9.2: Expected final NPK nutrient concentrations of fertiliser solution after FO desalination or in the final FDFO product water using brackish water as feed water (5,000 mg/L NaCl at 3.9 atm). CAN: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

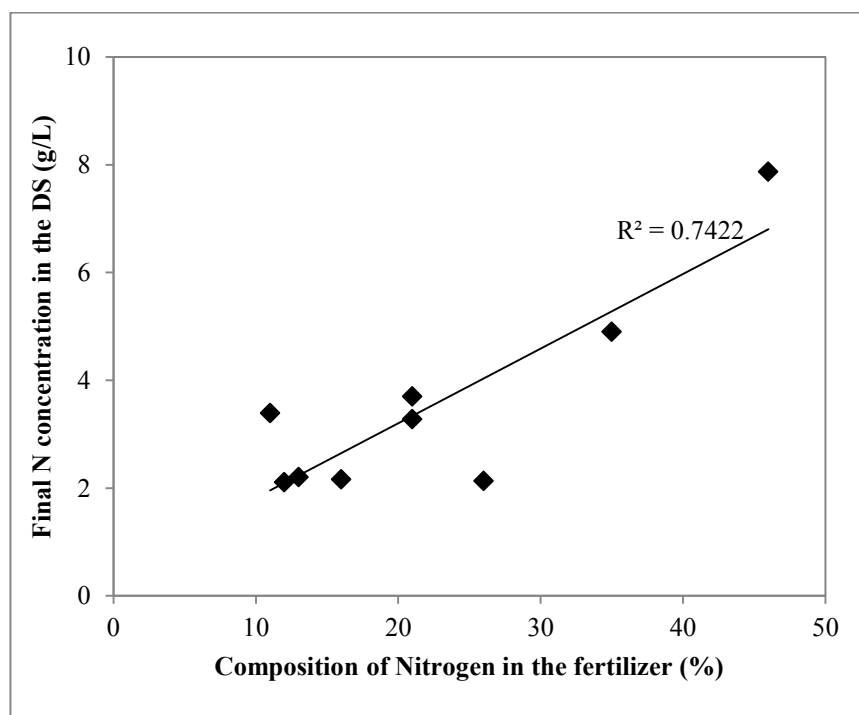


Figure 9.3: Comparison between % of N composition of N containing fertilisers and the N nutrient concentration in the final DS or desalted water with brackish water as feed water

9.4 FDFO desalination using fertiliser DS blended with two single fertilisers

9.4.1 Properties of the blended fertiliser draw solutions

Table 9.2 and Table 9.3 shows the pH and the osmotic pressure of the blended fertilisers DS. Most of the selected fertilisers could blend with each other and only few combinations resulted in the formation of precipitates especially when calcium containing fertilisers were blended with sulphate or phosphate fertilisers. For example, $(\text{NH}_4)_2\text{SO}_4$ and $\text{Ca}(\text{NO}_3)_2$ blend resulted in the formation of CaSO_4 (gypsum) precipitate while $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$ and KH_2PO_4 with $\text{Ca}(\text{NO}_3)_2$ formed CaHPO_4 precipitates. Therefore, these combinations are not suitable for fertiliser blending.

Blending also decreased solubility of some fertilisers. For example, when $(\text{NH}_4)_2\text{SO}_4$ was blended with KCl, one of the products formed is K_2SO_4 which has much lower solubility than their original basic fertilisers (Imas, 1999). The decrease in the solubility could reduce the recovery rate at which FDFO desalination can operate because recovery rates depend on the fertiliser solubility. Higher fertiliser solubility leads to higher osmotic pressure for a particular fertiliser draw solution and therefore higher feed recovery rates are possible.

The pH of all blended fertilisers in this study was within the range of pH 4.0 to 8.0, indicating that they are compatible with the commercially available cellulose acetate FO membrane.

When two different compounds were blended in the solution, the number and types of species formed varied depending on the type of fertiliser used. Speciation analysis using the OLI Stream Analyser indicated that urea was the only fertiliser that does not dissociate to form different species with any of the fertilisers blended at 25°C. Speciation is important because osmotic pressure is directly related to the number of species formed in the solution. While a number of species are important, the nature of the species is also important since non-charged species tend to diffuse more easily through the membrane.

In most blends, the osmotic pressure of the blended fertiliser solution was generally lower than the arithmetic sum of the osmotic pressures of the two individual fertiliser solutions, except for NH_4Cl blended with some fertilisers. For some fertiliser blends, the

net osmotic pressure significantly decreased, while in some cases the decrease was minimal. For example, most fertilisers blended with KNO_3 and DAP resulted in lowering osmotic pressure in some cases by more than 10% with the highest reduction observed for KNO_3 and DAP blend at 22.6%. NH_4NO_3 with KH_2PO_4 and $\text{Ca}(\text{NO}_3)_2$ and, NH_4Cl with $\text{Ca}(\text{NO}_3)_2$ also decreased the net osmotic pressure by more than 10%. The reduction in the resultant osmotic pressure of the blended solution may be due to the change in the properties of the blended fertiliser solutions probably due to the formation of more complex species.

Table 9.4 shows the comparative properties of KNO_3 and DAP and their blended solution as a typical example. When KNO_3 and DAP are blended (1 M : 1 M), the total number of species decreased to 4.45 M from 4.98 M for the combined species of the two different solutions and this has direct implications on the osmotic pressure. This blend also formed about 0.5 M of uncharged species (NH_4NO_3) which might played a role in lowering the osmotic pressure.

However, when NH_4Cl is blended with other fertilisers, the blended solution mostly resulted in increased osmotic pressure except when blended with urea, KNO_3 and $\text{Ca}(\text{NO}_3)_2$. The highest increase in osmotic pressure was observed for $(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{Cl}$ with about 10% increase. Urea has low osmotic pressure and therefore not suitable for use alone as DS. But when urea is blended with other fertilisers, there is no appreciable decrease in the net osmotic pressure except with $\text{Ca}(\text{NO}_3)_2$ and KNO_3 . This indicates that urea blended fertilisers can be used as DS for FO desalination and this is significant because, urea is one of the most commonly used N fertilisers in the world.

9.4.2 Water flux of blended fertiliser draw solutions

Water fluxes of the selected fertiliser blends are presented in Table 9.2 while more details of the all the blends are presented in Table 9.3. The highest water flux was observed for the $\text{NH}_4\text{NO}_3 + \text{NH}_4\text{Cl}$ blend, with $3.94 \mu\text{m/s}$ using DI water and $3.52 \mu\text{m/s}$ using BW as feed; while the lowest pure water flux was observed for urea+MAP blend with just $1.53 \mu\text{m/s}$ and $1.39 \mu\text{m/s}$ using DI water and BW as feed, respectively. Blends such as $\text{NH}_4\text{NO}_3 + \text{DAP}$, $\text{NH}_4\text{SO}_4 + \text{KNO}_3$, , $\text{KCl} + \text{NH}_4\text{Cl}$ and $\text{Ca}(\text{NO}_3)_2 + \text{NH}_4\text{Cl}$ all resulted in water fluxes comparatively higher than other blends. However, in almost all cases, the water fluxes of the blended fertiliser DS were slightly lower than the sum of

the two water fluxes if the two single fertilisers were used alone as DS with the exception of urea+KNO₃, urea+NaNO₃ and SOA+KNO₃ blends (with BW feed). The water flux for urea+KNO₃ blend was 2.83 µm/s, which is 16.2% higher than the sum of the individual fluxes of urea (0.58 µm/s) and KNO₃ (1.86 µm/s) used alone as DS. Likewise, the water flux for the urea+NaNO₃ blend was 2.36 µm/s, which is 11.6% higher than the sum of the individual fluxes of urea (0.58 µm/s) and NaNO₃ (1.53 µm/s). The increase in water flux with urea blend indicates a promising result since urea fertiliser itself as a DS has a very poor water flux in comparison to any other fertilisers.

Table 9.2 and Table 9.3 also shows the PR of water flux for the blended fertilisers. Depending on the type of blend, the PR ranged 8-19% with DI water and slightly less with BW feed. NH₄SO₄+KNO₃ and NH₄NO₃+NH₄Cl showed the highest PR of about 19% with DI water feed and about 17% with BW feed. The lowest performance ratio was observed for urea+MAP and NH₄SO₄+MAP blends, with only about 8% both using DI water and BW as feed. When the two fertilisers were blended in the solution, their PR was observed to be between the PR of the two fertiliser solutions tested individually. When two fertilisers with high PRs were blended together, the fertiliser blend generally tended to have a higher PR. Urea had the lowest PR amongst all the 11 selected fertiliser DS (Table 9.1); however, when urea was blended with other fertilisers, the PR of the DS significantly improved in comparison to using urea alone as the DS. Furthermore, these results also indicate that the PR of high performing fertilisers decreases when blended with low performing fertilisers. Therefore, it might be ideal to blend two high performing fertilisers containing different types of nutrients.

The decrease or increase in water flux for the blended fertilisers is explained as follows. Using DI water as feed water (bulk osmotic pressure of the feed is zero), the actual or experimental water flux J_w in FO mode is given by the following equation (McCutcheon and Elimelech, 2006; McCutcheon and Elimelech, 2007), which takes into account the influence of internal concentration polarisation (ICP) on the DS side facing the porous support layer of the membrane.

$$J_w = A \sigma [\pi_d \exp(-J_w K)] \quad (9.1)$$

Where A is the pure water permeability coefficient, π_d is the bulk osmotic pressure of the DS, σ the reflection coefficient (considered $\sigma = 1$ in this case) and K the solute resistance to diffusion within the membrane support layer. K is in fact a measure of how easily a draw solute can diffuse into or out of the membrane support layer and thus measures the severity of ICP (McCutcheon and Elimelech, 2006; McCutcheon and Elimelech, 2007). K is given by the following equation:

$$K = \frac{t\tau}{D\varepsilon} \quad (9.2)$$

Where t , τ and ε are all related to the structural properties of the membrane such as thickness, tortuosity and porosity of the membrane support layer and, D the diffusion coefficient of the draw solutes. Since all the experiments were performed using the same membrane, the performance of each DS is influenced by the diffusion coefficient of the draw solutes from equation (9.1) and (9.2) which in turn effects the solute resistivity value K . Therefore, blending different fertilisers would not only alter the types of species formed in the solution but the coexistence of different species could also alter the diffusivity of a particular species. This explains why the flux improves for urea+KNO₃ blend as DS.

Blended fertiliser solutions have multiple component species in comparison to single/straight fertiliser solutions. For concentrated solutions and solutions containing multiple component species, the diffusion coefficients are difficult to estimate because the solution does not obey the binary form of Fick's law however one of the exceptions is the mixture of weak electrolytes (Cussler, 2007). Urea being a weak electrolyte in this study, has been chosen as a typical example to explain the variations of flux and reverse diffusion of draw solutes in the blended draw solution.

For example, the average diffusion coefficient of KNO₃ in 1.0 M pure solution is $1.784 \times 10^{-9} \text{ m}^2/\text{s}$ however, its diffusion coefficient increases to $1.927 \times 10^{-9} \text{ m}^2/\text{s}$ in the urea+KNO₃ blended solution. The diffusion coefficient of urea did not alter significantly when blended with KNO₃. Similarly, the average diffusion coefficient of NaNO₃ also increased from $1.4241 \times 10^{-9} \text{ m}^2/\text{s}$ to $1.519 \times 10^{-9} \text{ m}^2/\text{s}$ when blended with urea in the solution. The average diffusion coefficients (D_{ave}) were calculated using equations provided elsewhere (Cussler, 2007; Tan and Ng, 2008) as follows:

$$D_{avg} = \frac{|Z_1| + |Z_2|}{(|Z_2|/D_1) + (|Z_1|/D_2)} \quad (9.3)$$

Where Z_i is the cation/anion charge of the ionic species and D_i is the individual diffusion coefficient of the cation/anion species in the water. The diffusion coefficients of each ionic species in the solution were determined by OLI Stream Analyser 3.2. This increase in the draw solute diffusivity helps in lowering the solute resistivity K (equation 9.2) and therefore decreasing the ICP effects on the porous side of the membrane thereby enhancing the water flux. ICP is one of the major factors responsible for limiting the water flux by FO process (Gray et al., 2006; McCutcheon and Elimelech, 2006; Tan and Ng, 2008; Tang et al., 2010; Wang et al., 2010a). Even at the same osmotic pressure, each type of DS has been observed to have different pure water flux indicating that, each type of DS offer different degree of ICP effects in the FO process (Achilli et al., 2010; Phuntsho et al., 2011b). The degree of ICP is higher at higher DS concentration and due to reduced diffusivity of the draw solutes at higher concentration (Tan and Ng, 2008).

9.4.3 Loss of nutrients by reverse diffusion of draw solutes during FDFO process

The loss of essential fertiliser nutrients due to reverse movement of only selected blended fertiliser draw solutes are also presented in Table 9.2. These results indicate that the fertiliser blend containing urea could still result in higher loss of N nutrient by reverse draw solute transfer. However, it is interesting to note that some blends result in either increased or decreased loss of nutrients in comparison to using single fertiliser as DS alone.

For example, when urea is blended with KH_2PO_4 , the loss of nutrients measured as N/P/K in g/L is 13.46/0.96/1.01. The loss of urea N in this case is significantly lower than when urea was used as DS alone (29.2 g/L); however, the loss of K and P are higher in urea+ KH_2PO_4 blended DS than for KH_2PO_4 alone. In the $(\text{NH}_4)_2\text{SO}_4$ + KH_2PO_4 blend, the loss of all the nutrients are lower than the loss of nutrient that occurs if they are used as DS alone. In contrast, the KH_2PO_4 + NaNO_3 blend resulted in increased NPK nutrient loss in comparison to their use as individual DS.

The reverse solute flux results for DS blended with two fertilisers indicate that the presence of multiple species (either in ternary system or in quaternary system) in the solution has a bearing on the net diffusion of species across the membrane for each type of species. At this stage, it is not well understood what causes this difference in reverse diffusion of draw solutes in the presence of multiple component species as this was not included within the scope of this study. Further study, including modelling of nutrient loss due to reverse movement of species, would provide an interesting inference on the influence of the multiple species in the draw solution.

9.4.4 Nutrient concentrations in the final FDFO product water using blended fertilisers as draw solutions

Table 9.2 and Table 9.3 also shows the final nutrient concentration in the product water by FDFO desalination using different types of blended fertiliser DS with BW. These results indicate that, blending of fertiliser in DS generally resulted in a significant reduction in the final nutrient concentration in comparison to using single fertilisers as the DS.

Urea fertiliser has one of the highest nitrogen contents (46.6%); therefore, when urea is used alone as the DS, the final nutrient concentration (measured as N/P/K in g/L) in the product water is 7.87/0/0 (Figure 9.2), which is significantly high for direct fertigation. However, when urea is blended with other fertilisers, the final nutrient concentration decreases appreciably. For example, when urea is blended with $(\text{NH}_4)_2\text{SO}_4$, their final nutrient concentration in the FDFO product water reaches 2.75/0/0, which is a decrease of about 65% from using urea as the DS alone. Likewise, when NH_4NO_3 with the next highest N (35%) fertiliser is blended with KH_2PO_4 , the final N concentration is 1.26/1.40/1.76, which has significantly lower N than using NH_4NO_3 alone as DS. Even by blending urea and NH_4NO_3 , both containing the highest N, the final N concentration in the FDFO product water decreases considerably.

The decrease of final nutrient concentration in the FDFO product water was more significant when fertilisers containing different major nutrients were blended together. For example, consider the blending of fertilisers containing only N as nutrient such as urea and NH_4NO_3 , with others such as KH_2PO_4 that do not contain N. The final nutrient concentrations of all major NPK nutrients for such blends decrease significantly in

comparison to using them alone as DS. It is also important to note that it will be easier to achieve significantly reduced nutrient concentration in the final FDFO product water, especially when two fertilisers containing different nutrients at low concentrations are blended together in the solution rather than blending fertilisers containing similar nutrients. For example, when MAP, which contains one of the lowest nutrient percentages (12%N and 27%P), is blended with KCl (containing only K), the final nutrient concentrations achieved in the FDFO product water are 0.61/1.35/1.70, which is one of the lowest in terms of NPK nutrients amongst all the blends studied here. Similar low nutrient concentrations were also achieved with $\text{KH}_2\text{PO}_4 + \text{NH}_4\text{Cl}$ blends. Although blending two fertilisers containing similar nutrients can also achieve significantly reduced nutrient concentrations in comparison to their parent single fertilisers, the final nutrient concentration for the common nutrient remains comparatively higher than when blending two fertilisers containing different nutrients. Blending to provide all NPK nutrients is even more effective in reducing the final concentration of the nutrients in the FDFO product water. These results confirm that blending two or more standard fertilisers could be useful in preparing a fertiliser DS that can produce FDFO product water of acceptable final nutrient concentration for direct fertigation.

Table 9.2: Performance of the selected fertiliser blend as DS in the FO process using DI water and BW as feed. J_{wt} : theoretical water flux calculated using equation (1), J_w : experimental water flux; PR: performance ratio (J_w/J_{wt}). Pure water permeability coefficient of the FO membrane ($A = 1.015 \pm 0.029 \text{ (L.m}^{-2} \text{ h}^{-1} \text{ atm}^{-1})$). Bulk osmotic pressure of the BW feed (5,000 mg/L NaCl) taken is 3.9 atm. RSF data is obtained from the DI water as feed. MAP: monoammonium phosphate - $\text{NH}_4\text{H}_2\text{PO}_4$, DAP: diammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$, SOA: sulphate of ammonia $(\text{NH}_4)_2\text{SO}_4$. CAN: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. RSF: Revers solute flux.

Fertiliser combinations 1M or (1M:1M)	π (atm)	DI as feed water			BW as feed water		
		J_w ($\text{L.m}^{-2} \text{ h}^{-1}$)	PR (%)	N/P/K loss by RSF (g/L)	J_w ($\text{L.m}^{-2} \text{ h}^{-1}$)	PR (%)	Final nutrient N/P/K (g/L)
Urea+SOA	68.6	7.78	11.2	9.41/0/0	7.24	11.0	2.75/0/0
Urea+MAP	66.2	5.51	8.2	10.71/0.26/0	5.00	7.9	2.36/1.74/0
Urea+KNO ₃	60.0	10.19	16.7	7.93/0/1.40	8.17	14.3	2.38/0/2.21
Urea+KH ₂ PO ₄	59.2	7.60	12.6	13.46/0.96/1.01	6.23	11.1	1.59/1.76/2.22
Urea+NaNO ₃	64.4	8.46	12.9	6.78/0/0	7.81	12.71	2.36/0/0
NH ₄ NO ₃ +KH ₂ PO ₄	78.5	10.12	12.7	1.04/0.01/0.72	9.68	12.8	1.26/1.40/1.76
NH ₄ NO ₃ +DAP	78.5	13.25	16.6	1.98/0.01/0	10.01	13.2	2.27/1.26/0
NH ₄ NO ₃ +NH ₄ Cl	74.8	14.18	18.7	1.55/0/0	12.67	17.6	1.92/0/0
SOA+MAP	89.6	7.52	8.3	0.818/0.624/0	7.38	8.5	1.72/1.27/0
SOA+KNO ₃	70.2	13.82	19.4	4.40/0/0.77	11.70	17.4	1.55/0/1.44
SOA+KH ₂ PO ₄	75.1	10.19	13.4	0.03/0.03/0.03	9.22	12.8	1.20/1.33/1.68
MAP+KCl	82.6	12.31	14.7	0.91/0.29/0.75	11.77	14.7	0.61/1.35/1.7
KCl+NH ₄ Cl	88.6	13.36	14.9	0.17/0/0.23	12.35	14.4	0.61/0/1.69
KH ₂ PO ₄ +NH ₄ Cl	82.6	11.45	13.6	0.27/0.01/0.24	11.34	14.2	0.61/1.35/1.70
CAN+NH ₄ Cl	82.0	13.03	15.6	0.74/0/0	12.38	15.6	1.71/0/0

Table 9.3: Details of different fertilisers blended as draw solution for FDFO desalination using brackish water feed. MAP: Monoammonium phosphate - $\text{NH}_4\text{H}_2\text{PO}_4$, DAP: Diammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$, SOA: sulphate of ammonia $(\text{NH}_4)_2\text{SO}_4$. A: Membrane permeability coefficient of the CTA FO membrane determined in RO mode at different pressure using DI water ($A = 1.015 \pm 0.029 \text{ (L.m}^{-2} \text{ h}^{-1} \text{ atm}^{-1})$). *Theoretical water flux of the blended fertiliser DS.

Fertiliser draw solution blends in 1M:1M (DS1+DS2)	Blend ed DS (pH)	Blend ed DS π (atm)	Sum of $\pi 1+\pi 2$ (atm)	M@3. 9 atm	N/P/K concentrations in the final FDFO product water using BW as feed (gL ⁻¹)			Actual Water Flux Jw (L.m ⁻² h ⁻¹)			J_{wt}^* (L.m ⁻² h ⁻¹)	Performance ratio (J _w /J _{wt} %)		
					DS1	DS2	Blended DS	DS1	DS2	Blende d DS		DS1	DS2	Blended DS
Urea Blended Draw Solutions														
Urea+NH ₄ NO ₃	4.96	56.9	57.4	0.059	7.87/0/0	4.90/0/0	3.30/0/0	2.05	7.67	8.75	57.74	8.5	22.9	15.1
Urea+SOA	5.14	68.6	69.8	0.0491	7.87/0/0	3.70/0/0	2.75/0/0	2.05	7.16	7.78	69.62	8.5	14.4	11.2
Urea+MAP	4.2	66.2	67.5	0.0561	7.87/0/0	2.11/4.68/0	2.36/1.74/0	2.05	5.29	5.51	67.18	8.5	11.7	8.2
Urea + KCl	7	66.9	67.7	0.0561	7.87/0/0	0/0/5.9	1.57/0/2.19	2.05	9.25	11.56	67.90	8.5	20.4	17.0
Urea+KNO ₃	6.98	60	60.9	0.0566	7.87/0/0	2.20/0/6.14	2.38/0/2.21	2.05	6.73	10.19	60.88	8.5	12.5	16.8
Urea+KH ₂ PO ₄	4.19	59.2	60.2	0.0567	7.87/0/0	0/4.86/6.14	1.59/1.76/2.22	2.05	6.23	7.60	60.08	8.5	17.5	12.6
Urea+Ca(NO ₃) ₂	6.8	69.9	72.5	0.0468	7.87/0/0	3.39/0/0	2.62/0/0	2.05	7.74	7.38	70.92	8.5	14.9	10.4
Urea+NaNO ₃	7	64.4	65.2	0.0563	7.87/0/0	2.16/0/0	2.36/0/0	2.05	5.54	8.46	65.34	8.5	11.8	12.9
Urea+ DAP	7.8	73.2	74.3	0.046	7.87/0/0	3.28/3.62/0	2.58/1.43/0	2.05	6.44	7.31	74.30	8.5	11.2	9.8
Urea+NH ₄ Cl	4.8	66.2	67.2	0.0561	7.87/0/0	2.13/0/0	2.36/0/0	2.05	8.93	9.83	67.18	8.5	20.3	14.6
Ammonium Nitrate Blended Draw Solutions														
NH ₄ NO ₃ +Urea	4.96	56.9	57.4	0.059	7.87/0/0	4.90/0/0	3.30/0/0	7.67	2.05	8.75	57.74	22.9	8.5	15.1
NH ₄ NO ₃ +SOA	5.15	79.6	79.8	0.0363	3.7/0/0	4.90/0/0	2.03/0/0	7.67	7.16	10.66	80.78	22.9	14.4	13.2
NH ₄ NO ₃ +MAP	4.13	74.7	77.5	0.0457	2.11/4.68/0	4.90/0/0	1.92/1.42/0	7.67	5.29	10.30	75.82	22.9	11.7	13.6
NH ₄ NO ₃ +KCl	4.93	76.5	77.7	0.0448	0/0/5.9	4.90/0/0	1.25/0/1.75	7.67	9.25	12.71	77.65	22.9	20.4	16.4
NH ₄ NO ₃ +KNO ₃	5.06	66.6	70.9	0.0461	2.2/0/6.14	4.90/0/0	1.94/0/1.80	7.67	6.73	11.27	67.57	22.9	12.5	16.7
NH ₄ NO ₃ +KH ₂ PO ₄	7.74	78.5	70.2	0.045	0/4.86/6.14	4.90/0/0	1.26/1.40/1.76	7.67	6.23	10.12	79.67	22.9	17.5	12.7
NH ₄ NO ₃ +Ca(NO ₃) ₂	5.18	75.7	82.5	0.0415	3.39/0/0	4.90/0/0	2.32/0/0	7.67	7.74	11.99	76.82	22.9	14.9	15.6
NH ₄ NO ₃ +NaNO ₃	5.09	72.4	75.2	0.0459	2.16/0/0	4.90/0/0	1.93/0/0	7.67	5.54	11.38	73.48	22.9	11.8	15.5
NH ₄ NO ₃ +DAP	7.7	78.5	84.3	0.0406	3.28/3.62/0	4.90/0/0	2.27/1.26/0	7.67	6.44	13.25	79.67	22.9	11.2	16.6

Fertiliser draw solution blends in 1M:1M (DS1+DS2)	Blend ed DS (pH)	Blend ed DS π (atm)	Sum of $\pi_1+\pi_2$ (atm)	M@3.9 atm	N/P/K concentrations in the final FDFO product water using BW as feed (gL ⁻¹)			Actual Water Flux J_w (L.m ⁻² h ⁻¹)			J_{wt}^* (L.m ⁻² h ⁻¹)	Performance ratio (J_w/J_{wt} %)		
					DS1	DS2	Blended DS	DS1	DS2	Blended DS		DS1	DS2	Blended DS
NH ₄ NO ₃ +NH ₄ Cl	4.75	74.8	77.2	0.0457	4.9/0/0	2.13/0/0	1.92/0/0	7.67	8.93	14.22	75.92	22.9	20.3	18.7
Ammonium Sulphate Blended Draw Solutions														
SOA+Urea	5.14	68.6	69.8	0.0491	7.87/0/0	3.70/0/0	2.75/0/0	7.16	2.05	7.78	69.62	14.4	8.5	11.2
SOA+NH ₄ NO ₃	5.15	79.6	79.8	0.0363	3.7/0/0	4.90/0/0	2.03/0/0	7.16	7.67	10.66	80.78	14.4	22.9	13.2
SOA+MAP	4	89.6	89.9	0.041	3.7/0/0	2.11/4.68/0	1.72/1.27/0	7.16	5.29	7.52	90.94	14.4	11.7	8.3
SOA+KCl	5.1	89.6	90.1	0.0353	3.7/0/0	0/0/5.90	0.99/0/1.38	7.16	9.25	11.95	90.94	14.4	20.4	13.2
SOA+KNO ₃	5.28	70.2	83.3	0.0368	3.7/0/0	2.20/0/6.14	1.55/0/1.44	7.16	6.73	13.82	71.24	14.4	12.5	19.4
SOA+ KH ₂ PO ₄	4	75.1	82.6	0.043	3.7/0/0	0/4.86/6.14	1.20/1.33/1.68	7.16	6.23	10.19	76.21	14.4	17.5	13.4
SOA+ Ca(NO ₃) ₂														
SOA+NaNO ₃	5.3	83	87.6	0.035	3.7/0/0	2.16/0/0	1.47/0/0	7.16	5.54	12.38	84.24	14.4	11.8	14.7
SOA+DAP	7.6	95	96.7	0.0344	3.7/0/0	3.28/3.62/0	1.93/1.07/0	7.16	6.44	9.11	96.41	14.4	11.2	9.4
SOA+ NH ₄ Cl	5	98.5	89.6	0.0343	3.7/0/0	2.13/0/0	1.44/0/0	7.16	8.93	12.24	99.97	14.4	20.3	12.2
Monoammonium phosphate Blended Draw Solutions														
MAP + Urea	4.2	66.2	67.5	0.0561	7.87/0/0	2.11/4.68/0	2.36/1.74/0	5.29	2.05	5.51	67.18	11.7	8.5	8.2
MAP+NH ₄ NO ₃	4.13	74.7	77.5	0.0457	2.11/4.68/0	4.90/0/0	1.92/1.42/0	5.29	7.67	10.30	75.82	11.7	22.9	13.6
MAP+SOA	4	89.6	89.9	0.041	3.7/0/0	2.11/4.68/0	1.72/1.27/0	5.29	7.16	7.52	90.94	11.7	14.4	8.3
MAP+KCl	4.1	82.6	87.8	0.0436	2.11/4.68/0	0/0/5.90	0.61/1.35/1.7	5.29	9.25	12.31	83.81	11.7	20.4	14.7
MAP+KNO ₃	4.12	69.6	81	0.045	2.11/4.68/0	2.20/0/6.14	1.26/1.40/1.76	5.29	6.73	10.04	70.63	11.7	12.5	14.2
MAP+ KH ₂ PO ₄	4.05	75.5	80.3	0.0438	2.11/4.68/0	0/4.86/6.14	0.61/2.72/1.71	5.29	6.23	8.21	76.64	11.7	17.5	10.7
MAP+ Ca(NO ₃) ₂	Precipitation occurs													
MAP+NaNO ₃	4.07	77.1	85.3	0.0447	2.11/4.68/0	2.16/0/0	1.25/1.39/0	5.29	5.54	10.94	78.23	11.7	11.8	14.0
MAP+DAP	6	83.5	94.4	0.0391	2.11/4.68/0	3.28/3.62/0	1.64/2.42/0	5.29	6.44	7.96	84.74	11.7	11.2	9.4
MAP+ NH ₄ Cl	4.04	88.5	87.3	0.0433	2.11/4.68/0	2.13/0/0	1.21/1.34/0	5.29	8.93	11.56	89.82	11.7	20.3	12.8
Potassium Chloride Blended Draw Solutions														
KCl+Urea	7	66.9	67.7	0.0561	7.87/0/0	0/0/5.9	1.57/0/2.19	9.25	2.05	11.56	67.90	20.4	8.5	17.0

Fertiliser draw solution blends in 1M:1M (DS1+DS2)	Blend ed DS (pH)	Blend ed DS π (atm)	Sum of $\pi_1+\pi_2$ (atm)	M@3.9 atm	N/P/K concentrations in the final FDO product water using BW as feed (gL ⁻¹)			Actual Water Flux J_w (L.m ⁻² h ⁻¹)			J_{wt}^* (L.m ⁻² h ⁻¹)	Performance ratio (J_w/J_{wt} %)		
					DS1	DS2	Blended DS	DS1	DS2	Blended DS		DS1	DS2	Blended DS
KCl+NH ₄ NO ₃	4.93	76.5	77.7	0.0448	0/0/5.9	4.90/0/0	1.25/0/1.75	9.25	7.67	12.71	77.65	20.4	22.9	16.4
KCl+SOA	5.1	89.6	90.1	0.0353	3.7/0/0	0/0/5.90	0.99/0/1.38	9.25	7.16	11.95	90.94	20.4	14.4	13.2
KCl+MAP	4.1	82.6	87.8	0.0436	2.11/4.68/0	0/0/5.90	0.61/1.35/1.7	9.25	5.29	12.31	83.81	20.4	11.7	14.7
KCl+KNO ₃	6.95	77.1	81.2	0.0437	0/0/5.9	2.2/0/6.14	0.61/1.35/3.42	9.25	6.73	9.11	78.23	20.4	12.5	11.6
KCl+ KH ₂ PO ₄	4.07	76.1	80.5	0.0438	0/0/5.9	0/4.86/6.14	0/1.36/3.43	9.25	6.23	12.02	77.22	20.4	17.5	15.6
KCl+ Ca(NO ₃) ₂	6.76	95.6	92.8	0.0326	0/0/5.9	3.39/0/0	0.91/0/1.27	9.25	7.74	11.09	97.02	20.4	14.9	11.4
KCl+NaNO ₃	6.97	83.7	85.5	0.0435	0/0/5.9	2.16/0/0	0.61/0/1.70	9.25	5.54	11.38	84.96	20.4	11.8	13.4
KCl+DAP	7.8	79.7	94.6	0.039	0/0/5.9	3.28/3.62/0	1.09/1.21/1.52	9.25	6.44	12.02	80.89	20.4	11.2	14.9
KCl+ NH ₄ Cl	4.8	88.6	87.5	0.0433	0/0/5.9	2.13/0/0	0.61/0/1.69	9.25	8.93	13.36	89.93	20.4	20.3	14.9
Potassium Nitrate Blended Draw Solutions														
KNO ₃ +Urea	6.98	60	60.9	0.0566	7.87/0/0	2.20/0/6.14	2.38/0/2.21	6.73	2.05	10.19	60.88	12.5	8.5	16.8
KNO ₃ +NH ₄ NO ₃	5.06	66.6	70.9	0.0461	2.2/0/6.14	4.90/0/0	1.94/0/1.80	6.73	7.67	11.27	67.57	12.5	22.9	16.7
KNO ₃ +SOA	5.28	70.2	83.3	0.0368	3.7/0/0	2.20/0/6.14	1.55/0/1.44	6.73	7.16	13.82	71.24	12.5	14.4	19.4
KNO ₃ +MAP	4.12	69.6	81	0.045	2.11/4.68/0	2.20/0/6.14	1.26/1.40/1.76	6.73	5.29	10.04	70.63	12.5	11.7	14.2
KNO ₃ +KCl	6.95	77.1	81.2	0.0437	0/0/5.9	2.2/0/6.14	0.61/1.35/3.42	6.73	9.25	9.11	78.23	12.5	20.4	11.6
KNO ₃ + KH ₂ PO ₄	4.1	63.9	73.7	0.0442	2.2/0/6.14	0/4.86/6.14	0.62/1.37/3.46	6.73	6.23	11.27	64.84	12.5	17.5	17.4
KNO ₃ + Ca(NO ₃) ₂	6.8	86	86	0.0329	2.2/0/6.14	3.39/0/0	1.38/0/1.29	6.73	7.74	11.63	87.26	12.5	14.9	13.3
KNO ₃ +NaNO ₃	6.97	73	78.7	0.0439	2.2/0/6.14	2.16/0/0	1.23/0/1.72	6.73	5.54	9.40	74.09	12.5	11.8	12.7
KNO ₃ +DAP	7.89	68	87.8	0.0404	2.2/0/6.14	3.28/3.62/0	1.70/1.25/1.58	6.73	6.44	12.28	69.01	12.5	11.2	17.8
KNO ₃ +NH ₄ Cl	4.93	76.5	80.7	0.0448	2.2/0/6.14	2.13/0/0	1.25/0/1.75	6.73	8.93	12.20	77.65	12.5	20.3	15.7
Potassium Dihydrogen Phosphate Blended Draw Solutions														
KH ₂ PO ₄ +Urea	4.19	59.2	60.2	0.0567	7.87/0/0	0/4.86/6.14	1.59/1.76/2.22	6.23	2.05	7.60	60.08	17.5	8.5	12.6
KH ₂ PO ₄ +NH ₄ NO ₃	7.74	78.5	70.2	0.045	0/4.86/6.14	4.90/0/0	1.26/1.40/1.76	6.23	7.67	10.12	79.67	17.5	22.9	12.7
KH ₂ PO ₄ +SOA	4	75.1	82.6	0.043	3.7/0/0	0/4.86/6.14	1.20/1.33/1.68	6.23	7.16	10.19	76.21	17.5	14.4	13.4
KH ₂ PO ₄ +MAP	4.05	75.5	80.3	0.0438	2.11/4.68/0	0/4.86/6.14	0.61/2.72/1.71	6.23	5.29	8.21	76.64	17.5	11.7	10.7

Fertiliser draw solution blends in 1M:1M (DS1+DS2)	Blend ed DS (pH)	Blend ed DS π (atm)	Sum of $\pi_1+\pi_2$ (atm)	M@3.9 atm	N/P/K concentrations in the final FDFO product water using BW as feed (gL ⁻¹)			Actual Water Flux J_w (L.m ⁻² h ⁻¹)			J_{wt}^* (L.m ⁻² h ⁻¹)	Performance ratio (J_w/J_{wt} %)		
					DS1	DS2	Blended DS	DS1	DS2	Blended DS		DS1	DS2	Blended DS
KH ₂ PO ₄ +KCl	4.07	76.1	80.5	0.0438	0/0/5.9	0/4.86/6.14	0/1.36/3.43	6.23	9.25	12.02	77.22	17.5	20.4	15.6
KH ₂ PO ₄ +KNO ₃	4.1	63.9	73.7	0.0442	2.2/0/6.14	0/4.86/6.14	0.62/1.37/3.46	6.23	6.73	11.27	64.84	17.5	12.5	17.4
KH ₂ PO ₄ + Ca(NO ₃) ₂														
KH ₂ PO ₄ +NaNO ₃	4.05	73.2	78	0.0439	0/4.86/6.14	2.16/0/0	0.61/1.36/1.72	6.23	5.54	5.47	74.30	17.5	11.8	7.4
KH ₂ PO ₄ +DAP	6.14	74.7	87.1	0.0393	0/4.86/6.14	3.28/3.62/0	1.10/2.44/1.54	6.23	6.44	8.82	75.82	17.5	11.2	11.6
KH ₂ PO ₄ + NH ₄ Cl	4.06	82.6	80	0.0436	0/4.86/6.14	2.13/0/0	0.61/1.35/1.70	6.23	8.93	11.45	83.81	17.5	20.3	13.6
Calcium Nitrate Blended Draw Solutions														
Ca(NO ₃) ₂ +Urea	6.8	69.9	72.5	0.0468	7.87/0/0	3.39/0/0	2.62/0/0	7.74	2.05	7.38	70.92	14.9	8.5	10.4
Ca(NO ₃) ₂ +NH ₄ NO ₃	5.18	75.7	82.5	0.0415	3.39/0/0	4.90/0/0	2.32/0/0	7.74	7.67	11.99	76.82	14.9	22.9	15.6
Ca(NO ₃) ₂ +SOA	Precipitation occurs													
Ca(NO ₃) ₂ +MAP	Precipitation occurs													
Ca(NO ₃) ₂ +KCl	6.76	95.6	92.8	0.0326	0/0/5.9	3.39/0/0	0.91/0/1.27	7.74	9.25	11.09	97.02	14.9	20.4	11.4
Ca(NO ₃) ₂ +KNO ₃	6.8	86	86	0.0329	2.2/0/6.14	3.39/0/0	1.38/0/1.29	7.74	6.73	11.63	87.26	14.9	12.5	13.3
Ca(NO ₃) ₂ +KH ₂ PO ₄	Precipitation occurs													
Ca(NO ₃) ₂ + NaNO ₃	6.81	96.8	90.3	0.0326	3.39/0/0	2.16/0/0	1.37/0/0	7.74	5.54	10.40	98.24	14.9	11.8	10.6
Ca(NO ₃) ₂ + DAP	Precipitation occurs													
Ca(NO ₃) ₂ +NH ₄ Cl	5.07	82	92.3	0.0407	3.39/0/0	2.13/0/0	1.71/0/0	7.74	8.93	13.03	83.23	14.9	20.3	15.6
Sodium Nitrate Blended Draw Solutions														
NaNO ₃ +Urea	7	64.4	65.2	0.0563	7.87/0/0	2.16/0/0	2.36/0/0	5.54	2.05	8.46	65.34	11.8	8.5	12.9
NaNO ₃ +NH ₄ NO ₃	5.09	72.4	75.2	0.0459	2.16/0/0	4.90/0/0	1.93/0/0	5.54	7.67	11.38	73.48	11.8	22.9	15.5
NaNO ₃ +SOA	5.3	83	87.6	0.035	3.7/0/0	2.16/0/0	1.47/0/0	5.54	7.16	12.38	84.24	11.8	14.4	14.7
NaNO ₃ +MAP	4.07	77.1	85.3	0.0447	2.11/4.68/0	2.16/0/0	1.25/1.39/0	5.54	5.29	10.94	78.23	11.8	11.7	14.0
NaNO ₃ +KCl	6.97	83.7	85.5	0.0435	0/0/5.9	2.16/0/0	0.61/0/1.70	5.54	9.25	11.38	84.96	11.8	20.4	13.4
NaNO ₃ +KNO ₃	6.97	73	78.7	0.0439	2.2/0/6.14	2.16/0/0	1.23/0/1.72	5.54	6.73	9.40	74.09	11.8	12.5	12.7
NaNO ₃ +KH ₂ PO ₄	4.05	73.2	78	0.0439	0/4.86/6.14	2.16/0/0	0.61/1.36/1.72	5.54	6.23	5.47	74.30	11.8	17.5	7.4

Fertiliser draw solution blends in 1M:1M (DS1+DS2)	Blend ed DS (pH)	Blend ed DS π (atm)	Sum of $\pi_1+\pi_2$ (atm)	M@3.9 atm	N/P/K concentrations in the final FDFO product water using BW as feed (gL ⁻¹)			Actual Water Flux J_w (L.m ⁻² h ⁻¹)			J_{wt}^* (L.m ⁻² h ⁻¹)	Performance ratio (J_w/J_{wt} %)		
					DS1	DS2	Blended DS	DS1	DS2	Blended DS		DS1	DS2	Blended DS
NaNO ₃ +Ca(NO ₃) ₂	6.81	96.8	90.3	0.0326	3.39/0/0	2.16/0/0	1.37/0/0	5.54	7.74	10.40	98.24	11.8	14.9	10.6
NaNO ₃ +DAP	7.84	50.7	92.1	0.0403	2.16/0/0	3.28/3.62/0	1.69/1.25/0	5.54	6.44	8.14	51.44	11.8	11.2	15.8
NaNO ₃ + NH ₄ Cl	4.95	81.5	85	0.0446	2.16/0/0	2.13/0/0	1.25/0/0	5.54	8.93	12.17	82.69	11.8	20.3	14.7
Diammonium Phosphate Blended Draw Solutions														
DAP+Urea	7.8	73.2	74.3	0.046	7.87/0/0	3.28/3.62/0	2.58/1.43/0	6.44	2.05	7.31	74.30	11.2	8.5	9.8
DAP+NH ₄ NO ₃	7.7	78.5	84.3	0.0406	3.28/3.62/0	4.90/0/0	2.27/1.26/0	6.44	7.67	13.25	79.67	11.2	22.9	16.6
DAP+SOA	7.6	95	96.7	0.0344	3.7/0/0	3.28/3.62/0	1.93/1.07/0	6.44	7.16	9.11	96.41	11.2	14.4	9.4
DAP+MAP	6	83.5	94.4	0.0391	2.11/4.68/0	3.28/3.62/0	1.64/2.42/0	6.44	5.29	7.96	84.74	11.2	11.7	9.4
DAP+KCl	7.8	79.7	94.6	0.039	0/0/5.9	3.28/3.62/0	1.09/1.21/1.52	6.44	9.25	12.02	80.89	11.2	20.4	14.9
DAP+KNO ₃	7.89	68	87.8	0.0404	2.2/0/6.14	3.28/3.62/0	1.70/1.25/1.58	6.44	6.73	12.28	69.01	11.2	12.5	17.8
DAP+KH ₂ PO ₄	6.14	74.7	87.1	0.0393	0/4.86/6.14	3.28/3.62/0	1.10/2.44/1.54	6.44	6.23	8.82	75.82	11.2	17.5	11.6
DAP+Ca(NO ₃) ₂	Precipitation occurs													
DAP+NaNO ₃	7.84	50.7	92.1	0.0403	2.16/0/0	3.28/3.62/0	1.69/1.25/0	6.44	5.54	8.14	51.44	11.2	11.8	15.8
DAP+ NH ₄ Cl	7.67	89.4	94.1	0.0389	3.28/3.62/0	2.13/0/0	1.63/1.21/0	6.44	8.93	11.38	90.72	11.2	20.3	12.5
Ammonium Nitrate Blended Draw Solutions														
NH ₄ Cl +Urea	4.8	66.2	67.2	0.0561	7.87/0/0	2.13/0/0	2.36/0/0	8.93	2.05	9.83	67.18	20.3	8.5	14.6
NH ₄ Cl +NH ₄ NO ₃	4.75	74.8	77.2	0.0457	4.9/0/0	2.13/0/0	1.92/0/0	8.93	7.67	14.22	75.92	20.3	22.9	18.7
NH ₄ Cl +SOA	5	98.5	89.6	0.0343	3.7/0/0	2.13/0/0	1.44/0/0	8.93	7.16	12.24	99.97	20.3	14.4	12.2
NH ₄ Cl +MAP	4.04	88.5	87.3	0.0433	2.11/4.68/0	2.13/0/0	1.21/1.34/0	8.93	5.29	11.56	89.82	20.3	11.7	12.8
NH ₄ Cl +KCl	4.8	88.6	87.5	0.0433	0/0/5.9	2.13/0/0	0.61/0/1.69	8.93	9.25	13.36	89.93	20.3	20.4	14.9
NH ₄ Cl +KNO ₃	4.93	76.5	80.7	0.0448	2.2/0/6.14	2.13/0/0	1.25/0/1.75	8.93	6.73	12.20	77.65	20.3	12.5	15.7
NH ₄ Cl +KH ₂ PO ₄	4.06	82.6	80	0.0436	0/4.86/6.14	2.13/0/0	0.61/1.35/1.70	8.93	6.23	11.45	83.81	20.3	17.5	13.6
NH ₄ Cl +Ca(NO ₃) ₂	5.07	82	92.3	0.0407	3.39/0/0	2.13/0/0	1.71/0/0	8.93	7.74	13.03	83.23	20.3	14.9	15.6
NH ₄ Cl +NaNO ₃	4.95	81.5	85	0.0446	2.16/0/0	2.13/0/0	1.25/0/0	8.93	5.54	12.17	82.69	20.3	11.8	14.7
NH ₄ Cl +DAP	7.67	89.4	94.1	0.0389	3.28/3.62/0	2.13/0/0	1.63/1.21/0	8.93	6.44	11.38	90.72	20.3	11.2	12.5

*experiment conducted at DS concentration of (0.625 M : 0.625 M) since at 1 M:1 M, the blend was not easily soluble.

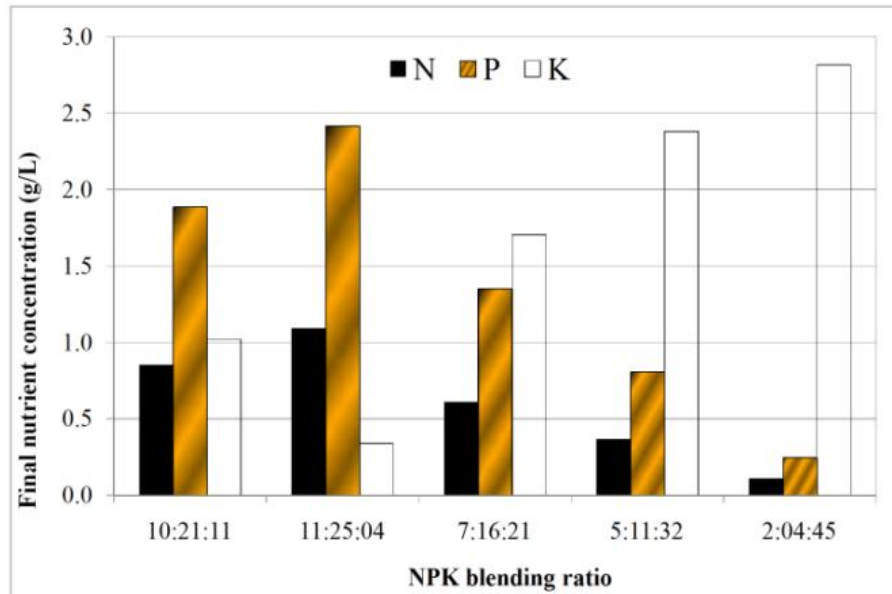
Table 9.4: Comparative properties of KNO₃, DAP and KNO₃+DAP fertiliser solutions

Properties	1.0 M KNO ₃ + 1.0 M		
	KNO ₃	DAP	DAP
pH	6.970	7.780	7.890
Osmotic pressure (atm)	37.190	50.560	68.030
Ionic strength (mol/mol)	0.017	0.051	0.058
EC (mS/cm)	89.729	137.073	140.397
K ⁺ (mol)	1.000		1.000
NO ₃ ⁻ (mol)	1.000		0.506
NH ₃ aqueous (mol)	0.026		
NH ₄ ⁺ (mol)		1.974	1.483
P ₂ O ₇ ⁴⁻ (mol)		0.011	
HPO ₄ ³⁻ (mol)		0.947	0.965
H ₂ PO ₄ ⁻ (mol)		0.021	
NH ₄ NO ₃ (aqueous) (mol)			0.494
Total charged species (mol)	2.000	2.952	3.950
Total uncharged species (mol)	0.026	NIL	0.494
Total species (mol)	2.026	2.952	4.448

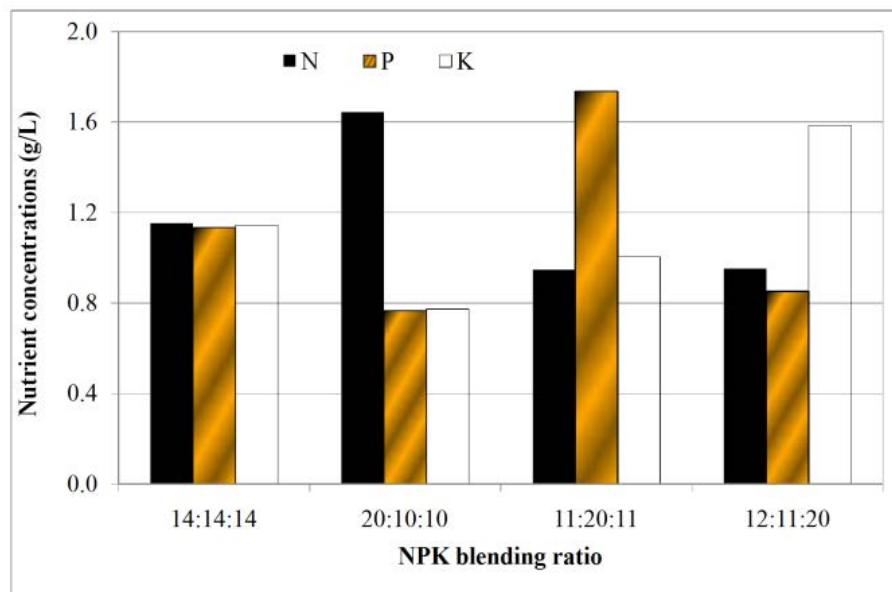
9.5 Influence of NPK blends in different ratios using two or more single fertilisers on the final nutrient concentrations

NPK fertiliser blends can be prepared either using two or more single fertilisers. The earlier data shows combinations for only two different fertilisers in equal molar ratio. Here, we show how blending of two or three single fertilisers to prepare different grades of fertilisers can influence the final nutrient concentrations in FDFO product water. Figure 9.4 shows that, it is possible to prepare DS containing different grades of N:P:K nutrients for particular crop requirement. MAP+KCl, was taken as a sample blend (Figure 9.4a) as this blend resulted in one of the lowest final nutrient concentrations (Table 9.2). It also shows that it is possible to achieve a very low concentration of a particular nutrient by adjusting the blends. For example, a DS with a fertiliser grade of 10:12:11 achieves final nutrient concentrations of 850/1890/1020 mg/L while DS grade of 2:4:45 can achieve about 100/300/2800 mg/L. It shows that, when the concentration of one of the nutrients is adjusted, the concentration of the other nutrients also varies, as their concentrations are dependent. This is not suitable as each nutrient requires different level of dilution to maintain required nutrient concentrations. However, it becomes more convenient to adjust all the nutrient concentrations as desired when more than two different fertilisers are used in the blend as shown with MAP+KCl+NH₄NO₃ in Figure 9.4b.

Table 9.5 shows comparative nutrient concentrations for fertigation of three selected plants (tomato, eggplant and cucumber). The DS was prepared by blending four selected fertilisers NaNO_3 , $(\text{NH}_4)_2\text{SO}_4$, KCl and KH_2PO_4 . While other fertiliser combinations are also possible, the combination that yielded the lowest nutrient concentration was selected for discussion in Table 9.5. The data shows that it is possible to formulate a specific grade of fertiliser blend suitable for each plant and this is important to avoid variable dilution required when multiple nutrients are present in the FDFO product water. The results in Table 9.5 indicate that, the nutrient concentrations in the final FDFO product water is still not suitable for direct fertigation and the process will still require dilution before application. For example, for fertigation of tomato, the final FDFO product will require a dilution of 4.8 times with feed TDS of 5,000 mg/L although it reduces to only about 2 times dilution when feed TDS is 2,000 ppm.



(a)



(b)

Figure 9.4: Final NPK nutrient concentrations of: (a) MAP and KCl blended, and (b) MAP, KCl and NH_4NO_3 blended in different ratios

Table 9.5: Estimated N/P/K nutrient concentrations in the final FDFO product water using blended fertiliser as DS and BW (5,000 mg/L NaCl with an osmotic pressure of 3.9 atm, assigned as BW5 in this table for clarity) as feed. DS consisted of blended fertiliser solution prepared in specific N:P:K ratios suitable for three selected plants using four different types of fertilisers [NaNO_3 , $(\text{NH}_4)_2\text{SO}_4$, KCl and KH_2PO_4] that yielded the minimum nutrient concentration in the final product water. BW2, BW3, BW4 and BW5 refer to brackish water feed of TDS 2,000, 3000, 4,000 and 5,000 mg/L of NaCl, respectively.

Plants	Recommended concentration (N/P/K mg/L)	Proposed DS grade N:P:K (%)	Final N/P/K using BW5 feed (mg/L)	Dilution required for different feed water BW2/BW3/BW4/BW5
Tomato	200/50/300	12:03:19	944/236/1147	1.9/2.8/3.8/4.8
Egg plant	170/60/200	13:04:15	1067/356/1255	2.5/3.7/5.0/6.3
Cucumber	200/50/200	14:04:14	1174/300/1168	2.4/3.5/4.7/6.0

9.6 Concluding remarks

The performances of straight fertilisers and blended fertiliser solutions have been investigated comparatively as DS for FDFO desalination process. It was demonstrated that, by using blended fertilisers as DS instead of single fertiliser, the final nutrient concentration of a particular nutrient could be significantly reduced in FDFO desalination process without additional process involved such as post-treatment or pre-treatment units. However, it was also observed that blending fertilisers generally resulted in slightly reduced bulk osmotic pressure and water flux in comparison to the sum of the osmotic pressures and water fluxes of the two individual DSs as used alone. The performance ratio or PR (ratio of actual water flux to theoretical water flux) of blended fertiliser DS was observed to be between the PR of the two fertiliser solutions tested individually. In some cases, such as urea, blending also resulted in significant reduction in N nutrient loss by reverse diffusion in presence of other fertiliser species. However, the study also shows that, because of the limitations offered by the osmotic equilibrium, achieving acceptable nutrient concentrations in the final FDFO product water will still remain a challenge especially when high salinity feed water is used therefore requiring different levels of dilution factor before direct fertigation.

CHAPTER 10



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NANOFILTRATION AS AN INTEGRATED OPTION to REDUCE NUTRIENT CONCENTRATIONS IN THE FERTILISER DRAWN FORWARD OSMOSIS DESALINATION PROCESS

10.1 Introduction

Although, it has been demonstrated in the earlier chapters that, several types of fertilisers can be used as draw solutions (DS), achieving acceptable final fertiliser nutrient concentration is an challenge with fertiliser drawn forward osmosis (DFFO) desalination process. The final DFFO product water usually exceeds the acceptable nutrient (NPK or nitrogen, phosphorous, potassium) for direct fertigation especially when feed water or feed solution (FS) with high total dissolved solids (TDS) such as seawater is used. Although, the minimum concentration of nutrient varies depending on the type of crops, type of nutrients, nutrient uptake by the plant, soil conditions and composition, nutrient availability, cropping season, plant growth stage, etc. (Bates, 1971; Baldwin, 1975; Hornick, 1992), excess fertiliser nutrient in is not only an economic waste but also could cause leaching and groundwater contamination. It can also increase soil salinity and cause plant toxicity. One easy method is to dilute the fertiliser solution by adding fresh water before fertigation, but such option is not desirable especially when fresh water sources are unavailable nearby and also when the dilution factor is high.

In Chapter 9, blended fertiliser was investigated as DS with the objective of reducing the concentration of a particular nutrient in the final product water from DFFO desalination process. It was observed that using blended fertiliser as DS could help significantly reduce the concentration of a particular nutrient in the final product water. However, even with the blended fertiliser as DS, it was apparent from the results in Chapter 9 that, the final nutrient concentrations will still be higher than the acceptable concentration for direct fertigation when a FS with higher TDS is used. Moreover, it was also pointed out in Chapter 5 that, operating FO process until the point osmotic equilibrium may not be economical as the water flux would be too low, not commensurate to the energy consumed by the pumps. This indicates that the final diluted DS concentration during the actual application of DFFO desalination will still contain fertiliser nutrient concentrations higher than the equivalent concentration of the FS.

The main objective of this study is to evaluate the integration of nanofiltration (NF) with DFFO desalination process as either pre-treatment or post-treatment in order to

achieve acceptable nutrient concentrations for direct fertigation thereby avoiding the need to further dilution using fresh water. The concept of NF as pre-treatment and post-treatment to FDFO desalination process was identified and briefly discussed in Chapter 5 as one of the potential options for achieving the nutrient concentrations in the final FDFO product water. NF is chosen because of its highly selective rejection properties (high rejection of divalent ions and modest rejection of monovalent ions) and also it can be operated at significantly lower pressure and produces higher water flux in comparison to RO process. NF as pre-treatment is one of the major breakthrough in the desalination process because of its energy efficiency (Hilal et al., 2004). Complete rejection is not the objective of the post-treatment process as the nutrients in the permeate water is necessary for fertigation of crops and NF process offers this alternative. The comparative performances of the FDFO desalination using NF as an integrated treatment option have been assessed in terms of nutrient concentrations in the final product water using simulated brackish groundwater (BGW) quality found in one of the salt interception schemes in the Murray-Darling Basin (MDB) in Australia.

10.2 Integrated FDFO-NF desalination process

10.2.1 FDFO desalination alone without NF process

Figure 10.1 shows the process diagram for FDFO desalination without integrating the NF process. Depending on the TDS of the FS, nutrient concentrations in the final FDFO product water could vary, requiring different degrees of dilution from additional fresh water before the final product water can be used for fertigation. This option is suitable when the existing fresh water resources are inadequate for irrigation and the desalinated water from FDFO process can be used in augmenting the fresh water for irrigation.

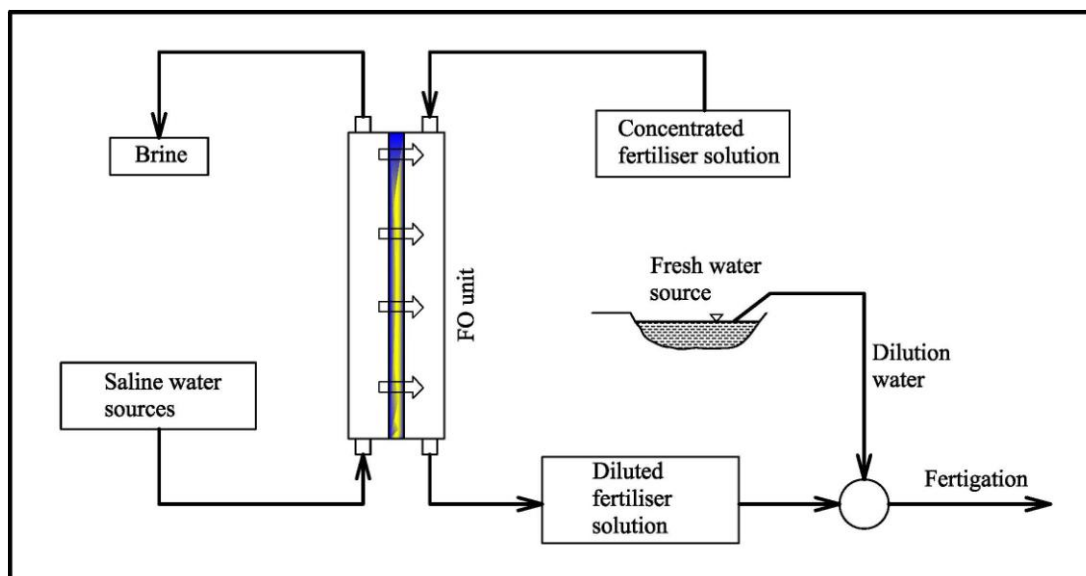


Figure 10.1: Conceptual process diagram for FDFO desalination alone without integrating NF process

10.2.2 NF as pre-treatment to FDFO desalination process

The minimum nutrient concentrations in the final FDFO product water depend on the TDS in the feed water. When TDS in the feed water are high, the final nutrient concentrations in the diluted fertiliser DS will also be proportionately high, as the osmotic equilibrium will occur at a DS concentration equivalent to that of the FS as discussed in Chapter 5. Pre-treatment of feed water using NF will significantly reduce the TDS of the FS as well as nutrient concentrations in the final FDFO product water. NF has high rejection of multivalent ions and moderate rejection of monovalent ions (Hassan et al., 1998; Childress and Elimelech, 2000; Bhattacharjee et al., 2001; Hilal et al., 2004). Since, BGW contains a significant proportion of multivalent ions, NF is a suitable choice for pre-treatment to reduce TDS in the feed. NF has been used as pre-treatment for seawater RO desalination due to its high flux and high retention of multivalent ions, as well as its ability to operate at low pressure (Hassan et al., 1998; Lu et al., 2002). Figure 10.2 presents the conceptual process flow diagram of the integrated FDFO-NF desalination process with NF as a pre-treatment option. NF is expected to remove most of the scaling and other organic fouling species, thereby enhancing the performance of FDFO process.

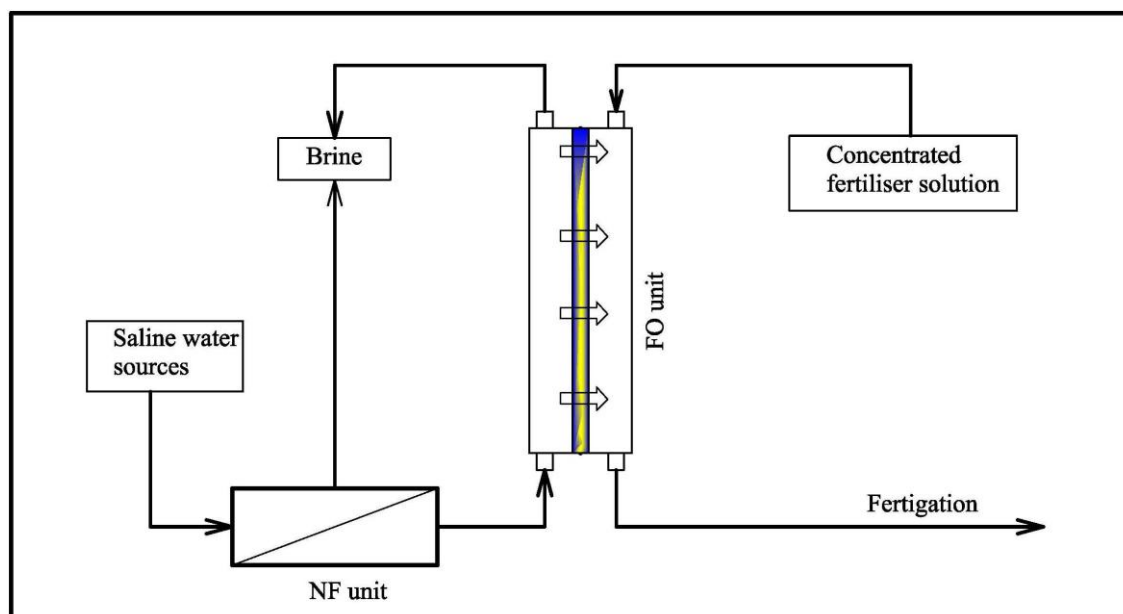


Figure 10.2: Conceptual process layout diagram for integrated FDFO-NF desalination process with NF as pre-treatment

10.2.3 NF as post-treatment to FDFO desalination process

NF as post-treatment serves two main purposes: reduction of fertiliser nutrient concentrations in the product water, thus making it suitable for direct fertigation and partial recovery, and recycling of excess nutrients for further reuse as DS. NF has selective rejection of ions, high rejection of multivalent ions and moderate rejection of monovalent ions. This property of NF makes it an ideal choice for post-treatment because complete separation and recovery of fertiliser draw solutes is not the objective. Recently, integrated FO-NF processes for desalination using seawater (Tan and Ng, 2010) and brackish water (Zhao et al., 2012b) have been reported using DS that contains divalent ions. They also reported that the FO-NF process is more advantageous than the RO desalination process in terms of energy. Since the quality of water needed for fertigation is lower than that required for drinking water, FDFO-NF is expected to be an ideal choice for meeting fertigation water quality standards. The other advantage of using NF for post-treatment is that the process can operate more efficiently since the final diluted DS contains only dissolved fertiliser and any scaling and fouling species present in the feed water would be removed during the FDFO process. Figure 10.3 shows the process layout of the FDFO desalination with NF as post-treatment option.

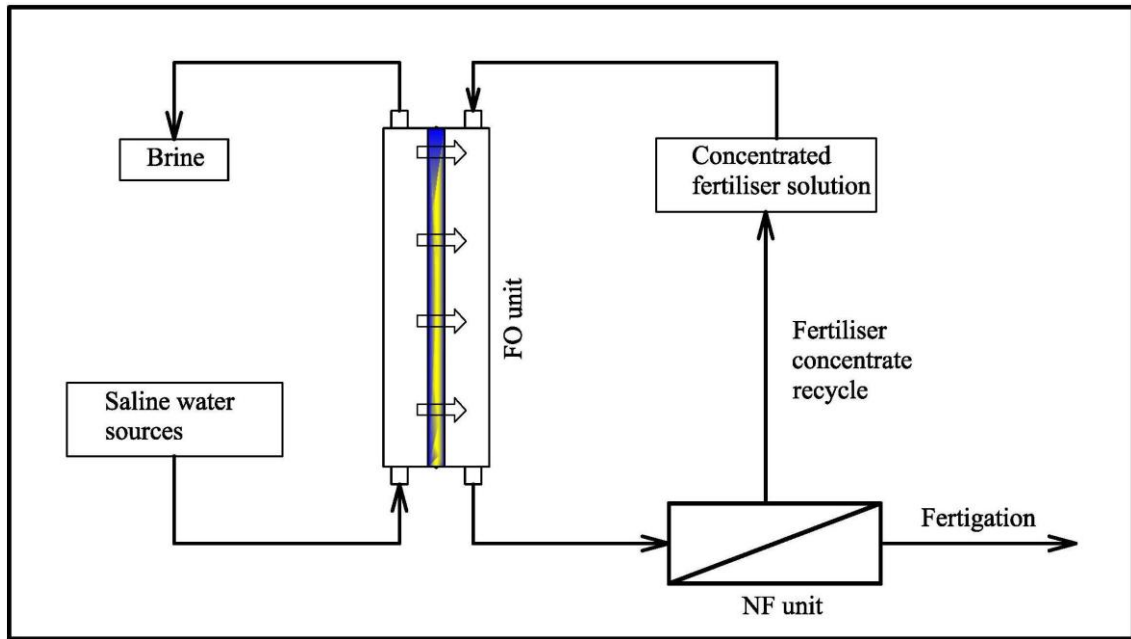


Figure 10.3: Conceptual process layout diagram for integrated FDFO-NF desalination process with NF as post-treatment

10.3 Experimental

All FO experiments were conducted using the CTA thin FO membrane and using eleven fertilisers as DS as described in Chapter 3. Unlike in other chapters, the study in this chapter has been performed using simulated brackish groundwater that is found at Buronga salt interception in the MDB. The composition of the BGW is provided in Table 3.2 under Chapter 3. In addition, blended fertilisers were also used as DS and the blending ratio for the major nutrients of NPK were prepared based on the ratio of the nutrient concentrations generally required by the crops. Two different blending options are included in this study: Blend 1 was prepared using three different fertilisers SOA, MAP and KNO_3 in specific proportions to make fertiliser blend of 15:4:23 (in %). Blend 2 was prepared using four different fertilisers SOA, KH_2PO_4 , NaNO_3 and KCl in specific N:P:K proportions of 12:4:17 (in %). This ratio has been designed to maintain the exact NPK nutrient ratio of the maximum recommended nutrient concentrations for plant (200 mg/L N, 50 mg/L P and 300 mg/L P) discussed in more detail later. While single fertilisers are used for growing crops, customised commercial fertilisers are often made available which are prepared based on the particular crop requirements and it contains most essential elements. However, the most commercial blended fertilisers are

often insoluble especially if they are prepared to include all the essential elements in the single fertiliser.

10.4 FDFO desalination of brackish groundwater without NF process

This particular study has two main components: performance assessment of FO process with fertiliser as DS and performance assessment of NF process with either BGW as feed water (during pre-treatment) or diluted fertiliser solution from FDFO desalination process as feed water (during post-treatment). The performance of the FO process with the eleven selected fertilisers as DS has been reported in our earlier publications (Phuntsho et al., 2011b; Phuntsho et al., 2012b). The experimental performance in this study is therefore mainly focussed on assessing the performance of the NF process and how it influences the outcome of the FDFO-NF desalination process in terms of the nutrient concentrations in the final product water. The performance of fertilisers as DS in FO process using BGW has been however briefly incorporated since our earlier studies did not specifically cover BGW. The assessment of the FO process in this study is mainly through theoretical calculations based on the osmotic equilibrium between the DS and FS. This was because the small membrane area used for the bench-scale experiment proved time-consuming and impractical to carry out the FO experimental run until the osmotic equilibrium has reached between the DS and the FS. However, when FDFO desalination process was assessed as standalone process, the experimental results are presented for the general benefit of the readers.

The ultimate goal of integrating the NF with the FDFO desalination processes is for achieving the nutrient concentrations in the final product water that is acceptable for direct fertigation of crops. The minimum or acceptable concentration of nutrients required for fertigation of crops vary considerably depending on many factors, such as type of crops, type of nutrients, soil conditions and composition, cropping season, plant growth stage, etc (Bates, 1971; Baldwin, 1975; Hornick, 1992; Phuntsho et al., 2012b). For example Table 10.1 shows the acceptable major nutrients NPK concentrations for tomato crops. Depending on the three different stages of plant growth, the acceptable nutrient concentrations for fertigation varies 120-200 mg/L N, 40-50 mg/L P and 180-300 mg/L K crops. The final product water from the FDFO desalination therefore must meet the water quality in terms of nutrient concentrations for direct fertigation.

Fertigation water containing fertiliser concentrations higher than this acceptable range would increase soil salinity and cause plant toxicity besides economic loss. Moreover these excess nutrients could reach water bodies and promote eutrophication and algal bloom, one of the devastating consequences of the excess nutrients in the environment.

Table 10. 1: Acceptable nutrient concentrations for direct fertigation of tomato plants (Imas, 1999).

Physiological Stages	N (mg/L)	P (mg/L)	K (mg/L)
Planting and establishment	120-150	40-50	180-220
Flowering	150-180	40-50	220-270
Ripening and harvest	180-200	40-50	270-300

10.4.1 Performance of FDFO desalination alone in terms of water flux

The experimental performance of the FO process using different fertilisers as DS is presented in Figure 10.4 in terms of water flux and the performance ratio (PR). PR is calculated as a ratio (in percentage) of actual water flux to theoretical water flux and indicates the bulk osmotic pressure available for effective generation of water flux across the membrane (McCutcheon et al., 2006; Phuntsho et al., 2012b). Theoretical water flux was calculated using the following equation:

$$J_{wt} = A \sigma \left[\pi_{D,b} - \pi_{F,b} \right] \quad (10.1)$$

Where J_{wt} is the theoretical water flux, A is the pure water permeability coefficient of the CTA FO membrane ($1.015 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) and $\pi_{D,b}$ and $\pi_{F,b}$ are the bulk osmotic pressures of 1.0 M fertiliser DS and the bulk osmotic pressure of the BGW feed used in this experiment. σ is reflection coefficient and its value was assumed unity for calculation.

Equation (10.1) has been derived based on the assumption that the osmotic equilibrium in a FO membrane module occurs when the osmotic pressure of the diluted DS is equal to the osmotic pressure of the fresh incoming feed solution. This is possible when the FO process is conducted with crossflow directions in the counter-current mode in the membrane module. Since the two solutions flow in opposite directions, the diluted DS at its outlet meets the incoming fresh feed solution on the other side and therefore can

still be diluted until the DS reaches osmotic equilibrium with the fresh feed solution. Therefore, in the counter-current crossflow mode of operation, the recovery rate of the feed does not affect the final concentration of the diluted DS but depends only on the concentration of the fresh feed solution.

FO performance experiments were carried out using 1.0 M fertilisers as DS and BGW5 and BGW35 as FS (properties of BGW shown in Table 3.2 in Chapter 3). From Figure 10.4(a), the highest water flux was observed for NH_4Cl DS, followed by KCl , NaNO_3 , and NH_4NO_3 , while MAP had the lowest water flux, consistent with our earlier findings (Phuntsho et al., 2011b; Phuntsho et al., 2012b). Blends 1 and 2 performed modestly in terms of water flux. As observed in our other study using pure water and brackish water as feed (Phuntsho et al., 2012b), urea showed the lowest water flux amongst the 12 selected DS, followed by MAP and DAP even using BGW feed.

Although water flux for all the DS has been ranked in decreasing order of magnitude (Figure 10.4(a)), their comparison in terms of PR, presented in Figure 10.4(b), indicates a different ranking. While NH_4Cl showed the highest PR, other DS, having much lower water fluxes such as NH_4NO_3 , showed comparable PR with NH_4Cl . Although the water flux of $\text{Ca}(\text{NO}_3)_2$ was ranked in fourth place, its PR is lower than most of the DS that are ranked lower in terms of water flux, except for DAP, MAP, and urea. $\text{Ca}(\text{NO}_3)_2$ has the highest MW among all the selected DS and, because of the large molecular size, its diffusivity within the membrane support layer is probably more restricted, causing more severe internal concentration polarization (ICP) effects. The PR of Blends 1 and 2 were slightly higher than $\text{Ca}(\text{NO}_3)_2$, although their water flux is much lower. The lowest PR was observed for urea, followed by MAP and DAP. The poor performance ratio of urea is attributed to its hydrophobic properties, which limit the diffusivity and contact of urea solutes within the membrane support layer causing severe ICP effects (Phuntsho et al., 2012b).

The other observation made in Figure 10.4 is the difference in DS performance using different feed TDS. While most fertilisers showed lower PR with BGW35, KH_2PO_4 , $\text{Ca}(\text{NO}_3)_2$, and MAP surprisingly showed higher PR with BGW35 than BGW5. This indicates that a higher percentage of the bulk osmotic pressure is effectively available with these DS when used with higher TDS FS. Urea has a net bulk osmotic pressure of

only about 5.1 atm with BGW35, but its water flux is negative, indicating that, due to its hydrophobic properties, urea concentration at the membrane surface within the membrane support layer is too low to generate positive water flux. The water flux for with BGW5 with most fertiliser DS in Figure 10.4(a) are slightly higher than the water flux reported with the simulated brackish water (5,000 mg/L NaCl) in our earlier studies (Phuntsho et al., 2012b). This is expected because the osmotic pressure of BGW5 (2.74 atm) is slightly lower than the osmotic pressure of the simulated brackish water feed (3.9 atm). In fact it was expected that the water flux could be affected by the formation of scales on the membrane surface due to the presence of scaling ions in the BGW. The water flux obtained in Figure 10.4(a) was however comparable to the water flux obtained using NaCl alone as DS in the earlier studies (Phuntsho et al., 2012b) indicating that the rejection of these scaling ions is high and therefore scaling is not significantly formed when 1 M concentration of fertilisers are used as DS.

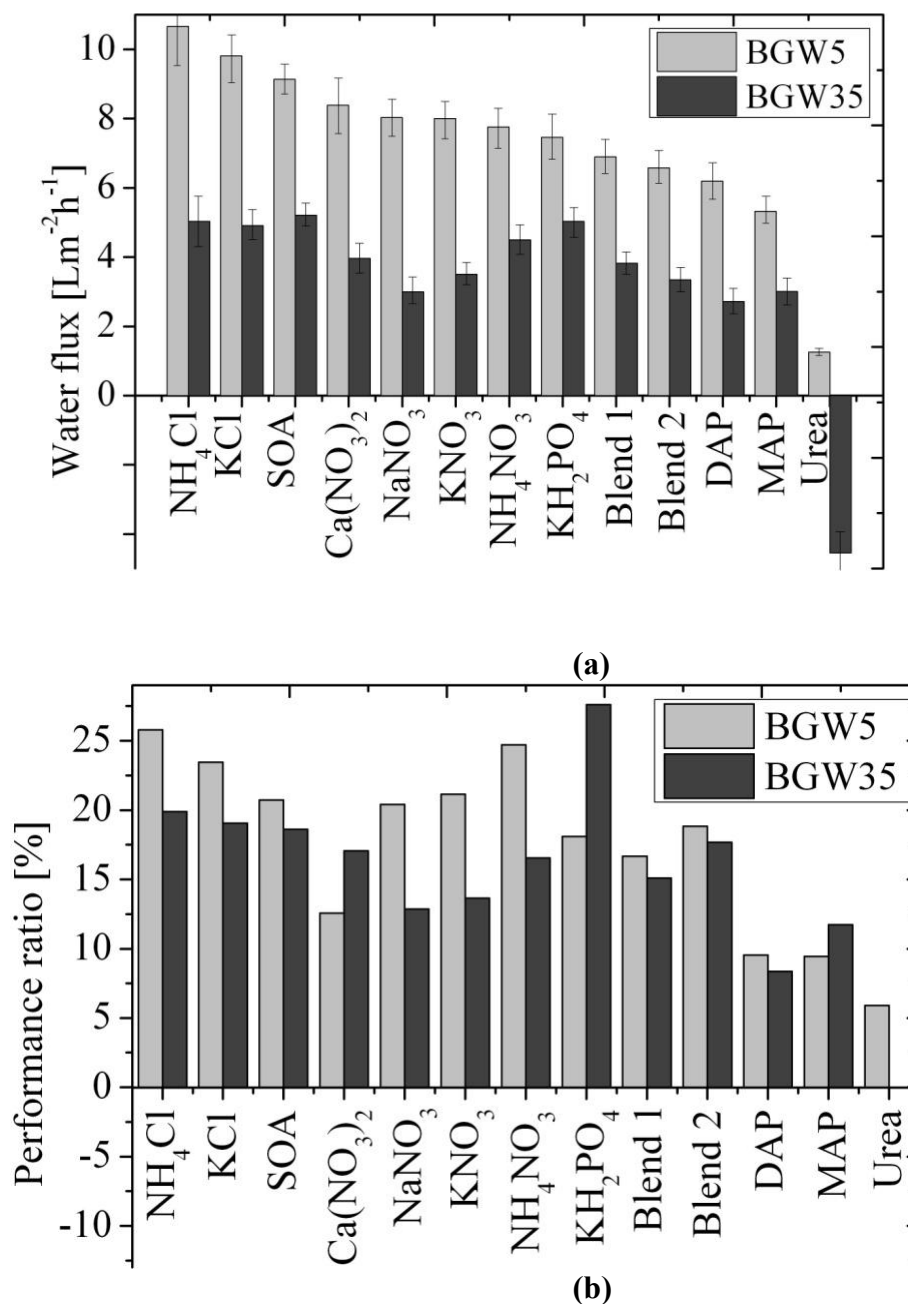


Figure 10. 4: Performances of the FDFO desalination process using fertilisers as DS (a) in terms of FO water flux and (b) performance ratio using 1.0 M fertiliser solutions as DS and BGW5 and BGW35 as FS.

10.4.2 Final nutrient concentrations from FDFO desalination alone

Table 10.2 shows the total water volume that a kilogram of each fertiliser as DS is expected to extract from a BGW with certain TDS and the expected nutrient concentrations in the final FDFO product water after desalination process. It must be clarified that, these are expected values because it was not practical using bench-scale FO unit to continue operating FO until the DS and FS concentrations achieved osmotic

equilibrium. These data have been arrived at based on the theoretical osmotic equilibrium between each fertiliser DS and the BGW FS and estimated using the following relationship derived based on mass balance:

$$V = \left(\frac{1000}{M_w C_M} \right) - 1 \quad (10.2)$$

where M_w is the molecular weight of the fertiliser compound and C_M is the molar concentration of the fertiliser solution that generates equal bulk osmotic pressure (osmotic equilibrium condition) with the osmotic pressure of the FS. The water extraction capacity of each fertiliser is important to estimate the nutrient concentrations in the product water. Similar approaches were adopted in our earlier studies to estimate the water extraction capacities of the draw solutes from brackish water to seawater although the equation was not presented (Phuntsho et al., 2012b). The water extraction capacity in our earlier studies was however simulated for saline water using NaCl as the only dissolved salt content. In this study however, the water extraction capacity has been simulated for BGW of different TDS that contains different types of salts as per the composition shown in Table 3.2 in Chapter 3. Based on the osmotic pressure of the particular BGW and the equivalent concentration of the DS predicted using OLI Stream Analyser 3.2, the water extraction capacity was estimated using equation (10.2).

It is clear from Table 10.2 that the total volume of water that can be extracted and the final N/P/K concentrations in the FDFO product water vary depending on the types of fertiliser used as DS and the TDS of the FS. The selected fertilisers can extract 120 to 311 L/kg of water from BGW5 and only 15 to 43 L/kg using BGW35. NH_4Cl is expected to extract the highest volume of water (311 L/kg) from BGW5 and about 43 L/kg from BGW35, followed by KCl with 223 L/kg from BGW5 and 31 L/kg from BGW35. KH_2PO_4 is expected to extract the lowest, removing only 120 L/kg, followed by $\text{Ca}(\text{NO}_3)_2$ with 132 L/kg from BGW5. Blend 1 can extract about 169 L/kg, while Blend 2 can extract 194 L/kg from BGW5, which is higher than most of the single fertilisers used as DS. Besides the feed TDS, the water extraction capacity of each fertiliser depends on the molecular weight of the fertiliser and the molar concentration of the fertiliser solution at osmotic equilibrium with the bulk osmotic pressure of the FS.

Based on the estimated water extraction capacity of the fertilisers, nutrient concentrations in the final FDFO product water have also been estimated and presented in the same Table 10.2. MAP, NH_4Cl , and NaNO_3 are expected to achieve minimum N concentrations of about 840 mg/L, closely followed by KNO_3 at 850 mg/L using BGW5 as the feed water source. NH_4NO_3 will result in the highest N concentration of 1,820 mg/L, followed by SOA at 1,370 mg/L. The lowest P concentration of 1,380 mg/L was achieved by DAP while the lowest K concentration of 2,340 mg/L was achieved by KCl using BGW5 as the FS. Nutrient concentrations are proportionately higher when BGW with higher TDS concentrations are used as FS.

Comparing Tables 10.1 and Table 10.2, it is amply clear that the nutrient concentrations in the final product water from FDFO desalination exceed the acceptable nutrient concentrations for fertigation indicating that the final diluted fertiliser DS cannot be directly applied for fertigation. The final nutrient concentrations must therefore be lowered by dilution to acceptable nutrient levels before fertigation. For example, when NH_4NO_3 or SOA is used as DS, the final product water from FDFO desalination requires a dilution factor that varies from 9 to 73, depending on the feed TDS. Although NH_4Cl and NaNO_3 achieve the lowest N concentrations, they still require a dilution factor between 4 and 30, depending on the feed TDS. Similarly, the dilution factor required for P is between 27 and 209 when DAP is used as DS, while the dilution factor required for K is between 8 and 55 when KCl is used. The dilution factor required is even higher when higher TDS FS is used.

The data in Table 10.2 also shows the expected final nutrient concentrations in the FDFO product water when a DS is prepared by blending more than two fertilisers together. The expected nutrient concentrations using Blend 1 fertiliser are 910/227/1365 with BGW5, which are much lower than the concentrations achieved when single or straight fertilisers are used as DS. The concentrations are even lower with Blend 2 at 614/153/922 with BGW5 as FS. This shows that Blend 1 and Blend 2 require dilution factors of 4.5 and 3.1 using BGW5 as FS, which is significantly lower than concentrations for most of the single or straight fertilisers used as DS. The concept and advantages of blending fertiliser DS has been extensively described in our earlier publication (Phuntsho et al., 2012b). However, when high TDS feed water is used, the

dilution factor required even with blended fertiliser DS is also proportionately higher, indicating the limitations of the FDFO process with high TDS FS.

Although, one of the options is to dilute the product water directly using fresh water before fertigation, the FDFO desalination process loses its merit if the required dilution factor is too high. A dilution factor equal to 2 or more means that an equal volume of fresh water or more will be required to dilute and make the product water suitable for direct fertigation. FDFO desalination that requires high dilution using fresh water is not a feasible technology given the fact that the very purpose of desalination is to solve fresh water scarcity issues. Therefore, NF has been assessed as an option to reduce nutrient concentrations in the final FDFO product water to acceptable limits.

However, it is important to note that, one of the assumptions made while calculating the water extraction capacity and final nutrient concentrations in Table 10.2 using equations (10.1) and (10.2) is that, the FO membrane is a perfect barrier to the solutes ($\sigma = 1$). This means that influence of feed solute that may cross the membrane towards the draw solutes or the reverse diffusion of draw solutes towards the feed is considered negligible on the water extraction capacity of the fertiliser draw solutes. These assumptions are reasonable given the recent synthesis of high performance and high rejecting membranes for FO applications (Wang et al., 2010a; Yip et al., 2010; Wei et al., 2011b; Wang et al., 2012).

Table 10. 2: Total volume of water a kilogram of fertiliser can extract (calculated using equation 10.2) and the expected nutrient concentrations in the final FDFO product water using BGW as feed. Blend 1 was prepared using SOA, MAP, and KNO₃ in an NPK ratio of 15:4:23 (in %), while Blend 2 was prepared using SOA, KH₂PO₄, NaNO₃, and KCl in an NPK ratio of 12:4:17 (in %).

Fertilisers	MW (g/mol)	π @1M atm	Water extraction capacity (L/kg)				Expected final nutrient concentrations (N/P/K in mg/L)			
			BGW5	BGW10	BGW20	BGW35	BGW5	BGW10	BGW20	BGW35
SOA	132.14	46.14	153	73	35	19	1370/0/0	2850/0/0	5940/0/0	10850/0/0
MAP	115.03	43.82	145	72	36	20	840/1850/0	1660/3670/0	3310/7320/0	5870/12980/0
DAP	132.06	50.56	168	83	40	21	1250/1380/0	2530/2800/0	5190/5740/0	9460/10460/0
KH ₂ PO ₄	136.09	36.51	120	59	28	15	0/1890/2380	0/3790/4780	0/7770/9810	0/14310/18060
KCl	74.55	43.96	223	112	56	31	0/0/2340	0/0/4640	0/0/9280	0/0/16450
KNO ₃	101.10	37.19	162	80	39	21	850/0/2380	1710/0/4760	3490/0/9750	6410/0/17890
NH ₄ NO ₃	80.04	33.68	191	92	43	23	1820/0/0	3770/0/0	7930/0/0	14690/0/0
NH ₄ Cl	53.49	43.47	311	156	78	43	840/0/0	1660/0/0	3330/0/0	5920/0/
NaNO ₃	84.99	41.53	194	97	48	26	840/0/0	1680/0/0	3390/0/0	6070/0/0
Ca(NO ₃) ₂	164.09	48.79	132	64	31	16	1280/0/0	2620/0/0	5290/0/0	9900/0/0
Urea	60.06	23.68	147	74	37	20	3140/0/0	6180/0/0	12280/0/0	21810/0/0
Blend 1	-	43.46	169	81	37	19	910/227/1365	1890/472/2836	4030/1007/6048	7642/1909/11468
Blend 2	-	37.15	194	93	44	23	614/153/922	1268/317/1903	2663/665/3996	4929/1231/7396

10.5 FDFO desalination of brackish groundwater with NF as pre-treatment

10.5.1 Performance of nanofiltration in the pre-treatment of brackish groundwater

The primary objective of NF pre-treatment here is to reduce the TDS of the feed prior to desalination so that osmotic equilibrium in the FDFO process can be reached at much lower DS concentrations and, thereby achieve significantly reduced nutrient concentrations in the final product water. The assessment includes performance of bench-scale NF pre-treatment in terms of water flux and salt or TDS rejection using four different types of BGW feed at different operating pressures. The performance of the FDFO desalination process following NF as pre-treatment is then simulated to determine the expected nutrient concentrations in the final FDFO product water. The experimental performances of the FDFO process in terms of water flux are not included here since the rejection rates of NF pre-treatment are adequate to estimate the nutrient concentrations in the FDFO product water based on the osmotic equilibrium. The FDFO process is naturally expected to perform significantly better when a pre-treated BGW feed is used instead of BGW feed without pre-treatment. The pre-treated BGW is of high quality with reduced TDS, scaling precursors and any other fouling species in the feed.

The performance of the NF process as pre-treatment of BGW is presented in Figure 10.5 in terms of specific water flux (SWF) and the fertiliser rejection. SWF is defined here as permeate flux per unit applied pressure and provides an indirect measure of the comparative energy required to produce unit product water from a diluted DS. Higher SWF will require lower energy to produce equal volume of product water by the NF process.

Although higher water fluxes were observed when NF was operated at higher applied pressure (data not shown here), the permeate fluxes did not increase linearly with the applied pressure. The SWF in Figure 10.5(a) indicate that the optimum operating pressure is about 20 bar for high TDS feed BGW20 and BGW35, while, for BGW5 and BGW10, the optimum operating pressure is about 15 bar. Operating NF beyond these optimum pressures with BGW is not likely to yield any economic benefit in terms of water flux per unit energy input or TDS rejection, except for higher recovery rates. The

reason for this decrease in SWF at higher applied pressure (non-linearity of the permeate flux with the applied pressure) is due to increased concentration polarisation at the membrane surface when the NF is operated at higher recovery rates or applied pressure (Wilf, 2007; Nilsson et al., 2008a; Silva et al., 2011). Operating NF above the critical flux increases the osmotic pressure of the feed at the membrane surface, which reduces the net driving force and the pressure drop across the membrane, ultimately affecting the overall permeate flux.

Figure 10.5(b) shows the TDS rejection of the BGW feed by the NF membrane at different applied pressures and feed concentrations. The results indicate that the TDS rejection is significantly influenced by the applied pressure (recovery rates) and the feed TDS. The first observation from Figure 10.5(b) is that the TDS rejection decreases with the increase in feed concentration. Based on the optimum pressure of the permeate flux described earlier, the TDS rejection rates for BGW5, BGW10, BGW20 and BGW35 were 83%, 74%, 67% and 53%, respectively. The second observation made from Figure 10.5(b) is the decrease in TDS rejection with the increase in applied pressure, although this decrease varied with the feed concentration.

Solute rejection by NF membranes is complex and influenced by several factors, such as membrane pore size, membrane surface charge density, feed solute properties, solution chemistry and the operational parameters (Waypa et al., 1997; Seidel et al., 2001; Schäfer et al., 2005). In the aqueous solutions, since anions are less hydrated than cations, anions approach more closely to the membrane surface. As a result, the membrane surface acquires a more negative zeta potential due to the presence of anions beyond the plane of shear (Childress and Elimelech, 1996). Membrane properties, especially the pore size and surface charge (type of charge and charge density), play a significant role in the rejection of solutes by NF. As the NF membrane (NE90) is negatively charged at the pH for all the BGW feed used in this study, electrostatic repulsion of anions present in the BGW plays an important role in the rejection rate of the NF membranes.

This low rejection at higher feed concentrations in Figure 10.5(b) is attributed to charge screening or shielding phenomenon (Cadotte et al., 1988; Wang et al., 1997; Diawara et al., 2003; Kim et al., 2010) and is usually interpreted using the Debye screening

length that decreases at higher salt concentrations (Nilsson et al., 2008b). At higher bulk feed concentrations, the salt concentration at the membrane surface, including cations (counter ions), increases and as a result, the negative charge of the membrane decreases. Such screening or shielding effect reduces the electrostatic repulsion between the anions and the membrane, causing solute rejection to decrease (Wang et al., 1997; Paugam et al., 2004; Kim et al., 2010). Moreover, a slight decrease in the pH of the BGW feed at higher TDS concentrations (Table 3.2, Chapter 3) may also contribute to reducing the negative charge of the membrane and hence the lower reduction.

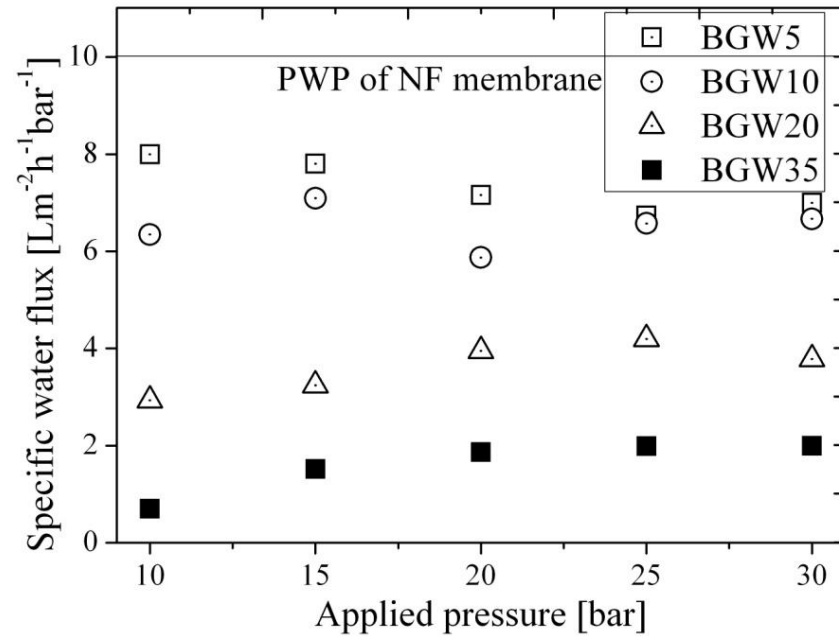
The decrease in TDS rejection with the increase in applied pressure can be explained as follows. At lower feed concentrations (BGW5 and BGW10), the TDS rejection decreased rapidly with increasing the applied pressure, while at higher feed concentrations (BGW10 and BGW35), the rejection slightly increased with increasing pressure up to 20 bar and then decreased at higher pressure. The decrease in the rejection at higher applied pressure is likely due to higher concentration of salts at the membrane surface, due to higher recovery rates (higher concentration polarisation), that enhances the permeation of salts due to increased convective and diffusive solute flux (Lee and Lueptow, 2001). This low rejection at higher recovery rates is also due to charge screening or shielding effect, a phenomenon similar to that explained earlier when higher feed concentration was used. However, the influence of this shielding effect is less prominent at higher TDS BGW. When a higher feed concentration is used as feed, the water flux is also comparatively lower and hence NF operates at lower recovery rates when compared with lower TDS feed. Therefore, the observed decrease in rejection rate is not as sharp as with low TDS feed. This also indicates that, at lower feed concentration, the permeate flux is higher, which in turn also induces higher convective flux of the solutes and thereby decreasing the TDS rejection.

Table 10.3 shows the water qualities of the permeate water following the NF pre-treatment of BGW. The data is presented only for the permeate composition operated at optimum applied pressure (15 bar for BGW5 and BGW10 and 20 bar for BGW20 and BGW35) as determined from Figure 10.5(a). The TDS of NF permeate were 454, 1,161, 4,222, and 11,049 mg/L using BGW5, BGW10, BGW20, and BGW35 FS, respectively. Crop salinity ratings in terms of TDS (mg/L) are as follows (ANZ-ECC and

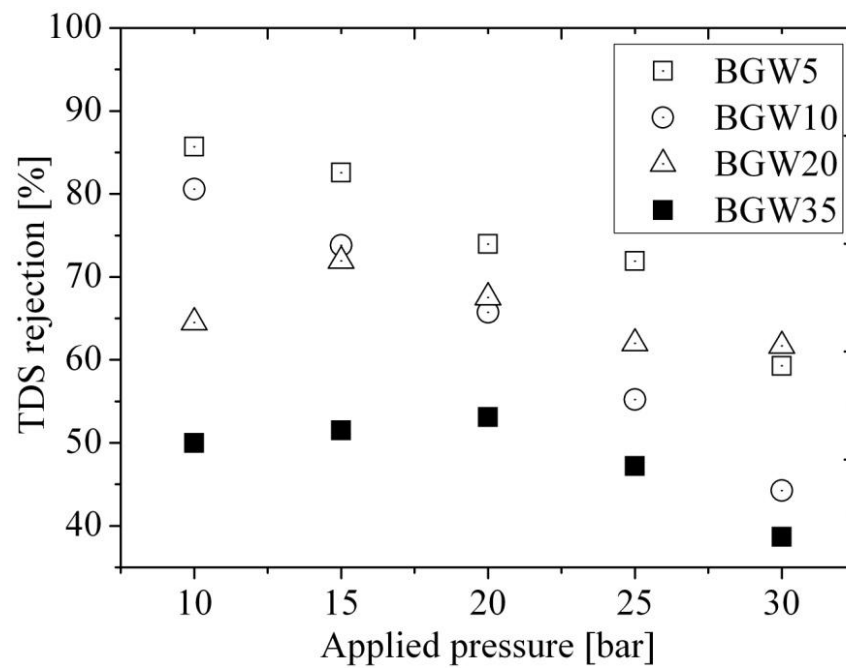
ARMCANZ, 2000): very low < 636, low: 636 to 1273, medium: 1273 to 3015, high: 3015 to 5159, very high: 5159 to 8174, and extreme > 8174. From the results in Table 10.3, the NF permeate using BGW5 and BGW10 falls below the low salinity ratings, while for BGW20 and BGW35, the water quality falls below high and extreme salinity ratings. This shows that, permeates from the BGW5 and BGW10 meet the salinity criteria for irrigation. However, besides salinity, water quality must also be assessed in terms of the sodium adsorption ratio (SAR), a value that measures the relative concentration of sodium (Na^+) to calcium (Ca^{2+}) and magnesium (Mg^{2+}). Calculation details for SAR are provided elsewhere (ANZ-ECC and ARMCANZ, 2000; Phocaides, 2007). Water containing high SAR value will cause sodicity (sodium toxicity) and loss of soil structure problems ultimately leading to soil degradation and poor crop yield (ANZ-ECC and ARMCANZ, 2000).

SAR value has been assessed for the permeate from the NF pre-treatment of BGW to see if the pre-treated BGW meets the water quality standard for irrigation. SAR is essential because the pre-treated water contains Na^+ ions that can cause sodicity problem if used for irrigation. SAR is not expected to be an issue when NF is used as post-treatment of diluted fertiliser solutions because Na^+ ions in the feed are expected to be completely removed during the FDFO desalination stage. Although the NF permeates from BGW5 and BGW10 have low salinity, the SAR values of the permeates are 13.7 and 23.0, respectively, higher than the recommended value for the water with above salinity and therefore, cannot be used directly for irrigation unless Ca and Mg concentrations are adjusted. The higher SAR value in the NF permeate in Table 10.3 is due to low rejection of NaCl and high rejection of divalent ions of Ca and Mg by the NF process that results in higher concentrations of Na relative to the Ca and Mg concentrations. The highly selective rejection of essential multivalent ions such as Ca and Mg is one of the disadvantages of NF or RO processes (Mrayed et al., 2011). NaCl rejection significantly decreases in the presence of divalent cations due to Donnan exclusions (Cadotte et al., 1988). Different crops have different tolerance to salinity (measured in terms of TDS or EC) and the groupings and the salinity ratings are provided elsewhere (ANZ-ECC and ARMCANZ, 2000). Moreover, the NF was operated at low recovery rates given the limited membrane area use for the lab-scale NF unit. If a much larger membrane area is used for FO tests, recovery rates would increase

and therefore it could result in lower rejection rates which could further impact the quality of the final product water.



(a)



(b)

Figure 10. 5: Performance of nanofiltration for the pre-treatment of BGW feed (a) NF permeate water flux and (b) specific water flux at different applied pressure. PWP: pure water permeability.

Table 10. 3 : Quality of the BGW following NF pre-treatment. The data is presented only for the optimum applied pressure for each feed (15 bar for BGW5 and BGW10 and 20 bar for BGW20 and BGW35). The osmotic pressure (π) in bar of the NF permeate was calculated using the equation: $\pi = 1.12 (273+T) \sum m_j$, where T is the temperature (25 °C) and $\sum m_j$ is the sum of molality concentration of all constituents in a solution (moles of solute/kg of solvent).

Compositions	BGW5	BGW10	BGW20	BGW35
Bicarbonate (mg/L)	10	10	10	20
Carbon (mg/L)	10	10	10	10
Sodium (mg/L)	149	419	1,342	3,544
Potassium (mg/L)	6	16	52	123
Calcium (mg/L)	1	5	27	73
Magnesium (mg/L)	10	27	138	358
Chloride (mg/L)	242	609	2,344	6,130
Sulphate (mg/L)	26	65	299	790
TDS (mg/L)	454	1161	4222	11049
Total molality (mol/kg)	14.50	38.06	135.62	355.49
Total molar mass (g/mol)	379.02	379.02	379.02	379.02
Osmotic pressure (bar)	0.31	0.80	2.86	7.49
SAR	13.7	23.0	32.7	53.6

10.5.2 Nutrient concentrations in the final product water from FDFO desalination after NF pre-treatment

Based on the permeate water quality from the NF pre-treatment for each BGW feed, the water extraction capacity and the final nutrient concentrations from FDFO desalination for each fertiliser DS have been estimated and presented in Table 10.4. The estimate is based on the osmotic equilibrium of the fertiliser DS with the pre-treated BGW whose composition is presented in Table 10.3. The equivalent concentration of the fertiliser solution was determined using OLI Stream Analyser 3.2. Due to reduced feed TDS by NF pre-treatment, the water extraction capacity of fertiliser significantly increases in comparison to FDFO alone (as shown earlier in Table 10.2). NH_4Cl and KCl are estimated to extract the highest volume of about 2.9 kL/kg and 2.1 kL/kg of water from BGW5 respectively, which are more than 9 times higher than FDFO alone. In fact all

fertilisers can extract more than 1 kL/kg of water from BGW5, although this capacity reduces substantially with higher TDS feed. Comparing BGW5 values from Tables 10.2 and 10.4 reveals that, if NF is used as a pre-treatment, the water extraction capacity of the fertiliser increases by 9 to 11 times depending on the type of fertiliser used as DS, although this is reduced when higher TDS feed is used.

The nutrient concentrations in the FDFO product water following NF as pre-treatment are also presented in Table 10.4. The results indicate that all fertilisers (except urea and NH_4NO_3) are able to achieve acceptable N concentrations of less than 200 mg/L using BGW5. While most K concentrations were quite close to the acceptable concentration of 300 mg/L, the P concentrations remained significantly higher indicating that meeting acceptable P concentration in the final product water will be a challenge with single or straight fertiliser compound as draw solutes. However, the results from the Blend 1 and Blend 2 fertilisers are promising. The final nutrient concentrations are significantly lower than the acceptable nutrient concentrations, indicating that only a certain portion of the BGW feed will be required to undergo the NF pre-treatment process in order to achieve a desirable N/P/K nutrient concentration of 200/50/300 mg/L. Based on these results, it has been estimated that about 85% (for Blend 1) and 80% (for Blend 2) of the total product water will have to come from FDFO desalination using NF as pre-treatment, while the remaining 15% (Blend 1) and 20% (Blend 2) can be used without NF pre-treatment. This is also true for the single fertilisers, such as SOA, NH_4Cl , NaNO_3 , and $\text{Ca}(\text{NO}_3)_2$.

Table 10. 4: Performance of the FDFO desalination process using NF as pre-treatment, measured in terms of the total volume of water extracted per kg of fertiliser and the expected nutrient concentration in the final FDFO product water. The estimation was performed based on the osmotic equilibrium between the fertiliser DS and the pre-treated BGW presented in Table 10.3. The equivalent concentration of the fertiliser solution was determined using OLI Stream Analyser 3.2.

Fertilisers	BGW5		BGW10		BGW20		BGW35	
	Vol (L/kg)	N/P/K (mg/L)	Vol. (L/kg)	N/P/K (mg/L)	Vol. (L/kg)	N/P/K (mg/L)	Vol. (L/kg)	N/P/K (mg/L)
SOA	1,628	162/0/0	583	477/0/0	146	1511/0/0	51	4779/0/0
MAP	1,345	112/242/0	506	310/687/0	138	915/2024/0	51	2695/5961/0
DAP	1,670	157/174/0	614	449/496/0	161	1369/1514/0	58	4191/4635/0
KCl	2,079	0/0/312	782	0/0/866	213	0/0/2556	79	0/0/7547
KH ₂ PO ₄	1,135	0/248/313	425	0/691/872	114	0/2061/2602	41	0/6260/7904
KNO ₃	1,530	112/0/312	574	312/0/871	155	929/0/2595	56	2817/0/7867
NH ₄ NO ₃	1,908	227/0/0	704	647/0/0	182	2000/0/0	63	6348/0/0
NH ₄ Cl	2,898	112/0/0	1,090	310/0/0	297	916/0/0	110	2710/0/0
NaNO ₃	1,822	112/0/0	684	311/0/0	186	921/0/0	68	2746/0/0
Ca(NO ₃) ₂	1,339	158/0/0	488	455/0/0	126	1405/0/0	45	4353/0/0
Urea	1,326	433/0/0	505	1186/0/0	141	3437/0/0	53	10006/0/0
Blend 1	1,719	90/22/135	630	245/61/368	162	952/238/1429	55	2745/685/4210
Blend 2	1,973	61/15/91	721	166/41/249	185	643/160/965	70	1680/419/2522

10.6 FDFO desalination of brackish groundwater with NF as post-treatment

The performance of FO process alone, using different fertilisers as DS has already been discussed under section 10.4. This section exclusively discusses the performance of NF as post-treatment to reduce the fertiliser or nutrient concentrations in the diluted DS following the FDFO desalination. NF experiments were carried out using different fertiliser concentrations that represent the final diluted DS concentrations after the FDFO desalination process.

10.6.1 Performance of NF in the recovery of excess fertiliser solutes

Figure 10.6 shows the variation of specific water flux (SWF) of NF post-treatment with types of fertilisers, fertiliser concentrations, and applied pressure. Although all fertiliser concentrations were prepared to simulate diluted fertiliser DS produced from the FDFO desalination process using BGW5 (2.74 atm) and BGW35 (18.56 atm) as FS, their SWF results varied significantly. This indicates that the performance of the NF process depends on other solute properties besides osmotic pressure of the feed solution (all fertiliser DS feeds have the same osmotic pressure as BGW5 and BGW10). At the lowest fertiliser concentration (BGW5), NH_4Cl solution showed the highest SWF, followed by Blend 1, SOA, and Blend 2, while KH_2PO_4 and $\text{Ca}(\text{NO}_3)_2$ showed the lowest SWF among the 13 fertiliser solutions. This difference in SWF indicates that each fertiliser can offer different advantages in terms of energy consumption during the NF post-treatment process. For example, the SWF of NH_4Cl is almost twice as high as that of KH_2PO_4 and therefore, the energy required for NF post-treatment will be comparatively lower. Similarly, other fertilisers with higher SWF, such as Blend 1, SOA, Blend 2, etc., will also require lower energy than KH_2PO_4 or $\text{Ca}(\text{NO}_3)_2$ solutions.

While lower SWF values are expected at higher fertiliser concentrations due to higher osmotic pressure, the ranking of SWF at higher fertiliser concentrations (BGW35) was slightly different from that at lower fertiliser concentration (BGW5). Fertiliser solutions that resulted in higher SWF at lower concentrations did not show high SWF at higher concentrations. Although, NH_4Cl solution resulted in the highest SWF at BGW5, its SWF at BGW35 was lower than that of many other fertiliser solutions. The highest SWF at BGW35 was observed for urea, followed by NH_4NO_3 , KNO_3 , MAP, and NaNO_3 , while fertilisers such as KH_2PO_4 , $\text{Ca}(\text{NO}_3)_2$, SOA, and DAP all showed lower

SWF. The SWF values of Blends 1 and 2 were, however, higher than those of SOA, $\text{Ca}(\text{NO}_3)_2$, and KH_2PO_4 . The highest SWF for urea at concentration equivalent to BWG35 is likely because of the poor retention properties of the urea. Urea has low molecular weight and neutral charged and therefore poorly retained by the NF membrane. Moreover, urea has hydrophobic properties and this enhances absorption of urea on the membrane, which further enhances its permeation through the membrane. Solutes with poor retention do not exert adequate osmotic pressure on the membrane and therefore this possibly resulted in higher water flux. This is not the case with the other fertilisers as their rejection is significantly higher than urea and therefore their water flux is proportionately lower at higher concentrations.

Figure 10.6 also shows a slight variation in the SWF for each fertiliser solution with applied pressure. At lower fertiliser concentration (BGW5), a slightly higher SWF was observed (consistent with all fertilisers) when the NF was operated at 10 bars than at 20 or 30 bars. At higher applied pressure, recovery rates of the NF process increase, but high recovery rates also contribute to enhanced concentration polarisation effects that likely result in lower SWF. However, at higher fertiliser feed concentrations (BGW35), the SWF increased slightly at higher applied pressures for most fertiliser solutions. The SWF for urea, NH_4NO_3 , and NaNO_3 did not vary significantly with applied pressure. At higher fertiliser concentrations, water flux in the NF process is comparatively low and therefore, the influence of ECP effects becomes insignificant, probably resulting in slightly higher SWF at higher applied pressure.

A comparison between the molecular weight (MW) of the fertiliser and the NF permeate flux (results not shown here) indicates that, fertilisers with larger MW generally resulted in lower SWF and vice versa. This is probably due to the higher rejection that occurs via size exclusion when salts with larger MW are used. As a result, a higher concentration of salts forms at the membrane surface, ultimately, increasing ECP effects, and hence lowering SWF. Although a comparison between the MW of all the fertilisers and their rejection by the NF membrane did not show a strong relation, nevertheless, it was evident that the salts with higher MW generally had higher rejection rates by the NF membrane, showing that size exclusion plays a vital role in NF rejection.

Figure 10.7 shows the variations of fertiliser salt rejection by NF during the post-treatment, according to the type of fertiliser salts used, their equivalent feed concentrations, and the applied pressure. From Figure 10.7(a), the highest rejection was observed for fertiliser salts containing multivalent ions such as DAP (96%), followed by SOA (95%), but excluding $\text{Ca}(\text{NO}_3)_2$ which had exceptionally lower rejection. Urea fertiliser had the lowest rejection of only 22%, followed by NH_4Cl (57%) and NH_4NO_3 (68%). MAP and KH_2PO_4 showed better rejections compared to other monovalent fertilisers such as KCl , NaNO_3 and KNO_3 . Fertiliser Blend 2 solution also showed moderate rejection while the rejection for Blend 1 was slightly lower.

The high rejection of DAP and SOA by NF is because of the presence of divalent anions, such as HPO_4^{2-} and SO_4^{2-} , which favours higher electrostatic repulsion by the negatively charged NF membrane. The high rejection of multivalent salts is one of the distinct characteristics of NF membranes. The rejections of MAP and KH_2PO_4 are higher than other fertilisers containing monovalent anions such as KCl , NaNO_3 and KNO_3 . This is because the effective size or (Stokes' radius) of H_2PO_4^- (0.323 nm) for MAP and KH_2PO_4 is higher than that of other monovalent anions such as Cl^- (0.120 nm) and NO_3^- (0.128 nm) (Wang et al., 2005; Hong et al., 2009; Disha et al., 2012) and therefore they are more rejected by NF due to size exclusion. Stokes' radius of Na^+ (0.183 nm) is also higher than K^+ (0.124 nm) (Wang et al., 2005) and for this same reason, NaNO_3 is more rejected by size exclusion than KNO_3 , although it has higher MW with the same anion than NaNO_3 .

The fertiliser Blends 1 and 2 contains multiple ions and therefore its rejection may a result of both size sieving and Donan exclusion. Since fertiliser Blend 2 was prepared using four different fertiliser compounds it contains Na^+ and Cl^- as additional ions compared to Blend 1 prepared using only three different fertilisers and therefore this might have resulted in slightly higher rejection of Blend 2 by NF. We have also seen earlier that Na^+ is more rejected by NF than K^+ .

The very low rejection for urea is due to its smaller size (lower molecular weight and no hydration layer), implying that NF cannot remove it by size exclusion. In addition, urea in aqueous solution remains neutral in charge and, therefore, electrostatic repulsion does not play a role in the rejection of urea (Lee and Lueptow, 2001). Urea rejection has also

been reported very poor in the FO process, as indicated by the high reverse solute fluxes (Phuntsho et al., 2012b; Yong et al., 2012). NH_4Cl has the lowest MW amongst all the selected fertiliser and therefore the low rejection is perhaps not surprising. Although NH_4Cl has lower MW than urea, its rejection is more than twice as high as urea, indicating that charge repulsion plays a significant role in the rejection of ionic N.

The low rejection of NH_4NO_3 is perhaps because it does not dissociate fully in water to form charged ions despite its highly solubility (Wishaw and Stokes, 1953; Robinson and Stokes, 1959a). Speciation analysis by OLI Stream Analyser 3.2 shows that about 16% and 42% of NH_4NO_3 remains non-dissociated at similar concentrations to BGW5 and BGW35 respectively, which could significantly affect the NF rejection. The NH_4NO_3 solutes, which are not dissociated, could easily pass thorough the membrane by both convective and diffusive phenomenon, which is further worsened by the low molecular size of the NH_4NO_3 .

Although $\text{Ca}(\text{NO}_3)_2$ contains divalent ion, its rejection rate is low and this low rejection can be explained as follows. Since NE90 membrane is negatively charged at the pH of BGW feed, complex formation of the divalent Ca^{2+} ion with the NF membrane surface becomes electrostatically favourable (Childress and Elimelech, 1996). The high adsorption of divalent cations (Ca^{2+}) cause the membrane surface to become less negatively charged (Childress and Elimelech, 1996). This reduction in negative charge enhances the attraction of anions (NO_3^{-1}) towards the membrane, thereby increasing permeation of $\text{Ca}(\text{NO}_3)_2$ salt through the membrane and reducing the rejection rates.

Figure 10.7(a) also shows the variation of NF rejection at different applied pressures. This data only shows the fertiliser concentration at osmotic equilibrium with BGW5, but a similar trend was observed for BGW35. Most fertilisers show improved rejection at higher applied pressure except for the few fertilisers listed on the right-hand side of Figure 10.7(a). At higher applied pressure, the convective flux dominates the diffusive flux, resulting in slightly lower solute diffusion in the permeate and, therefore, higher rejection rates are observed (Hilal et al., 2004). However, the decreased rejection rates at higher applied pressure for those fertilisers on the right-hand side of Figure 10.7(a) are probably due to higher concentration polarisation from the increased solvent flux at higher applied pressure (Lee and Lueptow, 2001). At lower applied pressure, the

diffusive flux becomes significant, resulting in a relative increase of salt diffusion across the membrane, which leads to reduced rejection rates. This is further supported by the lower salt rejection rates that occur when higher fertiliser concentrations are used as FS as shown in Figure 10.7(b). Low rejection at higher salt concentrations is explained due to screening or shielding effect similar to one described earlier although, in this case only single fertiliser compound is used, unlike in the earlier case with BGW feed, which contained multiple ionic species. This was evident with all the fertiliser DS when tested at higher concentrations equivalent to BGW35 shown in Figure 10.7(b).

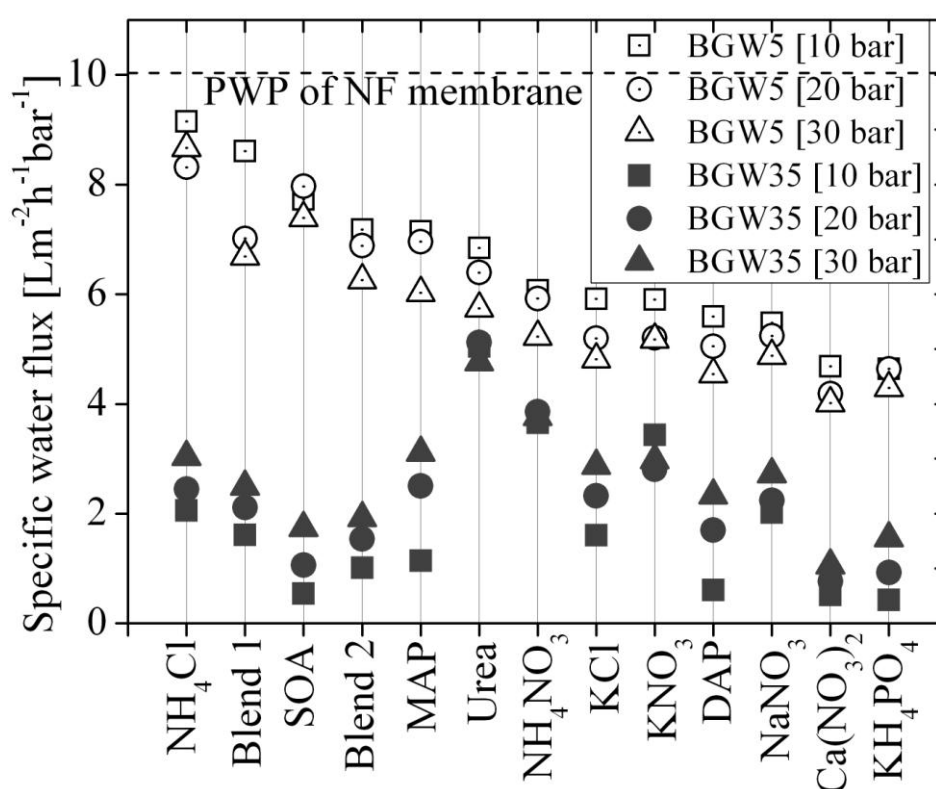


Figure 10. 6 : Variation of specific water fluxes with applied pressure for all fertiliser DS used as DS for NF post-treatment. BGW5 and BGW35 in the legend represent the concentrations of diluted fertiliser DS from a FDFO desalination process, using BGW5 and BGW35 as FS (solution temperature at 25 °C and crossflow rate at 400 ml/min or 8.5 cm/s). PWP: pure water permeability.

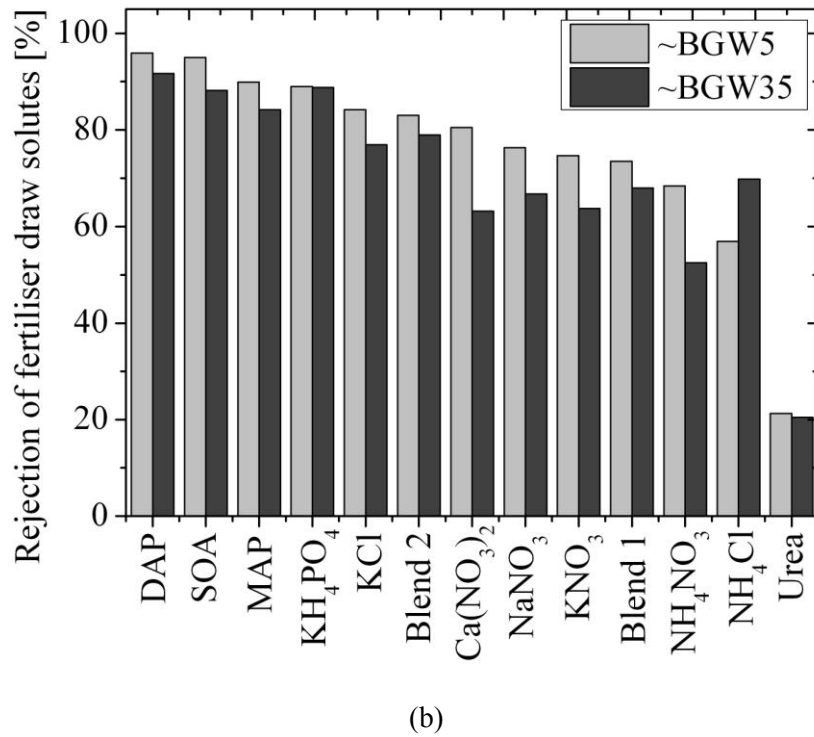
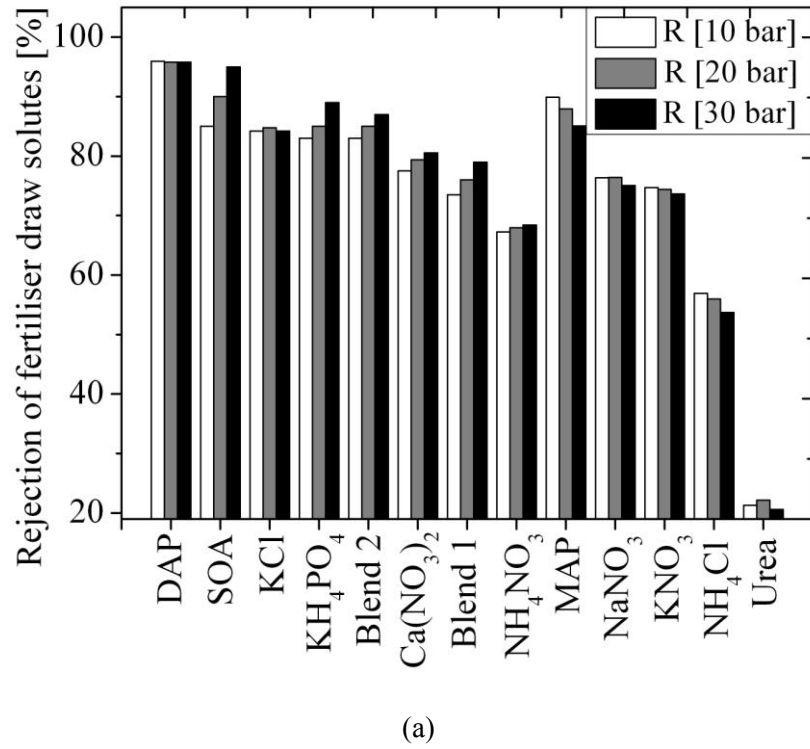


Figure 10. 7: Rejection of fertiliser draw solutes by NF membrane (NE90) (a) at different applied pressure using diluted fertiliser DS which has osmotic pressure equal to BGW5 and (b) at different FS concentrations using diluted fertiliser DS which has osmotic pressure equal to BGW5 and BGW35 at an applied pressure of 10 bar. Solution temperature at 25 °C and crossflow rate at 400 ml/min (8.5 cm/s).

10.6.2 Nutrient concentrations in the final FDFO product water with NF as post-treatment

The water extraction capacity and the resulting nutrient concentrations in the final FDFO product water for each fertiliser using NF as post-treatment are shown in Table 10.5. The water extraction capacity increased substantially since the rejected draw solutes from the NF post-treatment are recycled to FDFO process for further reuse. The highest volume of water can be extracted from BGW5 using DAP (4.2 kL/kg), followed by SOA (3.1 kL/kg) and KCl (1.5 kL/kg) which are several orders of magnitude higher than that in FDFO used alone for desalination, indicating that NF as post-treatment can significantly increase the water extraction capacity of fertiliser draw solutes therefore effectively reducing nutrient concentrations in the final product water.

When BWG5 is used as the feed source, SOA, MAP, DAP, KNO_3 , NaNO_3 , Blend 1, and Blend 2 were able to achieve N concentrations lower than the acceptable N concentrations of 200 mg/L. DAP, Blend 1, and Blend 2 were able to achieve P concentrations lower than or closer to acceptable nutrient concentrations. K concentration for KH_2PO_4 was lower than the target concentration of 300 mg/L, while for KCl, the concentration was slightly higher. However, at higher fertiliser concentrations (BGW10 and above), the NF permeate exceeded nutrient concentrations for most fertilisers, except P concentrations for Blends 1 and 2. The N concentrations were closer to acceptable nutrient concentrations for MAP and DAP, although the P concentration was still much higher than 50 mg/L. Therefore, nutrient concentrations in the final FDFO product water, even after NF post-treatment, still remained high for direct fertigation, especially with high TDS feed. This indicates that, in order to further reduce nutrient concentrations to acceptable limits, the NF permeate must undergo second pass before the product water can be used for fertigation.

The results from Figures 10.6 and 10.7 indicate that, NF can be suitably used as the post-treatment process for reducing the fertiliser nutrient concentration and recycle to extract more water by FO process. It is however important to note some of the limitations of this study and how the results must be used with caution especially in terms of the absolute values. The NF rejection and the final nutrient concentrations are based on the bench-scale experimental set up in which the NF process was operated at

low recovery rates due to small membrane area (0.002 m^2). As discussed earlier, when NF is operated at higher recovery rates, the rejection would decrease and therefore the final nutrient concentrations would be higher than the ones presented in Table 10.5. These results will also vary if the post-treatment is carried out using NF with different pore sizes (MWCO) and charge density as their rejection rates would vary.

Table 10. 5: Final nutrient concentrations (N/P/K in mg/L) in the NF permeate after post-treatment of diluted fertiliser DS by NF following FDFO desalination. The data relates only to NF operated at an applied pressure of 10 bar and at a temperature of 25 °C. Acceptable N/P/K concentrations are 120-200/40-50/180-300 mg/L.

DS	BGW5		BGW10		BGW20		BGW35	
	Vol (L/kg)	N/P/K (mg/L)	Vol (L/kg)	N/P/K (mg/L)	Vol (L/kg)	N/P/K (mg/L)	Vol (L/kg)	N/P/K (mg/L)
SOA	3077	69/0/0	480	442/0/0	223	951/0/0	166	1280/0/0
MAP	1439	85/187/0	496	245/543/0	168	725/1605/0	131	929/2056/0
DAP	4173	51/56/0	837	253/281/0	272	779//862/0	266	797/0/0
Ca(NO ₃) ₂	474	360/0/0	151	1130/0/0	55	3111/0/0	33	5241/0/0
KH ₂ PO ₄	1097	0/208/261	316	0/720/906	140	0/1633/2054	142	0/1605/2019
KCl	1472	0/0/355	565	0/0/925	177	0/0/2691	138	0/0/3781
KNO ₃	643	215/0/600	271	512/0/1426	88	1572/0/4378	60	2323/0/6472
NaNO ₃	825	200/0/0	327	504/0/0	139	1185/0/0	82	2017/0/0
NH ₄ Cl	723	362/0/0	357	732/0/0	175	1500/0/0	147	1786/0/0
NH ₄ NO ₃	607	577/0/0	232	1507/0/0	88	3963/0/0	50	6978/0/0
Urea	190	2455/0/0	92	5064/0/0	45	10308/0/0	27	17324/0/0
Blend 1		132/8/138		297/25/324		727/60/759		1441/123/1479
Blend 2		200/11/205		454/33/482		1108/91/1149		2294/191/2293

10.6.3 Comparative performances of fertiliser solutions for NF as post recovery process

An ideal fertiliser candidate would be one that performs best in both NF and FO processes. Since NF is expected to consume significantly higher energy than FO, it is logical to select the fertiliser that performs well with NF so that overall energy consumption is lower for the entire process. An interesting observation is made by comparing water fluxes of the NF process to those of the FO process (Figure 10.8 (a)), as well as NF rejection (Figure 10.8(b)) for all of the fertilisers together. The dashed line represents strong linear correlation between the parameters considered. Although there was no correlation between the FO flux and water flux for all the fertilisers considered together, it was interesting to observe in Figure 10.8(a) that few fertilisers, such as NH_4Cl , SOA, Blend 2, NH_4NO_3 , and DAP, were closer to the dashed line. The comparison has been considered only within the two limits of the NF SWF obtained for all of the fertilisers, excluding urea at an applied pressure of 10 bar.

While the trend in Figure 10.8(a) may not reveal anything significant, it is logical to assume that fertiliser salts that generate higher water fluxes both in FO and NF are ideal candidates for the integrated FDFO-NF desalination process. It is clear from Figure 10.8(a) that NH_4Cl results in the highest water fluxes in both FO and NF processes, followed by SOA. Fertiliser Blends 1 and 2 and MAP are also proposed as a potential candidate as they have higher NF fluxes than other fertilisers. However, flux alone is not an adequate parameter and the ideal candidate must facilitate high rejection in the NF process.

Figure 10.8(b) shows the comparative plot of NF fluxes versus salt rejection of all the fertilisers together. The above potential candidate must have high flux and high NF rejection. Although NH_4Cl possesses high FO flux and NF flux, as indicated in Figure 10.8(a), its rejection by NF is the lowest (excluding urea) and it is, therefore, not an ideal candidate. SOA, with the next highest FO and NF fluxes (Figure 10.8(a)), also facilitates high rejection and is, therefore, the most suitable fertiliser candidate for integrated FDFO-NF desalination. The NF rejection of MAP and Blends 1 and 2 is also high indicating that these fertilisers are also suitable to be used for integrated FDFO-NF desalination. In addition, fertilisers, such as SOA, MAP, and Blends 1 and 2, all have

nutrient concentrations in the final product water below the acceptable concentrations and can, therefore, be directly used for fertigation. However, adjustment to P and K concentrations may be necessary before fertigation.

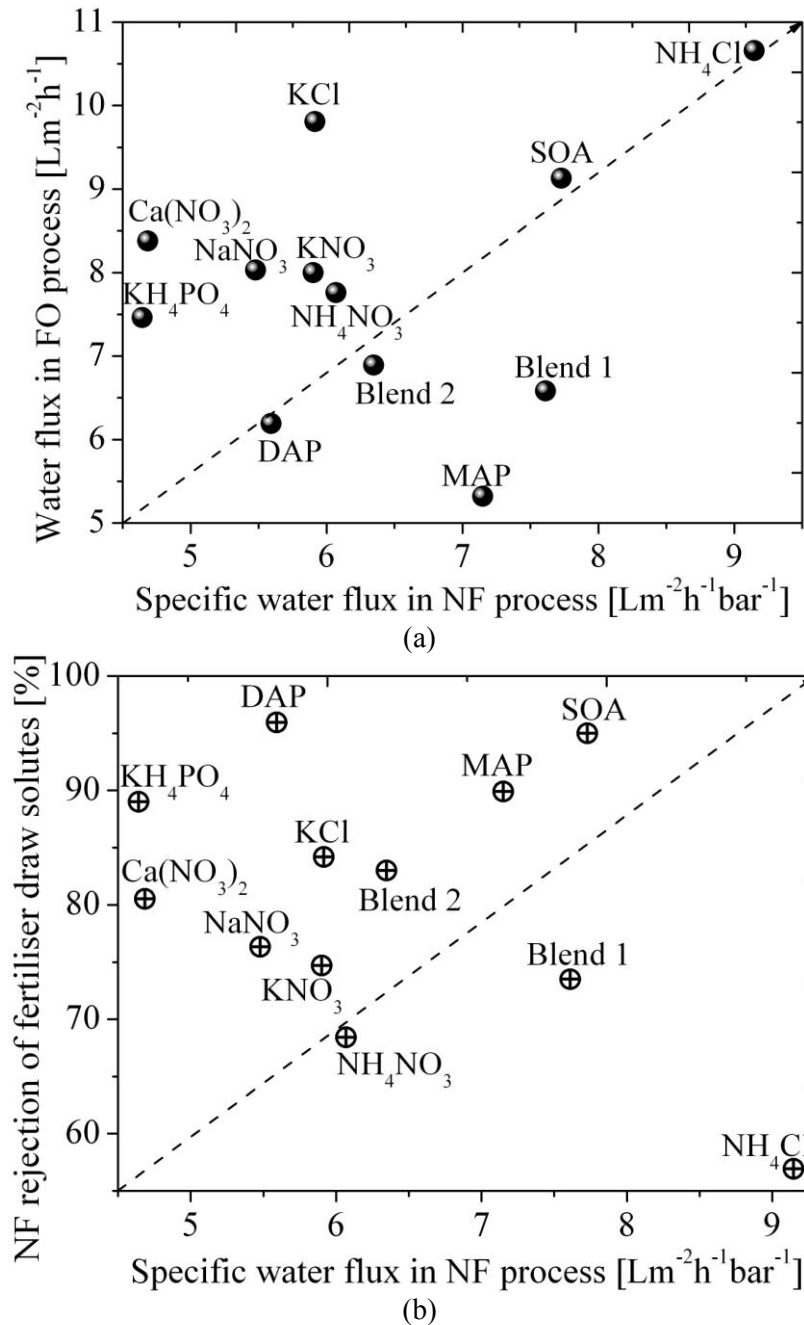


Figure 10. 8: Correlation between the performances of fertiliser salts in terms of (a) water flux in the NF process compared to the FO process and (b) NF fluxes with the NF rejection for all fertilisers together. The SWF for NF is obtained at an applied pressure of 10 bars, a temperature of 25 °C, and crossflow rates of 500 ml/min and uses FS that represents diluted fertiliser DS from the FDFO desalination process using BGW5 as FS. FO flux is obtained using 1.0 M fertilisers as DS with BGW5 as FS at a solution temperature of 25 °C and counter current crossflow rates of 400 ml/min in a system operated in FO mode.

10.7 Comparison of NF as pre-treatment and post-treatment with FDFO process alone

Although the absolute energy data could provide a comparative advantage of each process, the energy estimation is not straightforward and require complex considerations. The comparative advantages of each process are therefore assessed in terms of their technical feasibility to achieve acceptable nutrient concentrations and also in terms of process advantages.

Table 10.6 shows the comparative performances of the three different FDFO desalination processes assessed in terms of the N/P/K nutrient concentrations in the final product water using BGW5 and BGW35. The data in Table 10.6 was compiled from Tables 10.2, 10.4 and 10.5. The ideal choice of the FDFO desalination is to use as a standalone process because the energy consumption will be minimum; however, the quality of the product water in terms of the nutrient concentrations limits the application for direct fertigation. One simple option is to dilute the product water directly using fresh water before fertigation as discussed earlier, but this option is possible only when fresh water is already available. Moreover, if the dilution factor is too high, the volume of water provided by FDFO desalination process becomes insignificant. Therefore, FDFO desalination process cannot be used as a standalone for fertigation and hence option such as NF is necessary to be integrated with the FDFO system.

When low TDS BGW is used as FS, all multivalent fertilisers, such as SOA, MAP, DAP, and KH_2PO_4 , excluding $\text{Ca}(\text{NO}_3)_2$, will have lower N/P/K concentrations in the final product water when NF is used as post-treatment instead of pre-treatment. This is due to high rejection of multivalent ions by the NF process during the post-treatment of diluted fertiliser DS. Monovalent fertiliser salts, such as KCl, KNO_3 , NH_4NO_3 , NH_4Cl , and NaNO_3 including urea, $\text{Ca}(\text{NO}_3)_2$ all contain high N/P/K concentrations when used as post-treatment process. This is due to low rejection of monovalent fertiliser ions by NF. However, when a higher TDS BGW source is used, all fertilisers (except for NH_4NO_3 , $\text{Ca}(\text{NO}_3)_2$, urea, and Blend 2) can have significantly lower nutrient concentrations by using NF as post-treatment. This is due to comparatively higher rejection of fertiliser solutes than BGW as it contains higher concentrations of monovalent ions.

The above results indicate that, NF as a post-treatment could be more advantageous both in terms of reducing nutrient concentrations in the final product water and the resulting lower energy consumption. When NF is used as post-treatment, feed water quality is significantly high as it has already passed through the high rejecting FO membrane and therefore, NF can operate more efficiently without the issues of inorganic scaling and organic fouling further reducing the energy need. Scaling potential for fertiliser solution as feed is less because most fertiliser solution contains only single compound with high solubility, mostly higher than 3.0 M except for KH_2PO_4 (only 1.9 M). Scaling will be one of the major issues when NF is used as pre-treatment of BGW because of the presence of scaling ions such as Ca^{2+} , SO_4^{2-} .

However, some of the advantages of NF as pre-treatment of BGW must also be acknowledged. When NF is used as pre-treatment process, it removes the majority of scaling precursor ions, including any organic fouling species if present in the BGW feed. When high quality feed water is available, FDFO desalination can be operated with the membrane porous support layer facing the FS and the active layer facing the DS. Although, this membrane orientation is termed as pressure-retarded osmosis (PRO) and used mainly for osmotic power generation however, the water flux for this mode of membrane orientation is comparatively higher than when it is operated in normal FO mode due to elimination of dilutive ICP effects that occur in normal FO mode (Gray et al., 2006; Xu et al., 2010). This could significantly reduce the total membrane area required for the FO process and therefore the capital cost of the FO process.

It's important to note here that, this study was limited to only one type of NF membrane (NE90). Currently, a wide range of NF membranes are available in the market with varying pore sizes and charge density. It is important that, a membrane with high permeate flux and a suitable rejection is selected for the process whether for use as pre-treatment or post-treatment options. Although, it might be reasonable to assume that the lowest cost of the NF system will be the NF membrane with high permeate flux and high rejection nevertheless, there is always a trade-off between the two properties and therefore optimisation study is indispensable for the proper choice of NF membrane in any desalination processes (Hilal et al., 2005; Mohammad et al., 2007).

Table 10. 6: Comparative performances of FDFO and integrated FDFO-NF processes in terms of nutrient concentrations in the final product water. Data are compiled from Tables 2, 5, and 10. NF+FDFO: FDFO desalination with NF as the pre-treatment process. FDFO+NF: FDFO desalination with NF as the post-treatment process. Operating pressure for NF pre-treatment (15 bar for BGW5 and BGW10 and, 20 bar for BGW20 and BGW35) and NF post-treatment (10 bar for all concentrations).

Fertilisers	BGW5			BGW35		
	FO alone	NF + FO	FO + NF	FO alone	NF + FO	FO + NF
SOA	1370/0/0	162/0/0	69/0/0	10850/0/0	4779/0/0	1280/0/0
MAP	840/1850/0	112/242/0	85/187/0	5870/12980/0	2695/5961/0	929/2056/0
DAP	1250/1380/0	157/174/0	51/56/0	9460/10460/0	4191/4635/0	797/882/0
KH ₂ PO ₄	0/1890/2380	0/248/313	0/208/261	0/14310/18060	0/6260/7904	0/1605/2019
KCl	0/0/2340	0/0/312	0/0/355	0/0/16450	0/0/7547	0/0/3781
KNO ₃	850/0/2380	112/0/312	215/0/600	6410/0/17890	2817/0/7867	2323/0/6472
NH ₄ NO ₃	1820/0/0	227/0/0	577/0/0	14690/0/0	6348/0/0	6978/0/0
NH ₄ Cl	840/0/0	112/0/0	362/0/0	5920/0/	2710/0/0	1786/0/0
NaNO ₃	840/0/0	112/0/0	200/0/0	6070/0/0	2746/0/0	2017/0/0
Ca(NO ₃) ₂	1280/0/0	158/0/0	360/0/0	9900/0/0	4353/0/0	5241/0/0
Urea	3140/0/0	433/0/0	2455/0/0	21810/0/0	10006/0/0	17324/0/0
Blend 1	910/227/1365	90/22/135	132/8/138	7642/1909/11468	2745/685/4210	1441/123/1479
Blend 2	614/153/922	61/15/91	200/11/205	4929/1231/7396	1680/419/2522	2294/191/2293

10.8 Concluding remarks

One of the inherent limitations of FDFO desalination is that fertiliser nutrient concentrations in the final product water are governed by the TDS or osmotic pressure of the FS. When high TDS BGW feed sources are used, the essential N/P/K nutrient concentrations in the final product water always exceed acceptable limits, making the product water unfit for direct fertigation without further dilution using fresh water sources. This study investigated the integration of NF with FDFO desalination as either pre-treatment or post-treatment to reduce nutrient concentrations in the final product water so that it can be directly used for fertigation.

NF as pre-treatment was able to significantly reduce the TDS of the BGW because of its high rejection of multivalent ions. This ultimately helped in significantly enhancing the water extraction capacity of the fertiliser draw solutes and therefore achieving much reduced nutrient concentrations in the final product water from the FDFO desalination process. Most fertilisers were able to achieve nutrient concentrations lower than acceptable nutrient concentrations for direct fertigation however, the nutrient concentrations were still higher than for direct fertigation when high TDS BGW was used as feed. The other significant observation made in this study was that, when NF was used as pre-treatment, the feed water quality to the FDFO was high and therefore there is a potential for FDFO process to be operated in PRO mode of operation where water flux is significantly higher than in FO mode of operation.

NF as post-treatment is applied to reduce the nutrient concentrations in the final product water, while recovering excess salts for further extraction of water by FDFO process. Due to higher rejection of multivalent ions by NF, most fertilisers were able to achieve nutrient concentrations acceptable for direct fertigation. However, at higher TDS concentrations, the permeate requires a second pass through the NF system before fertigation.

A comparative study on NF as a pre-treatment or post-treatment option indicates that NF post-treatment could be more advantageous in terms of process efficiency and the energy consumption because of the high quality feed received for the NF from the FDFO process.

It is however important to note that this study was limited to a bench-scale NF experimental set up operated at very low recovery rates constrained by the small membrane area. The NF results are likely to vary when it is operated at higher recovery rates where the salt rejection would decrease and therefore the final nutrient concentrations would be higher. Moreover, this study was carried out using only one NF membrane (NE90) with a MWCO of 220 kDa. There is wide range of NF membranes available in the market and the absolute values of nutrient concentrations presented in this study with NE90 must be therefore used with caution especially when a NF membrane with different properties are to be considered for commercial applications.

CHAPTER 11



University of Technology Sydney

Faculty of Engineering & Information Technology

CONCLUSIONS AND RECOMMENDATIONS

11.1 Conclusions

Agriculture worldwide consumes over 70% of the total fresh water withdrawn from natural sources. The rapid growth in the world's population has driven the demand for fresh water, putting tremendous stress on already limited fresh water resources. With most fresh water sources either unavailable at affordable cost or already over-exploited, the only way we can satisfy the increasing demand for fresh water is by improving current water use efficiency and by creating new water from otherwise impaired water sources, such as seawater. It has been recognised that desalination could play a significant and reliable role in creating a new source of water, using the earth's unlimited saline water sources. However, current desalination technologies are generally energy intensive, with energy alone contributing about 45% of the total cost of desalinated water. Since the sources of energy in the world are mostly fossil fuel based, energy becomes a significant impediment for desalination because it results in increased greenhouse gas emissions that have direct consequences for global warming and climate change. Energy also becomes a significant issue if desalination technologies are targeted for large-scale water uses such as irrigation.

To address the global water scarcity problem through desalination, extensive investment in research to identify new and robust methods of purifying water using lower energy and at affordable cost is necessary. If low cost desalination technologies were made available, their impact on the agriculture sector would be significant for drought stricken countries like Australia where saline water is abundant in the form of seawater along coastal areas and as brackish groundwater in inland areas. Low energy and low cost desalination technology would also make desalination affordable for all the countries facing severe water shortages. Given dwindling freshwater supplies and the competition from other beneficial uses, desalination for irrigation could become a viable option for the irrigation of high value crops.

Of the new desalination technologies being investigated, forward osmosis (FO) has recently been recognised as one of the most promising and practical low energy technologies. Since FO desalination is based on the principle of a natural osmotic process driven by the concentration gradient rather than by hydraulic pressure, as in the RO desalination process, desalination can be achieved using very low energy. In the FO

desalination process, an artificially concentrated draw solution (DS) that generates high osmotic pressure is used to draw water from the saline water sources through a special membrane. Depending on the end-use of the product water, the diluted DS is usually further processed to separate and recover the draw solutes. Besides consuming almost negligible energy, FO has other advantages such as low membrane fouling potential, unlike the RO process, in which fouling is a major operational issue.

It has been acknowledged that the lack of a suitable DS has limited the application of FO desalination for potable water. Since the quality standard for drinking water is high, the separation of draw solutes from fresh water requires an additional post-treatment process that still requires energy, making the process uncompetitive with the existing state of the art RO desalination process in terms of energy and total cost of desalted water.

This study has identified that the FO process offers novelty for those applications where complete separation and recovery of draw solutes is not necessary and the final diluted DS can be used directly because it adds value to the end use. Fertiliser drawn forward osmosis (FDFO) desalination for fertigation was therefore proposed in the study and addresses most of the issues faced by FO desalination for potable purposes. Conclusions drawn from specific studies on the FDFO desalination process are mentioned below.

11.1.1 Fertiliser drawn forward osmosis desalination: concept, potential applications and limitations

The underlying premise of the FDFO desalination process is based on the concept that the diluted fertiliser DS after desalination can be used directly for fertigation because fertilisers are in any case used for agriculture. When fertilisers are used as the draw solutes in the FDFO desalination process, the diluted fertiliser solution after desalination can be directly applied for fertigation, thereby avoiding the need for separation and recovery of the DS.

This novel concept of the FDFO desalination process was explained, and the advantages in terms of energy need were compared based on the literature. The energy required for FDFO for direct fertigation was estimated to be less than 0.24 kW/m^3 of fertigation water which is not only comparatively lower than the most efficient current desalination

technologies but is also lower than the theoretical minimum energy required for desalting seawater based on the law of thermodynamics. Since FDFO is a low energy process, this particular technology can easily be powered by renewable energy, such as solar and wind energy, which exists in abundance in many arid and semi-arid countries, including Australia. Since fertilisers are extensively used for agricultural production, FDFO desalination does not create additional environmental issues related to fertiliser usage. In fact, FDFO desalination could add more value to irrigation water, thereby providing greater opportunity for improving the efficiencies of water and fertiliser use. It was also shown that FDFO desalination can be operated at very high feed recovery rates without significant extra energy use, unlike the RO process in which energy usage increases with the increase in the feed recovery rates. Depending on the types of fertilisers used as DS and the feed TDS, the simulation showed that the recovery rate would theoretically vary; nevertheless, most fertilisers achieved recovery rates higher than 80% with seawater.

It is recognised that that FDFO desalination has practical limitations. A major limitation identified in this study was the process limitation of osmotic equilibrium. Based on the principles of natural osmosis, 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. This indicates that if the seawater is used as the FS, the final diluted DS will still have a concentration (or osmotic pressure) equivalent to seawater. It is theoretically not possible to render the diluted DS concentration lower than the FS concentration without external influence. A model was presented to explain the osmotic equilibrium in the FDFO desalination process, and this osmotic equilibrium is one of the factors that limits the amount of water a unit mass of fertiliser can extract from a feed of particular TDS. This model was proposed based on the operation of cross flows in counter-current flow directions.

The water extraction capacities of each fertiliser DS were calculated for feed solutions with a different range of TDS, based on the limits of osmotic equilibrium. The water extraction capacity of the fertiliser DS was found to depend on factors such as the molecular weight of the fertiliser compound, its osmotic pressure and the concentrations of the FS. The study on eleven selected fertilisers indicates that each kilogram of

fertiliser can extract between 425 and 1090 L of water from brackish water feed with TDS 5,000 mg/L, although this reduces to between 9 and 28 L from seawater.

Based on the water extraction capacity of each fertiliser, the expected fertiliser nutrient concentrations in the final FDFO product water were then estimated in terms of N/P/K concentrations. By comparing the expected nutrient concentrations with the acceptable nutrient concentrations for different crops, it is clear that achieving acceptable nutrient concentrations for direct fertigation will be a major challenge for the FDFO desalination process. The remainder of the study therefore focussed mainly on investigating processes and options that would reduce the nutrient concentrations in the final FDFO product water for direct fertigation. Relevant options are dilution using fresh water sources, the use of blended fertilisers as the DS, integrating nanofiltration as either a pre-treatment or post-treatment process, and using a hybrid system of desalination and wastewater treatment in a dual stage FO process. The last option was outside the scope of this study and was not included.

Fertiliser drawn forward osmosis (FDFO) desalination technology has universal application, but due to process limitations in its current form, its potential application was discussed more in the context of water issues in the Murray Darling Basin (MDB) in Australia. *The draft basin plan* proposes to cut water allocations for consumptive use by 2,750 GL per year and under such circumstances, FDFO desalination technology is a suitable option for augmenting irrigation water by using brackish groundwater. FDFO desalination can be easily integrated with existing salt interception schemes where brackish water is pumped out every day and simply allowed to evaporate, losing precious water in the process.

11.1.2 Factors influencing the performance of the FO desalination process

Investigations included a study on the influence of various factors affecting the performance of the FO desalination process before the FDFO desalination process was evaluated. Four major factors responsible for the performance of FO desalination process were thoroughly investigated and their implications to the overall process discussed. The major factors assessed include membrane properties, DS properties, FS properties and finally the operating conditions. The influences of all these factors were measured in terms of water fluxes and the reverse diffusion of draw solutes.

A new and proprietary polyamide based thin film composite FO membrane (TFC-FO) membrane was introduced and its performance compared with two commercial cellulose triacetate FO (CTA-FO) membrane and TFC-RO membrane. The performance of new TFC-FO membrane in terms of water flux and SRSF was significantly higher than CTA-FO membrane and TFC-RO membrane indicating that water flux can be significantly improved by modifying the structural properties of the membrane support layer. High performing membrane will have significant implications on the capital and operation cost of the desalination plant.

The study on the influence of DS indicated that, the types of DS have more significant influence on the FO process than the osmotic pressure of the DS. Although adequate osmotic pressure of DS is desirable for FO process, the influence of DS osmotic pressure was observed less significant at higher osmotic pressure and therefore selecting an optimum initial osmotic pressure may be essential for FO process to reduce pumping energy as pumping energy is affected by fluid density and viscosity. A critical DS concentration has been hypothesized based on the implications of DS concentrations on the capital and operational cost of the FO desalination plant. The initial DS concentration must be selected so that feed recovery is not too high that can accelerate scaling of membrane.

The study observed that, the TDS of the feed plays a significant role in the performance of FO process although its influence was less significant for feed TDS higher than 20,000 mg/L indicating that FO has a promising potential for use with high TDS feed water. Although, water flux decreased at higher feed TDS, the RSF and SRSF is also lower at higher feed TDS. This is significant, as it would help reduce the loss of draw solutes and replenishment costs when high TDS feed such as seawater is used.

The influence of operating parameters included influence of crossflow velocity and the crossflow direction on the performance of FO process. The influence of crossflow velocity was effective only to certain extent beyond which the influence was not significant. The influence of crossflow direction on the FO water flux could not be clearly established in this study probably because of the limitation offered by the small cell dimension.

The study on the influence of temperature and temperature difference on the performance of the FO desalination process indicates that these elements play a significant role in enhancing the performance of the FO desalination process. The water flux increased by 12.3% and 45.4% when the temperatures of the DS and the BW FS were increased from 25°C to 35°C and 45°C, respectively. For every degree rise in temperature of the DS and FS above 25°C, water flux with BW increased on average 1.2% at 35°C and 2.3% at 45°C. Therefore, an FO desalination process operated at 45°C will be able to gain water flux per unit heat energy input that is twice as high as an FO process operated at 35°C. The percentage gain in water flux per unit rise in temperature varied with DS concentration showed a modal distribution, indicating that operating the FO process at higher temperature reduces the concentrative ECP effects, especially at higher DS concentrations. Operating the FO desalination process at higher temperature can reduce the reverse draw solute flux and increase feed salt rejection rates. The CTA FO membrane used in this study was found to be thermally stable at 45°C.

When a temperature difference was created between the DS and the FS, the performances of the FO desalination process improved significantly. Increasing the temperature of the DS only from 25°C to 45°C improved water flux on average by more than 21%, while this increase was only about 15% when the temperature of the BW FS was elevated to 45°C. This has significant implication for the FO process, since heating only the DS can substantially reduce the large amount of heat energy required if the temperature of the FS solution has to be increased.

The study on the performance of the FO process using temperature difference indicates that the thermodynamic properties of the DS play a more influential role on the water flux in the FO process than the thermodynamic properties of the FS at higher temperature. Increasing the DS temperature significantly reduced the ICP effects, although this study could not establish which particular thermodynamic property of the DS was more influential in the FO process at elevated temperature. For the BW FS, the increase in water flux results mainly from the reduction in viscosity, and only very little is due to decreased concentrative ECP effects.

This study indicates that, by optimizing the various parameters that relates to the membrane, FS and DS properties and the operating conditions, it is possible to improve the performance of FO desalination process.

11.1.3 Selected straight/single fertiliser solutions as the DS in the performance of the FDFO desalination process

The performance of the fertiliser DS was tested using a bench-scale FO desalination unit with a membrane area of 20.02 cm². It was observed that any soluble fertiliser that can generate osmotic pressure in excess of the osmotic pressure of the FS can draw water by the osmotic process; however, only eleven chemical fertilisers commonly used for agriculture worldwide were selected for this study. The selection of fertiliser DS was also based on the solubility and compatibility of the pH (between 4.0 and 8.0) with the CTA FO membrane used in this study. Different fertilisers had different solution properties and therefore showed different osmotic potential. Ca(NO₃)₂ had the highest osmotic pressure, while KNO₃ and urea had the lowest osmotic pressures amongst the selected fertilisers.

It was observed that the water flux in the FDFO desalination process increased with the increase in fertiliser DS concentrations; however, the increase in water flux with the DS concentration was observed to be non-linear but logarithmic. This non-linearity between the experimental water flux and the bulk osmotic pressure of all the selected fertiliser DSs indicates that the nature of the ionic species formed in the solution has significant influence on the CP in the FO process although it does not affect the osmotic potential of the solution.

The highest water flux was shown by KCl as DS, while NH₄H₂PO₄ or MAP and (NH₄)₂HPO₄ or DAP showed the lowest pure water flux amongst the selected fertilisers. It was also observed that the experimental water flux was much lower than the predicted flux for all cases studied because of the CP effects. In terms of the performance ratio or PR (ratio of actual water flux to theoretical water flux), KCl and NaNO₃ resulted in the highest PR, which was much better than all the other selected fertilisers. The performance of fertiliser DSs in terms of RSF varied widely depending on the type of fertiliser used. The ammonium compounds of sulfate and phosphate, and Ca(NO₃)₂

containing divalent anions, had very low RSF, which is very significant for any FO process.

11.1.4 Performance of blended fertiliser solutions as the DS for the FDFO desalination process

It was hypothesised that if the DS is composed of multiple nutrients, the final concentration of each nutrient could be lower than if single nutrient fertilisers (single or straight fertilisers) were used as the DS. The performances of the straight fertiliser and blended fertiliser solutions as the DS for the FDFO desalination process were investigated comparatively through both simulation and bench-scale experiments. It was demonstrated that, by using blended fertilisers as the DS instead of single fertilisers, the final nutrient concentration of a particular nutrient could be significantly reduced in the FDFO desalination process without the involvement of additional processes such as post-treatment or pre-treatment units. However, it was also observed that blending fertilisers generally resulted in slightly reduced bulk osmotic pressure and water flux compared to the sum of the osmotic pressure and water flux of the two individual DSs used alone. The PR of the blended fertiliser DS was observed to be between the PR of the two fertiliser solutions tested individually. In some cases, such as urea, blending also resulted in a significant reduction in N nutrient loss by reverse diffusion in the presence of other types of fertiliser. However, the study also shows that because of the limitations imposed by osmotic equilibrium, achieving acceptable nutrient concentrations in the final FDFO product water is still a challenge, especially when high salinity feed water is used, therefore requiring different levels of dilution factor before direct fertigation.

11.1.5 Integrated FDFO-NF desalination process for fertigation

All the above studies indicated that the inherent limitations of FDFO desalination relate to fertiliser nutrient concentrations in the final product water, and this final concentration is dictated by the TDS or osmotic pressure of the FS. When high TDS brackish groundwater (BGW) feed sources are used, the essential N/P/K nutrient concentrations in the final product water always exceed acceptable limits, making the product water unfit for direct fertigation without further dilution using fresh water sources. An integrated FDFO-NF desalination process was investigated in which

nanofiltration (NF) was used either as a pre-treatment or post-treatment process to reduce nutrient concentrations in the final product water, so that it could be used directly for fertigation.

NF as pre-treatment was able to significantly reduce the TDS of the BGW because of its high rejection of multivalent ions. This ultimately helped in significantly enhancing the water extraction capacity of the fertiliser draw solutes and therefore achieving much reduced nutrient concentrations in the final product water from the FDFO desalination process. Most fertilisers were able to achieve nutrient concentrations lower than acceptable nutrient concentrations for direct fertigation however, the nutrient concentrations were still higher than for direct fertigation when high TDS BGW was used as feed. The other significant observation made in this study was that, when NF was used as pre-treatment, the feed water quality to the FDFO was high and therefore there is a potential for FDFO process to be operated in PRO mode of operation where water flux is significantly higher than in FO mode of operation.

NF as post-treatment is applied to reduce the nutrient concentrations in the final product water, while recovering excess salts for further extraction of water by FDFO process. Due to higher rejection of multivalent ions by NF, most fertilisers were able to achieve nutrient concentrations acceptable for direct fertigation. However, at higher TDS concentrations, the permeate requires a second pass through the NF system before fertigation.

A comparative study on NF as a pre-treatment or post-treatment option indicates that NF post-treatment could be more advantageous in terms of process efficiency and the energy consumption because of the high quality feed received for the NF from the FDFO process.

11.2 Recommendations and future works

The idea of engineering natural osmosis for desalination with minimum energy using fertiliser as the DS is indeed a novel concept. However, it was identified in this study that, because of the process limitations, the fertiliser nutrient concentration in the final product water exceeds the level acceptable for direct fertigation of crops. This problem is more significant when the saline water with high TDS is used as a source of water for

desalination. Therefore, meeting the water quality standards for irrigation is perhaps the cornerstone to the success of the FDFO technology for direct fertigation. Water quality from the FDFO desalination process must meet the required standards both in terms of salinity (salt index) and in terms of the nutrient concentration, otherwise over-fertilisation of a particular nutrient could cause harm to the plants.

One of the options identified and investigated in this study was the use of blended fertiliser as a DS, instead of a single/straight fertiliser. Although the final nutrient concentration of a particular nutrient was significantly reduced by using a blended DS containing multiple nutrients, the final nutrient concentrations were still above the acceptable limit when a high TDS feed was used for desalination. The second option identified and investigated was the use of an integrated FDFO-NF desalination process. The integrated FDFO-NF was observed to be very effective in reducing the nutrient concentrations in the final product water; nevertheless, NF is a pressure based membrane process and could therefore still suffer from similar problems to the RO process, although the energy consumed by the NF process is expected to be significantly lower than that used by the RO process.

For the FDFO desalination process to be an ideal low energy desalination process and remain energy efficient in comparison to existing desalination technologies, the FDFO desalination process must produce product water of acceptable quality for direct fertigation. This requires that the issue of process limitation of the FDFO desalination that limits the final concentrations of the diluted fertiliser DS must be addressed, either through process modifications or through alternative arrangements. The following options and modifications are suggested and recommended as a potential approach, and they include a futuristic approach for reengineering the FDFO desalination process so that it would not only lower the final nutrient concentrations but also have the potential to improve the energy efficiency of the FDFO desalination process.

11.2.1 Pilot testing of the integrated FDFO-NF desalination process in the Murray-Darling Basin

The study on FDFO desalination so far indicates that the integrated FDFO-NF is currently the most practical desalination process for direct fertigation. Although there have been numerous recent studies on the FO process, most of these studies are limited

to bench-scale investigations. The first pilot scale FO desalination unit was installed at Yale University (Elimelech, 2007) but the findings of that study have not been reported so far. Recently, the performance of a pilot scale level FO process was reported by Kim and Park (2011), but the focus of this report was mainly on the operational aspects of the newly commercialised modules by HTI. The same company has recently announced the commercialisation of the polyamide based thin film composite (TFC) FO membrane and its modules, which has a water flux more than twice as high as the HTI CTA FO membrane used in this study (Gullinkala et al., 2012; Smoke, 2012).

It is important that the long-term performance of FDFO desalination be assessed at a pilot-scale level using the new TFC FO membrane and that its potential for commercial scale application is evaluated. The use of the TFC FO membrane would also allow the use of fertilisers with a wide range of pH, unlike the CTA FO membrane where the pH was limited to between pH 5.0 and 8.0.

All eleven fertilisers tested in this study were found to be compatible with the FDFO desalination process; however, the experiments were carried out for short periods of 10 hours, or slightly more, and were not tested for long-term operation. When the duration of FO operation is longer, the issue of the stability of certain fertilisers (especially those containing ammonium salts) may arise due to oxidation or other unknown processes and this therefore requires further evaluation. It is recommended that a pilot-scale testing of the FDFO-desalination unit be carried out in the field to test the robustness of the technology and provide an opportunity to showcase the potential application of such technology for irrigation. The pilot scale unit was designed based on this study and the unit has been already built at UTS. The pilot FDFO-NF desalination unit is currently being tested in the UTS laboratory and will later be tested at one of the salt interception schemes within the MDB.

11.2.2 FDFO desalination process using pressure assisted osmotic (PAO) process

It was discussed that the concentration of the final diluted DS from the FDFO desalination will have equal osmotic pressure with the bulk feed concentration (state of osmotic equilibrium). It was also mentioned that it is theoretically impossible to have a net transfer of water taking place towards the DS from the FS during osmotic equilibrium without external influence. Here, an external influence is proposed that can

extend the net water transfer beyond the point of osmotic equilibrium. When an external hydraulic pressure (ΔP) is applied on the feed side of the membrane, water flux can be induced from the feed site towards the DS. The advantage with this concept is that the applied pressure does not have to overcome feed osmotic pressure (as in RO or NF) due to the state of osmotic equilibrium created by the presence of the DS on the other side of the membrane. In fact, the water flux could be equivalent to pure water flux if ICP and ECP effects are excluded in this concept.

Recently, the concept of pressure assisted osmosis was presented by Lutchmiah et al. (2012) with the main aim of improving the water flux and reducing ICP effects. However, the main objective of this recommendation is to use PAO as an external influence to induce water flux beyond the osmotic equilibrium and to assist the further dilution of the DS.

This concept could be applied with either a single stage FO process or a two-stage FO process; however, the two-stage FO process is presented here, as shown in Figure 11.1(a). In the first stage FO process, normal FDFO desalination is carried out; the flux model in such situations has been already described in several earlier chapters. In the second pass FDFO process, the DS and FS concentrations are in osmotic equilibrium initially and water flux will be generated only when external hydraulic pressure is applied. The standard flux under such circumstances is modified as follows to include the influence of the applied pressure.

$$J_w = A [\pi_{D,b} - \pi_{F,b} + \Delta P] = A \Delta P \quad (11.1)$$

Where A is the pure water permeability, $\pi_{D,b}$ and $\pi_{F,b}$ are the bulk osmotic pressures of DS and FS respectively and ΔP is the applied external pressure on the feed. If the influence of the length of the membrane along the module is considered, however, the feed concentrations will increase while the DS concentration will decrease along the length of the channel, and the state of osmotic equilibrium would no longer exist. As such, the flux equation in Eq. (11.1) would have to be modified to accurately represent the change in FS concentration depending on the recovery rates. It is important to note the difference between the modified flux equation shown by equation (11.1) under PAO with the standard flux equation of the RO process given by the following equation.

$$J_w = A [\Delta P - \Delta \pi] \quad (11.2)$$

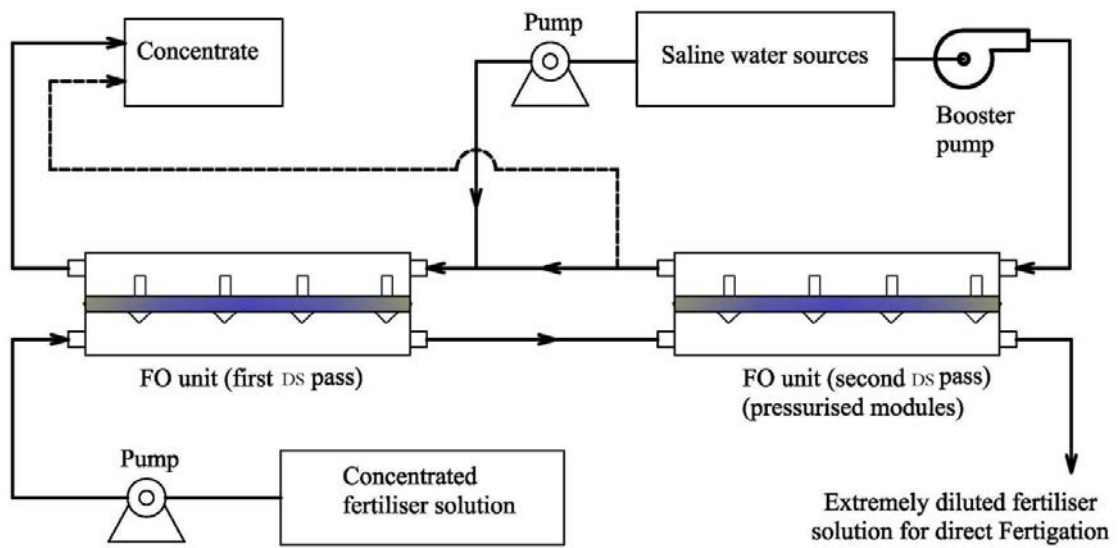
Where $\Delta \pi$ represents the osmotic pressure of the FS. Here the presence of the osmotic pressure of the FS opposes the applied pressure ultimately reducing the net driving force. The presence of DS on the other side of the membrane nullify this opposing osmotic pressure and therefore, the full applied pressure is available a net driving force in the PAO process.

When external pressure is applied at osmotic equilibrium, the water flux generated will result in the alteration of the solute concentrations at the membrane boundary layer, and the influence of the dilutive ICP and concentrative ECP (for the FO mode of operation) will become significant and therefore must be considered. Considering the CP effects, the flux Eq. (11.1) can be modified as follows to account for CP effects in the FO mode.

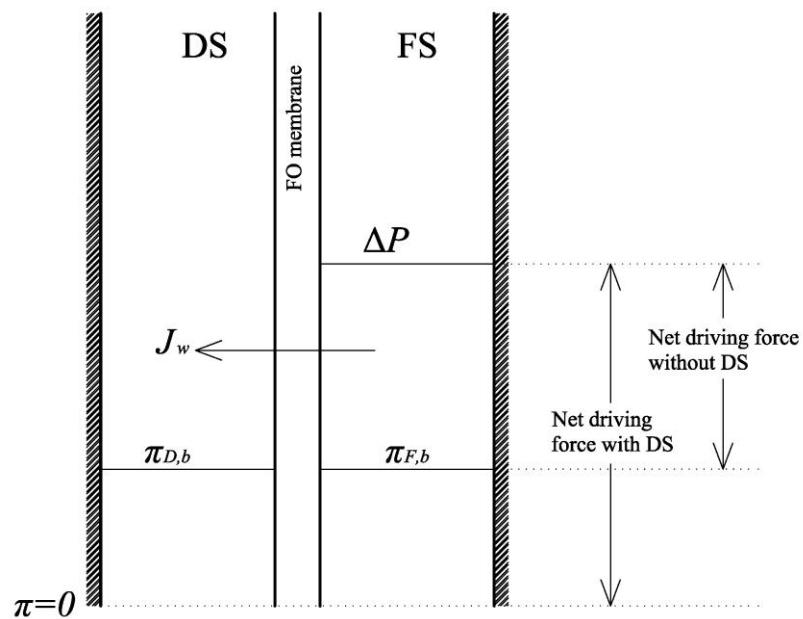
$$J_w = A [\pi_{D,b} \exp(J_w K) - \pi_{F,b} \exp(J_w / k) + \Delta P] \quad (11.3)$$

The concept of FDFO using PAO offers the following advantages:

- The FDFO desalination process can be continued beyond the state of osmotic equilibrium between the feed and the DS, thereby further diluting the DS
- It avoids the need for a different pressure based membrane process such as RO or NF to achieve further dilution of the DS, because the same FO unit can be used for PAO
- The osmotic pressure generated by the DS is effectively used to lower the osmotic pressure of the feed and thereby reduce the osmotic pressure that needs to be overcome for the net transfer of water



(a)



(b)

Figure 11.1: FDFO desalination process using pressure assisted osmosis (a) two-stage FDFO desalination process using PAO and (b) model explaining the net driving force in PAO

11.2.3 The use of osmotic fillers with the fertiliser DS

In commercial grade fertilisers, other elements in the form of mixtures (either soluble or insoluble, organic or inorganic) are found, together with the major macro NPK nutrients either as a fillers or as essential secondary nutrients (Stewart et al., 2005). The presence

of additional elements or ionic species in commercial fertilisers has the effect of lowering the composition of a particular nutrient and the same concept was applied when the use of blended DS was proposed in this study. An investigation of the influence of such soluble impurities in commercial fertilisers on the performance of the FDFO desalination process in terms of water flux and final nutrient concentration was not included in this study. However, the use of commercial fertilisers containing these impurities or additional ionic species has a potential to help reduce the concentration of particular nutrient in the final FDFO product water.

Likewise, it is also possible to add impurities to the fertilisers and to use their presence as mere osmotic fillers. The concept of an osmotic filler has therefore been proposed here for application in the FDFO desalination process. An osmotic filler is defined here as an additional draw solute that can be used for FDFO desalination, either by mixing it with the fertiliser or using it separately. An osmotic filler is proposed mainly as a means to provide additional osmotic or ionic species that will help to generate a higher osmotic pressure for the fertiliser DS. The presence of an osmotic filler with the fertilisers also reduces the percentage composition of the nutrients, and this in turn can help to achieve a lower nutrient concentration in the final FDFO product water. The ideal osmotic filler should have the following properties:

- It should generate high osmotic pressure
- It should be compatible with the fertiliser solution
- It should have easy separation from the fertiliser solutes for further recycling and reuse
- It should result in low reverse solute flux in the FO process
- It should be environmentally benign and should not cause plant toxicity
- It should be cheap and easily available

There are two possible options for using osmotic fillers in FDFO desalination, as described in the following subsections.

11.2.3.1 Osmotic filler and fertiliser mixed as a DS

In this approach, an osmotic filler and a fertiliser can be mixed together and used as the DS for the FDFO desalination process. The elemental constituents of the osmotic filler

should be useful for agricultural purposes, in which case, the separation and recovery process is not essential. Chemigation, which involves the application of agrochemicals such as herbicides, pesticides/insecticides, fungicides, nematicides, growth regulators, and so on to crops, together with irrigation water, is commonly practised in farming (Papadopoulos, 1999). This has led to extended terms such as herbigation, insectigation, fungigation, nemagation, etc., to describe various types of chemigation. Mixing agrochemicals such as pesticides has been common for many years because they serve the dual purpose of crop nutrition and pest control (Jacob, 1954). While some agrochemicals are insoluble and are often used in colloidal suspension form, soluble agrochemicals, such as water soluble pesticides, are widely available to agriculture industries for a variety of purposes (Appleby et al., 2000). Even the adjuvants used with chemicals for weed control such as nonionic surfactants could also provide enhanced osmotic pressure, provided they do not interfere with the fertiliser ionic species. However, the agrochemicals must be compatible with the fertilisers and mixing them should not result in the formation of complex products that may be detrimental to the desalination process, crops and the receiving environment.

11.2.3.2 Osmotic filler used as a DS separately to the fertiliser DS

In this concept, an osmotic filler can be separately used as a DS for the FDFO process in parallel with the fertiliser DS. The final diluted osmotic filler DS can be processed for the separation and recovery of draw solutes for recycling and further reuse. The final product water, free of osmotic filler or containing only a very low concentration of filler solutes, can be used for dilution of the product water obtained using fertiliser as the DS.

11.2.4 A self-powered FDFO desalination process for irrigation using osmotic energy

Gibbs free energy of mixing is dissipated when fresh water from rivers flows into the sea, and this energy can be harnessed for sustainable power generation (Yip and Elimelech, 2012). Pressure retarded osmosis (PRO) has the potential to harness osmotic power by taking advantage of both natural and manmade salinity gradients (Post et al., 2007; Achilli and Childress, 2010). In the PRO mode of operation, a small hydrostatic pressure is applied to the concentrated DS during the osmotic process so that the water transport across the membrane is partly retarded. The transport of water from the low-

pressure diluted solution to the high-pressure concentrated solution results in pressurisation of the expanding volume of transported water in the DS (Yip et al., 2011). This pressurised volume of transported water can be used to run a hydro-turbine and generate electrical power. Figure 11.2 shows the concept of generating osmotic power by the fertiliser drawn PRO process.

A novel engineered osmotic process that desalinates salt water for irrigation while simultaneously generating osmotic energy/power is proposed and recommended. This concept is termed a fertiliser drawn pressure retarded osmosis (FD-PRO) desalination process because fertiliser solution is used as the DS for osmotic desalination in PRO mode. Both the FDFO process and the FD-PRO process are driven by concentration/osmotic gradient; however, desalination in the FD-PRO process is re-engineered by reversing the normal mode of membrane orientation, i.e. the fertiliser DS now faces the active layer and the saline feed (SF) water faces the membrane support layer. Osmotic power cannot be harnessed in the normal FO process because the active layer facing the DS cannot withstand the hydraulic pressure created by the water flow.

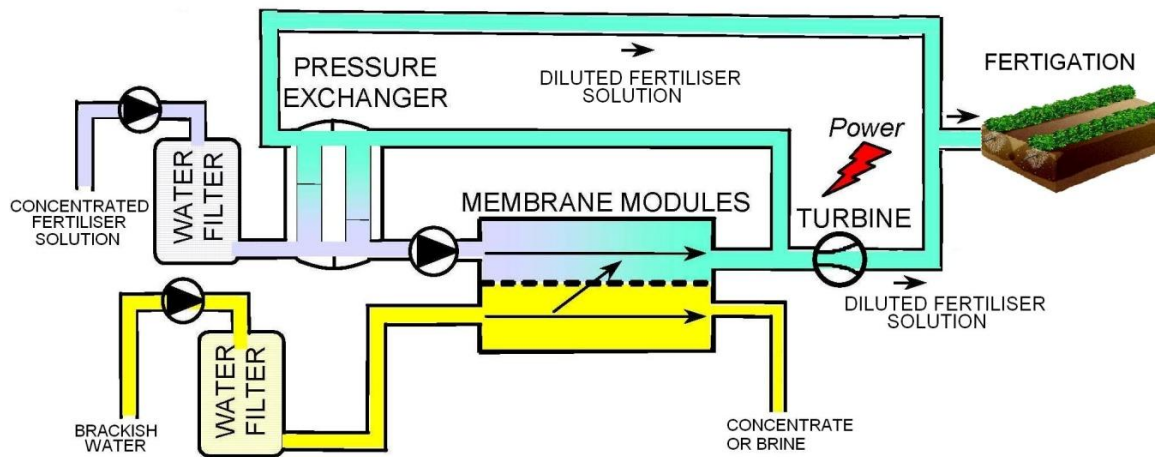


Figure 11.2: Concept of osmotic energy from a salinity gradient by fertiliser drawn - pressure retarded osmosis

Two different approaches to harnessing osmotic energy by the FD-PRO desalination process have been conceived, as explained below.

Osmotic energy to osmotic power: When a small external pressure, less than the net osmotic pressure difference between the DS and the FS is introduced on the fertiliser solution in the FD-PRO desalination process, the expanding volume and pressurised DS

can be used to run a hydro turbine generating osmotic power. Two phenomena occur simultaneously in this process: the desalination of the brackish feed water by osmotic process, and the generation of osmotic power, both as a result of the salinity/osmotic gradient. Three different stages have been identified as having potential for harnessing osmotic power from the FDFO desalination process during the application of FD osmotic power generation for fertigation, as illustrated in the schematic diagram in Figure 11.3.

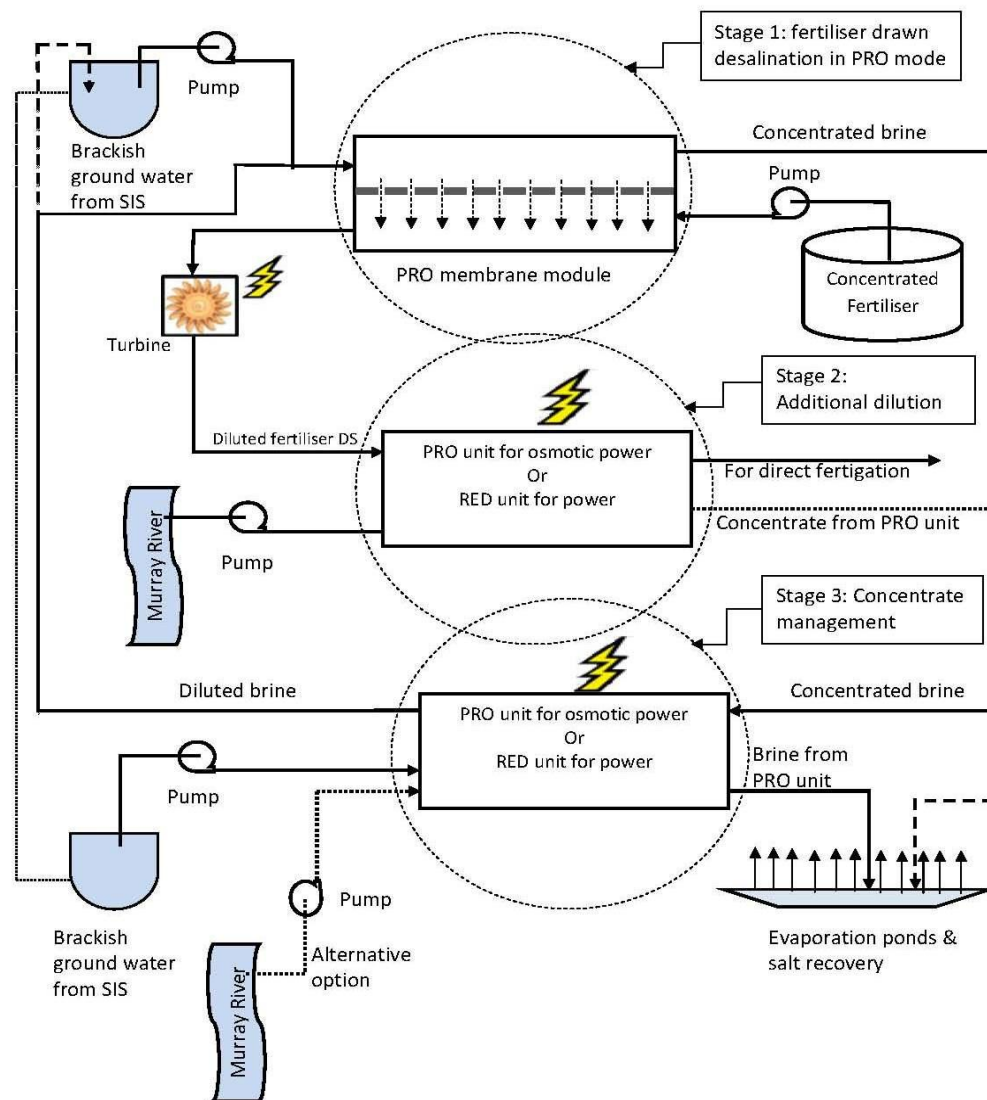


Figure 11.3: Schematic of the FDFO desalination process showing the various potential points for the generation of osmotic power

Osmotic energy can be used directly as hydraulic energy: The other approach to harnessing osmotic energy from the FD-RO desalination process is to utilise the hydrostatic pressure created by the expanding volume of incoming water flux to use as

hydraulic pressure for driving the nanofiltration (NF) or RO process used as post-treatment. The NF/RO in this case can be directly driven by using a suitable pressure exchanger, without the need for external high-pressure pumps. This post-treatment is applied to separate and recover the excess fertiliser salts before fertigation and subsequent reuse; the concept is explained in Figure 11.4.

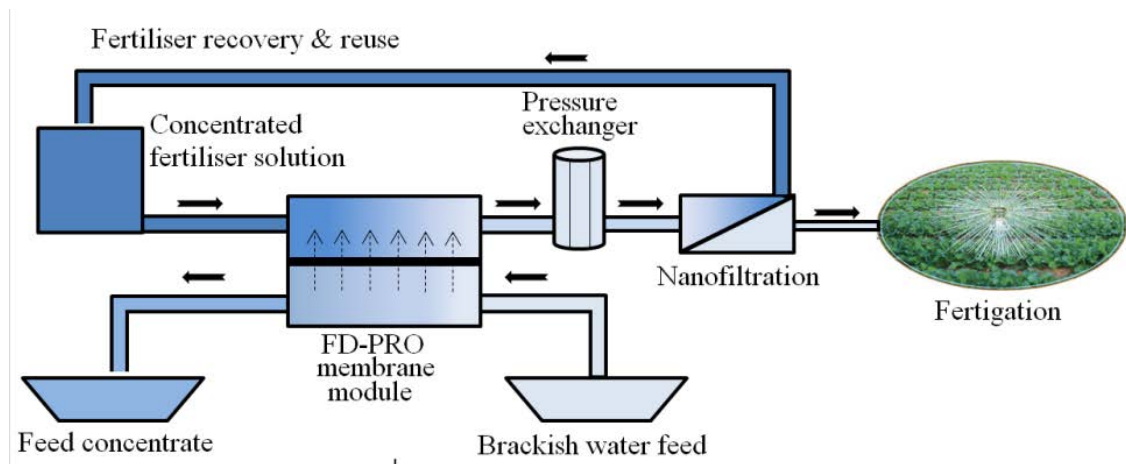


Figure 11.4: Osmotic energy from the FD-PRO desalination process can be directly used to drive the NF/RO post treatment process

FD-PRO desalination has the following qualities:

- Desalinates saline water using fertiliser as DS
- Generates osmotic energy/power simultaneously by reengineering the process design
- The power generated from the FD-PRO desalination can be used to self-power the desalination unit and the excess power can be sold to the commercial grid
- FD-PRO could potentially serve as a stand-alone desalination unit for irrigation in remote regions of Australia where power is not easily accessible
- No additional membrane for power generation is necessary because the same membrane modules can be used for both osmotic desalination and osmotic power generation, although additional accessories such as a booster pump and pressure exchangers are necessary

11.2.5 Other recommendations

It has been demonstrated in this study that the FDFO desalination process can be operated at high recovery rates, and theoretically up to 100% for some fertilisers, without substantial extra energy. However, at such high recovery rates, membrane fouling due to inorganic scaling becomes an issue that affects the performance of the FDFO desalination process. Therefore, it is recommended that the influence of inorganic scaling in the FDFO desalination process should be evaluated in future studies. It is also likely that this scaling would be influenced by several factors including feed composition, types of fertilisers used and operating conditions.

It is likely that scaling could occur within the membrane support structure, although this has nothing to do with the recovery rates. This phenomenon is possible when the feed rejection is lower and the diffusion of feed solutes towards the support layer meets the draw solution species that together may form precipitates that in turn form scaling compounds. The influence of such an occurrence also requires further investigation, because it may affect or accelerate ICP effects during the FDFO desalination process.

The presence of boron was not observed in the brackish groundwater in the MDB, but the issue is worth evaluating, especially for the application of FDFO desalination for seawater desalination. The existence of boron higher than the recommended concentration in the irrigation water could cause boron toxicity to the plants and affect the plant yield. Very few studies are available on boron rejection, indicating the need for further study, since boron is critical for irrigation water.

The energy requirement for the FDFO desalination process for direct fertigation has been assessed based on the available literature. However, it is recommended that a full life cycle analysis for FDFO desalination be carried out to understand the true merits of the FDFO desalination process for fertigation.

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Appendix A

Table A1: Compositions of the brackish groundwater at Burronga salt interception scheme, NSW. Source: NSW State Water.

Bore No	Test date	Cl	Ca	Mg	K	Na	Fe	Mn	NO ₃ -N	SO ₄	HCO ₃	CO ₃	TDS	EC	pH
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	(µS/cm)	
40895	9-Apr-03	8300	230	45	730	4900	18	1.4	10	1700	78		16,012	24300	7.9
40895	10-Apr-03	8900	220	42	790	5400	17	1.3	10	1800	79		17,259	25600	7.9
40895	11-Apr-03	9200	240	47	860	5400	17	1.2	10	1900	84		17,759	26500	8
40895	12-Apr-03	9300	230	45	840	5300	16	1.2	10	1900	85		17,727	26600	8
88461	14-Sep-02	4400	200	480	23	2800	58	0.9	20	2400	92		10,474	16300	7.9
88461	15-Sep-02	24000	420	2200	150	12000	6.2	0.83	100	6800	150		45,827	64500	8
88461	12-Sep-02	50000	520	4000	210	29000	4	0.75	100	10000	120		93,955	111000	7.8
88463	24-Sep-02	470	12	22	5.5	700	9.4	0.28	2	400	960		2,581	3460	8.2
88463	23-Sep-02	24000	440	2000	100	13000	9	0.64	10	4400	140		44,100	57500	6.8
88463	22-Sep-02	43000	520	4200	190	26000	4.5	0.84	20	10000	110		84,045	98100	6.9
88464	20-Sep-02	1000	12	42	12	860	9.2	0.094	2	250	630	52	2,869	4680	8.9
88464	19-Sep-02	33000	520	2900	150	18000	4.6	0.64	100	8500	150		63,325	82100	7.9
88464	18-Sep-02	48000	550	4400	280	24000	8.1	0.9	100	12000	110		89,449	108000	7.7
88465	26-Sep-02	43	11	7.7	2.6	33	4.5	1.1	0.9	0.8	84		189	345	7.4
88465	26-Sep-02	63	16	11	3.6	45	8.3	0.82	2	1	110		261	405	7.1
88465	25-Sep-02	36000	510	3600	240	17000	5.9	0.65	100	10000	140		67,597	84900	6.9
88467	12-Oct-02	320	14	23	5.3	370	6.4	0.18	36	240	410	6.7	1,432	2060	8.4
88467	11-Oct-02	39000	380	3500	260	2100	6	0.98	20	9400	1100		55,767	93000	7
88467	10-Oct-02	53000	440	4600	350	3300	7.2	0.89	100	1400	100		63,298	116000	7
88469	15-Nov-02	18000	390	1400	72	8700	11	0.59	10	3400	160		32,144	43600	6.9
88469	16-Nov-02	16000	390	1400	72	8800	11	0.59	20	3600	160		30,454	43800	6.9
88469	18-Nov-02	16000	390	1400	70	8200	12	0.59	20	3400	160		29,653	43400	6.8
Average		20091	303	1653	246	8905	12	1	36	4250	237	29		48916	6.8-8.9