MEMBRANE FOULING DURING FERTILISER DRAWN FORWARD OSMOSIS DESALINATION USING BRACKISH GROUNDWATER

By

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A thesis submitted in fulfilment for the degree of

Master of Engineering

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October 2013

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

Fezeh Lotfi

For my wonderful husband, Dr. Behnam Fatahi

ACKNOWLEDGEMENTS

Well here it is, my thesis, finished! It's taken a long time to get to this point and I have a lot of people to thank. Each of the following people has my lasting gratitude for helping me reach this exciting milestone.

Firstly, I'd like to express my deep gratitude to my supervisor Dr. Ho Kyong Shon for his direction, wisdom, insight and patience. I'm also much obliged to my co-supervisor Dr. Sherub Phuntsho for his goading, exhortation and encouragement.

My most profound thanks, my most heartfelt appreciation, my deepest gratitude goes to my husband Dr. Behnam Fatahi without whom none of this could have been accomplished. Also I must express my gratitude to Mr Parviz Lotfi, my Dad and Mrs Akhtarosadat Yosofi my Mum, thanks for your unwavering confidence in me, for your love and sacrifice. Special thanks to Dr. Behzad Fatahi for his support and encouragement. Finally, thanks to my sisters (Temi and Forough).

I sincerely acknowledge the help I received from my colleagues, without whose support I would not have been able to complete this thesis on time. In particular, I want to acknowledge the contribution made by Mr. Tahir Majeed, Mr. Soleyman Sahebi, Miss. Laura Chekli and Miss Jung Eun.

I also acknowledge the administrative and logistic supports received from Mrs. Phyllis Agius, Craig Knowles, Tim and Van Lee during my research.

This research was supported by the National Centre of Excellence in Desalination Australia, funded by the Australian Government through the Water for the Future initiative.

LIST OF ABBREVIATIONS

FO: Forward osmosis

FDFO: Fertiliser drawn forward osmosis

RO: Reverse osmosis

PRO: Pressure retarded osmosis

BGW: Brackish groundwater

DS: Draw solution

CP: Concentration polarisation

ICP: Internal concentration polarisation

ECP: External concentration polarisation

CTA: Cellulose triacetate

PA: Thin film composite polyamide

HTI: Hydration Technology Innovations

NF: Nanofiltration

TDS: Total dissolved solids

DI water: Deionised water

DAP: Diamminium phosphate or $(NH_4)_2HPO_4$

MAP: Monoammonium phosphate or $NH_4H_2PO_4$

SOA: Sulphate of ammonia or $(NH_4)_2SO_4$

CAN: Calcium nitrate tetra hydrate

MW: Molecular weight

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Abstract

Freshwater has become a scarce resource in many parts of the world and has been recognised as a critical global issue. By far, agriculture is the largest consumer of global freshwater, reaching a proportion that exceeds 70% of the total water consumption, mainly in the form of irrigation. In 2006, 54% of the total water use in Australia related to the irrigation of farms and pastures although the figure was much higher in previous years. Due to the rapid growth in the world's population, water demand for agriculture will keep increasing to meet the corresponding food demands. Creating new water sources can reduce pressure on the existing fresh water resources. Hence, desalination can play a key role in creating a new water sources because saline water sources exist in abundance. However, current desalination technologies are energy and cost intensive and this can have negative impacts on the environment and natural resources.

Forward osmosis (FO) has been recognised as one of the most promising low energy processes for desalination. The FO process, as an alternative to conventional desalination techniques, has attracted much attention in recent years. The driving force in the FO process is generated by the osmotic pressure difference between the feed water and the concentrated draw solution (DS).

Where a natural source of high concentration DS is available, FO can be highly attractive due to its significantly lower energy demand for pumping. Fertiliser drawn forward osmosis (FDFO) desalination has been recently studied as one of

the most practical applications of FO for irrigation. The study indicated that most commercially available fertilisers can be used as osmotic draw solutes. This led to the idea of applying FO technology in agriculture where the diluted fertiliser DS containing desalinated water can be used directly for fertigation (fertilised irrigation) instead of further subjecting it to a separation process.

Despite the many benefits of membrane technologies, the unavoidable issue of membrane fouling during membrane filtration remains a problem. Membrane fouling is a process where solute or particles deposit onto a membrane surface or into membrane pores. Membrane fouling causes a reduction in the permeate yield and a decrease in the quality of water produced, which leads to an increase in the operational and capital costs of the entire membrane filtration process.

It is generally accepted that fouling reduces the performance of membrane. When the fouling occurs, a thick gel layer and cake layer are formed on and in the membrane, causing the permeate flux to decline and increasing the operational costs due to the need for higher energy, cleaning frequency and/or the reduced life of the membrane. Mechanisms of fouling in pressure-driven membrane processes have been investigated extensively. By contrast, only a few studies have so far targeted membrane fouling during the FO process.

This study investigates the influence of various factors affecting the water flux behavior and membrane fouling during the desalination of brackish groundwater by FDFO process. The major factors responsible for the performance of FDFO water flux behavior are thoroughly investigated and their implications to the overall process were discussed. The major factors assessed include membrane properties, DS properties and FS properties. The influences of all these factors have been measured in terms of water flux decline. A membrane autopsy has also been conducted to identify the inorganic scaling that forms on the membrane surface. Foulants have been analysed using Scanning Electron Microscopy (SEM), energy dispersive spectroscopy (EDS) and X-Ray Diffraction (XRD).

Six commercially available fertilisers (Potassium chloride, potassium nitrate, ammonium sulphate, monoammonium phosphate or MAP, diammonium phosphate or DAP, calcium nitrate) have been selected as DS to observe the effects of different fertilisers in water flux behavior during the FDFO process. DAP, having one of the highest osmotic pressures amongst the six selected fertiliser solutions has been found to produce unexpected water flux behavior with severe flux decline during the FDFO desalination of brackish ground water (BGW).

The XRD results indicate that the scales formed on the membrane surface during FDFO process using DAP as DS are mainly composed of magnesium phosphate ($MgHPO_4$) and magnesium ammonium phosphate ($MgNH_4PO_4.6H_2O$) or struvite. These insoluble compounds are formed because of the reverse diffusion of DAP towards the feed during the osmotic process which then reacts with the magnesium ions present in the FS.

This study shows that, the selection of fertiliser as DS is important for several reasons. Fertilisers that generate higher water flux at lower concentrations are preferable as these can contribute to significant cost savings in terms of both capital and operational costs. The other important characteristic of DS is that, it should have lower membrane scaling and fouling potential. Fertilisers that produce steady water flux and lower membrane scaling and fouling during long-term operation are preferable for FDFO application.

This work also seeks to show that besides the selection of suitable fertiliser as DS during the long term FDFO process, the selection of an appropriate membrane for the selected fertiliser is also essential. The interaction between fertiliser properties and membrane characteristics has a significant influence in water flux behavior.

As in real situations, varied types of foulants always coexist in natural waters. In addition to inorganic scaling by super saturation of calcium and sulfate ions, which are common in brackish groundwater, organic fouling is also possible due to prevalent natural organic matters. Therefore, alginate, albumin (BSA), and humic acid (HA) have been chosen as model organic foulants to study the effect of combined fouling in water flux behavior during the long term operation of the FDFO desalination process. 60 mg/l alginate has been found to aggravate inorganic scaling leading to a decrease in water flux of more than 30%.

Physical cleaning with cross-flow rates similar to normal FDFO process has been adopted to evaluate the effectiveness of restoring the membrane flux after inorganic scaling. The flux recovery is about 80-97% depending on the type of

the DS. However, when the cross-flow rate is increased, the water flux is restored almost in full, irrespective of the type of DS and DS concentration used.

CHAPTER 1

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INTRODUCTION

1.1 Introduction

With worldwide concerns about water scarcity, agriculture is under pressure to improve its water management and explore available options to match supply and demand. Desalination is a technological option to increase the availability of freshwater both in coastal areas with limited fresh water resources and in areas where brackish waters – such as saline groundwater are available.

In the past, the high cost of desalinating and the energy required have been major constraints on large-scale production of freshwater from brackish waters (BW) and seawater (SW). However, desalinated water is becoming more competitive for urban use because desalinating costs are declining while the availability of the fresh water resources such as surface water and groundwater is decreasing and their costs are increasing. In spite of the advancement in the desalination technologies, the costs of desalinated water are still too high for large-scale water use such as irrigated agriculture, with the exception of intensive horticulture for high-value cash crops, such as vegetables and flowers (mainly in greenhouses), grown in coastal areas (where safe disposal of concentrated brine is easier than in inland areas). For agricultural use, RO is the preferred desalination technology because of the cost reductions driven by improvements in membranes in recent years. Desalinated BW and SW are not used worldwide for irrigated agriculture because of energy issues and high membrane fouling potential in the RO process.

The emerging forward osmosis (FO) membrane process has received increasing attention as a promising technology for wastewater reuse and sea/brackish water desalination. FO utilises natural osmotic pressure generated by a concentrated draw solution (DS) as the driving force to pull water molecules from the feed solution (FS) through a semi-permeable membrane to the DS by natural osmosis. Where a natural source of high concentration DS is available, FO can be highly attractive due to its significantly lower energy consumption. Fertiliser drawn forward osmosis (FDFO) desalination has been recently studied as one of the most practical approaches to FO irrigation applications.

The FDFO desalination process is not significantly different from the conventional FO desalination process except that it does not require a DS recovery process. The DS in this particular case consists of only soluble fertiliser which after extraction of water can be used directly for fertigation without the need for further dilution. Water is extracted from the saline water due to the high osmotic gradient between the concentrated fertiliser DS and the FS. Therefore, in the FDFO process, saline water is used 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 cross-flow system, to minimise the influence of the concentration polarisation (CP) effects. Due to the osmotic gradient across the semi-permeable membrane, water flows from the FS with lower concentration towards the highly concentrated fertiliser DS, desalting the saline water in the process (Phuntsho, 2012).

For any successful application of FO process, several important aspects of the process should be evaluated. One critical issue that demands considerable research effort is FO membrane scaling and fouling (Valladares Linares et al., 2012, Li et al., 2012, Zou et al., 2011, Mi and Elimelech, 2008a). Membrane fouling in the pressure based membrane processes is controlled by adopting pretreatment of source water and membrane chemical cleaning, which incurs increased energy consumption and also additional costs (Elimelech and Phillip, 2011).

A slow flux decline and high flux recovery rate was observed in the FO process, compared to the RO process and this lower fouling potential with the FO process was attributed to less compaction of the fouling layer in the absence of hydraulic pressure (R. Holloway, 2007). In order to demonstrate the fouling mechanisms in the FO process, the atomic force microscopy (AFM) measurements were employed to study the role of membrane–foulant and foulant–foulant interactions in the organic fouling and gypsum scaling of FO membranes (Mi and Elimelech, 2008b, Mi and Elimelech, 2010c). This study discerned that (1) foulant–foulant interaction significantly affected the rate and extent of organic fouling in the FO process and (2) membrane properties played a significant role in gypsum scaling. In addition, the FO membranes cleaning efficiency was investigated (Mi and Elimelech, 2008b, Mi and Elimelech, 2010c). This demonstrated that, depending on membrane materials, membranes fouled by organics or gypsums could clean by adopting simple physical rinsing processes using water devoid of any chemical cleaning agents. The effects of critical flux and internal concentration polarization on the flux decline behavior during the FO membrane process were also studied. Severe ICP was observed for higher DS concentrations and higher flux levels, and for the AL-facing-FW configuration. These observations agreed well with the ICP model. In contrast, the AL-facing-DS configuration was highly prone to flux reduction under fouling conditions due to the pore clogging enhanced ICP effect in addition to the reduced membrane permeability. The enhanced ICP effect was more dominant at higher flux levels. (Tang et al., 2010).

1.2 Research objectives

Understanding the fouling behavior in the FDFO process is particularly important as both sides of the FO membrane are in constant contact with solutions of different properties: the active layer with saline water and the support layer with fertiliser solution. Therefore, there is a critical need for a systematic understanding of the membrane scaling and fouling behavior and for the development of strategies for fouling mitigation during the FDFO process, especially for the desalination of brackish groundwater (BGW).

The main objective of this study is to investigate the impact of membrane scaling and fouling on the flux decline during the desalination of BGW by the FDFO process. The specific objectives of this study are to:

- Evaluate the factors that govern the water flux behavior during the FDFO desalination of BGW.
- Investigate the influence of six different fertilisers as DS on the membrane scaling and fouling during the long-term operation of the FDFO desalination of the BGW.

- Compare the influence of different FO membrane materials (cellulose triacetate or CTA, polyamide or PA thin film composite membrane or TFC) on the membrane scaling/fouling on the water flux decline.
- Elucidate the effects of combined organic and inorganic scaling using albumin, humic acid and alginate selected as organic foulant during the FDFO desalination process.
- Examine a membrane autopsy to identify the types of scales and the compounds responsible for membrane scaling during the FDFO desalination process
- Evaluate the effectiveness of simple physical/hydrodynamic rinsing in the water flux recovery after scaling/fouling of the membrane during the FDFO desalination with the BGW.

1.3 Outline of thesis

This thesis presents a study on membrane scaling and fouling during the FDFO process using a laboratory-scale FO setup. The introduction, describing the background about the necessity for this study is presented in Chapter 1. The review of existing literature on membrane processes and fouling, including a few recent studies on membrane fouling and scaling in the FO process, has been included in Chapter 2. The materials and methods explaining the lab-scale experimental design and setup of the FDFO membrane system and their detailed operating conditions are presented in Chapter 3. Chapter 4 discusses the preliminary studies on the various factors affecting the water flux behavior due to membrane scaling and fouling in the FDFO desalination process using six different fertilisers as DS. Chapter 5 focuses on a detailed study of the influence of di-ammonium phosphate (DAP) DS on the membrane scaling and fouling. Conclusions and recommendations for improvements are presented in Chapter 6.

CHAPTER 2

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LITERATURE REVIEW

2.1 Water purification membranes

Membrane filtration is a process where a membrane is used as a physical barrier to separate compounds by applying a driving force across the membrane. In a membrane system, a feed water solution is separated into two solutions, the product or permeates, containing solutes that have passed through the membrane and the concentrate containing solutes and particles rejected by the membrane (Niriella, 2006). The early history of membrane filtration started over 250 year ago when the French cleric Abbé Nollet found that water transports across a pig bladder covering the mouth of a jar containing wine (Nollet, 1748, Nollet, 1752, Lonsdale, 1982). One hundred years later in 1867, Moritz Traube prepared the first artificial membrane (Traube, 1867).

In 1950, Hassler introduced the first concept of membrane desalination describing “salt repelling osmotic membranes” and “perm selective films” (Hassler, 1950, Glater, 1998). In the late 1950s, the basis for modern-day reverse osmosis was laid by research with cellulose acetate membranes by Reid and Breton (1959) and Loeb and Sourirajan (Loeb, 1960, Loeb, 1963). Reid and Breton were the first to demonstrate that cellulose acetate films could produce potable water from saline solutions. Loeb and Sourirajan (1963) are credited with the invention of asymmetrical cellulose acetate membranes offering improved salt rejection and water flux thereby making membrane desalination practical. The first spiral-wound element was developed by General Atomics in 1963. The oldest patents for reverse osmosis are dated 1964 (Hassler, 1964) and 1965 (California, 1965). In the 1970s, thin film composite membranes were introduced and, in time, enhancements were made to improve the water flux and rejection properties and reduce the feed pressure.

The history of membrane science is described in several reviews (Lonsdale, 1982, Brandt, 1993, Böddeker, 1995, Baker, 2004). Membrane operations can be classified according to the parameter’s driving force, separation mechanism and rejection properties. Four pressure driven membrane filtration processes can be discerned based on the differences in feed pressures and membrane rejection capacities: microfiltration, ultrafiltration, nanofiltration and reverse osmosis, ranked by increasing pressure (Figure 2.1). The categorization of membrane filtration shows four categories of pressure driven membrane processes. As shows in Figure 2.1 there are four categories of pressure driven membrane processes: reverse osmosis (RO), ultrafiltration (UF), microfiltration (MF) and nanofoltration (UF). That microfiltration and ultrafiltration are low pressure membranes and nanofiltration and reverse osmosis are high pressure membranes.

2.1.1 Low pressure membranes

RO and NF processes are usually applied for the removal of dissolved constituents including both inorganic and organic compounds and these processes operate at pressures significantly higher than MF and NF. Low pressure membrane processes are usually applied for the removal of particulate and microbial contaminates.

Low pressure membrane (LPM) filtration, which includes ultrafiltration (UF) and microfiltration (MF), is one of the most energy efficient technological in water treatment in the past two decades. Microfiltration filters particles of size ranging from 0.1 to 0.5 microns and ultrafiltration filters particles of size ranging from 0.005 to 0.05 microns. The LPM filtration process is, hindered by the problem of membrane fouling. Membrane fouling due to the accumulation of particles on or within the membrane is observed with LPM filtration process during water treatment.

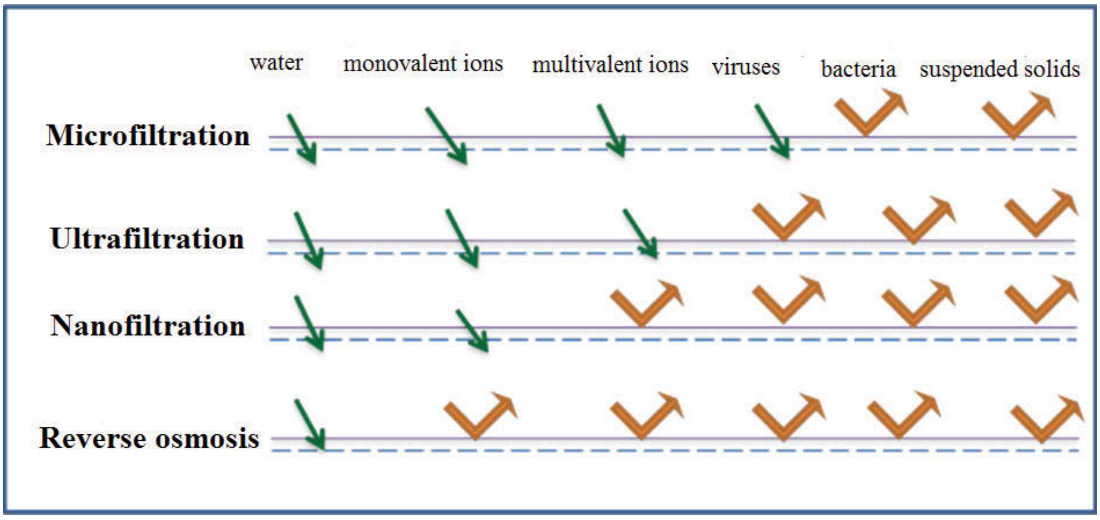


Figure 2.1: Scheme of different pressure-driven membrane filtration processes and rejection capacities

2.1.2 High-pressure membranes

Nano filtration is applied for removal of divalent ions e.g. sulfate and hardness, natural colour (humic acids) and partial removal of monovalent ions e.g. sodium and chloride. Reverse osmosis (RO), isone of the most applicable methods for water desalination that energy consumption in RO process is quite high. Therefore more researches need to minimise these drawbacks in RO process. RO membranes are able to remove more than 99% of mono and divalent ions. The pores in NF and RO membranes are smaller than 1 nm. RO and NF are pressure driven membrane separation processes in which a dense membrane allows diffusion of the solvent and solutes. Diffusion of solutes like salts, (low) molecular weight compounds and particles is low compared to water, resulting in a rejection of those substances. RO is the membrane process used for desalination of brackish and seawater.

2.1.3 Forward osmosis membrane process

The development of FO can be attributed to the phenomenon of osmosis. This process can best be described as a system of communicating vessels where a membrane separates high and low salt solutes. Water from the low saline solute diffuses through the semi-permeable membrane to the more concentrated saline solute. This diffusion of water through a semi-permeable membrane is called osmosis. The volume of the high saline solute increases and the saline concentration is reduced, while the volume of the low saline solute decreases and the saline concentration increases on the other side of the membrane, until “osmotic equilibrium” is reached. The history of FO involves membranes, draw solutions, processes and energy generations. Osmosis is a ubiquitous physical observation, which can be found in all living cells. In the early days of mankind, the osmotic process was primarily used to desiccate food for long term preservation (McCutcheon et al., 2005). The test and evaluation of Pressure Retarded Osmosis (PRO), which utilises the concept of FO for power generation, has been disclosed to the public since the 1960s (Kalele et al., 2009). From the 1970s, more and more attention was directed to the research area of FO applications, such as food processing (Lee et al., 2008) and wastewater treatment (Narain et al., 2007, Robinson et al., 2007). However, researchers tested the FO performance in different configurations using mostly RO membranes and the results were lower than anticipated (Du et al., 2009). The reason behind this was the progressive understanding acquired through the development of FO and other closely related processes (Li et al., 2004, Cai and Wan, 2007, Klug and Alexander, 1974). RO membranes may induce severe internal concentration polarisation (ICP) within the membrane when operated in a zero hydraulic pressure environment. The inevitable ICP can greatly lower the effective driving force of a FO process. Accordingly, if we use RO membranes tested in a FO environment, the FO performance in terms of water flux is never satisfactory.

By understanding the crucial role of FO membrane structure, which determines the degree of concentration polarisation (CP), Hydration Technologies Inc. (HTI, USA) successfully commercialised the FO membrane with a much improved FO performance in 1990s (McCutcheon et al., 2005). In the 21st century, more FO membranes designed with novel structures started to appear in the publications. Wang et al reports doubled-skinned FO membranes of reduced ICP within a porous sublayer and this was a breakthrough in the development of FO membranes (Ling et al., 2010). Later, Zhang et al investigated the fabrication of double-skinned FO membranes using different substrates (Ge et al., 2010). Su et al reports the broad studies of FO membranes made from cellulose acetate, which is a promising material for FO applications (Ling et al., 2011, Ling and Chung, 2011, Ge et al., 2012a). In terms of osmotic energy generation, Statkraft in 2009 built the first pilot-scale osmotic power plant in Norway (Ge et al., 2012b). The energy was generated from the natural osmotic pressure between two solutions. The rapid development of osmotic power generation in recent years is believed to play a significant role as the source of future renewable and eco-friendly energy.

Forward osmosis (FO) process utilizes a high osmotic pressure draw solution (DS) that can produce high osmotic pressure as a driving force for separation (Cath et al., 2006b, Zhao et al., 2012b, Loo et al., 2012). FO can be combined with pressure driven membrane processes such as RO to improve performance of water treatment (Yangali-Quintanilla et al., 2011, Zhao et al., 2012a, Shaffer et al., 2012). Lack of an ideal DS is one of the critical drawback that hampers the efficiency of FO application (McCutcheon et al., 2005). However efforts have been made to develop an ideal DS (McGinnis and Elimelech, 2007, Yen et al., 2010, Bowden et al., 2012, Ling et al., 2010), DS with high osmotic pressure and high recovered rate that can regenerated with low energy and cost have not yet been successfully identified (Achilli et al., 2010). However, FO does not always need draw solute recovery (Hoover et al., 2011). In FO process seawater or brackish ground water are diluted with an impaired water source (e.g., treated wastewater effluent) and then sent to the desalination RO plant. Dilution of seawater or brackish ground water reduces the required hydraulic pressure in the RO process and the energy consumption for desalination (Cath et al., 2010). Therefore, successful application of osmotic dilution processes could significantly improve the efficiency of waste water treatment and sea water desalination (Hancock et al., 2012).

FO process uses the osmotic pressure gradient ($\Delta\pi$) between FS and DS as the driving force to pull water across the semipermeable membrane. RO uses the difference in hydraulic pressure as the driving force for the transport of fresh water. Pressure retarded osmosis (PRO) can be viewed as the process between FO and RO, where hydraulic pressure is applied in the opposite direction of the osmotic pressure gradient, similar to RO. The general equation to describe water transport in FO, RO, and PRO is Eq.1.1:

$$J_w=A(\sigma\Delta\pi-\Delta P) \qquad (1.1)$$

Where Jw is the water flux, A the water permeability constant of the membrane, σ the reflection coefficient, and ΔP is the applied pressure. For FO, ΔP is zero; for RO $\Delta P>\Delta\pi$; and for PRO $\Delta\pi>\Delta P$. The flux directions of the permeating water for FO, PRO, and RO are illustrated in Figure 2.2

FO consumes only about 20% of the electrical energy required by other desalination processes (McGinnis and Elimelech, 2007). In addition, FO also has higher recovery, resulting in less brine discharge to the environment (Cath et al., 2005). Promising FO applications include seawater desalination (Kravath and Davis, 1975), green power production (Aaberg, 2003, Lee et al., 1981, McGinnis et al., 2007), wastewater reclamation (Cartinella et al., 2006, Cath et al., 2005), industrial wastewater treatment (Holloway et al., 2007), and liquid food processing (Jiao et al., 2004).

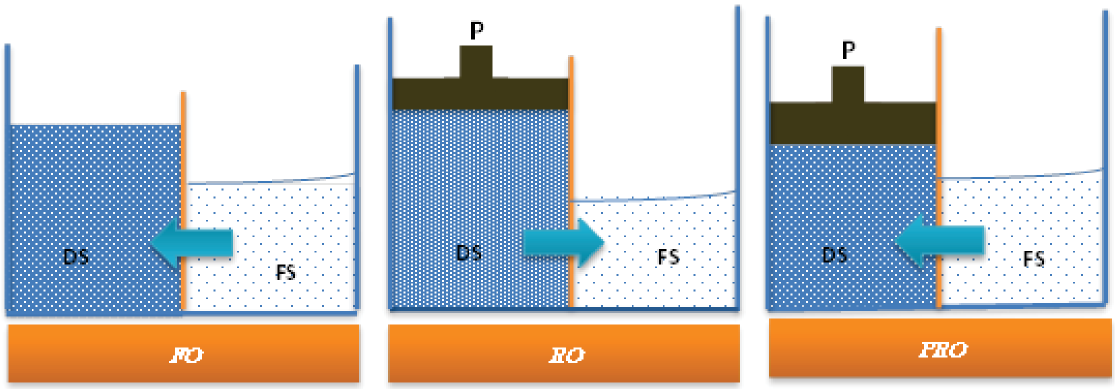


Figure 2.2: Water flows in FO, PRO and RO process. For FO process, ΔP is approximately zero and water transports to the higher osmotic pressure side of the membrane. For PRO process, water transports to the more saline liquid that is under positive pressure (Δπ>ΔP). For RO process, water transports to the lower osmotic pressure side due to hydraulic pressure (ΔP>Δπ).

2.1.3.1 Concentration polarisation in FO process

In the FO process the water flux is almost always less than expected because of concentration polarisation (CP). CP is the dynamic accumulation of particles at the surface of a membrane due to the balance of convective transport toward the membrane and the rate of back diffusion away from the membrane (Cheryan, 1998a). The result of this accumulation is a boundary layer near the membrane surface that is commonly referred to as the "gel layer," as it is thought that super saturation of rejected species may result in localised gelation near the membrane surface. Increases in viscosity due to filtration and declines in fluid velocity due to friction result in laminar flow in this gel layer (Cheryan, 1998a). While it is not fouling in the strictest sense of the word, concentration polarisation leads to an observable flux decline. Two mechanisms may cause this decrease (Marshall et al., 1993, Daufin, 1995). The gel layer simply hinders the passage of permeating species and the large osmotic pressure formed at the membrane surface acts against the process' driving force.

Two independent solutions are involved in the FO process: the draw solution (DS) and the feed solution (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 CP: concentrative CP on the membrane surface facing the FS and dilutive CP on the membrane surface facing the DS (Figure 2.3). Mainly, in any pressure based membrane processes the feed solute concentration at the membrane surface is higher than the bulk solute concentration which increases the osmotic pressure of the feed solution at the membrane surface, thereby decreasing the net osmotic pressure and the water flux. This phenomenon is called a concentrative CP effect, in the FO process a similar phenomenon exists on the feed side of the membrane

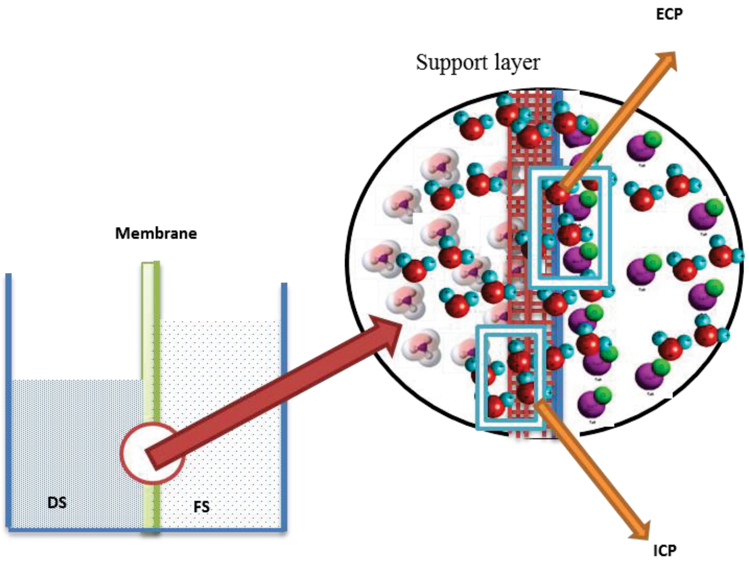


Figure 2.3: A schematic of concentrative polarisation

The FO process also experiences dilutive CP that occurs on the membrane surface facing the DS. As water transports through the membrane from the FS 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 osmotic pressure. Concentrative CP occurs only on the feed solution side of the membrane, while dilutive CP occurs on the DS side of the membrane that both of them significantly influence the water flux in the FO process (McCutcheon et al., 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 2.4 illustrates the concentration polarisation effects in the FO process using a symmetric membrane.

The CP effects model in Figure 2.4 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. 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 (Cath et al., 2006a).

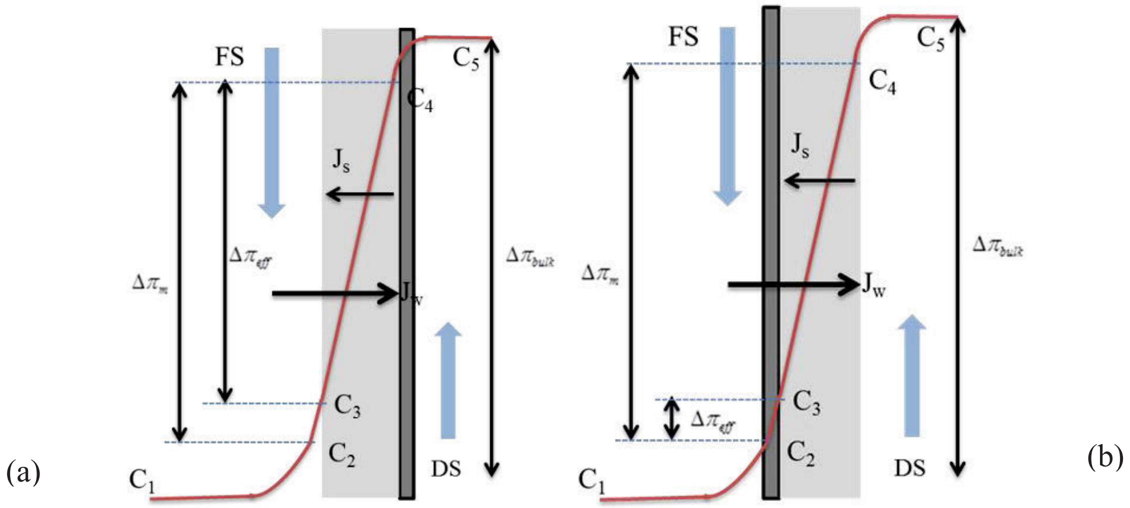


Figure 2.4: Influence of concentration polarization in the water flux, Concentrative (a) and dilutive (b) ICP. is bulk osmotic pressure difference, is the membrane osmotic pressure difference (less than due to ECP), is the

effective osmotic pressure difference across the membrane active layer (less than due to ICP) (Cath et al., 2006a).

2.2 Membrane fouling in the pressure based membrane process

Membrane fouling is referred to as the deposition of the particles contained in the feed stream on the membrane surface or in the membrane pores. Membrane fouling has a negative impact on filtration performance as it decreases the permeate flux. It can also change the characteristics of the membrane and reduce the recovery of the desired product (Niriella, 2006).

Many researches have been focused on the mechanisms governing the fouling of membrane based processes and to alleviate fouling such as pre-treating feed water (Jin et al., 2009, Shon et al., 2008, Zhou et al., 2009, Asatekin et al., 2006, Vrouwenvelder et al., 2009). Fouling is a major obstacle for efficient use of pressure driven membrane systems. Fouling reduces the performance of the membrane surface. When the fouling occurs, a thick layer is formed on the membrane, causing the permeate flux to decline and increasing the operating costs for chemical cleaning or replacing the membrane. Chemical cleaning impairs membrane selectivity and shortens membrane life but is also unsustainable as it consumes additional energy so alternative membrane processes that can reduce or even eliminate chemical cleaning are strongly preferred (Ang and Elimelech, 2007, Ang et al., 2006).

Soluble particles can enter the membrane pores and then build up on the pore wall, leading to a reduction of the total section area of the membrane pore, causing pore plugging into the membrane and increasing the membrane resistance (Xing, 2002). Membrane fouling is strongly influenced by solutions characteristics, operating conditions and membrane characteristics.

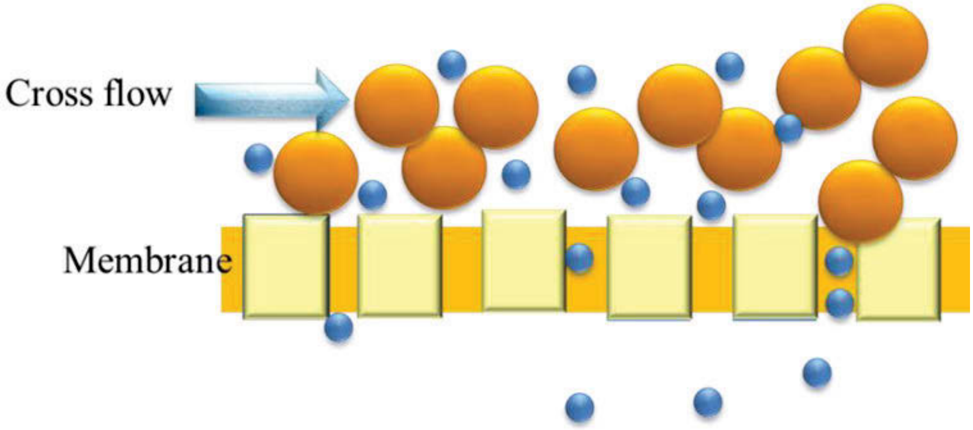


Figure 2.5: Water passes through the semipermeable membrane

Membrane filtration refers to the separation of components from a feed solution that the separation is initially the result of size differences. The liquid stream passing through the membrane, the permeate, is free of feed components larger than the membrane pores whereas the liquid stream leaving the membrane module unfiltered, the retentate, will have a higher concentration of retained particles (Figure 2.5). In cross flow filtration the feed flows tangentially to the membrane surface thereby remove some of the deposited particles and reducing the accumulation of feed components at the membrane surface. A schematic for cross flow filtration is shown in Figure 2.6.

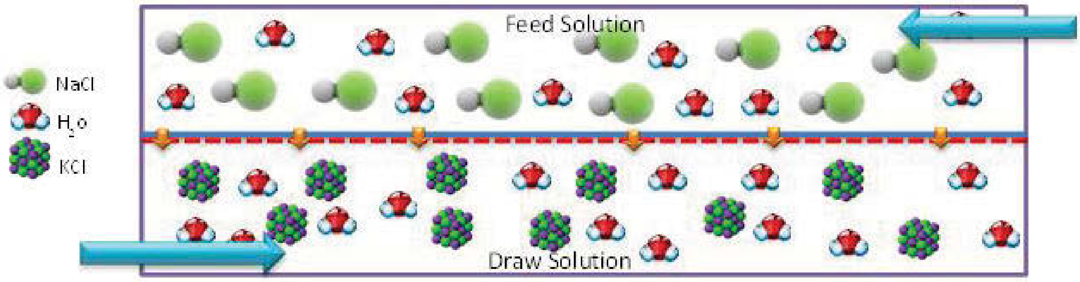


Figure 2.6: A schematic for cross-flow filtration

2.2.1 Organic fouling

The Effluent Organic Matters (EfOM) are considered as main organic foulants have been investigated (Jarusutthirak et al., 2002, Laabs, 2006, Shon et al., 2006, Amy, 2008). EfOM in wastewater is from three sources: natural organic matters (NOM), synthetic organic compounds (SOC), and soluble microbial products (SMP) (Amy, 2008, Barker and Stuckey, 1999, Drewes and Fox, 1999).

NOM in drinking water is attributed to fouling in low pressure membrane process (Hallé, 2009, Kennedy et al., 2008, Huang et al., 2007), EfOM foulants in the membrane process of treated domestic wastewater are different to NOM foulants in drinking water. The foulants from SE reduce the permeability of UF more than those from surface water but the formed fouling shows a higher reversibility. Also the high molecular organic compounds demonstrate severe fouling effect than other organic fractions (Jarusutthirak et al., 2002).

Dissolved naturally occurring organic substances have been recognised as a cause of membrane fouling in facilities that treat natural waters. The major component of NOM in aquatic environments is typically humic substances (Letterman, 1999). Humic substances do not have a well-defined structure and are typically low to moderate molecular weight. Hong and Elimelech (Hong and Elimelech, 1997) found increased flux decline is associated with larger molecular weight (MW) species. Depending on the type of substance, dissolved organic matter fouling can change the charge properties of the membrane. Organic fouling can occur in surface water systems with total organic carbon (TOC) greater than 3-6 mg/L. Organics are typically removed by coagulation, sedimentation, and filtration. Integrated membrane systems (IMSs) can also be used to limit organic fouling. While the reality of organic fouling is known, the significance of this type of fouling compared to others is not (Duranceau, 2004).

Though there are many filtration system designs available, no process is exempt from fouling. Membrane systems can be configured for dead end cross-flow filtration. In the former, the fluid is fed perpendicular to the surface of the membrane. In the latter, the fluid is pumped tangentially over the surface of the membrane. The general form of flux decline is different in each configuration (Figure 2.7).

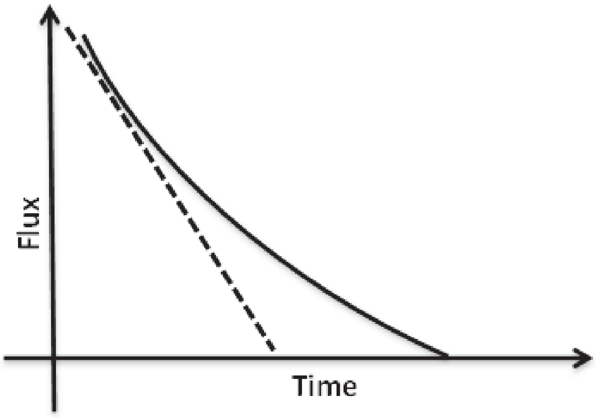


Figure 2.7: Flux decline during dead end (- -) and cross-flow (___) filtration processes.

Cross-flow filtration is commonly used in industrial applications because it permits longer run times between cleaning cycles. Because of its industrial ubiquity, only cross-flow filtration will be examined in this review. Once a steady state has been reached, cross-flow filtration processes may be operated in constant flux or constant pressure mode. The former indicates that permeate flux is held constant by increasing TMP, as foulant accumulates on the membrane. The latter indicates that a constant TMP is maintained while permeate flux is allowed to decline, as fouling limits membrane permeability.

Feed characteristics, membrane type, and processing conditions all contribute to the level of foulant build up.

2.2.2 Inorganic fouling/ scaling

Inorganic fouling is caused by the accumulation of inorganic precipitates and scales on membrane surfaces or within the pore structure (Li, 2008). In the RO and NF process precipitation of inorganic compounds is a major concern that are formed when the concentration of these chemical species exceed their saturation concentrations. During UF process and MF process, inorganic fouling due to concentration polarisation (CP) is much less profound, but can exist due to interactions between ions and other fouling materials (Liang et al., 2008, Costa et al., 2006). If pre-treatment processes for membrane filtration such as coagulation or oxidation are not designed or operated properly, they may introduce metal hydroxides into the fouling matrix. Inorganic fouling and scaling can be a significant issue for chemical cleaning to enhance water flux (Liu, 2006).

When the solubility of a sparingly soluble salt is exceeded, the resulting precipitation is mineral scaling (Nemeth, 1997). Calcium carbonate and sulfate salts are examples of sparingly soluble salts which were initially and remain the driving force of most pretreatment chemical selection for RO processes. Silica, hydrogen sulfide, iron, manganese, and aluminum are some of the other constituents to consider. Historically, acid addition for pH adjustment has been used to prevent scaling in membrane systems. Systems with the potential for calcium carbonate scale formation and scaling by other inorganic compounds typically use a combination of acid addition and scale inhibitors. The type of anti-scalant and the required dosage can be determined by calculating the solubility limit of the Limiting Salt. The Limiting Salt is found by analysing the feed water quality and solubility products of potential limiting salts.

There have been significant advances made in the area of scale inhibitors. Many of today's proprietary pretreatment chemicals offer solutions to a variety of membrane applications. Some applications were previously a significant challenge to treat and others, where the water was accepted as poor quality resulted in increased operation and maintenance costs. A specific scale inhibitor is typically best suited for a particular source water. Factors for selection of a scale inhibitor include feed water source, water quality, recovery, water temperature, membrane material, and the presence of other contaminants such as biological containments (Kinslow, 2004).

As membrane systems are integrated treatment processes for the removal of a variety of constituents, the treatment of scaling cannot be viewed in a vacuum. While membrane manufacturers typically provide a recommended pH level to prevent scaling in their system, this pH level is usually not ideal for other applications or unit processes. An example is removal of hydrogen sulfide in feed water. The presence of hydrogen sulfide in gaseous form is a secondary standard issue for odour and, as Sulfate and elemental sulfur, it can irreversibly damage reverse osmosis membranes. To combat these effects, it is common practice to operate a system where the feed water supply and membrane system itself exclude the introduction of air to protect the membranes. A post-treatment such as counter-current forced draft aeration is used to remove the gaseous fraction to reduce odours.

Christopher et al (Christopher, 2002) found that optimising acid addition feed locations was a way to limit scaling while also optimising hydrogen sulfide removal in the post–treatment two stage wet scrubber. The original plant operation included one acid addition feed point prior to cartridge filtration where the pH of the raw water feed was lowered using sulfuric acid to prevent scaling in the membranes and improve removal of gaseous hydrogen sulfide efficiency in the scrubber. Trying to accomplish both pretreatments at one injection point resulted in a pH significantly lower than what the manufacturer recommended for scaling and a high acid demand because the Floridan aquifer source water had a high alkalinity. Lowering the pH was also detrimental to removal of dissolved ions of sulfide species as the pH forced the distribution to the gaseous forms. The resulting permeates plus blend water had a high chlorine demand since the dissolved sulfide species were not removed by the membranes. By adding a second acid feed point after the membranes, the facility was able to reduce acid dosage, increase control of hydrogen sulfide, increase removal of total sulfide species, and reduce the amount of chlorine needed for disinfection. Optimising the use of acid is important as plants move toward scale inhibitor only pretreatment of membranes.

2.3 Fouling mechanism in pressure based membrane process

The common thread among all forms of fouling is that they describe an interaction between the foulant and the membrane that is only reversible with cleaning. Adsorption occurs when foulant adheres to the surface of the membrane. This may take place on top of the membrane or in the membrane's pores. Adsorption within the pores reduces flux by narrowing the channels for permeate passage. Adsorption at the membrane surface can lead to the formation of so-called cake layers. Cake layers are created when particles aggregate to form bridges and piles that cover sections of the membrane. These aggregates are made up of large particles that would typically be concentrated and smaller ones that could potentially be separated. Because of the wide range of particle size within this matrix, the layer can be firmly compressed if allowed to remain on the membrane's surface, thus adding an additional layer of resistance to permeate flow. Pore blocking involves the superficial plugging of a pore. This form of fouling takes place when a particle that is slightly larger than the pore becomes lodged at the pore's entrance. Depth fouling occurs when a large particle, such as one involved in a pore blocking scenario, is forced deep into a pore through which it would not normally pass. This is often due to the application of excessive TMP. As with pore blocking, depth fouling acts to reduce flux by decreasing the number of available pores through which permeate can pass. While the forms of fouling that take place on the membrane surface can often be removed with proper cleaning techniques, foulant within the pores is much more difficult to get at, and may remain bound to the membrane (Renner, 1991). Irreversibly bound foulant such as this limits the membrane's usable lifespan (Renner, 1991).

2.3.1 Fouling caused by concentration polarisation

In membrane process, the solvent passes through the membrane and the accumulation of solute causes the local concentration to increase (Bowen, 1995). The accumulation of solute on the membrane could be either particle polarisation or concentration polarisation which leads to reduce osmotic pressure. The basic equation describing the relationship between flux and driving force is as follows:

$$J = \frac{\Delta P - \Delta \Pi}{\eta (R_m + R_d)} \qquad (1.8)$$

Where

Rd = Resistance due to reversible or irreversible deposition of solute onto the membrane surface

$\Delta\Pi = \Pi(cm) - \Pi(cp)$, the difference of osmotic pressure

$\Pi(cm)$ = the osmotic pressure at the membrane surface

$\Pi(cp)$ = the osmotic pressure in the permeate

As in low pressure membrane processes for water treatment, the osmotic pressure is negligible, osmotic effects are frequently ignored by calculation (Bowen, 1995). However, the CP effect is important in respect to the formation of membrane fouling. During filtration, the accumulated solutes at the membrane surface have a tendency to diffuse back into bulk solution according to Fick's law of diffusion. At a steady condition, the solute mass balance on the membrane surface can be achieved which gives the rate of convective transport of solute towards the membrane surface equal to the rate of solute leakage through the membrane plus the rate due to back diffusion. When the hydraulic resistance disappears, the fouling is considered reversible. Concentration polarisation leads to an irreversible build up under certain conditions. For example, when the concentration of macrosolutes at the membrane surface reaches its solubility limit and precipitates to form a solid or thioxotropic gel layer, the consolidated structure is slow in diffusing into water and leads to a flux reduction, a fraction of which could be irreversible. Current analysis (Wang et al., 2008) has found that the formed gel layer in wastewater filtration effluent is a three dimensional network consisting of macromolecular compounds. The interactions between these organics and membrane are assisted or strengthened by bridging via multivalent metals and specific molecules.

2.3.2 Particle blocking

Hermans and Bredée (Hermans, 1935) proposed filtration laws to describe the accumulation of foulants on membranes. Gonsalves (Gonsalves, 1950) made a critical research of the physical models used to derive these laws. The accumulation of foulants was classified into four filtration models, a) complete pore blocking model, b) intermediate pore blocking model, c) standard pore blocking model and d) cake layer formation model. Figure 2.6 illustrates each type of model schematically.

In the complete pore blocking model, every particle can block one membrane pore when it reaches the membrane surface. This causes a decrease in the available pores that can increase the resistance. In the intermediate pore blocking model, not all of the particles block the membrane pore. Some particles can overlap existing particles. As with partial pore blocking, the available pores is reduced. In the standard blocking model, small particles deposit/adsorb onto the membrane surface as well as on the inner walls of the membrane pores. The deposition/adsorption of the particles on the membrane walls decreases the pore diameter and results in an increase in the resistance. In the cake formation model, particles accumulate, forming a cake layer on the membrane surface and resulting in an increase in the resistance (Ye, 2009).

Hermia (Hermia, 1982b) developed a mathematical model that describes the fouling of membranes based on the four filtration laws for the constant pressure filtration conditions. The characteristic form of the model is:

$$\frac{d^2t}{dV^2} = K_{i_n}\left(\frac{dt}{dV}\right)^n \tag{1.2}$$

Where the t [s] and V [m3] are the filtration time and cumulative permeate volume, dt/dV is the inverse of the permeate flow rate and the rate of variation of the dt/dV with respect to filtrate volume V is defined as the resistance coefficient which is d2t/dV2. The n value is different for the different filtration laws: for complete blocking, n = 2; for standard blocking, n = 1.5; for intermediate blocking, n = 1; and for cake layer formation, n = 0. Kin is the blocking constant and is different for each filtration law. For a constant flow and variable pressure systems, the Hermia's model yields equations 1.3 to 1.6 for the four different fouling laws.

Cake fouling: $$P_t = P_0 + K_c V \tag{1.3}$$

Intermediate blocking: $$P_t = P_0 e^{kv} \tag{1.4}$$

Standard blocking: $$P_t = \frac{P_0}{(1+\frac{1}{2}k_s V)^2} \tag{1.5}$$

Complete blocking: $$P_t = \frac{P_0}{1-k_b V} \tag{1.6}$$

Where the Pt [Pa] is the TMP at time t and P0 is the initial The Hermia's model was developed assuming dead-end filtration with no back transport.

Field et al. (Field et al., 1995) modified the Hermia's model for the cake formation, intermediate blocking and complete blocking filtration laws, by assuming that under these three laws, the particle can transport back into the bulk solution.

$$-\frac{dJ}{dt}J^{n-2} = K_{i_n}(J - J^*) \qquad (1.7)$$

Where the J is the permeate flux (dV/dt/A), J* is the critical flux defined by Field et al. (Field et al., 1995) that fouling will not happen when the permeate flux is below the critical flux and the kin is the blocking constant for different filtration laws.

The back transportation of the particle has been suggested to occur predominantly due to three mechanisms for which models have been designed. In the shear-induced diffusion model, particles subjected to a shear, flow randomly, "bump into", and tumble over each other as well as the membrane surface, resulting in net displacement of the particles away from the membrane surface (Zydney, 1986). In the inertial lift model, particles subjected to a laminar cross-flow velocity distribution near the membrane surface undergoe rotation resulting in a lateral movement away from the membrane due to the differential pressure induced by the velocity gradient of the rotating particles (Green and Belfort, 1980). The surface transport models suggest that the particles at the membrane surface roll along the surface due to tangential flow along the membrane surface (Belfort et al., 1994).

The three models suggest that particle back transport is significantly affected by the shear rate (as well as the particle size and concentration) (Belfort et al., 1994).

However, the particle transport models were developed for constant laminar cross-flow conditions at the membrane surface. In a gas sparged membrane systems, the hydrodynamic conditions at the surface are highly variable and turbulent. Therefore, the above models cannot be applied directly to gas sparged membrane systems. Nonetheless, the models do suggest that particle back transport in gas sparged systems is likely to be affected by the shear rate (Ye, 2009).

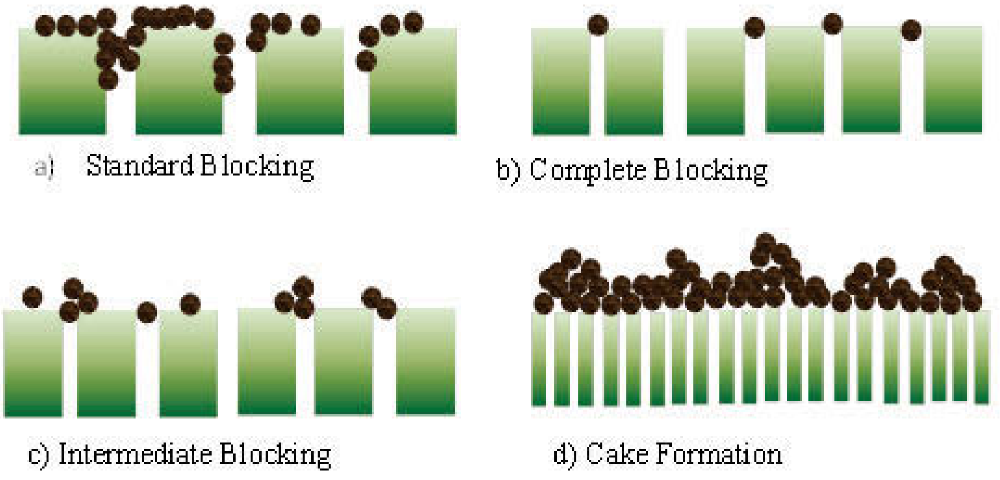


Figure 2.8: Filtration models (Blocking lows)

The four models are the Standard Blocking, Intermediate Blocking, Complete Blocking and Cake Filtration Laws. The physical phenomena associated with each of these models is summarised in Figure 2.6. As will be explained below, each model is more relevant at different conditions depending on the ratio between the pore and foulant particle sizes. They are useful in analysing empirical results and provide information about the nature of fouling occurring in a system (Ye, 2009).

In the standard blocking or pore constriction model (Figure 2.8 (a)), the particles are much smaller than the pores and tend to foul the membrane by depositing on the membrane surface and on the sides of the pores. Thus, over time, the diameter of the pores will decrease which results in an increase in the hydraulic resistance to permeation as the total pore area decreases and so flux declines.

Under the complete blocking or pore plugging model (Figure 2.8 (b)), the particles are around the same size as the pores and so when reaching the membrane tend to discretely block entire pores. Thus the flux declines and resistance increases as the number of pores available for permeation (and thus total pore area) decreases.

The intermediate blocking model (Figure 2.8 (c)) is a compromise between the standard and complete models (Hlavacek and Bouchet, 1993). Unlike the previous models, the intermediate law assumes particles can land across the entire membrane surface and on other particles, rather than exclusively blocking pores or reducing their volume. The model considers the probability that a particle (of approximately the same size as the pores) will block a pore (Hermia, 1982a).

This reduction in total pore area increases the resistance, reducing the flux.

The final model is the cake filtration law (Figure 2.8 (d)). In this model, the particles are much larger than the pores and collect on the surface, forming a cake. This cake adds a second resistance layer in the series to the membrane resistance. This extra resistance reduces the flux.

2.3.3 Stages of fouling

After concentration polarisation and fouling have been initiated, the membrane is not the only resistance which dictates the process separation. In fact, once the foulant layer has been laid down, it contributes a much larger resistance than the membrane itself (Fritsch, 2008). Hanemaaijer et al. (Hanemaaijer, 1989) noted that the resistance due to the foulant layer and concentration polarisation can be between 10 to 50 times that of the resistance contributed by the membrane itself in the case of UF. A generalized trend of flux decline in cross-flow membrane processes is depicted in Figure 2.9.

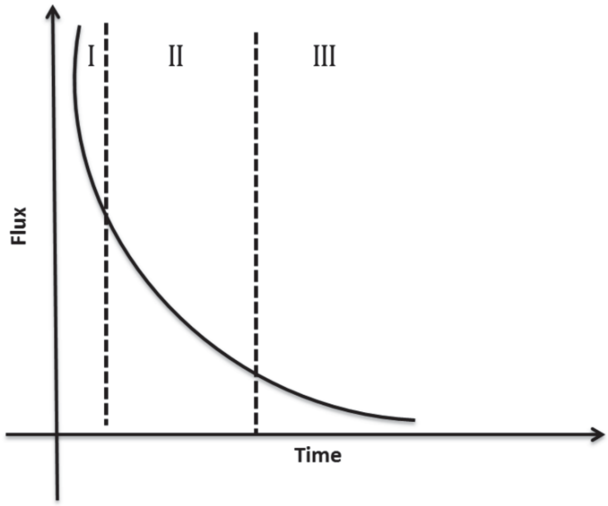


Figure 2.9: The three stages of flux decline during cross-flow filtration. Adapted from, Marshall and Daufin (1995).

Because concentration polarisation promotes fouling, it is often associated with stage I of flux decline (Marshall et al., 1993). This phase occurs early in the process (within seconds or minutes) and is characterized by a rapid drop in membrane flux. However, immediate foulant adsorption also contributes to this initial flux decrease, as rapid (within 5 min) adsorption of protein to the membrane surface has been noted to occur even without the effects of concentration polarisation (Tong, 1988, Rudan, 1990). If the membrane being used is easily deformable, as many polymeric varieties are, membrane compaction may also be responsible for suppressing the flux during this initial stage (Marshall et al., 1993).

According to Marshall and Daufin (Marshall, 1995), stages II and III of UF flux decline are due to fouling. The initial deposition of foulant onto the membrane is responsible for the drop during stage II (Marshall, 1995). This decrease is less dramatic than the decline due to concentration polarisation. Stage III shows an asymptotic decline and is due to additional deposition and compaction of the foulant layer (Marshall, 1995). Belfort et al. (Belfort et al., 1994) offered a similar progression for MF fouling with colloidal solutions: after solutes and colloidal particles adsorb to the surface of the membrane, monolayers (cake layers) are formed, these monolayers overlap to form multilayers, then the multilayers are compacted under the system's TMP.

2.4 Factor affecting membrane fouling in pressure based membrane process

2.4.1 Effects of feed properties

The properties of the feed solution such as solid concentration, particle properties, pH and ionic strength strongly influence membrane fouling. . Increase in the feed concentration results in a decline in the permeate flux. This is because of the increase in membrane fouling by the presence of a higher foulant concentration. In a filtration process, the particle sizes in the feed often cover a wide range. The presence of fine as well as coarse particles results in a lower cake porosity as the fine particles can slide between the large ones, filling the interstices. The particle size distribution plays a key role in the selective deposition at high cross-flow. In addition to the particle size, the particle shape affects the porosity of the cake formed on the membrane surface. In general, the lower the particle sphericity, the greater is the porosity (Vyas and Bennett, 2000).

The other factors, such as: pH, ionic strength, and electric charges of particles, are also important. The pH and ionic strength of the feed affect the charge on the membrane, the charge on the particles, conformation and stability of, and the adhesiveness of particles and the size of the cake. For example, a study of the impact of pH of the latex emulsion on membrane fouling showed that the latex emulsion pH should be high enough to prevent the coagulation of latex particles, and hence, to increase the antifouling properties of the latex emulsion. Moreover, a reduction in pH can decrease the molecular size of NOM so enhance adsorption onto membrane, resulting in a significant fouling.

According to film theory, an engineering model that predicts flux decline according to mass transfer effects, flux decreases exponentially with an increasing concentration of the feed fluid (Cheryan, 1998b). While film theory addresses concentration polarisation specifically, it impacts fouling as described above. Generally speaking, increasing the concentration of a feed stream increases the level of reversible foulant (that which can be removed by cleaning). This amounts to an increase in observed cake layer formation and a decline in flux (Marshall et al., 1993). Increasing the concentration factor (CF) during a membrane process has the same effect on fouling as increasing the feed concentration because the feed solids build up to a greater extent on the retentive side of the membrane.

2.4.2 Effects of membrane properties

Membrane materials strongly influence membrane fouling capacity for any particular compound and the reversibility. There are variety polymer membranes with either a hydrophilic or hydrophobic surface, that changing their interaction with potential foulants (Thorsen et al., 2004).

Ho and Zydney (Ho and Zydney, 1999) determined that a MF membrane's pore structure plays a large role in the initial rate of flux decline during protein (BSA) fouling. Membranes with highly interconnected pore systems exhibited slower rates of initial flux decline (i.e., slower fouling) than membranes with straight-through pores (i.e., no interconnectivity) because permeate was able to manoeuvre around foulant deposited on and just below the surface of the interconnected-pore membrane. In addition, membrane porosity was found to be inversely proportional to the initial rate of flux decline, at least at relatively low porosities. In this low porosity region, an increased number of pores allowed more foulant to be applied without diminishing flux. However, porosity was eventually increased to a point at which flux decline was no longer mitigated because localized areas of foulant build up obstructed more than one pore, offsetting the benefit of additional pores. Bacchin et al. (Bacchin et al., 2006) indicate that by increasing the membrane's porosity further still, pores could eventually become so close to one another that foulant deposition would be limited by particle-particle steric repulsions. When interconnected pore structures are not present, the pore's shape has been shown to impact a membrane's critical flux (the maximum flux prior to rapid fouling). Microsieves are membranes, usually made from metals, which have a well-defined pore structure which is created by precision etching. Bacchin et al. (Bacchin et al., 2006) indicated that microsieves with slotted pores have been shown to exhibit higher critical flux values when compared to those with circular pores.

The channel shape within a membrane through which the product flows may also be of importance in regard to fouling. When working with membranes containing star-shaped channels at cross-flow velocities between 0.6 and 2 m/s, Chiu et al. (Chiu, 2005) noted that a higher critical flux could be expected using this design than might be observed with traditional circular channels. This observation was attributed to the star-shaped channel's ability to promote turbulent flow at the membrane surface. In 1999, Technologies Avancees & Membrane Industrielles (TAMI) produced a patent regarding the creation of non-circular membrane channels which were triangular in nature (Grangeon, 1999). Aside from increasing the amount of surface area in a given element volume, this design is purported to confer the following advantages over circular designs: reduced headloss within the support structure and increased flow speed of permeate through the channels.

2.4.3 Effects of membrane operating parameters

The effects of cross-flow velocity and membrane flux on membrane fouling depend heavily on one another. In general, increasing the cross-flow velocity increases the limiting flux (Marshall and Daufin, 1995). When operating in constant flux mode, flux is maintained and pressure on the permit side of the membrane is allowed to increase until the system flux is too low and the system must be cleaned or the process is completed. The chosen flux in this operating scheme impacts fouling in the system because an increased flux at a constant pressure increases convection toward the membrane surface which fouls the membrane to a greater extent.

Shear stress at the membrane surface can be increased by increasing the cross-flow velocity on the permeate side of the membrane. Furthermore turbulent flow is promoted. This turbulence scours the surface of the membrane to break up the reversible foulant layer and provides inertial lift from the membrane surface which mitigates concentration polarisation, thus reducing the potential for fouling (Belfort et al., 1994). Below this ratio, the MF membranes did not foul appreciably and the process exhibited longevity. Above this ratio, rapid fouling was noted because convective forces toward the membrane exceeded erosion of the foulant layer. Similarly, Grandison et al. (2000) determined that increasing shear stress at the membrane wall (at a constant TMP) and decreasing the TMP lessened the resistances due to reversible and irreversible fouling. Polymeric flat sheet membrane systems are also capable of being operated at high cross-flow velocities (Belfort et al., 1994). However, polymeric spiral-wound membrane systems are generally limited to about 1 m/s to prevent delamination of the spiral polymeric membrane structure.

2.5 Fouling reduction, conventional methods of cleaning in pressure based membrane process

Membrane cleaning methods can be classified into a) physical, b) chemical and c) physio-chemical. Physical cleaning methods followed by chemical cleaning methods are widely used in membrane applications. The chemical cleaning methods are usually applied for RO desalination and physical cleaning can apply for FO process.

2.5.1 Physical membrane cleaning methods

In physical cleaning methods the mechanical forces use to remove foulants from the membrane surface. Physical methods include forward and reverse flushing, sponge ball cleaning, backwashing, air flushing, ultrasonic, electrical fields, magnetic fields and CO2 back permeation (Ebrahim, 1994; Al-Amoudi&Lovitt, 2007).

2.5.2 Sponge ball cleaning

Sponge balls made of polyurethane are inserted into the membrane modules for a few seconds for scrubbing the foulant from the membrane surface (Ebrahim, 1994). Sponge balls are usually used for cleaning large diameter tubular membranes when treating polluted solution such as wastewater and industrial process water (Psoch and Schiewer, 2006).

2.5.3 Forward and reverse membrane flushing

During forward flushing permeate water at high cross-flow velocity pumps through the feed side to remove foulants from the membrane surface (Ebrahim, 1994). More rapid flow resulting turbulence, particles absorbed to the membrane are released and discharged. The direction of the permeate flush is alternated for a few seconds in the forward and for a few seconds in the reverse direction in the reverse flushing method (Figure 2.10). Forward flush techniques are specifically useful in removing colloidal matter.

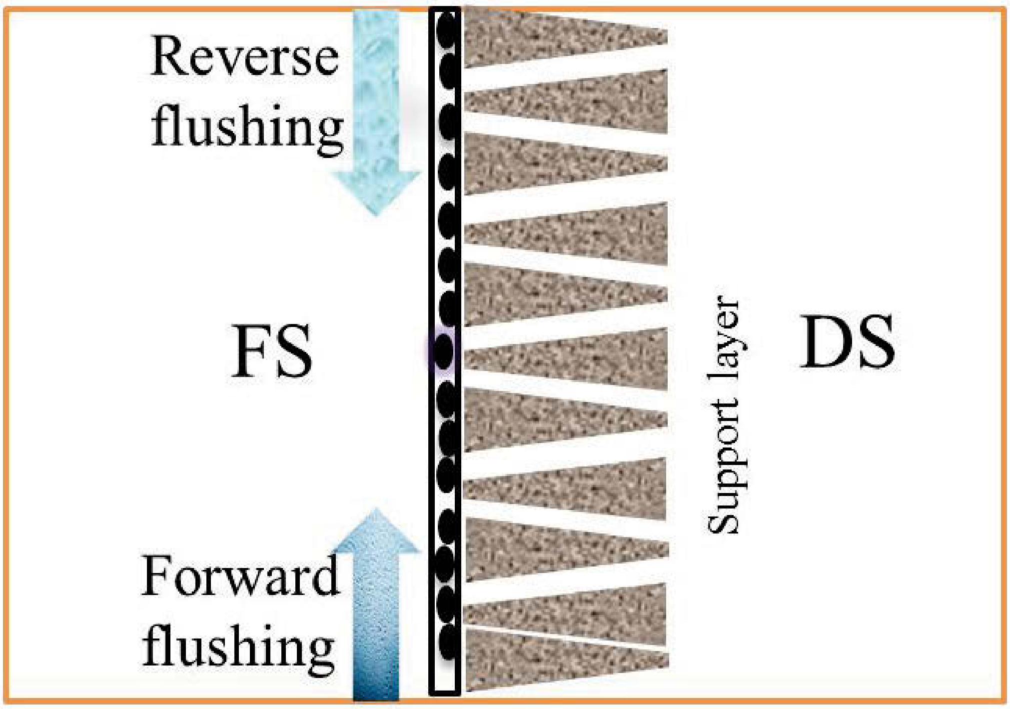


Figure 2.10: Physical cleaning (reverse flushing)

2.5.4 Backwashing membrane cleaning

Membrane backwashing is areversed filtration process that permeate water flux is flushed on the membrane surface. When the backward flush is applied, the pores are flushed inside out. The pressure on the membrane surface is higher than the pressure within the membranes, causing the pores to be cleaned (Figure 2.11). In the RO membranes, backwash cleaning is based on flow induced by osmotic pressure as direct osmotic cleaning. This physical cleaning process is based on negative driving pressure between the operating pressure and the osmotic pressure of the water solution in the feed side. This can be done either by increasing the permeate pressure or reducing operation pressure below the osmotic pressure of the feed solution (Sagiv and Semiat, 2005). Pure water backwashing to the feed side of the membrane expands the thickness of the fouling layer and fluidises it. Usually forward flush is used to wash out the fouled layer or dilute the fouling layer. The best cleaning performance is generally reached optimising the two flows. The significant factors affecting physical cleaning during forward and backward flushing are: duration of backwash, the production interval between cleans, and pressure during forward flush (Chen et al., 2003).

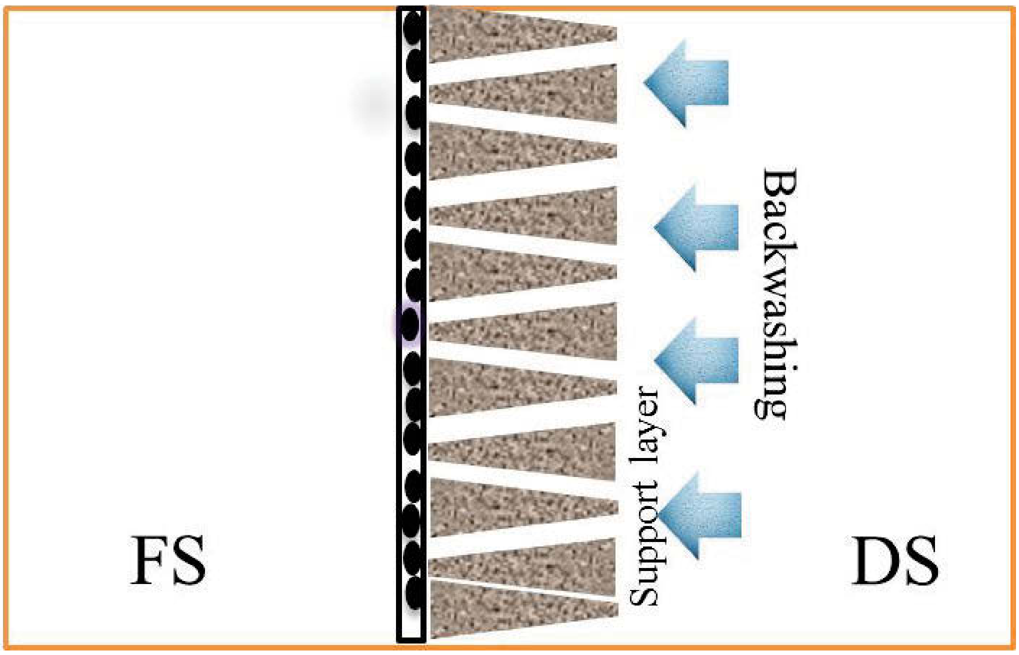


Figure 2.11: Physical cleaning (backwashing)

The significant factor of the backwash cleaning is the driving force that is a combination of concentrations and applied pressures from both sides of the RO membrane. Backwash cleaning classified into two forms: a) with zero feed velocity and applied pressure, and b) with feed velocity and pressure. Some research have shown that methods without pressure seem to have some advantages over methods with pressure (Sagiv and Semiat, 2005).

2.5.5 Pre-treatment process

Membrane fouling in reverse osmosis plants is generally caused by physical blockage, scaling and biofouling.

- Physical blockage is the result of poor pretreatment which results in the deposition of particles on the RO membrane surface.

- Scaling is the result of the precipitation of inorganic salts as the concentrate within the membrane exceeds its solubility (typically di- and tri-valent cations with various anions).

- Many organics form complexes with calcium ions so the removal of calcium can also remove a portion of the dissolved organic compounds (DOC). Organics also form the food for some bacteria, which can cause biofilm formation.

Traditionally, conventional softeners are used to remove cations. However, in "dirty water" applications (e.g. produced water, groundwater and treated effluent), the pre-treatment processes required for conventional technology make these processes less feasible.

RO desalination of saline water process (SWRO) is being increasingly emphasised as a strategy for the conservation of limited resources of freshwater. Desalination methods have been developed over the last few decades, the SWRO operation is still affected by membrane fouling. The membrane fouling during SWRO has a significant impact on the operation of desalination plants. The SWRO foulants consist of a) biofouling (around 48%), b) inorganic colloids (~ 18%), c) organic compounds (~ 15%), d) silicites/silicates (~ 13%), e) mineral deposits (~ 6%) and f) coagulants (~ 5%)

(Khedr, 2000). Organic compounds in seawater consist of particulate organic matter and dissolved organic matter. The concentration of the organic matter in seawater is relatively low (1–3 mg/L) so the portion of organic foulant is small in comparison with inorganic constituents. However, seawater organic matter is a more difficult issue to be solved in the SWRO as it leads to biofouling. To examine organic fouling on the membrane surface, a number of membrane fouling indices have been developed in terms of the silt density index (SDI) and modified fouling index (MFI) using microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) (Schippers and Verdouw, 1980, Boerlage et al., 2000, Boerlage et al., 2002). The MFI study has been investigated in correlation with different pretreatment methods and membrane autopsies (Khirani et al., 2006, Van der Vaart and Stahel, 1988). Fouling potential reduction was observed more than 80% by MFI–UF with pretreatment. The removal efficiency of ozonation and biological activated carbon filtration using the MFI0.45 test was around 60% and 50%, respectively. The removal efficiencies observed for the MFI0.45 and SDI do not correspond and the MFI0.45 results are considered to be more reliable. Membrane characterisation after each MFI experiment is one of the most effective indicators to determine the MFI performance on membrane fouling (Shon et al., 2004). Scanning electron microscopy (SEM), energy dispersive x ray (EDX), atomic force microscopy (AFM), zeta potential, contact angle, pyrolysis-gas chromatography/mass spectrometry (GC/MS) and attenuated total reflection–Fourier transform infrared spectroscopy (ATR–FTIR) can be used to better understand membrane fouling. The zeta potential value is an index of the surface charge of SWRO membranes. ATR–FTIR gives a detailed screen of the molecular functional groups contributing to membrane fouling. SEM and EDX are used for visual investigation of membrane fouling and elemental analysis on foulants. AFM provides information on membrane roughness. Contact angle represents hydrophobicity of the membrane.

2.6 Methods to estimate fouling in pressure based membrane process

2.6.1 Fouling coefficient

One way to determine the extent of fouling after a membrane process is to calculate a fouling coefficient based on the water flux of the system before and after processing under standard conditions. By maintaining a consistent applied pressure on the membrane surface at a given temperature, a processor can determine how much of the initial membrane permeability is lost due to the addition of firmly deposited foulant material on the membrane. To calculate a fouling coefficient, the “fouled water” flux (which is determined after the membrane is rinsed with RO water, but not cleaned with chemical agents) is divided by the initial “clean water” flux and the quotient is subtracted from 1 (Rao, 2002). A higher fouling coefficient indicates a greater degree of membrane fouling, with a value of 1 corresponding to complete membrane blockage.

2.6.2 Hydraulic resistance

Another method to estimate fouling that relies on membrane permeability involves calculating the resistances contributed by various flux reduction phenomena. This is done by first calculating the resistance due to the clean membrane using Equation (1) under standard conditions with pure water. Once the membrane resistance is established, additional sources of resistance may be estimated as described in Caric et al., (2000) and Fritsch and Moraru (2008). By soaking the membrane in the feed material then conducting a fouled water flux measurement, a rough estimation of the resistance due to general adsorption may be quantified after subtracting out the membrane's resistance. An overall gauge of the resistance due to the final foulant layer may be established after processing as in the description for the fouling coefficient above. The concentration polarisation component of flux reduction may then be accounted for by deducting the adsorption and membrane resistances from the overall resistance during steady state process flux. Of course, these measurements would all need to be conducted under the same thermal and hydrodynamic conditions to maintain relative precision.

2.6.3 Membrane imaging

If there is no need to determine the flux reduction caused by fouling, imaging techniques may be used to examine the membranes before and after processing to elucidate the distribution of foulant material. Most commonly, scanning electron microscopy, atomic force microscopy, and X-ray photoelectron spectroscopy have been used in the past (James et al., 2003; Fritsch and Moraru, 2008). Scanning electron microscopy can be used to image cross sections of membranes to examine internal fouling structures. By using this technique, Fritsch and Moraru (2008) determined that multichannel ceramic MF membranes foul to a greater extent within channels at the periphery of the membrane when compared to more interior channels. This finding was attributed to the existence of a velocity gradient within the diameter of the membrane element. Atomic force microscopy is better suited to visualising surface fouling or characterising clean membrane surface roughness, as cross sections usually prove to be too irregularly shaped for this method. While not a form of microscopy, X-ray photoelectron spectroscopy has the benefit of being able to detect the chemical makeup of the membranes. It should be considered, that each of the above techniques are highly invasive and would require the destruction of the membrane for analysis. Furthermore, because these methods require extensive preparation of the membrane before imaging, the original form of the foulant may be altered prior to analysis (Chan and Chen, 2004).

2.7 Membrane fouling and scaling in the FO process

Despite several advantages of the forward osmosis (FO) process, its applications in real situation have been hindered by three challenging problems. 1) draw solution (DS) that create a high osmotic pressure solution that can be recover efficiently, 2) membranes designed for osmotically driven FO processes are needed, as commercially available semi-permeable membranes are primarily designed for pressure-driven processes And 3) compared to abundant research that has been conducted on pressure-driven membrane processes, a systematic understanding of the fouling mechanisms and cleaning effectiveness of the FO process is lacking. Advances in FO technologies lag far behind those in pressure-driven membrane technologies.

Membrane fouling is a major issue faced by FO process that can decrease membrane life and increase the membrane maintenance cost and energy consumption of operation. Therfore, developing strategies to reduce membrane fouling potential have drawn researchers' interest.

Until now, a few studies on FO membrane fouling have been reported in the literature so the underlying membrane fouling and cleaning mechanisms in the FO process are basically unknown (Achilli et al., 2009, Cornelissen et al., 2008, Mi and Elimelech, 2008). There are some fundamental questions that need to be answered, including 1) whether the lack of hydraulic pressure in FO processes mechanistically alters the membrane's fouling and cleaning behavior and 2) whether membrane materials affect the fouling and cleaning behavior and which factors should be considered in the development of a new FO membrane. Thus, fundamental and systematic research is required to elucidate the fouling/cleaning mechanisms of FO membranes.

2.7.1 Colloidal and organic fouling

In colloidal fouling, significant flux decline rates can be observed with thick or less porous fouling layers composed of large particles or a mixture of particles, respectively. The back diffusion of salts that permeate water flux from the DS are hindered by the colloidal fouling layer and, consequently, the salt concentration on the membrane surface increases dramatically (Boo et al., 2012).

Foulant–foulant interaction plays a key role in determining the rate and extent of organic fouling in the FO process. FO fouling is governed by the influence of chemical interaction. Calcium binding, permeation drag, and hydrodynamic shear force are the main factors governing the development of a fouling layer on the membrane surface. The dominating factors controlling membrane fouling is different from foulant to foulant. Before a compact cake layer is formed, the fouling rate is affected by hydrodynamic conditions and the intermolecular adhesion forces (Mi and Elimelech 2008).

Organic fouling such as alginate in the FO process is almost fully reversible with simple water rinse without any chemical cleaning reagents (more than 98% recovery) . The fouling reversibility of the FO process can be attributed to the less compact organic fouling layer formed on the membrane surface due to the lack of hydraulic pressure (Gu, 2012).

2.7.2 Inorganic scaling and fouling

When the concentration of soluble salts in the feed water becomes supersaturated inorganic scaling occurs. Precipitation of these salts may occur on the membrane surface, leading to significant membrane flux decline. A previous research on gypsum scaling found that the lack of hydraulic pressure in FO process helps improve membrane cleaning efficiency (Mi and Elimelech, 2010). Due to its abundance in natural waters and low solubility in water (Den and Wang, 2008), silica is the common inorganic types of salt that cause membrane scaling (Mi and Elimelech, 2012).

Ro desalination of seawater or brine shows insignificant water flux decline, which implies a negligible effect on particulate and organic matter in the seawater or brine on fouling of the FO membrane support layer. Fouling of the membrane active layer may be increased by using an enriched synthetic wastewater effluent containing of both inorganic and organic foulants, focusing on the impact of permeate drag force on fouling layer formation. Higher permeate water flux causes an increase in the concentration build-up of foulants at the membrane surface (Boo et al., 2013).

The intraction between alginate fouling and gypsum scaling observed in the combined fouling experiment that the coexistence of foulants (organic and inorganic) cause faster flux decline than the individual foulants. Alginate acts as nuclei in gypsum crystal growth, so significantly increasing the size of gypsum crystal and accelerating crystallisation kinetics. Also in the presence of alginate, the dominating scaling mechanism switches from bulk crystallisation to surface crystallisation. The direct observation results indicate that alginate shortens the nucleation time, increases the gypsum growth rate, and changes the morphology of gypsum crystals. The fouled membrane cleaning efficiency by combined foulants is less than that for membranes fouled by individual foulants (Liu and Mi, 2012).

Membrane fouling was mainly attributed to external fouling, which was closely related to the movement of cell population to the membrane surface and inorganic precipitation at the membrane surface. The major composition of the inorganic foulant was identified as $MgNH_4PO_4.6H_20$ (struvite), whose deposition together with the microbial cells attached at the membrane surface played a significant role in the formation of the strongly attached cake layer limiting membrane permeability. The struvite precipitation/deposition mechanisms were examined thoroughly in relation to the chemical composition of the influent wastewater and the subsequent anaerobic decomposition in the membrane bioreactor. The conceptual resistance-in-series model was applied to assess the fouling characteristics (Jin et al.).

Only a few works were devoted to temperature influence on struvite precipitation. Aage et al. (Aage et al., 1997) determined the struvite solubility product with a radiochemical method at various temperatures. Burns and Finlayson (Ronteltap et al., 2007) used pH and concentration measurements to investigate the influence of temperature on the solubility product of struvite.

The activity coefficients and ionic concentrations of species were calculated by EQUIL, a Fortran computer program used for chemical equilibrium computation.

According to these results, a steady increase in solubility is observed with an increase in temperature.

From a practical point of view, the Ksp value depends, on the one hand, on the experimental precision, and on the other hand on the thermodynamic method used to calculate the equilibrium constant values, at different temperatures, for all the equilibrium relations involved during the precipitation of struvite.

It is important to highlight that the final values of Ksp presented in the dedicated literature are dramatically impacted by the conditions and assumptions associated with the thermodynamic data. Table 2.1 illustrates the variation range of Ksp values proposed by several authors. The published pKsp values at 25 ◦C range from 9.41 to 13.27.

Table 2.1: Reported experimental values of the K_{sp} for struvite (25 $\circ$C).

pKsp	Ksp	Reference
13.15	7.08×10^{-14}	Taylor et al. (Taylor et al., 1963)
9.41	3.89×10^{-10}	Borgerding (Stratful et al., 2001a)
12.60	2.51×10^{-13}	Snoeyink and Jenkins (Nixon, 1980)
13.12	7.59×10^{-14}	Burns and Finlayson (Ronteltap et al., 2007)
9.94	1.15×10^{-10}	Abbona et al. (Abbona et al., 1982)
13.27	5.37×10^{-14}	Ohlinger et al. (Ohlinger et al., 1998)

2.8 Fertiliser drawn forward osmosis (FDFO) desalination

The forward osmosis (FO) desalination process is an attractive option if the diluted DS after process can be used directly as it is and does not require the further separation and recovery of draw solutes. This is possible when used draw solute adds value to the product water. Therefore, the diluted DS can be used directly, thereby avoiding the need for additional separation and recovery process (Hoover et al., 2011). A promising area of FO application is agriculture, desalination for irrigation using fertilisers as the draw solutes (Moody, 1977). When fertilisers are used as the DS, the diluted DS after desalination can be directly used for irrigation (fertigation), thereby avoids the need for separation and recovery. As fertilisers are extensively used in agricultural production, this process would provide nutrient-rich water for direct fertigation from any saline water source such as seawater and brackish ground water (Phuntsho et al., 2011).

2.8.1 The concept of FDFO process

The concept of using fertilisers as a draw solute in FO process to extract fresh water from saline water for irrigation was first reported by Moody and Kessler (1976). Despite the potential for such an application is immense, works on this particular concept did not receive attention until now and this is mainly due to the lack of a suitable membrane for the FO application. In the FO process, two different solutions are used: saline water as the feed solution (FS) on one side of the membrane, and highly concentrated fertiliser solution as the draw solution (DS) on the other side of the membrane. FS and DS are continuously kept in contact with the membrane through a modest cross-flow system, to minimise the influence of concentration polarisation (CP) effects. Based on osmotic gradient across the semi-permeable membrane, water flows from the FS with lower concentration towards the highly concentrated fertiliser DS. After FO process, the fertiliser DS becomes diluted, with the extent of dilution. If diluted fertiliser solution meets the water quality standards for irrigation in terms of salinity and fertiliser (nutrient) concentration, it can be used directly for fertigation. If the final fertiliser concentration exceeds the nutrient limit, further dilution may be necessary before it can be applied for fertigation.

The energy required for FDFO for direct fertigation was estimated to be less than 0.24 kW/m3 of fertigation water which is not only comparatively lower than the most efficient current desalination technologies but is also lower than the theoretical energy required for desalting saline water based on the law of thermodynamics (phuntsho, 2012). FDFO is a low energy process; this technology can easily be powered by renewable energy, such as solar and wind energy, which exists in many arid and semi-arid countries. Since fertilisers are extensively used for agricultural production, FDFO desalination does not create additional environmental issues related to fertiliser usage. In fact, FDFO desalination adds more value to irrigation water, thereby providing greater opportunity for improving the efficiencies of water and fertiliser use. Also FDFO desalination can be operated at very high feed recovery rates without significant extra energy use. Depending on the types of fertilisers used as DS and the feed TDS, the recovery rate would theoretically vary; nevertheless, most fertilisers achieved recovery rates higher than 80% with seawater (Phuntsho et al., 2011).

2.8.2 Prospects of FDFO desalination process

The FDFO desalination process is appropriate for areas with groundwater (GW) that cannot be used directly for irrigation due to high salinity which promotes the sustainable use of brackish groundwater (BGW). The use of GW will reduce the pressure on the river water and make more water available for environmental flows in the river system. Although, direct irrigation using groundwater is impractical due to the high salinity content, the salinity in some area 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), so BGW has to be desalted first, to make it fit for irrigation. Current desalination technologies are energy intensive, thus low energy FDFO desalination could play a key role in BGW for irrigation. Thus, 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. Moreover, this technology is more 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. FDFO desalination process offer multiple advantages, including: making water available for irrigation; the sustainable use of groundwater; and reducing dependence on river water for irrigation while still serving the original purpose of salt interception. FDFO desalination process is more applicable for the areas where saline water such as SW and BGW is plentiful and where the existing fresh water source is inadequate for irrigation.

2.8.3 Fouling potential in the FDFO process

Freshwater sources are becoming scarcer every year in many part of the world, low energy desalination processes such as FDFO desalination technology could play a significant role in increasing water for irrigation. Besides making suitable water for irrigation from saline water sources at lower energy, 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.

Membrane fouling is a main obstacle to the efficient application of membrane technology in applications involving seawater desalination, wastewater reuse, and water treatment. One potential advantage of using FDFO is that it operates with no hydraulic pressure that may result in a lower membrane fouling propensity in compare of pressure-driven membrane processes due to lesser cake layer compaction.

Understanding the fouling behavior in the FDFO desalination process is particularly important as both sides of the membrane are in constant contact with impaired waters: the support layer with fertiliser solution and the active layer with BGW. As a consequence, there is a critical need for a systematic understanding of membrane scaling and fouling behavior and for the development of strategies for fouling mitigation.

CHAPTER 3

University of Technology Sydney

Faculty of Engineering & Information Technology

MATERIALS AND METHODS

3.1 Introduction

A series of experiments have been carried out to attain the objectives outlined in Chapter 1. This chapter describes the experimental procedures adopted in this study to evaluate various factors responsible for causing membrane fouling and membrane scaling.

3.2 Feed solutions for the FDFO process

A model brackish groundwater (BGW) was used in this study that simulates the actual BGW found at the Borronga salt interception scheme under the Murray-Darling Basin (Phuntsho et al., 2011b). The detailed composition of the simulated BGW is shown in Table 3.1. Since salinity varies throughout the year, it was appropriate to simulate the BGW of different Total Dissolved Solids (TDS). Accordingly, this study used three different types of simulated BGW as the FS with its TDS varying from 7.824 to 27,382 mg/L (Table 3.2). The TDS of the originally proposed BGW were 10,000, 20,000 and 35,000 mg/L for BGW 10, BGW 20 and BGW 35 respectively, but their actual concentrations after subtracting the mass of the water from the hydrated mass were lower. All the chemicals used for the preparation of the FS were of technical grade and obtained from Sigma-Aldrich Australia. The FS was prepared by dissolving the salts in DI water with the help of a magnetic stirrer at 200-300 rpm for 30 minutes to ensure that all salts were fully dissolved and uniformly mixed before starting the experiments. Also, during the experiment, the FS was continuously stirred to avoid precipitation (Phuntsho et al., 2011b).

Table 3.1: 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 the OLI Stream Analyser 3.2 (OLI Systems Inc., Morris Plains, NJ, US).

Compounds	BGW 10 (g/L)	BGW 20 (g/L)	BGW 35 (g/L)
NaCl	3.713	7.426	13.0
Na_2SO_4	1.794	3.588	6.280
KCl	0.134	0.268	0.470
$CaCl_2.2H_2O$	0.317	0.634	1.110
$MgCl_2.6H_2O$	3.947	7.895	13.820
$NaHCO_3$	0.094	0.189	0.330
Total TDS (g/L)	7.824	15.647	27.382
π (atm)	5.35	10.56	18.56
pH	7.72	7.93	7.33

Table 3.2: Type of FS used for FDFO studies. Osmotic pressure of the FS was determined by the OLI Stream Analyser

Type of FS	Osmotic pressure (atm)	Total dissolved solids (TDS)	Measured pH
BGW 10	5.35	7.824 g/L	7.68
BGW 20	10.56	15.647 g/L	7.79
BGW 35	18.56	27.382 g/L	7.98

3.3 Draw solutions for the forward osmosis experiments

The choice of fertiliser DS for FDFO desalination for fertigation will be reached by taking into account many factors, including fertiliser economics and the performance of a particular fertiliser as DS 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 DS in the FO process, such as solubility, pH compatibility with the FO membrane used, the types of species formed in the solution, and the water extraction capacity, which depends on the molecular weight and osmotic pressure of the fertiliser DS. The final selection will also reached by taking into account the nutrient requirements for the particular target crop (Moody and Kessler, 1976). The existing commercial CTA FO membrane has a limited pH range of between 4.0 and 8.0, while the thin-film composite membrane has been reported to have a significantly higher pH range (Yip et al., 2010; Wang et al., 2012) and hence the fertiliser's DS must provide a suitable pH environment so as not to undermine the chemical stability of the CTA membrane.

However, only those fertilisers commonly used in Australia were considered for assessment as DS for the FDFO desalination process. All these fertilisers had been already studied for FDFO process for desalination of brackish water and brackish groundwater (Phuntsho et al., 2011b, Phuntsho, 2012). 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 $NH_4H_2PO_4$, diammonium phosphate (DAP) or $(NH_4)_2HPO_4$ and others.

Six different types of fertiliser that are commonly used for agriculture were selected as the DS and are listed in Table 3.3. All the FO experiments were conducted using technical grade fertilisers such as the DS. The DS 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 30 minutes at room temperature before the start of the experiments.

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

Name of fertiliser	Chemical formula	MW (g/mol)	Osmotic pressure (atm) 1M	Purity (%)
Potassium chloride (KCl)	KCl	74.6	43.964	99.0
Mono-ammonium phosphate (MAP)	$NH_4H_2PO_4$	115	43.822	98.0
Di-ammonium hydrogen phosphate (DAP)	$(NH_4)_2HPO_4$	132.1	50.563	98.5
Potassium nitrate (KNO3)	KNO_3	101.1	37.191	99.0
Ammonium sulphate (SOA)	$(NH_4)_2 SO_4$	132.1	46.139	99.0
Calcium Nitrate Tetra hydrate (CAN)	$Ca(NO_3)_2.4H_2O$	236.1	48.788	98.5

3.4 Organic foulants

Bovine serum albumin (BSA), sodium alginate, and humic acid (HA) were used as model organic foulants. Stock solutions for BSA and alginate (10 g/L) were prepared by dissolving the foulant in deionized (DI) water. Mixing of the stock solution was performed for over 24 hours to ensure complete dissolution of the foulant. The stock solution was stored in sterilized glass bottles at 4 °C without further purification.

For preparing the solution of humic acid, 10 g of humic acid was added to 1 litre of DI water. Subsequently, aliquots of a NaOH solution were added to the solution of humic acid until a pH 9 was reached. After shaking the solution for 24 hours, the pH was reduced by adding HNO_3 to pH 3, and the solution was continuously stirred. The pH of the solution was adjusted to 7 with the addition of the NaOH solution.

Groundwater usually has a very low or negligible organic concentration. Despite this, its composition has been included in this study to evaluate its implications in membrane scaling and fouling.

3.5 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 and these were marked as cartridge membrane. According to the manufacturer, the cartridge membrane is made up of cellulose triacetate (CTA) with an 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).

The second FO membrane used was a polyamide (PA) based thin film composite flat sheet membrane recently synthesised by Woongjin Chemicals Co. (Korea). This membrane was a hand-casted and non-optimised membrane and was therefore only used for comparative study. All the other FO experiments in this study were conducted using the CTA FO membrane unless otherwise stated. The detailed chemistry of the PA membrane and CTA membrane appears in Tables 3.4.

Table 3.4: Physical and chemical properties of membranes as provided by the manufacturer for TFC FO membranes and from various literature relating to the CTA membrane (Gu et al., 2013).

Membrane	Pure water permeability A 10-12 m/s Pa	Salt permeability B $(10^{-7}$ m/s$)$	NaCl Rejection R (%)	Contact angle (°)	Zeta potential at pH6 (mV)	RMS surface roughness[d] (nm)
CTA	2.8 ± 0.1 [a]	17.5 ± 0.5 [a]	89.5[a]	77 ± 1 [b]	-2.1 ± 03 [b]	30 ± 6
PA	5.0 ± 0.7 [c]	9.4 ± 1.9 [c]	93.4[c]	45 ± 4 [c]	-10 ± 5	105 ± 11

a A, B values, NaCl rejection of CTA membrane are obtained from (She et al., 2012b).

b Contact angle and zeta potential of CTA membrane are obtained from (Jin et al., 2012).

c Characterization of TFC membrane are obtained from (Wei et al., 2011a).

d Measured for active layer of both membranes.

Extensive efforts have been made to develop high performance FO membranes with high water flux and low salt passage by modifying the structural properties of the membrane, particularly the support layer, to reduce the ICP effects. Many research groups have focused on the thin-film composite polyamide (PA) membrane. Recently, we have received a new modified PA membrane from a different research group with a very thin support layer and this membrane has been designated as PA-2 in this study. The new TFC PA membrane (PA-2) has been compared to the CTA membrane and PA membrane. The properties of the PA-2 membrane are presented in the table 3.5.

Table 3.5: Physical and chemical properties of the PA-2 membranes

Membrane	Active layer material	Contact angle (°)		Zeta potential at pH 6 (mV) Active layer	Operating pH	Membrane thickness (mm)
		Active layer	Support layer			
PA-2	Polyamide	15	15	69	2–12	83 ± 3

Membrane	NaCl Rejection R (%)	Pure water permeability A		Salt permeability B (10^{-7} m/s)	B/A (10^{2} kPa)
		$\text{l m}^{-1}\text{ h}^{-1}\text{ bar}^{-1}$	10^{-12} m/s Pa		
PA-2	69 ± 5	15 ± 1.12	43	29	0.7

3.6 Bench scale cross-flow forward osmosis experimental set-up

All the experimental investigations for the FO process in this study were performed using a bench-scale cross-flow FO membrane unit, the schematic of which is shown in Figure 3.1. 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 x 10^{-3} m^2 (Figure 3.2). Two channels are provided on both sides of the membrane to allow FS to flow on one side of the membrane and DS on the side of the membrane.

Unless otherwise stated, all the FO performance experiments in this study were carried out at a cross-flow rate of 400 ml/min in which gives a turbulent flow with a cross-flow velocity of 8.5 cm/s. The co-current flow was also introduced into the two channels. The temperature of all solutions was maintained at 25±1°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 continuously recorded by connecting the DS to a digital mass scale connected to a computer for online data logging at three-minute intervals. The water flux Jw (in $Lm^{-2}h^{-1}$) was calculated using the following relationship:

$$Jw = \frac{\text{Change in DS volume (L)}}{\text{Time (h) x membrane area (m2)}} \qquad (3.1)$$

The initial volume of both the DS and FS was 2.0 L each. The solutions, after passing through the membrane, were returned or recycled back 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 over time. However, the water flux (*Jw*) was selected from the point at which a stable flux was observed from the plot of flux (*Jw*) versus time, which usually happened within the first 30 minutes of operation (Phuntsho, 2012). Each experiment was carried out for duration of at least 20 hours in order to obtain an adequate observation of the trend in the flux decline.

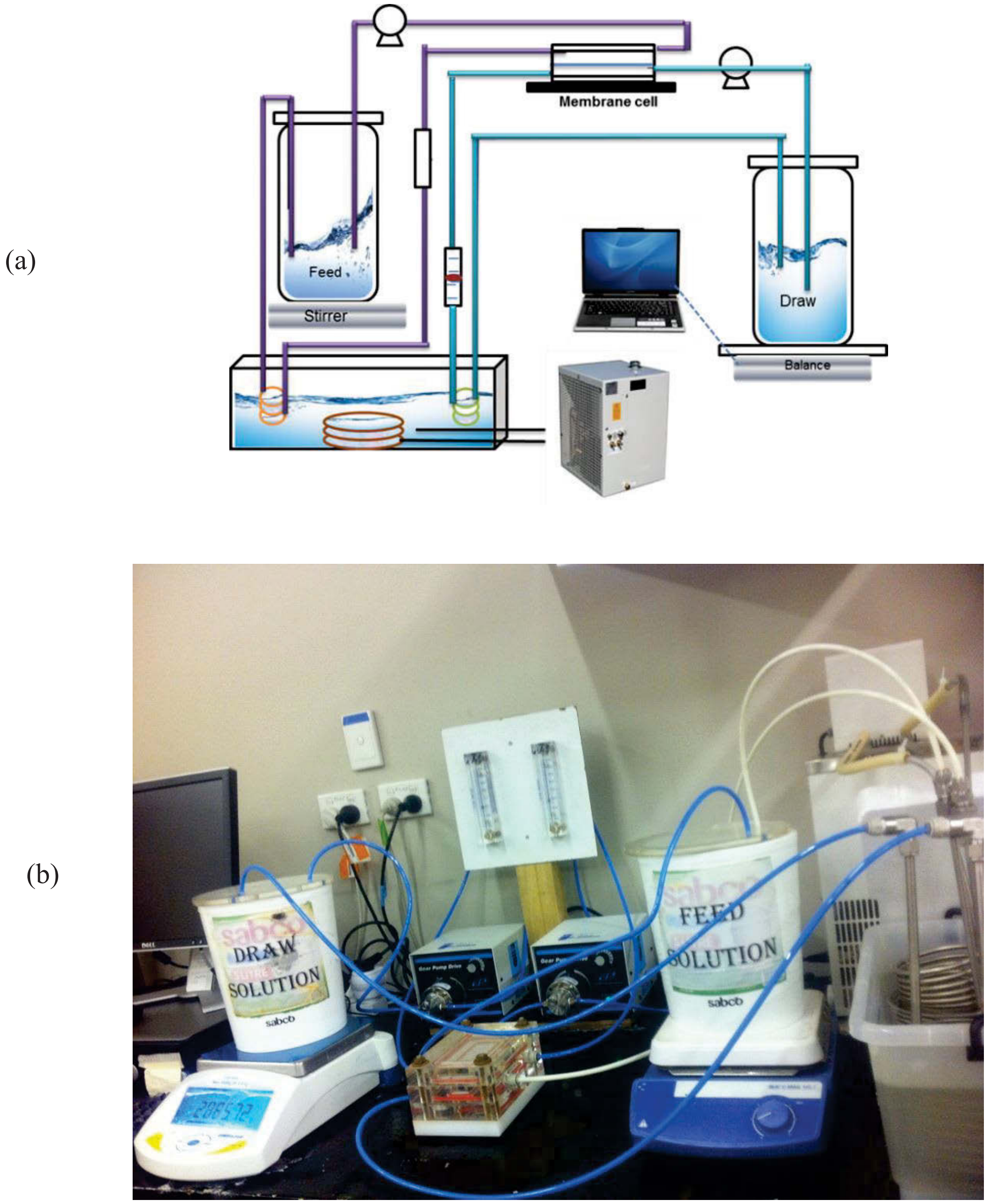
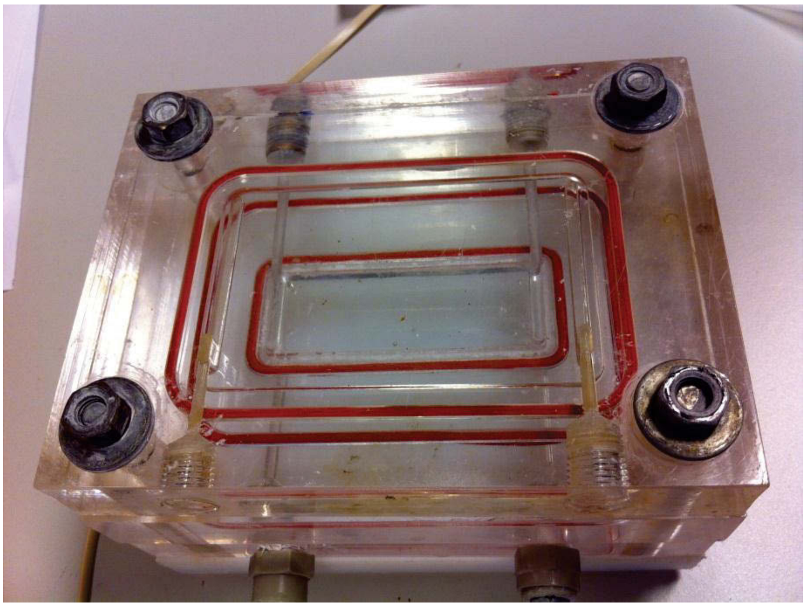


Figure 3.1: Bench-scale cross-flow forward osmosis experimental setup (a) Schematic of the bench-scale cross-flow FO membrane unit and (b) the bench-scale FO unit used for all FO experiments

a)



b)

Figure 3.2: a) Close up of FO membrane cell, b) Inside the FO membrane cell

3.7 Protocols of fouling and cleaning experiments

The procedure to conduct FO membrane fouling and cleaning experiments is described as follows (Figure 3.3). First, a fresh new FO membrane was placed in the membrane cell in FO mode with an active layer facing feed FS (AL-FS). Then, the whole membrane system was stabilized with DI water on both sides of the membrane at 25 ± 1°C for 30 min. The baseline experiment was performed for 4 hours to obtain the initial membrane flux. The fouling experiment started with 2 L of BGW FS and 2 L of fertiliser solution as DS. It continuously ran at the same temperature for about 20 hours at a cross flow rate 400 ml/min in or 8.5 cm/s. The permeate water was collected in the DS tank. The corresponding changes in the weight of DS were monitored, recorded, and later converted to changes in membrane flux. After the fouling experiment, membrane cleaning was immediately performed using DI water at the same temperature at a cross flow rate of 400 ml/min in. After membrane cleaning, the baseline experiment was conducted again to determine the membrane flux recovery ratio.

Figure 3.3: Experimental protocol

3.8 Membrane fouling identification methods

3.8.1 Scanning electron microscopy (SEM)

The qualitative analysis of the membrane fouling was performed using scanning electron microscopy (SEM). SEM is useful for judging the membrane surface structure and identifying scale and biological fouling. It can also be used for the morphological identification of scaling material present. SEM was employed as an additional tool for high resolution imaging of the fouling intergrowth at the membrane surface. For SEM imaging, a membrane is normally required to be completely dry and a scale layer of the membrane needs to brush off. All samples must also be an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. The fouled membrane is cut to a size of approximately 5 mm * 5 mm area using a diamond-wafering saw. The small membrane is then placed on to an aluminium SEM stub with carbon tape and the fouled surface of the membrane is pointed upward.

The SEM equipment that was used in this study was FEI Quanta 200 ESEM with Gatan CF302 continuous flow liquid helium cold stage. The FEI Quanta 200 Environmental Scanning Electron Microscope (ESEM) is a thermal tungsten gun instrument capable of imaging under three vacuum regimes, High-vacuum (< 6e-4 Pa), Low-vacuum (10 - 130 Pa) and ESEM-vacuum (10 - 2600 Pa). It is capable of SE imaging at the following resolutions for the given settings:

- High-vacuum: 3.0 nm at 30 kV or 10 nm at 3 kV
- Low-vacuum: 3.0 nm at 30 kV or < 12 nm at 3 kV

- ESEM-vacuum: 3.0 nm at 30kV

The Quanta is equipped with a Gatan MONOCL3 system for acquiring cathodoluminescence spectra and images. It has a Czerny Turner monochromator with a Peltier cooled Hamamatsu R943-02 PMT UV-Vis detector and a liquid nitrogen cooled Hamamatsu R-5509-72 PMT IR detector. A Gatan C1002 liquid nitrogen cold stage is available for cooling samples to 80 K while a Gatan CF302 continuous flow liquid helium cold stage is available for cooling to 5 K. A Melles Griot HeCd 100 mW dual wavelength laser is available for simultaneous PL studies with excitation at 325 and 442 nm.

3.8.2 Energy dispersive spectroscopy (EDS)

In this study an Oxford EDS system, capable of elemental characterisation as an HKL Electron Backscatter Diffraction (EBSD) system for crystal orientation, is used for analysis and mapping. Elemental composition of fouled membrane specimens is quantified by energy dispersive spectroscopy (EDS).

EDS is an analytical technique used for the elemental analysis or chemical characterization of a sample. It uses the x-rays emitted by the sample as it is exposed to the electron beam in the SEM to get the elemental information of the material being analysed. It relies on the investigation of an interaction between some sources of X-ray excitation and a sample. Its characterization capabilities are due, in large part, to the fundamental principle that each element has a unique atomic structure allowing for a unique set of peaks on its X-ray spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. This is so the major constituents of the inorganic foulants will appear in the EDS spectra, the extent of which will depend on the density of the sample.

3.8.3 X-ray diffraction (XRD)

X-Ray Diffraction (XRD) is a characterisation technique used for examining the fine structure of matter. It is used in the determination of crystal structure, qualitative phase identification, quantitative phase analysis, particle size and strain measurements, and the study of preferred orientation in crystals. The XRD equipment that was used in this study was a Siemens D5000 diffractometer that facilitates the automatic measurement of up to 40 samples. This is particularly suitable for routine analysis of a large number of samples. All the scale layer of the collected membrane surface was recorded overnight. This was due to agglomeration and the irregular particle shapes that were produced by grinding the XRD patterns. A grazing incidence attachment is available on this diffractometer which allows the measurements of thin films, surfaces and multilayers. Data analysis capabilities for the XRD include the use of the ICDD-JCPDS CD-ROM database consisting of more than 120,000 patterns for qualitative phase identification, as well as the SIROQUANT software package (Rietveld refinement method) for crystal structure determination and quantitative phase analysis.

CHAPTER 4

University of Technology Sydney

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WATER FLUX BEHAVIOR AND MEMBRANE FOULING DURING FERTILISER DRAWN FORWARD OSMOSIS PROCESS

4.1 Introduction

Forward osmosis (FO) process experiences membrane scaling and fouling however, the absence of hydraulic pressure in the FO operation has been found advantageous in terms of the fouling rate and cleaning efficiency. In fact, several studies have demonstrated that inorganic scaling and organic fouling are almost fully reversible by adopting simple physical cleaning measures without the need for chemical cleaning reagents (Mi and Elimelech, 2010b, Mi and Elimelech, 2010a, Lee et al., 2010). In some cases, the FO process is observed to have low fouling potential or a slower fouling rate than the the RO process (Achilli et al., 2009, Cornelissen et al., 2008, Holloway et al., 2007, Zhang et al., 2012). Fouling in the FO process is influenced by the feed water quality like that of the RO process. In addition, scaling and fouling in the FO process could be influenced by additional factors that are not present in the RO process.

To date, membrane fouling and water flux behavior during the fertiliser drawn forward osmosis (FDFO) desalination process has not been studied. FO has the potential to achieve higher feed recovery rate when high fertiliser DS concentrations are used and hence scaling may become a significant issue both due to supersaturation and reverse diffusion of fertiliser salts. The objective of this study is to investigate the flux decline due to inorganic scaling of membranes during the desalination of BGW by the FDFO process. Factors affecting membrane fouling during the FDFO process have been evaluated. These include: feed properties, DS properties and membrane properties. The study includes an investigation into the effects of physical or hydraulic cleaning. It also examines how effective physical or hydraulic cleaning is in relation to membrane flux recovery.

4.2 Methodology

Six different fertilisers were selected as DS. They include: potassium chloride (KCl), monoammonium phosphate (MAP), diammonium phosphate (DAP), potassium nitrate (KNO_3), ammonium sulphate (SOA) and calcium nitrate ($Ca(NO_3)_2.2H_2O$).

The feed solution consisted of a synthetic brackish groundwater (BGW) with different total dissolved solids (TDS). These were prepared and designated as BGW 10, BGW 20 and BGW 35. They contained TDS of 7.824, 15.647 and 27.382 g/L respectively. Full details of the BGW can be found in Chapter 3.

A commercial flat sheet cellulose triacetate (CTA) FO membrane (Hydration Technology Innovations or HTI, Albany, USA) was used, however, a thin film composite polyamide (PA) membrane was tested to observe the influence of the different membrane materials on water flux decline and membrane fouling in the FDFO process.

Before starting the experiments, a fresh new FO membrane was used and the whole membrane system was stabilised for 20 mins with DI water on both sides of the membrane. The initial baseline flux of the virgin membrane was then obtained using 1.0 M NaCl as DS and DI as FS. All the FO experiments were conducted in the batch mode of operation in which the initial volumes of both DS and FS were fixed at 2.0 L each. As the volume of DS increased, its concentration was decreased over time.

Correspondingly, the volume of the FS decreased over time thereby becoming more concentrated.

After the FDFO experiment, the membrane cleaning regime was performed to evaluate the flux recovery after the FO membrane was subjected to inorganic scaling. The DS and FS tanks were replaced with the DI water and the membrane was subjected to a similar operation as the FO process (cross-flow of 8.5 cm/s) for 20 mins. Following this physical cleaning, the second baseline flux for flux recovery was obtained using 1.0 M NaCl as DS and DI as FS. The percentage ratio of the recovery baseline flux to initial virgin baseline flux (normalised) was assessed as a flux recovery rate.

4.3 Influence of draw solution properties on inorganic scaling

The influences of the DS properties were investigated in terms of water flux behavior and membrane scaling of the FO desalination process using the CTA FO membrane. The DS properties mainly included different types of DS and the influence of DS concentration on the FO performance.

4.3.1 Influence of the types of draw solution on the water flux decline

Fertilisers are made up of compounds that contain major essential elements for the plants such N, P, K, Ca, Mg and S. However, when such compounds are used as DS during the FO process (especially for the desalination of BGW containing several scaling precursor ions) they can adversely affect the membrane process. Ca^{2+}, Mg^{2+} and PO_4^{3+}/HPO_4^{2-} ions are all scaling precursors that accelerate membrane scaling and fouling thereby undermining the efficiency of the RO desalination plants (Lee and Elimelech, 2006, Hatziantoniou and Howell, 2002, Li and Elimelech, 2004). These ions can interact with the feed ions and promote membrane scaling and membrane fouling which results in flux decline and a diminution of process efficiency.

The osmotic pressure of each DS is shown in Table 4.1. Diammonium phosphate (DAP) with 50.56 atm has the highest osmotic pressure amongst all selected fertilisers at 1.0 M concentration. The water fluxes as a function of operation time for the six fertilisers (as DS tested at 1 M concentration) are presented in Figure 4.1, using BGW 10 as FS. Most fertilisers showed a gradual decrease in the water flux with time except for DAP. This gradual decrease in the water flux is because of the decrease in the driving force (osmotic pressure difference) over time. Since the FO process is operated under batch mode, in which both the DS and FS are recirculated, the DS becomes diluted and the FS tank becomes concentrated over time. However, a rapid decline in water flux observed for DAP as DS is quite in contrast to the other DS used. In fact, after about 4 hours of operation, the water flux rapidly declines almost reaching zero. These results indicate that, long-term observation of the performances of the fertiliser DS is important as some of the DS could promote membrane scaling and fouling of the membrane. Such significant flux decline was not observed during the short-term experiments in the laboratory experiments using BGW in earlier studies (Phuntsho et al., 2013).

The ranking of the six DS in terms of water flux at equal DS concentration (1 M) was CAN>KCl>SOA>KNO_3>MAP>DAP (Figure 4.1). This ranking is consistent with earlier studies (Phuntsho et al., 2011b, Phuntsho, 2012).

Table 4.1: DS bulk osmotic pressures (π) were calculated using OLI stream analyser.

Name of fertiliser	**Osmotic pressure (atm) 1M**
Potassium chloride (KCl)	43.964
Mono-ammonium phosphate (MAP)	43.822
Di-ammonium hydrogen phosphate (DAP)	50.563
Potassium nitrate (KNO_3)	37.191
Ammonium sulphate (SOA)	46.139
Calcium Nitrate Tetra hydrate (CAN)	48.788

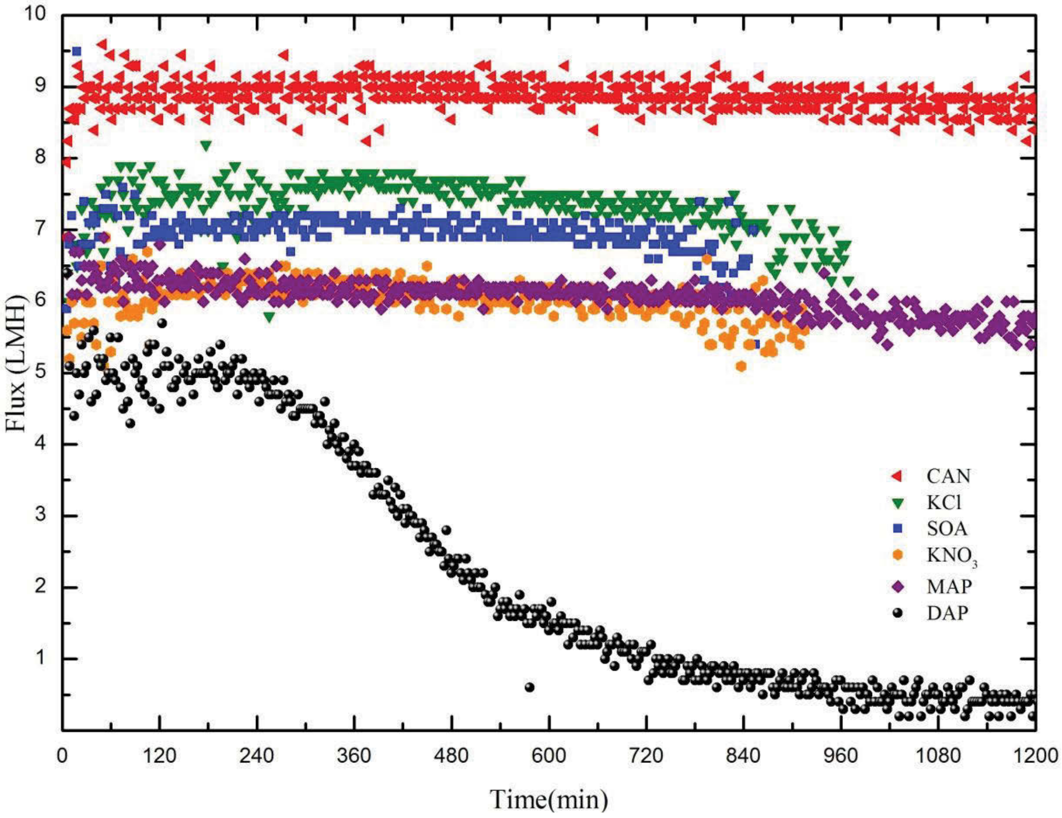


Figure 4.1: Variation of water flux over time for the six different fertiliser solutions during the FDFO process for the desalination of BGW, (Experimental conditions, DS: 1M of each fertiliser, FS: 10 g/L BGW, cross-flow velocity: 400 ml/min and temperature 25±1°C, CTA membrane)

It should be remembered that the choice of fertiliser as DS will play a very important role in a low energy demanding FDFO process where the diluted DS can be directly used for irrigation.

4.3.2 Influence of the draw solution concentration on the water flux decline

In the FDFO process water transfer from BGW as FS to fertiliser solution as DS by natural net osmotic pressure will occur as long as the osmotic pressure of the fertiliser solution remains higher than the BGW. As a consequence, the fertiliser solution with the higher concentration can extract more water. Increasing the DS concentration doesn't lead to a proportionate increase in the water flux and the increase is non-linear as reported in other studies (Xu et al., 2010). The net osmotic pressure increases by increasing the DS concentration thereby generating a higher water flux. The increased incoming water flux however causes enhanced dilutive internal concentration polarization (ICP) within the membrane support layer. This, in turn, means that the overall gain in water flux is lower. At higher DS concentrations, the water flux itself acts as a limiting factor and reduces the performance of the DS. This indicates that no matter how high the osmotic pressure is that a DS can generate, it will still not be able to produce a proportionate water flux by the FO process (Phuntsho, 2012).

Operating the desalination plant at a higher water flux is preferable because, this will require less membrane area for the particular capacity that relates to cost saving. During desalination by a fixed membrane area, operating the membrane at higher flux will reduce the operational time required for the desalination of a fixed volume of water. Beyond this, using a very high DS concentration has other negative impacts on the design and operation of the desalination plant (Phuntsho et al.).

The first impact of using a high concentration of DS is the increase in the pumping cost because of the increased specific weight and viscosity of the DS during desalination. The performance of the pump is influenced by the characteristics of the solution e.g. specific weight or density, particulate content, viscosity, and vapour pressure (Hydraulic Institute, 2006). The following equation shows the energy rating of the pump:

$P = Q \rho g H$ (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 ($9.81 \ m/s^2$) and H is the pressure head (m). A solution with higher viscosity consumes more energy during the pumping process because of its increased shear thereby requiring additional power to overcome this drag on the the pump's efficiency (Hydraulic Institute, 2006).

With the increase in DS concentration, the specific weight of the DS increases, thereby enhancing the energy requirements for the pumps. Similarly, the viscosity of the DS increases at higher DS concentrations which also increases the energy required for pumping the DS. The other impact of using high concentrated DS is the recovery at which the desalination plant can be operated. As the FO process operates under batch mode if a very high initial DS concentration is used, the feed recovery rates will be proportionately higher. Although, at very high recovery rates, the potential for scaling on the FS will also increase because, it has been substantiated 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 adverse effects on the water flux although this scaling is mainly expected to occur on the membrane surface. Therefore, the initial DS concentration must be selected so that it does not promote scaling of the membrane that could have a corresponding negative impact on the overall performance of the FO desalination plant. The scaling may also be influenced by the type of ions present in the feed and their concentration.

The other potential implications of using high concentration DS are the negative impacts on the some part of desalination plant such as the pumps and pipes that could affect the life of the desalination plant (Phuntsho, 2012).

What is the best DS concentration to begin with for the FO desalination? To find the answer to this, different concentrations of DS in the FDFO process were investigated.

Five different concentrations (1 M, 1.5 M, 2 M, 2.5 M and 3 M) of each selected fertiliser were adopted to obtain the influence of the DS concentration on the water flux behavior. At room temperature, the solubility of monoammonium phosphate (MAP) and potassium chloride (KCl) is usually about 2 M so 1 M, 1.25 M, 1.5 M, 1.75 M and 2 M were used for experimental works.

It can be seen in Figure 4.2 that the water fluxes were obviously different even under the same DS concentrations. These differences in terms of flux behaviors were even more significant at higher osmotic pressures. These flux differences indicate that the degrees of the dilutive ICP using six types of DS are significantly different. More specifically, the dilutive ICP using MAP as the DS was more serious than that which used ammonium sulphate (SOA) as DS. These differences in the degree of dilutive ICP may be reasonably explained by the diffusivity and viscosity of the DS (Hancock and Cath, 2009). Also, experimental results in Figure 4.2 demonstrate that the FO flux is non-linear with respect to the apparent driving force (the concentration difference between the DS and the FS) as a result of concentration polarization (CP). Further, 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, 2012).

Moreover, if scaling compounds are present in the FS, the increased feed recovery rate at higher DS concentration will build up scaling and therefore lead to a reduction in the water fluxes. The 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 will accelerate scaling. When this initial critical DS concentration is used, the membrane area must also be sufficient so that the DS becomes diluted up to the point of osmotic equilibrium with the feed water. In such a way, the DS does not require further pumping for more dilution (Phuntsho, 2012).

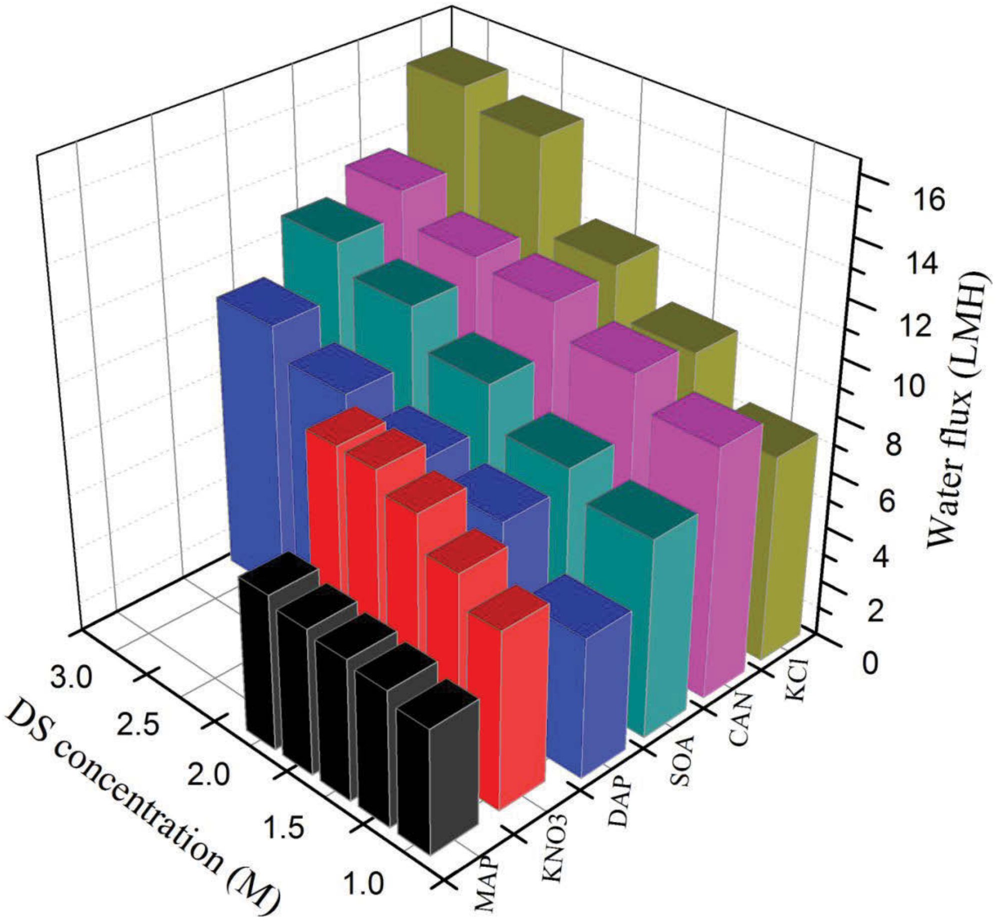


Figure 4.2: Effect of DS concentration in the water flux, (Experimental condition; FS: 10 g/l BGW, cross-flow velocity: 400 ml/min in; and temperature 25±1˚C, CTA membrane)

Consequently, higher water flux can be generated using higher DS concentrations. The other implication of using higher DS concentration, could be the higher loss of draw solutes due to the reverse diffusion and complications on the FS (Xiao et al., 2011; Ge et al., 2012).

The increase in monoammonium phosphate (MAP) concentration increases the water flux proportionately without any sudden or sharp flux decline, as shown in Figure 4.3, unlike DAP. Similar observations were made with the other fertilisers as DS and hence only MAP has been presented as a representative experimental result (Figure 4.3). The influence of ICP during experiments using different concentrations of MAP as DS causes a small difference between the water fluxes results.

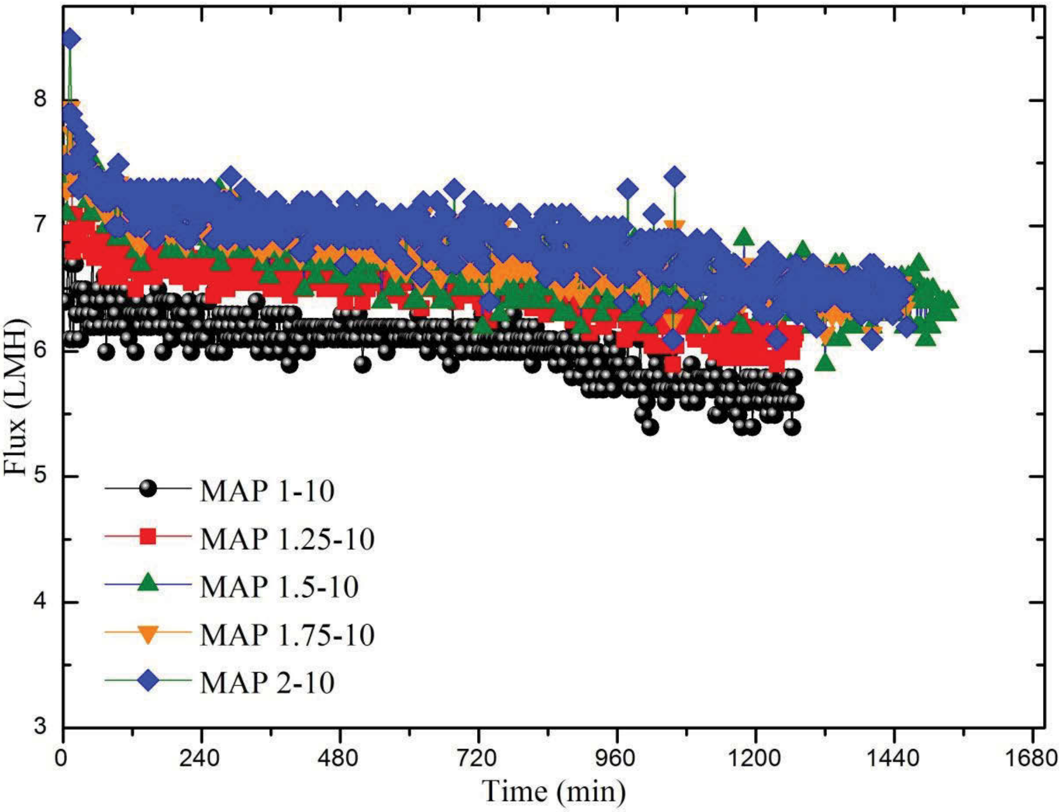


Figure 4.3: Variation of FO water flux with time during the FO process at different concentrations of MAP. (Experimental conditions; DS: DAP (1 M, 1.25 M, 1.5 M, 1.75 M, 2 M) FS: BGW 10 g/L, water cross-flow velocity: 400 ml/min, CTA membrane and a temperature of 25±1°C)

Figure 4.4 illustrates average water fluxes for 3 M concentration of each fertiliser as DS and 10 g/l BGW as FS. Interestingly, 3 M KCl as DS produced the highest water flux amongst the other fertilisers. While osmotic pressure of KCl is 200 atm less than MAP for 3 M concentration.

The above results indicate that the selection of suitable DS concentration is important for several reasons. Draw solutes that produce higher water flux at lower concentrations are desirable as these can contribute to significant cost savings in terms of both capital and operation costs. The other important reason is when higher DS concentrations are used, the reverse draw solute flux increases as it is a direct function of the concentration gradient (ΔC) (Boo et al., 2012, Hancock and Cath, 2009, She et al., 2012a, Phillip et al., 2010). Hence,it increases the rate of scale formation at the membrane surface thereby resulting in a stronger flux decline.

Further increasing the DS concentration was even less effective in increasing the water flux appropriately. Such reduced effectiveness of DS concentration has been reported previously by several research groups and has been attributed to ICP, i.e., the accumulation (or dilution) of solutes in the porous support layer of the FO membrane (Loeb, 2002, Tang et al., 2010, McCutcheon and Elimelech, 2006, Gray et al., 2006)

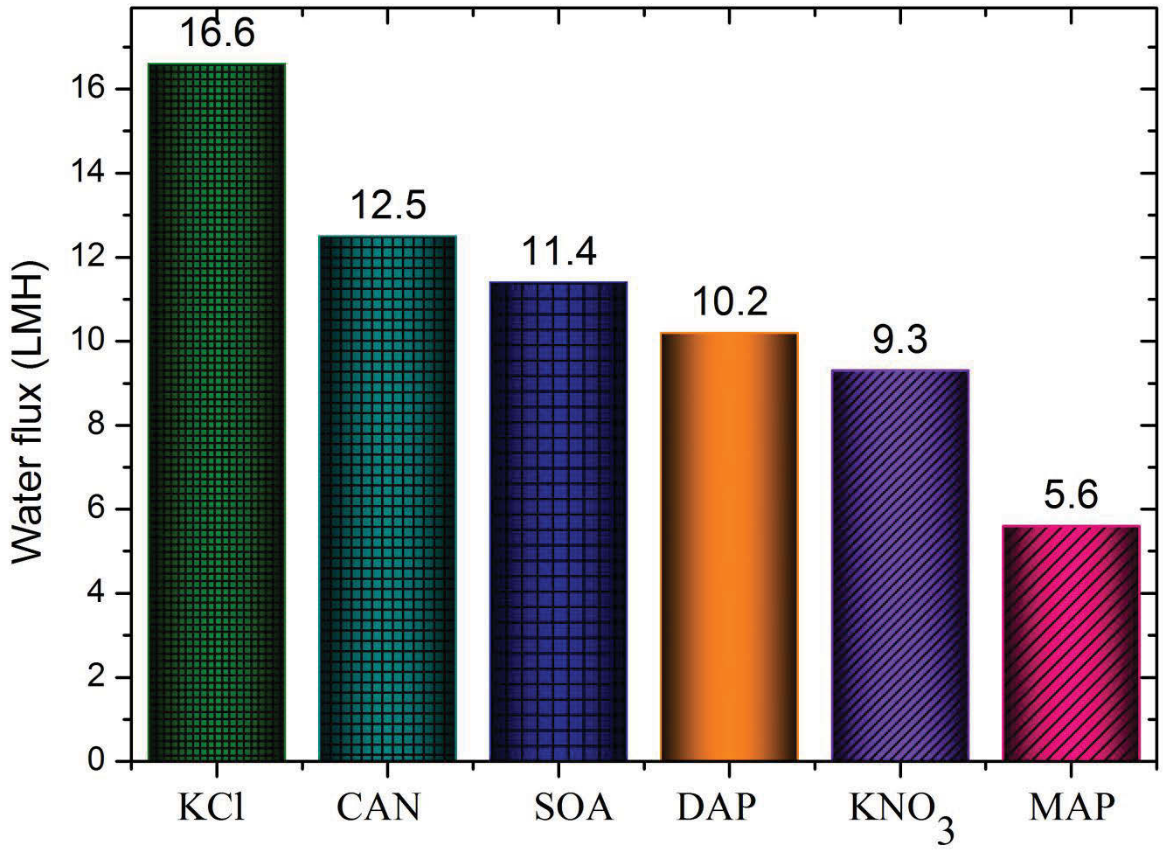


Figure 4.4: Average water flux for different fertilisers in 3 M concentration, (Experimental conditions; FS: 10g/l BGW, cross-flow velocity: 400 ml/min, temperature 25±1°C and CTA membrane)

4.4 Influence of feed solution; TDS, type, concentration on the water flux decline

Feed solution (FS) properties play a strong 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 can directly affect the performance of the FO process. According to film theory, the water flux model that predicts flux decline according to mass transfer effects, flux decreases exponentially with increasing concentration of the feed concentration (Cheryan, 1998). In general, increasing the concentration of a FS increases the level of reversible foulant. This amounts to an increase in observed cake layer formation and a decline in flux (Marshall et al., 1993).

In this particular study, only the influence of feed TDS has been considered. Three types of FS conditions were used that simulate brackish ground water (BGW 10, BGW 20 and BGW 35 corresponding to TDS of 10, 20 and 35 g/L respectively) as FS and 3 M of each fertiliser as DS. The average water fluxes of six different fertilisers as DS in terms of FS concentration have been presented in Figure.4.5. This shows that the water flux decreased with the increase in feed TDS and this is expected because of the decrease in the net osmotic pressure. The DS concentration was kept constant while the FS osmotic pressure increased at a higher TDS concentration, thereby reducing the net driving force. (McCutcheon et al., 2006).

DAP shows a significant difference in average water flux for different FS TDS. When a BGW with higher TDS is used, the reverse diffusion of DAP from the DS has more access to the scaling ions such as Ca and Mg resulting in rapid scaling and thicker cake layer formation responsible for rapid flux decline. Further discussion about DAP can be found in Chapter 5.

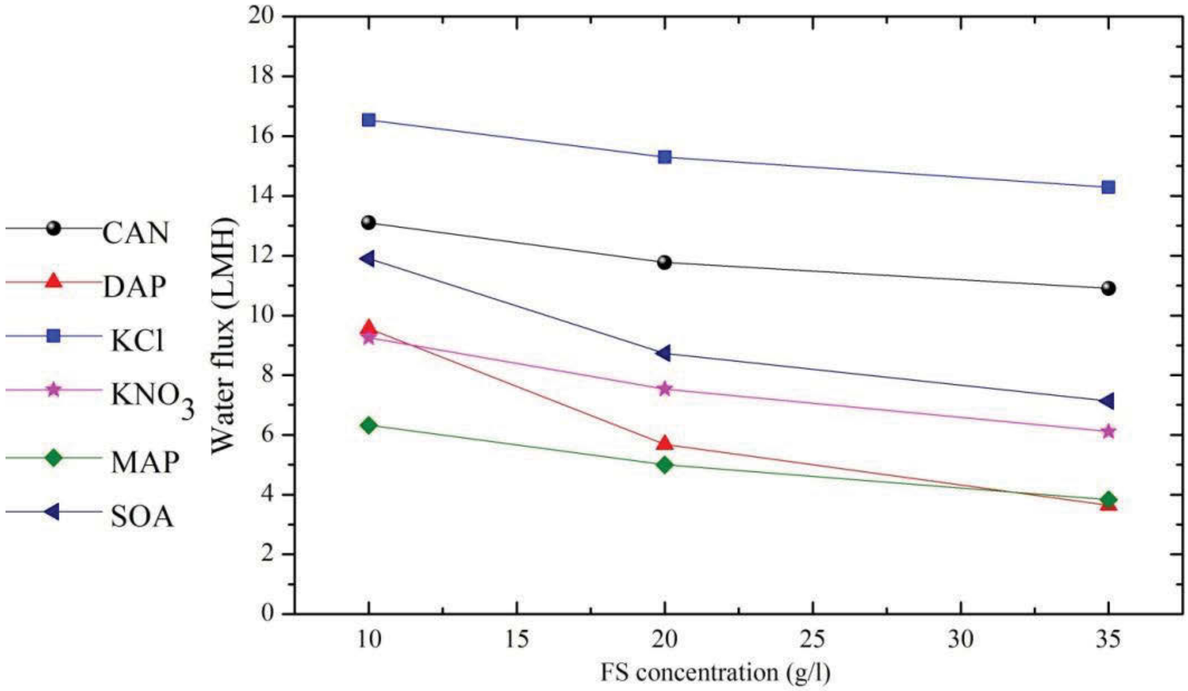


Figure 4.5: Effect of FS concentration in water flux decline, (Experimental conditions, DS: 3M of each fertiliser, FS: BGW 10, BGW 20 and BGW 35, temperature: 25 ± 1°C and cross-flow rates : 400 ml/min in with membrane active layers facing FS)

The decrease in the effective driving force in this situation is the particular function of the feed properties as the same DS condition is used for all the experiments. This situation shows the osmotic pressure of FS at higher TDS plays a less significant role in the performance of the FO process. At higher feed TDS, the water flux is lower and this lower flux reduces the dilutive ICP. This finding has considerable implications because it indicates that the FO has promising application for feed water containing high TDS or salt concentrations such as RO concentrate.

4.5 Influence of membrane properties on the water flux decline

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 water flux behavior.

Inorganic scaling in membrane processes can be administered by one of two different mechanisms: (1) heterogeneous or surface crystallisation, where crystals grow directly on the membrane surface, and (2) homogeneous crystallisation, where crystals are formed in the bulk solution and then deposit on the membrane surface (Mi and Elimelech, 2010a). In addition, it was found in the previous study that a variation in membrane materials and surface properties may alter the dominating inorganic scaling mechanism from homogeneous to heterogeneous crystallisation (Mi and Elimelech, 2010a). Investigation of gypsum scaling using the same method indicated two different crystallisation mechanisms for the CTA and the PA surface. Gypsum scaling on PA seemed to be dominated by surface crystallisation, while gypsum in the CTA membrane system seemed to crystallise in the bulk prior to surface deposition (Mi and Elimelech, 2010c).

To better control membrane fouling, it is necessary to elucidate the relationship between membrane fouling and membrane properties such as their structures and materials. One of the reasons for differences among the findings of previous studies is that membrane properties such as pore size, pure water flux and membrane structure, which also contribute to membrane fouling, are not constant. Subsequently, it is necessary to clarify the influence of the membrane material in water flux behavior and membrane fouling. To date, many groups have been attempting to synthesize high performance membranes for the FO applications by modifying the structural properties of the PA membrane support layer (Wei et al., 2005, Tiraferri et al., 2011, Wei et al., 2011b). The synthesis of the high performance FO membrane is still in its infancy. The modification includes decreasing the support layer thickness and increasing the porosity of the membrane. The only commercial FO membranes are made from cellulose triacetate (CTA) which has an approximately narrow range of pH tolerance as well as relatively low pure water permeability and solute rejection (Vos et al., 1966, Yip et al., 2011). This limits their application in water purification. Concurrently, significant progress has been achieved in developing high performance PA FO membranes that exhibit higher water permeability and better selectivity compared to commercial CTA based FO membranes (Wang et al., 2010, N.Y. Yip, 2010, Wei et al., 2011b, Yip et al., 2010). As there are considerable differences between CTA and PA polyamide membranes, it is important to compare the performance between the two types of FO membranes.

Three fertilisers (i.e. CAN, KCl, DAP) were selected to observe the influence of membrane properties on the water flux behavior. The comparison of average water flux between the PA and the CTA membranes is shown in Figure 4.6. Experimental conditions were, 3M of each fertiliser solution as DS, 35 g/l BGW as FS, with both CTA membrane and the PA membrane. Water flux from the baseline experiment for the PA membrane was 15% higher than the CTA membrane. These baseline results confirm the findings of previous researachg which shows that the PA produce higher water flux in comparison to that of the CTA membrane due to the modifications of the membrane support layer that helped in reducing the structural parameter of the membrane. Figure 4.7 shows the comparative cross sectional SEM images of the two membranes. The cross sectional image of the PA membrane in Figure 4.7 (a) indicates that the support layer is highly porous with many finger-like macro-voids ranging in some cases as large as 15 μm. The SEM images in Figure 4.7 (b) doesn't show the presence of a support structure that hinders easy diffusion of draw solutes and therefore results in lower water flux in the FO process with the CTA membrane rather than the PA membrane.

Interestingly, the comparison of water flux behavior between CTA and the PA membranes using DAP as DS shows a significant difference. The water flux with the PA membrane is more than 45% higher than the CTA membrane using DAP as DS. Also, the water flux is slightly higher with the CTA membrane than the PA membrane using calcium nitrate (CAN) as DS. This probably indicates that fouling behavior is related to interaction of the membrane and DS physicochemical properties. This suggests that different scaling mechanisms may exist between the two membranes.

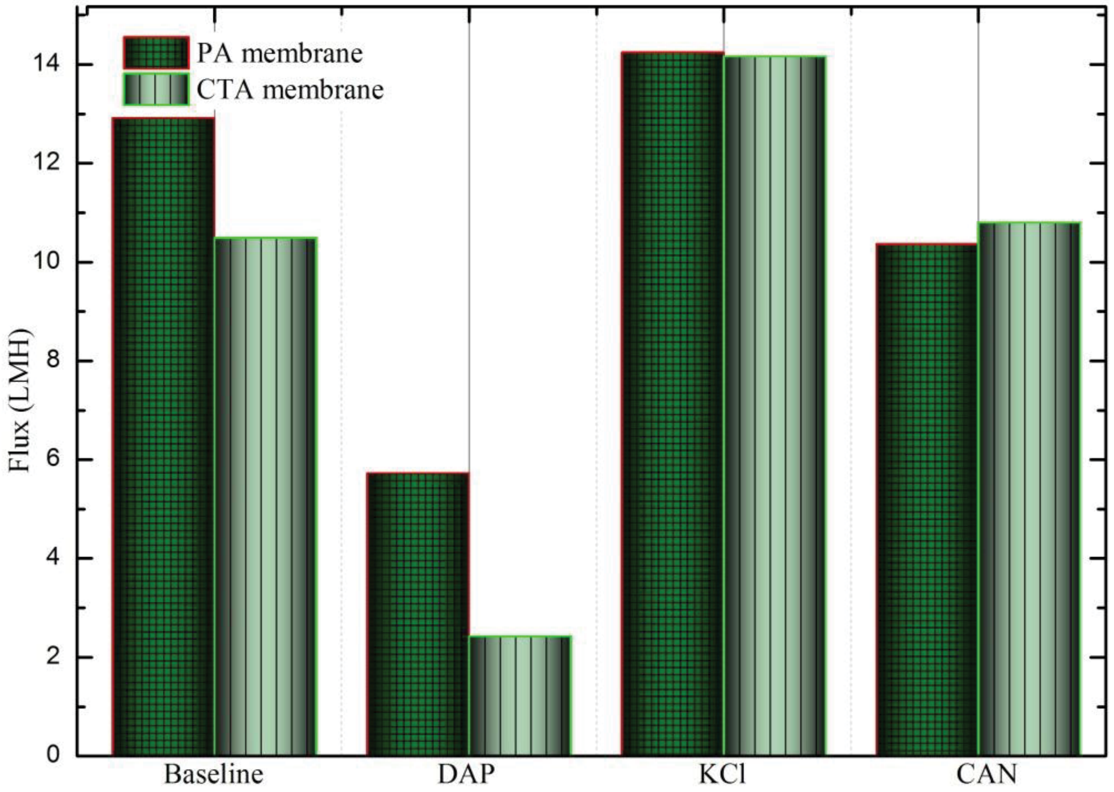


Figure 4.6: Comparison of average water flux on the fresh CTA and PA membranes, (Experimental conditions, DS: 3 molar of each fertiliser, FS: 35 g/l BGW as FS, cross-flow velocity: 400 ml/min and temperature 25±1°C)

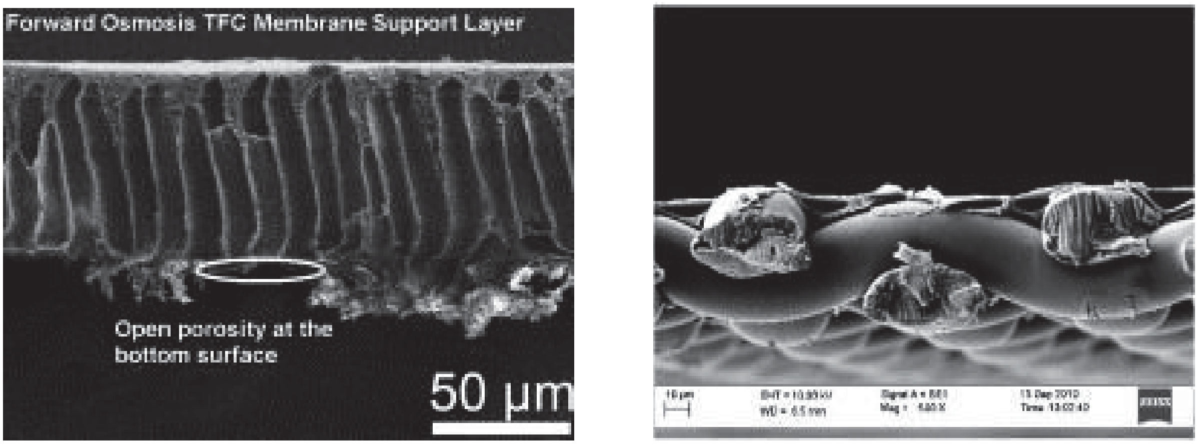


Figure 4.7: Comparative SEM images of the cross section of the two membranes (a) PA membrane, (b) CTA membrane (Qiu et al., 2012)(Wei et al., 2005)

4.5.1 Comparison of water flux behavior and membrane fouling between two PA membranes

Extensive efforts have been made to develop high performance FO membranes with high water flux and low salt passage by modifying the structural properties of the membrane, particularly the support layer, to reduce the ICP effects. Many research groups have focused on the thin-film composite polyamide (PA) membrane. Recently, we have received a new modified PA membrane from a different research group with a very thin support layer and this membrane has been designated as PA-2 in this study. The new TFC PA membrane (PA-2) has been compared to the PA membrane used in earlier section (designated as PA-1). The properties of these two membranes are presented in Chapter 3. Figure 4.8 shows the comparison of the water flux with 3 M KCl as DS and 35 g/l BGW as FS between PA-1 and PA-2 membranes. The gradual water flux declines without any sudden flux decline and no significant membrane fouling is observed for both membranes. The water flux with PA-2 membrane is ~17 $Lm^{-2}h^{-1}$ in FO mode. The same experiment produced ~12 $Lm^{-2}h^{-1}$ water flux with PA-1 membrane, (Figure 4.8). These results indicate that, water flux on the recently fabricated PA-2 membrane performs significantly better than the PA-1 membrane in the FO process. Moreover, the support structure of this PA-2 membrane appears to have larger finger-like macro-voids and therefore is comparatively more porous than the reported PA-1 membranes. PA-2 exhibits the high permeate water flux, a characteristically higher water flux which is due to a fabrication procedure that enables property optimisation of membrane.

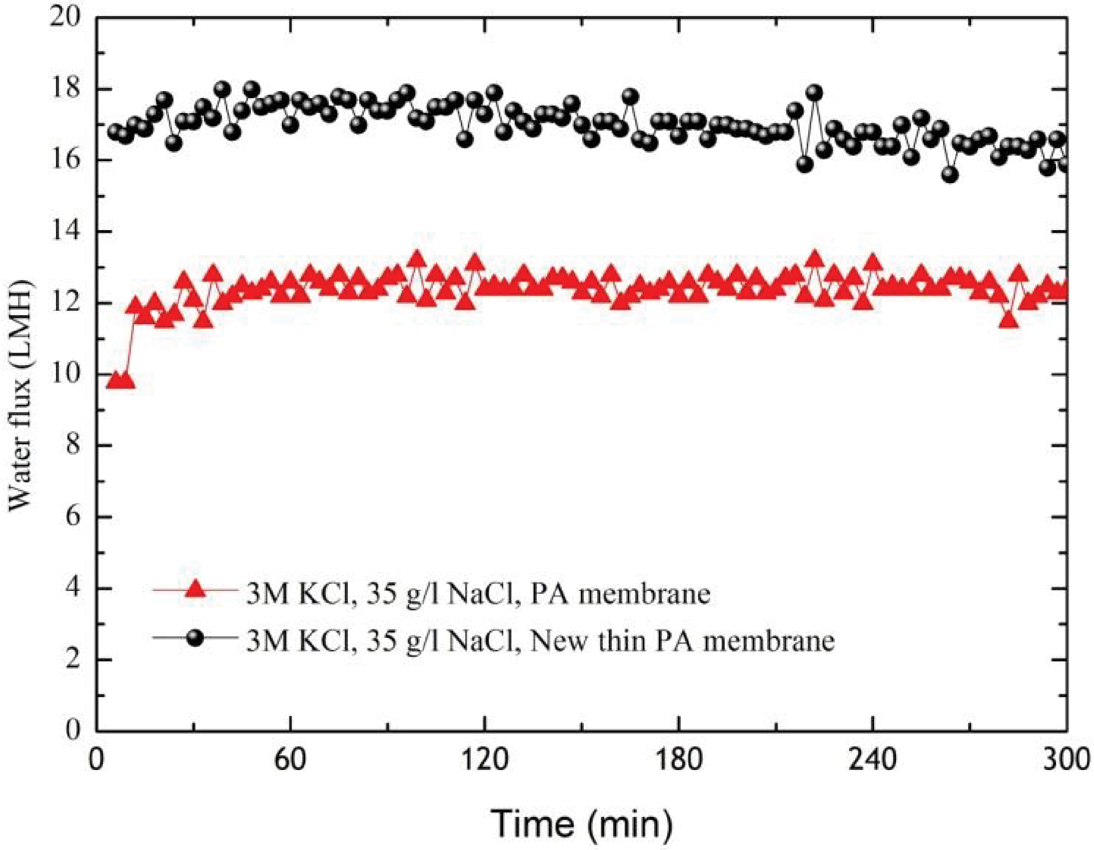


Figure 4.8: Variation of water flux in terms of different membrane materials, (Experimental conditions, DS: 3M KCl, FS: 35 g/l BGW, temperature: 25±1°C and cross-flow rate: 400 ml/min in with membrane active layers facing FS)

4.6 FO fouling reversibility by cleaning

A laboratory-scale cross-flow FDFO set-up was used in this study. Figure 4.9 illustrates the protocols for the fouling and cleaning experiments. Before each fouling experiment, a new membrane coupon was installed in the membrane unit and stabilised to obtain a constant flux. All the fouling and cleaning experiments performed in this study are operated in the FO mode, where the membrane dense (active) layer faces the FS. The effectiveness of physical cleaning on the water flux recovery of the FDFO desalination with BGW using six different fertilisers as DS was studied. Before the membrane was subjected to the FDFO process, the baseline flux was obtained by using 1 M NaCl as DS and DI water as FS. After the FDFO experiments, the membranes were subjected to physical cleaning using DI water on both sides of the membrane at the same cross-flow velocity as the fouling experiment 400 ml/min in or (8.5 cm/s) for 20 mins. The experimental conditions for the fouling experiments were 3 M fertiliser solution as DS, 35 g/l BGW as FS and 60 mg/l alginate as organic foulant using CTA membrane. The baseline flux was again obtained using 1 M NaCl as DS and DI water as FS to study the restoration of water flux. All the fouling and cleaning experiments performed in this study are operated in the FO mode, where the membrane dense (active) layer faces the FS. The percentage of water flux restored was observed as a percentage ratio of the restored flux to the initial baseline flux (normalised) of the virgin membrane.

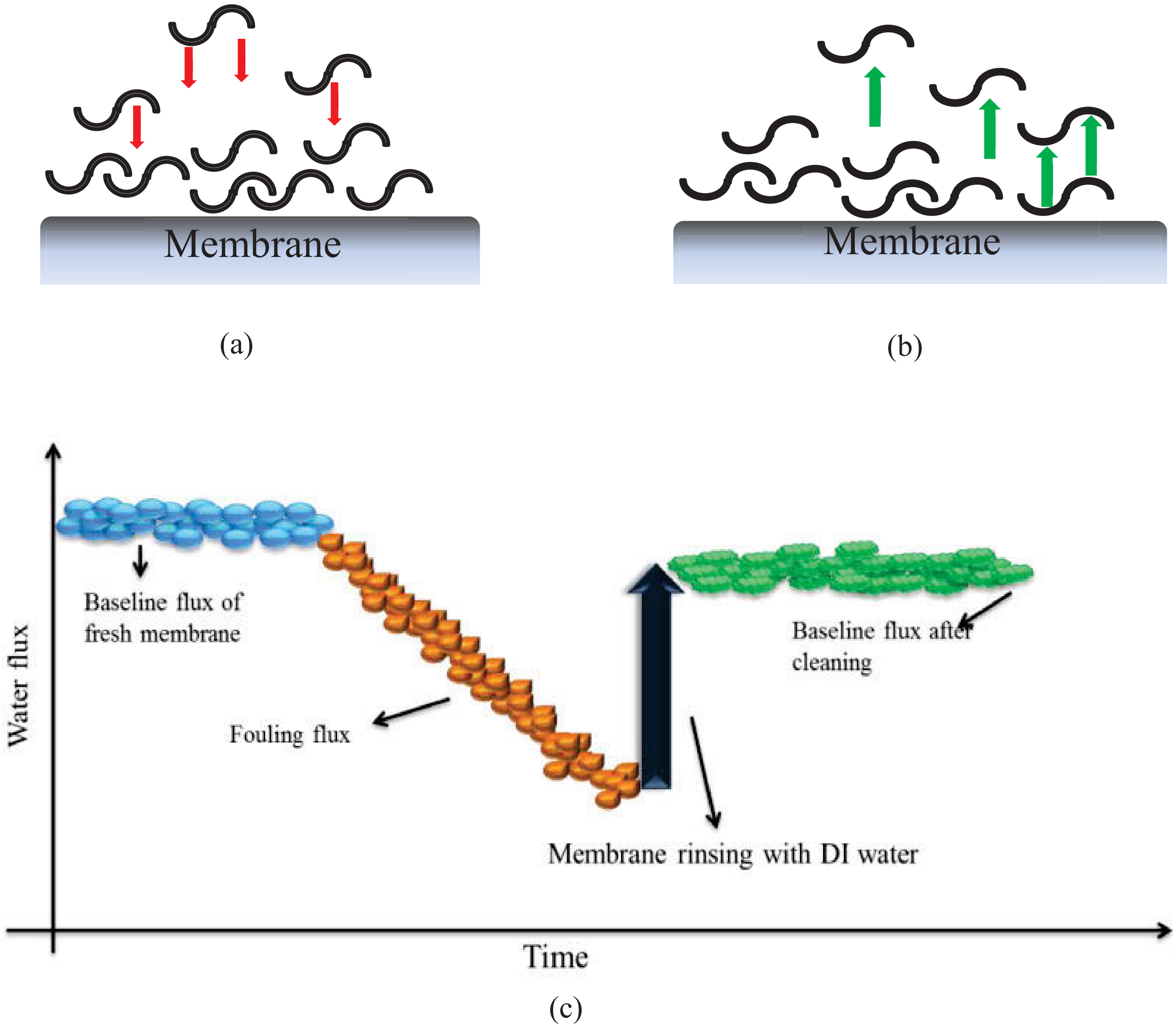


Figure 4.9: Membrane cleaning and fouling mechanism, (a) membrane fouling and (b) membrane cleaning (c) membrane cleaning protocol

Water flux recovery values of each fertiliser as DS on the CTA membrane are presented in Figure 4.10. For DAP as DS the recovered flux after combined fouling was about 80% of the original flux on the CTA membrane. The recovery rate for KNO_3 was remarkably 98% after only a 20 min cleaning without chemicals and with low cross-flow. When the FO membrane was subjected to both organic and inorganic fouling, the flux recovery was lower than where the membrane was subjected to single foulant. With the combined fouling experiment it clearly indicates that a synergistic effect exists between alginate fouling and inorganic scaling during the FDFO experiment by using DAP as DS. The co-existence of these two types of foulants on flux decline is greater than their individual effects. Accordingly, it is important to understand mechanisms that influence the synergistic effect in order to develop future effective strategies for controlling the combined fouling. This observation indicates that the cleaning is mainly attributed to physical removal of the fouling layer by the sheer force generated by the cross-flow.

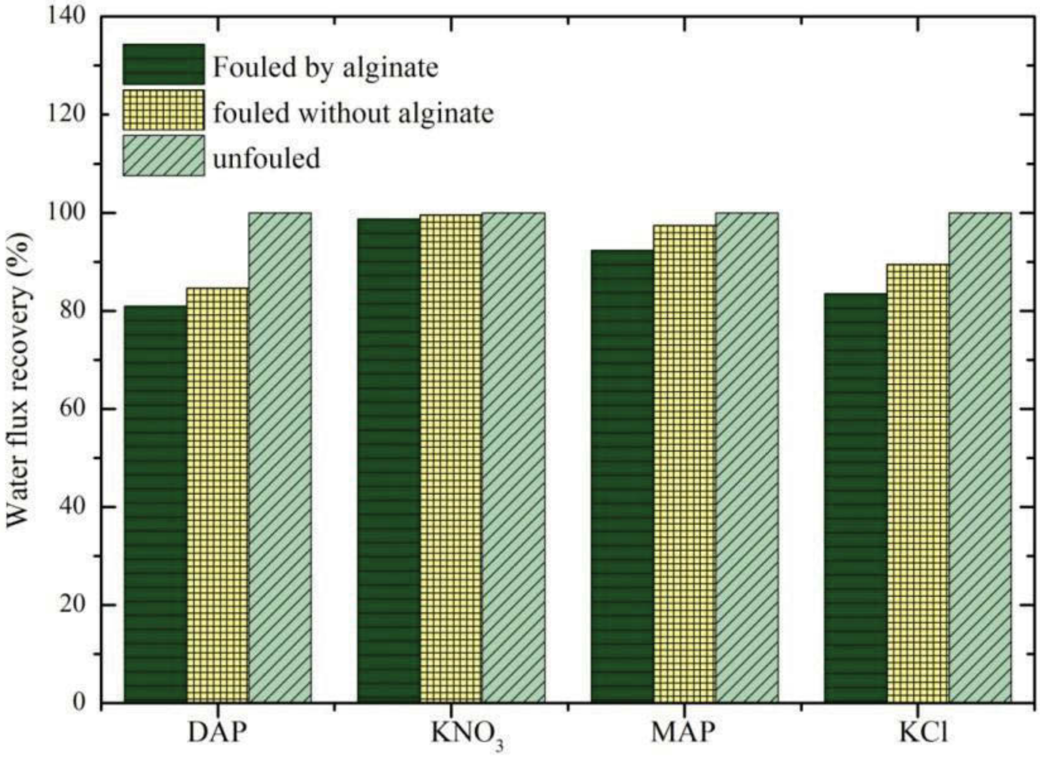


Figure 4.10: Comparison of average baseline water fluxes on fouled membrane after cleaning with water flux on the fresh new membrane, (Experimental conditions: fouling experiment 3M of DS, FS: BGW 35 g/L , 60 mg/l alginate, Baseline experiment condition: 1 M NaCl as DS and DI as FS)

A noticeable flux decline was not observed with the other fertilisers as DS, other than DAP. However, in order to evaluate the existence of surface crystals, three different fertilisers were selected for flux recovery: calcium nitrate (CAN), KNO_3 and DAP. These resulted in severe membrane scaling during the FDFO fouling experiment using 1 M of each dertiliser as DS and BGW 10 as FS. The results in Figure 4.11 show that, the physical cleaning is able to restore the water flux almost completely for both the CAN and the KNO3 indicating the absence of any scale surface crystallisation. However, for DAP as DS, the water flux could be restored only up to about 80% when the normal cleaning regime of 400 ml/min in for 20 min is applied. This shows that a higher cross-flow velocity or longer duration is required to clean the membrane more effectively.

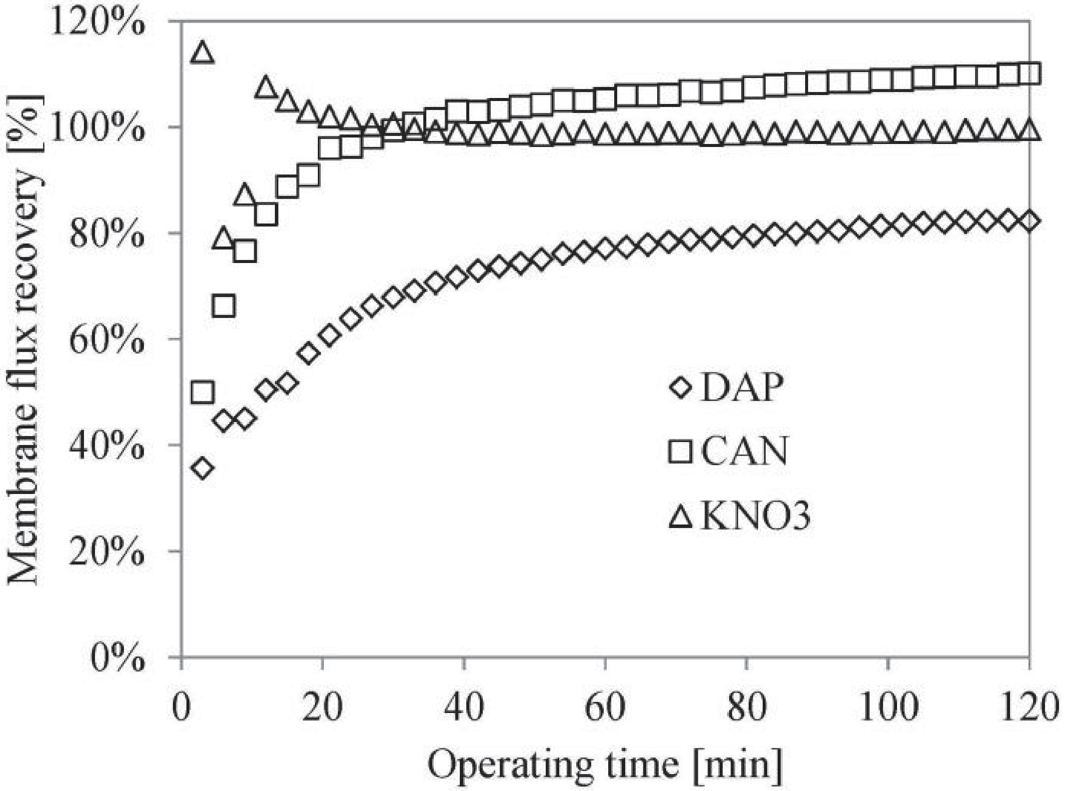


Figure 4.11: Flux recovery of the FO membrane after membrane has been fouled by inorganic foulant (a) using three different types of DS and (b) using DAP as DS at different concentrations. All cleaning regimes were conducted at cross-flow rates of 400 ml/min in for 20 minutes.

4.7 Concluding remarks

In this study, the membrane scaling and flux decline in the FDFO process during the desalination of brackish groundwater using six different fertilisers as DS has been investigated. The effectiveness of physical cleaning on the membrane flux recovery has also been evaluated. The following inference has been drawn from this study:

- Most fertilisers showed a gradual water flux decline over time with the exception of DAP. A rapid decline in water flux observed for DAP as DS is quite in contrast to other DS that have been used. These results indicate that, long-term observation of the performances of the fertilisers as DS is important as some of the DS could promote membrane scaling and fouling of the membrane. Such significant flux decline is not usually observed in short-term laboratory experiments.

- This work also reveals that besides the selection of suitable fertiliser as DS during the long term FDFO process, selecting an appropriate membrane for the selected fertiliser is also essential. Interaction between fertiliser properties and membrane characteristics has s significant influence in water flux behavior.

- Physical cleaning with cross-flow rates similar to the normal FDFO process was adopted to evaluate the effectiveness of restoring the membrane flux after inorganic scaling. The flux recovery was about 80-97% depending on the type of the DS.

CHAPTER 5

University of Technology Sydney

Faculty of Engineering & Information Technology

FACTORS AFFECTING SEVERE FLUX DECLINE DURING FERTILISER DRAWN FORWARD OSMOSIS PROCESS USING DIAMMONIUM PHOSPHATE AS DRAW SOLUTION

5.1 Introduction

Inorganic scaling and organic fouling pose a significant challenge for the efficient operation of any membrane process including forward osmosis (FO) processes. Scaling not only increases energy consumption but also increases operation and maintenance costs and significantly shortens membrane life. Scaling in the salt rejecting membrane processes occurs either by surface crystallisation or bulk crystallisation or both depending on the operating conditions (Gilron and Hasson, 1987, Hasson et al., 2001, Liu and Mi, 2012a).

The most common scaling salts are calcium sulfate, barium sulfate and calcium carbonate during desalination of seawater or brackish water by the RO/NF process however, phosphate scaling is a major issue when the RO process is applied to wastewater treatment (Antony et al., 2011, Chesters, 2009, Zach-Maor et al., 2008). In fact, the presence of phosphate ions can cause serious scaling problems for the RO membrane process and even anti-scaling agents are not quite effective in preventing scaling (Chesters, 2009).

For successful application of the fertiliser drawn FO (FDFO) desalination process some important aspects of the process should be evaluated. One critical issue that demands considerable research is significant membrane scaling during the FDFO desalination process when fertilisers containing scaling precursors are used such as diammonium phosphate (DAP) or $(NH_4)_2HPO_4$ as draw solution (DS). The relative flux reduction became progressively severe during this experiment. This significant flux decline in membrane filtration is the result of an increase to the membrane resistance and the development of another resistance layer on the membrane surface. More research is needed to systematically investigate the effect of different parameters on the critical flux value during the FDFO desalination of brackish groundwater (BGW) using DAP as DS.

Understanding the fouling behavior in the FDFO desalination process using DAP as DS is particularly important because DAP is one of the world's most widely used phosphorus (P) fertilisers so the factors underpinning this phenomenon need to be fully explored. DAP is made from two common constituents in the fertiliser industry and it is popular because of its relatively high nutrient content and its excellent physical properties. DAP fertiliser is an excellent source of P and nitrogen (N) for plant nutrition and it is gradually converted to nitrate by soil bacteria, resulting in a subsequent drop in pH. Highly soluble, it thus dissolves quickly in soil to release plant-available phosphate and ammonium.

Some other benefits of DAP are:

- DAP has uniform granule size which provides good flow characteristics and is ideal for seeding equipment
- It is a cost effective product providing readily available nitrogen and phosphate

- It can be used in forestry situations where both nitrogen and phosphate are required

The objectives of this chapter are to better understand the fouling behavior of FO membranes in the FDFO desalination of the BGW process using DAP as DS and to evaluate the effectiveness of operational conditions to mitigate severe membrane fouling. The water flux behavior and membrane fouling is evaluated in this chapter and the factors determining the extent of fouling and subsequent flux decline are investigated. Added to this,, the influence of the feed channel spacer on critical flux is evaluated.

The key parameters investigated include (1) DAP concentrations, (2) FS properties, (3) membrane orientation, and (4) the use of feed spacer.

5.2 Materials and methods

The DS (draw solution) and FS (feed solution) were prepared based on the procedures described in Chapter 3. In this chapter, only diammoniun hydrogen phosphate (DAP) solution has been used as DS. The FS used consisted of the brackish ground water (BGW) of different total dissolved solids or TDS of 10,000 mg/L, 20,000 mg/L, 35,000 mg/L as represented by BGW 10, BGW 20 and BGW 3, respectively. FO mode (active layer facing FS) orientation was adopted and PRO mode (active layer facing DS) was applied where the effect of membrane orientation was investigated. The influence of membrane material on the water flux decline during the FDFO process using DAP as DS on the cellulose triacetate (CTA) and thin film composite polyamide (PA) membranes was investigated.

5.3 FDFO desalination of BGW using DAP as DS

Fouling in the FO process is influenced by the feed water quality like in any membrane process such as the RO process. In addition, scaling and fouling in the FO process could be influenced by additional factors that are not present in the RO process. Reverse diffusion of draw solutes has been cited as one of the major challenges of the FO process because it not only results in the economic loss from replenishment cost, but also complicates feed concentrate management and membrane fouling potential. Reverse diffusion of draw solution salt towards the feed has been observed to play a significant role in influencing colloidal and organic fouling (Boo et al., 2012, Lee et al., 2010). It also exacerbates the cake enhanced osmotic pressure on the membrane surface in contact with the feed water thereby reducing the effective driving force and consequent flux decline (Lee et al., 2010). When a DS containing divalent ions such as Mg or Ca is used, the reverse diffusion of Mg or Ca or both could interact with some of the dissolved organic matter present in the feed to form a bridging effect which significantly affects the cake formation and flux decline (Lee and Elimelech, 2006, Hatziantoniou and Howell, 2002).

There are two possible reasons for severe membrane scaling in the FO process. The first relates to the supersaturation of feed ions and the second relates to the reverse diffusion of draw solute ions that may interact with the feed ions. In pressure based membrane processes such as RO and NF, scaling occurs due to the complex phenomenon that involves both crystallisation and transport mechanism (Antony et al., 2011). Nucleation and growth of inorganic scales on the membrane surfaces is a common problem for any RO system (Antony et al., 2011). Crystallisation occurs due to the permeation of feed water, which leaves salts or ions behind on the membrane surface resulting in the supersaturation of ions that promotes nucleation, which then induces the growth of crystals and then scale formation on membrane surfaces (Gilron and Hasson, 1987, Hasson et al., 2001, Liu and Mi, 2012a). Scaling in the RO process therefore increases with the increase in the feed recovery rates as the super- saturation point is reached earlier.

A similar scaling mechanism may be involved during the FDFO process because the GW feed contains several scaling precursor ions such as Mg^{2+}, Ca^{2+} and HCO_3^- and SO_4^{2+} which could precipitate to form scales such as $CaCO_3$, $MgCO_3$ $CaSO_4$. However, if this mechanism was responsible for the scale formation, the flux decline would have been observed for almost all the fertiliser DS once the supersaturation point was reached. In chapter 4, most fertilisers showed a gradual decrease in the water flux over time with the exception of DAP. A rapid decline in water flux observed for DAP as DS is quite in contrast to the other DS used. In fact, after about 4 hours of operation, the water flux rapidly declined almost reaching zero. Given that the flux decline was observed only for DAP this is an indication that the scale formation in this particular FDFO process is mainly due to the DS properties.

An autopsy of the fouled membrane with DAP as DS was conducted to study the composition of the scales formed during the FO process using DAP as DS. The membrane autopsy involved both destructive and non-destructive observation of fouled membrane which can provide an understanding of the scaling and fouling phenomenon at a microscopic level (Phuntsho et al., 2011a, Li et al., 2003). Figure 5.1 (a) presents the SEM images showing the formation of significant scales on the membrane surface using DAP as DS. Scales were observed on both the surfaces of the active layer and the support layer as shown in Figure 5.1 (b) however, the scales formed on the active layer surface (facing the FS) were more significant. A closer observation of the scaling layer reveals a flaky crystal layer formed on the membrane surface which was mainly responsible for the sharp flux decline when DAP was used as DS (Figure 5.1 (c)). The scales were also observed on the walls of the acrylic membrane cell facing the FS (Figure 5.1 (d)).

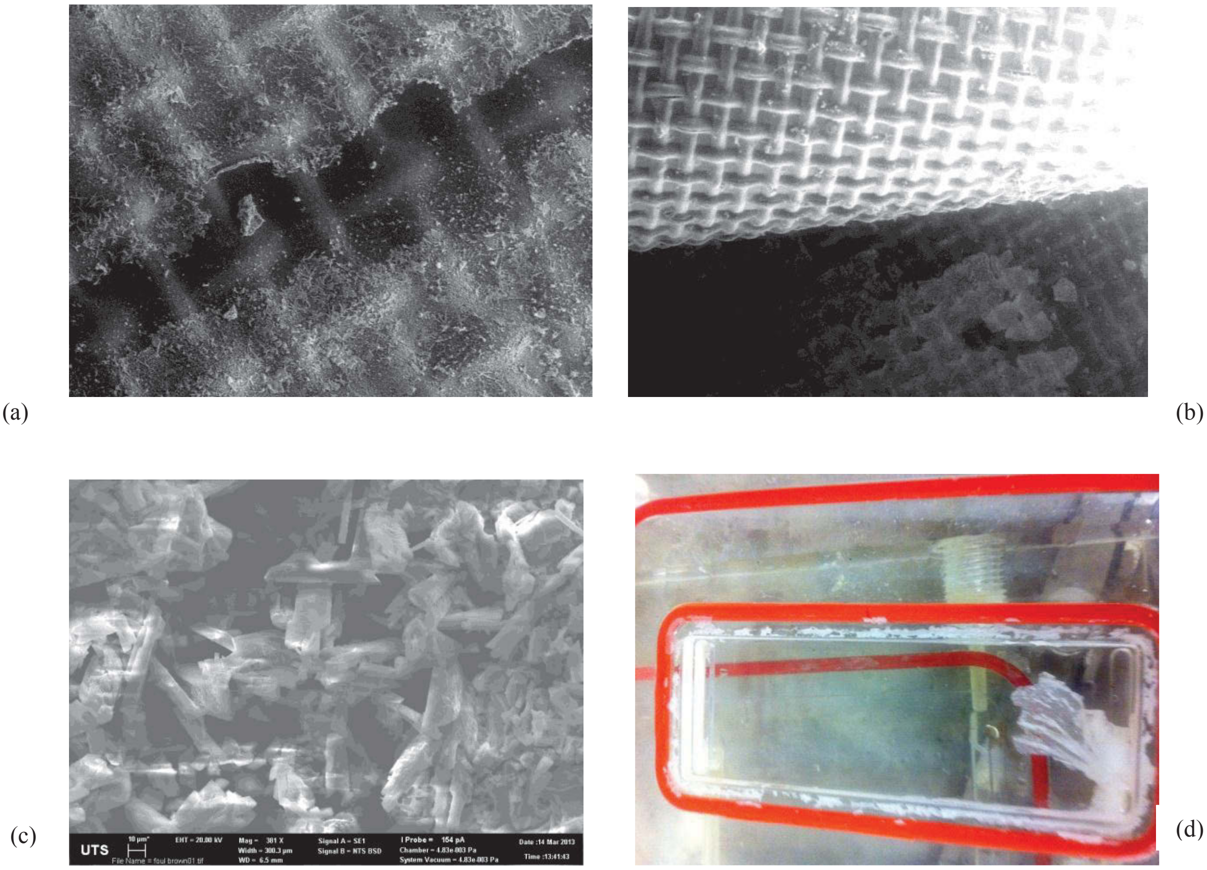


Figure 5.1: SEM images of CTA membrane after experiment with DAP as DS and BGW as FS. a) active layer of the membrane surface, (b) both active layer and support layer of the FO membrane, (c) on the wall of the acrylic membrane cell facing FS and (d) magnified image of the scaling layer.

In the FO process, the draw solutes diffuse towards the feed in the opposite direction to the water flux and this phenomenon is commonly described as reverse solute flux. The reverse diffusion of draw solutes or ions towards the FS from the DS could interact with feed ions forming insoluble scaling compounds. Reverse diffusion of certain draw solute ions such as Ca^{2+} and Mg^{2+} has also been found responsible for accelerating organic fouling by interacting with the colloids and organic matter (Boo et al., 2012, Lee et al., 2010).

In order to identify the composition of the scaling layer, EDS analysis was carried out on the active layer of the scaled membrane to determine the composition and the scaling layer. Immediately after the FO experiment, the scaled membrane was removed from the FO cell and then rinsed thoroughly with the DI water to remove any residual solution from the scales. The membrane was then dried overnight in the desiccator before the thick and loose top layer of the scale was brushed off before EDS analysis. The EDS results are presented in Figure 5.2. The results show that the scaling layer is composed of a large proportion of Na, Ca, Mg and P. Other than P, all other elements shown in Figure 5.2 are already present in the FS and are hence related to the feed properties. The presence of P in the scaling layer on the active layer side of the FO membrane further confirms that the reverse diffusion of DAP from the DS might have played a role in the formation of scales. The reverse diffusion of DAP across the membrane could react with the ions present in the FS such as Mg and Ca. Their combination particularly with Ca, and Mg could result in the formation of scales resulting in severe flux decline during the FO process.

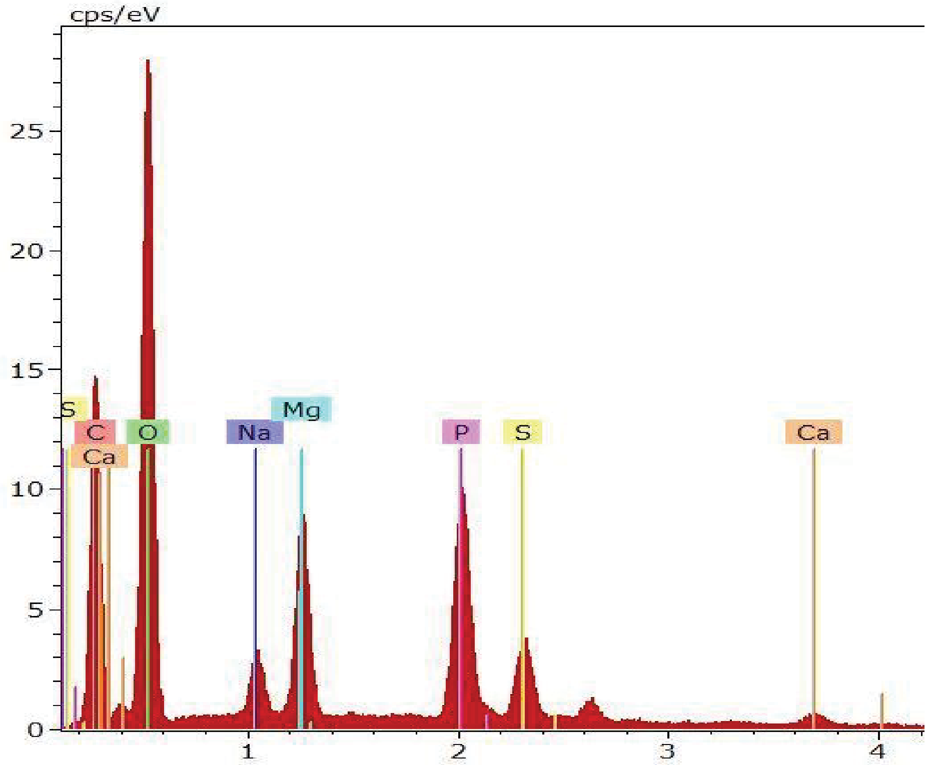


Figure 5.2: The EDS spectrum for the active layer of the membrane after the fouling experiment. The scale deposit mainly consists of phosphorous, sulphate, calcium and magnesium.

Calcium phosphate and magnesium phosphate scaling is usually a major issue when the RO process is applied for wastewater treatment because of the presence of phosphate nutrients (Antony et al., 2011, Chesters, 2009, Zach-Maor et al., 2008). The combined effects of increased phosphate levels with high calcium and bicarbonate levels increases the phosphate scale formation on the membrane (Chesters et al., 2007). Therefore, these results indicate that, despite the absence of phosphate in the BGW FS, phosphate scaling will be a significant issue if DS containing phosphate ions are used for the desalination of BGW by the FO process although not all phosphorous compounds could form severe scaling. Moreover, phosphate may also have a bridging effect that could create a thick cake layer on the active layer of the FO membrane. Figure 5.3 (a) shows formation of scaling in the membrane active layer and Figure 5.3 (b) presents the bridging effect of phosphate during the FDFO process using DAP as DS.

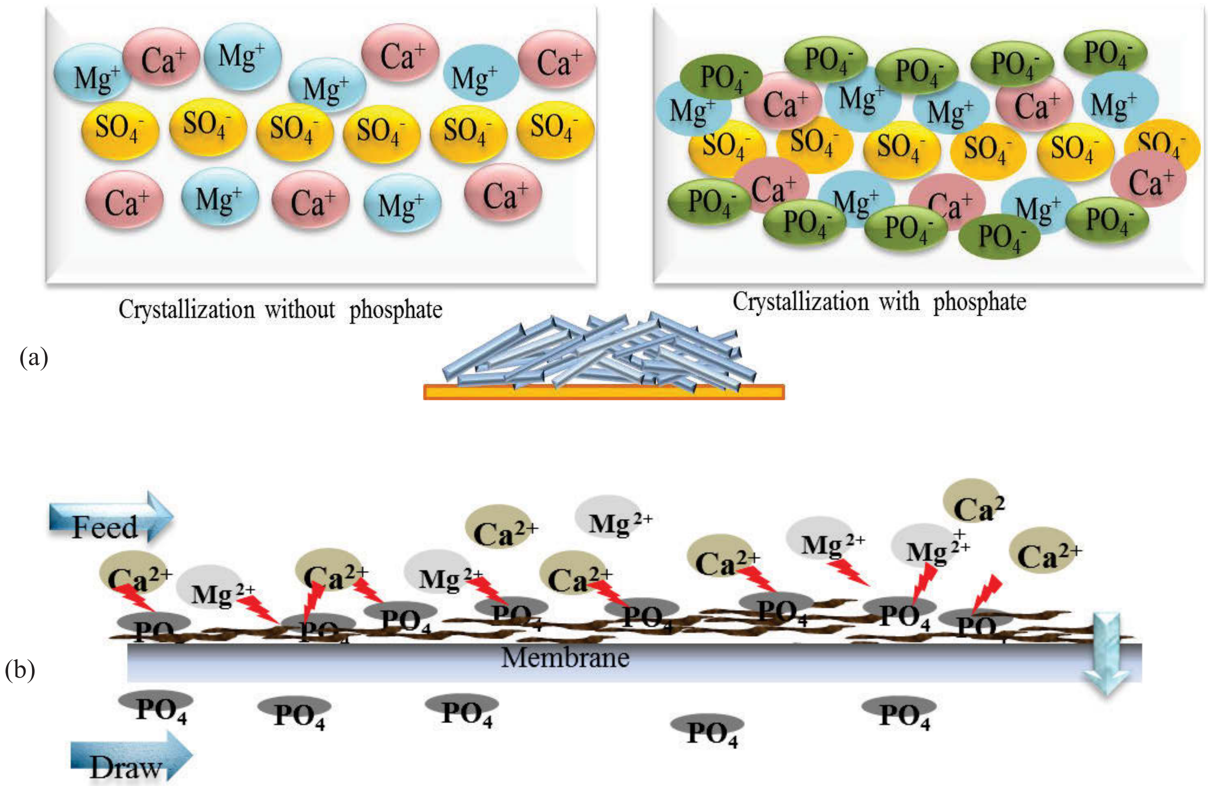


Figure 5.3: (a) Illustration of inorganic crystal formation in the membrane active layer due to reverse diffusion of phosphate, (b) Bridging effect of phosphate during cross flow filtration

As discussed earlier, scaling in the pressure-based membrane processes such as RO and NF starts with nucleation that induces growth of crystals on the membrane surface (Gilron and Hasson, 1987, Hasson et al., 2001, Liu and Mi, 2012a). However, given the low recovery rate at which the lab-scale FDFO process was operated, the potential of nucleation and surface crystallisation is not very significant. Bulk crystallisation could have been mainly responsible for the FDFO process using DAP as DS because a significant amount of scales were also observed on the walls of the acrylic membrane cell, and these are not expected if surface crystallisation is the dominating factor for scale formation. The presence of a small amount of Na and Cl in Figure 5.2 might be because of the salt remains after the membrane has been dried and not necessarily the scales formed during the FO process, as most sodium and chloride compounds are highly soluble.

5.4 Factors affecting severe flux decline during the FDFO desalination process using DAP as DS

This study investigates the influence of various factors affecting the membrane scaling in the FDFO desalination process when DAP is used as a DS. The major factors responsible for the performance of the FDFO water flux behavior were thoroughly investigated and their implications to the overall process discussed. The major factors assessed include membrane properties, DAP concentration, and FS properties. The influences of all these factors were measured in terms of water flux decline.

5.4.1 Influence of DAP concentration on water flux decline

In order to identify the influence of DAP concentration on critical water flux during the FDFO desalination of the BGW process, FO experiments were conducted with five different DAP concentrations (1 M, 1.5 M, 2 M, 2.5 M and 3 M). Clearly, greater initial water flux was observed at higher DAP concentrations and this is due to the increased driving force across the membrane.

However, the increase in DS concentration also caused rapid flux decline which occurred much earlier when higher DAP concentrations were used. As previously discussed, FO is known to have lower fouling propensity and hence the flux decline should usually be slow and mild as observed in the earlier fouling experiments in Chapter 4. However, several recent studies on FO fouling have shown that substantial flux decline can occur due to inorganic scaling (Mi and Elimelech, 2010a) or the synergistic effects between organic and inorganic foulants (Liu and Mi, 2012b).

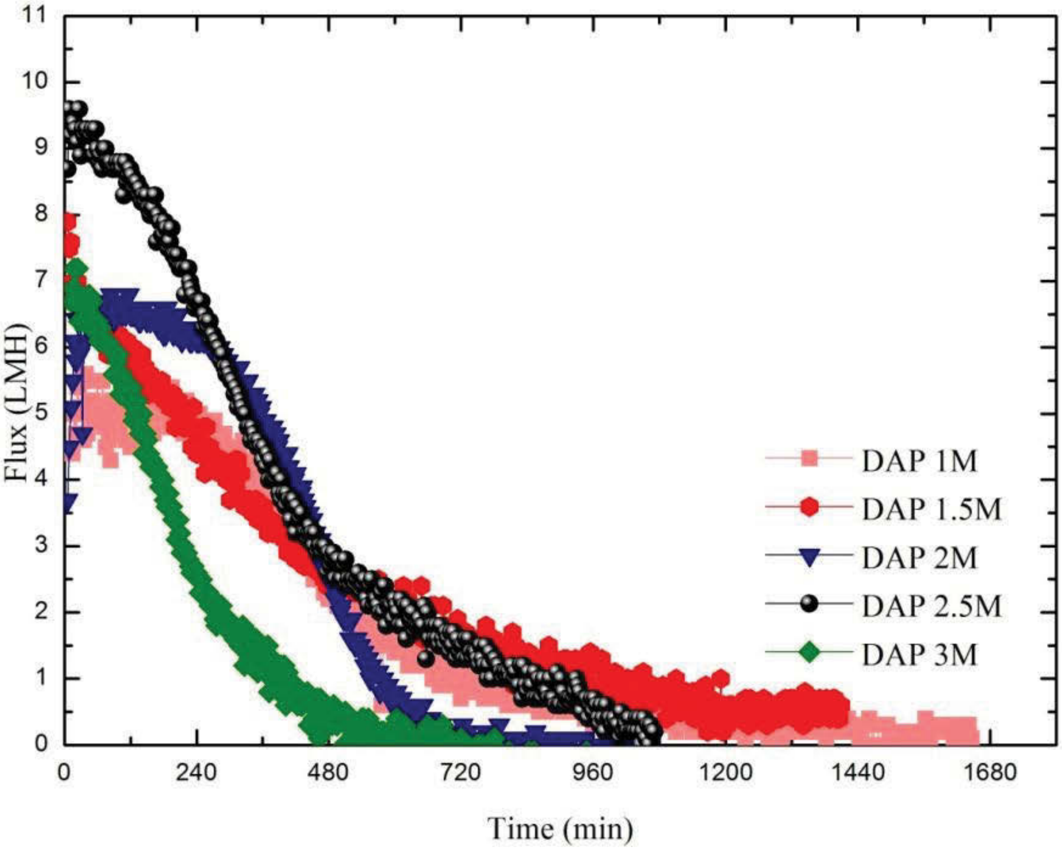


Figure 5.4: Effect of DAP concentration on water flux decline (Experimental conditions; DS: DAP (1M, 1.5M, 2M, 2.5M, 3M), FS: BGW 10 g/L, water cross-flow velocity: 400 ml/min, membrane: CTA and a temperature: 25±1°C)

Figure 5.4 indicates that, if the reverse diffusion or reverse draw solute flux is increased, the rate of scale formation may also increase and this can proportionately increase the severity of flux decline. The reverse draw solute flux increases when a higher DS concentration is used. Therefore, FDFO experiments were conducted to see how the DS concentration affects the scaling potential and the flux decline during the FDFO process using BGW as FS.

However, DAP concentration showed a significant influence on the membrane scaling and flux decline as shown in Figure 5.4. When higher DAP concentrations were used, the flux decline observed was not only severer but also occurred much earlier than when lower DAP concentrations were used. This shows that when higher DS concentrations are used, the reverse draw solute flux increases as it is a direct function of the concentration gradient (ΔC) (Boo et al., 2012, Hancock and Cath, 2009, She et al., 2012a, Phillip et al., 2010). Owing to this, the rate of scale formation at the membrane surface increases which, in turn, results in more severe flux decline.

5.4.2 Influence of FS concentration on water flux decline

BGW contains a variety of inorganic compounds and these components have been noted to foul membranes to varying degrees. It is generally accepted that inorganic compounds such as calcium, magnesium and sulphate account for the majority of the foulant in membranes during desalination of BGW.

The influence of feed properties on the flux decline was investigated using 1 M DAP as DS and by varying the feed water quality in terms of TDS. The results are presented in Figure 5.5. When a BGW as FS with higher TDS was employed the initial water flux was not only lower but the flux decline was also more rapid and occurred much earlier. When a BGW with higher TDS is used, the reverse diffusion of DAP from the DS has more access to the scaling ions such as Ca and Mg resulting in the rapid scaling and thicker cake layer formation that is responsible for rapid flux decline. The mechanisms described above explain the dense fouling layer and the ensuing substantial flux decline during the FDFO experiments when a FS with higher TDS was employed.

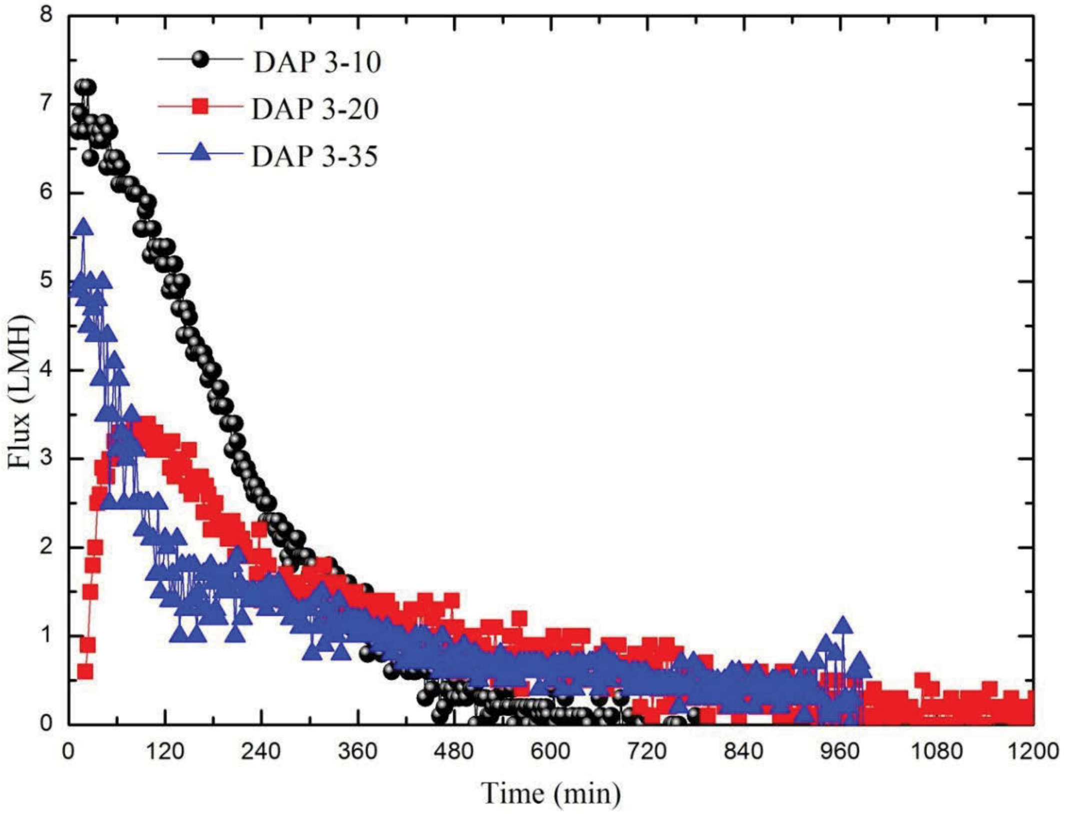


Figure 5.5: Effect of FS concentration on water flux decline (Experimental conditions; DS: 3M DAP, FS: BGW (10 g/L, 20 g/l, 35 g/l), cross-flow velocity: 400 ml/min, membrane: CTA and temperature: 25±1°C)

5.4.3 Influence of FS chemistry

In order to assess which cation (Ca or Mg) was more responsible for scale formation, experiments were conducted with 3 M DAP as DS and by removing either Ca or Mg or both from the FS and replacing them with NaCl to maintain similar TDS. The results presented in Figure 5.6 show that when both Ca and Mg ions are absent in the FS, the water flux is quite normal with only a gradual decline which can be attributed to a decrease in the driving force due to the batch operation of DS and FS. These results confirm that, Ca and Mg are mainly responsible for the formation of the scales during the FO process using DAP as DS and BGW as FS. When one of the ions Mg or Ca was removed from the FS, the water flux decline was still observed although the flux decline was more severe when the Mg ion was removed and only the Ca ion was present as a precursor. This indicates that Ca is responsible for more severe fouling than Mg during the FDFO process with DAP. Although the flux decline was still observed even in the absence of Ca ions, the rapid flux decline only occurred after a period of time had elapsed.

There are several types of phosphate salts because phosphate can form different polymeric ions and the most thermodynamically stable forms are calcium hydroxyapatite (HAP) and calcium fluoroapatite (Chesters et al., 2007). In order to identify the scaling compounds on the membrane, XRD analysis was carried out for the fouled membrane samples. The XRD results indicate that the scales formed on the membrane surface are mainly composed of magnesium phosphate ($MgHPO_4$) and magnesium ammonium phosphate ($MgNH_4PO_4.6H_2O$) or struvite (Figure 5.7). These insoluble compounds are formed because of the reverse diffusion of DAP as DS towards the feed during the osmotic process which then reacts with the magnesium ions present in the FS. Struvite precipitation is one of the major operational problems during the wastewater treatment works (Williams, 1999) including the RO treatment process (Chesters, 2009). A slight increase in FS pH (8.0) was observed after the FO process commenced which might also constitute ideal conditions for the formation of struvite as alkaline pH is the most condusive environment for struvite formation (Stratful et al., 2001).

Although, calcium phosphate and calcium sulphate could also be responsible for scale formation, the XRD analysis could not clearly confirm the presence of calcium phosphate in the scaling layer. Calcium phosphate, mainly hydroxyapatite or $Ca_5(PO_4)_3(OH)$, has been found to cause serious inorganic scaling during the RO process (Antony et al., 2011). However, the absence of calcium scaling in this case is likely because the Ca concentration in the BGW510 FS was significantly lower than the Mg in the BGW 10 FS thereby making the Mg ions more available for interaction with the phosphate ions.

Another potential scaling compound is $CaSO_4$ or gypsum since the FS contains both Ca^{2+} and SO_4^{2-} in the BGW FS. Gypsum is one of the most significant scaling compounds in the RO membrane process (Chesters, 2009, Tang et al., 2011, Greenlee et al., 2009) and the FO process (Mi and

Elimelech, 2010a, Zhao and Zou, 2011). However, neither the EDS analysis nor the XRD analysis could detect the presence of sulphur or sulphate and hence gypsum scaling did not form in this study. This is reasonable given that these lab-scale FO experiments were conducted at very low feed recovery rates (less than 5%) and hence supersaturation of $CaSO_4$ at this recovery rate is not expected.

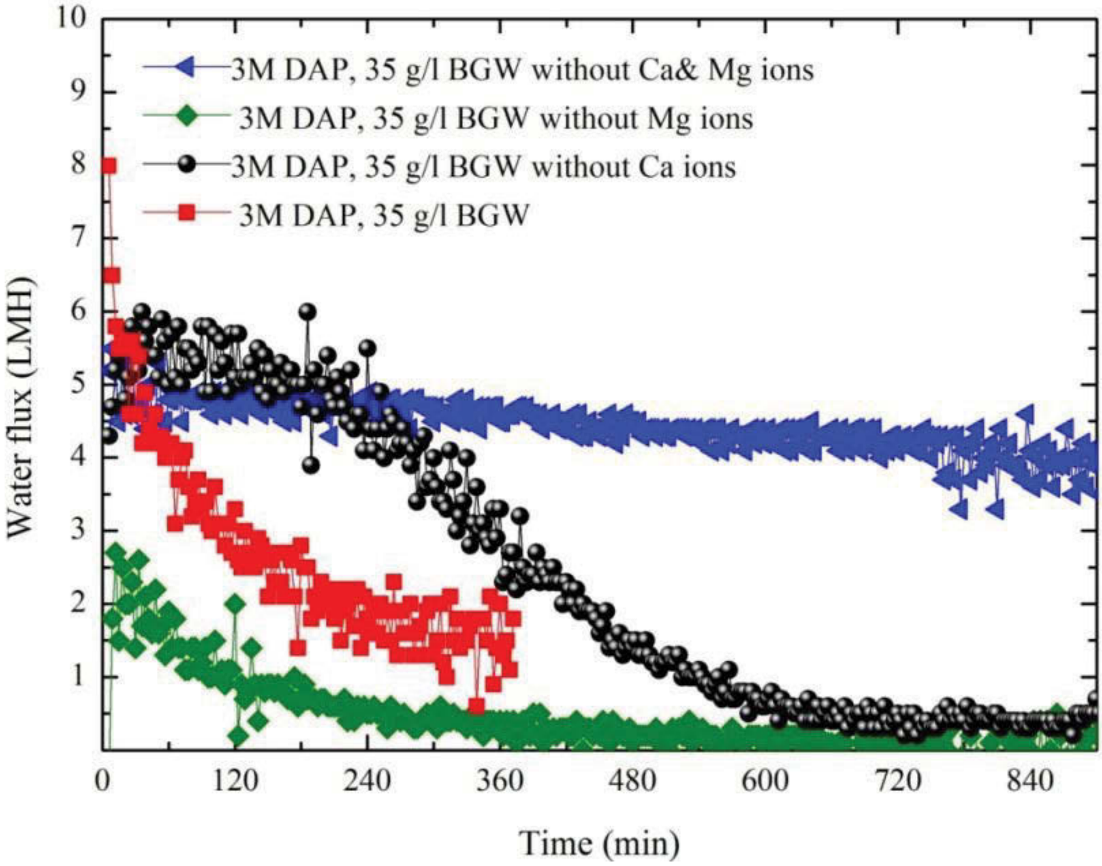


Figure 5.6: Influence of feed chemistry (Experimental condition: DS: 3M DAP, FS (35 g/L BGW, 35 g/L BGW without Mg, 35 g/L BGW without Ca, 35 g/L BGW without Mg and Ca), water cross-flow velocity: 400 ml/min, the CTA membrane and temperature:25±1°C)

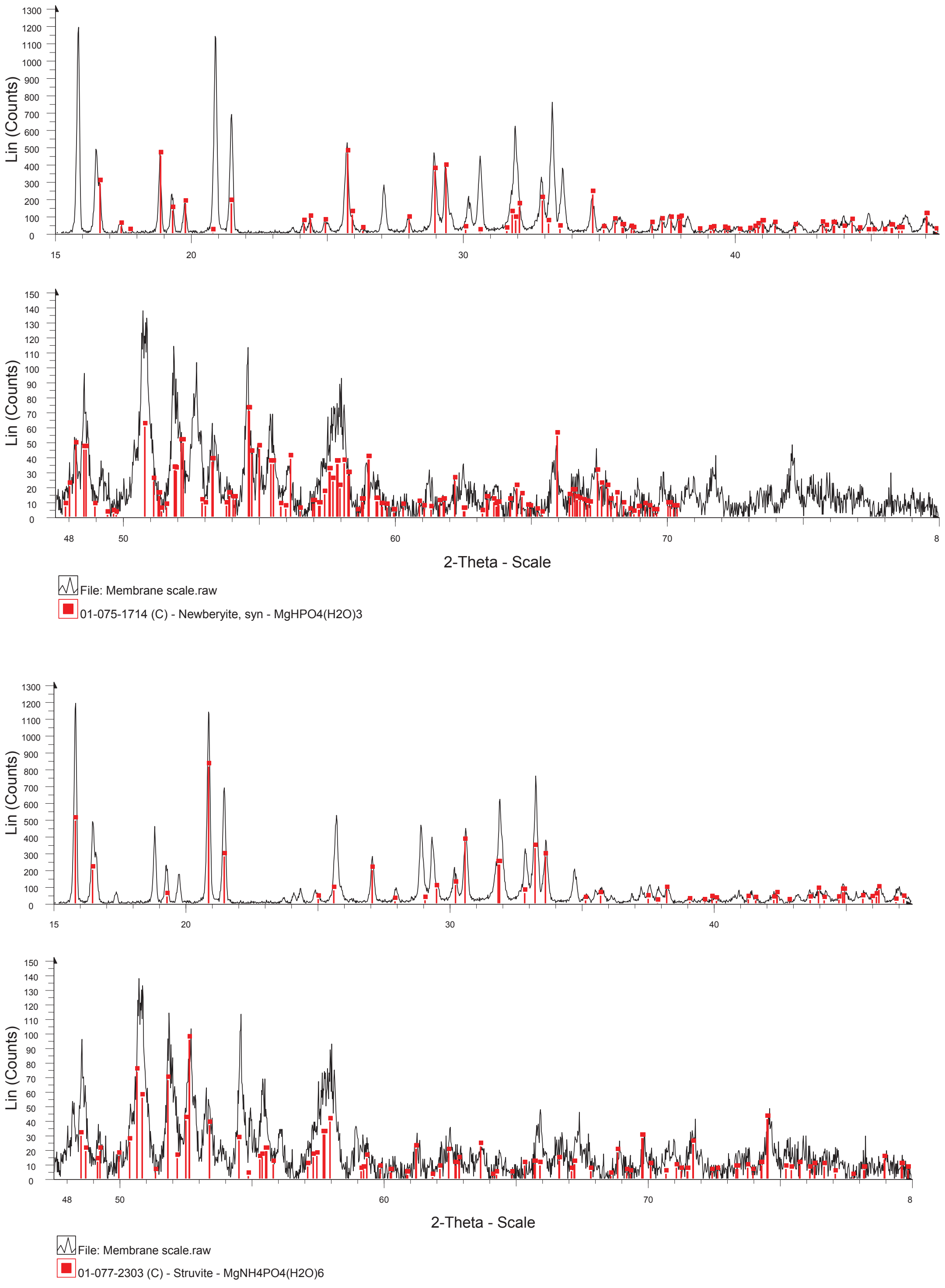
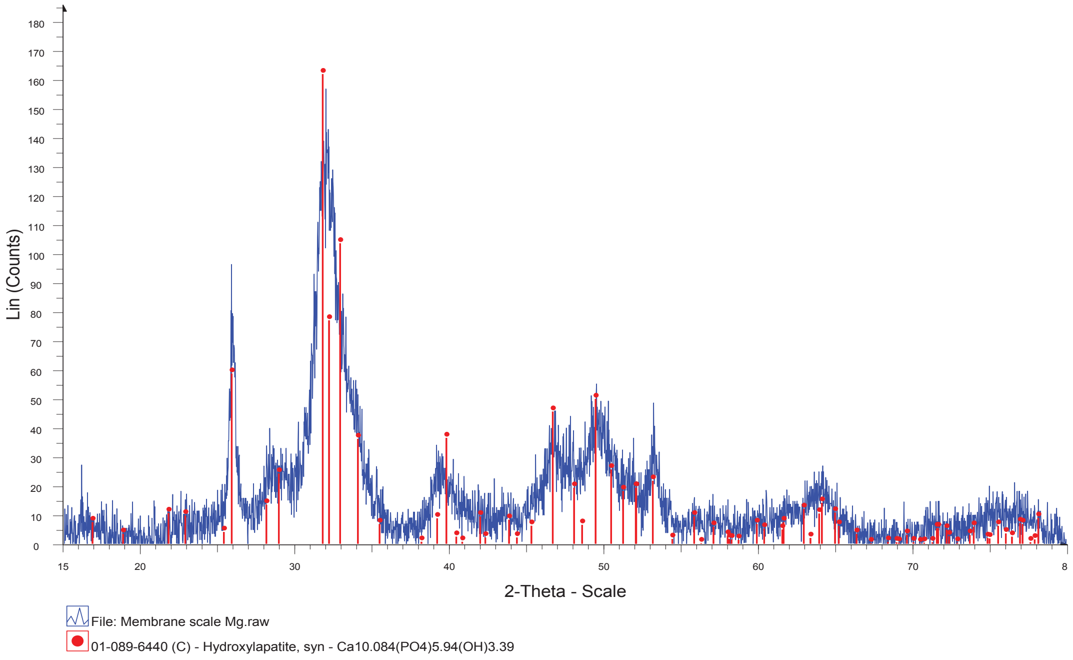


Figure 5.7: XRD analyses of deposition on the membranes after the specific duration of operation by employing the DAP experiment and BGW without calcium.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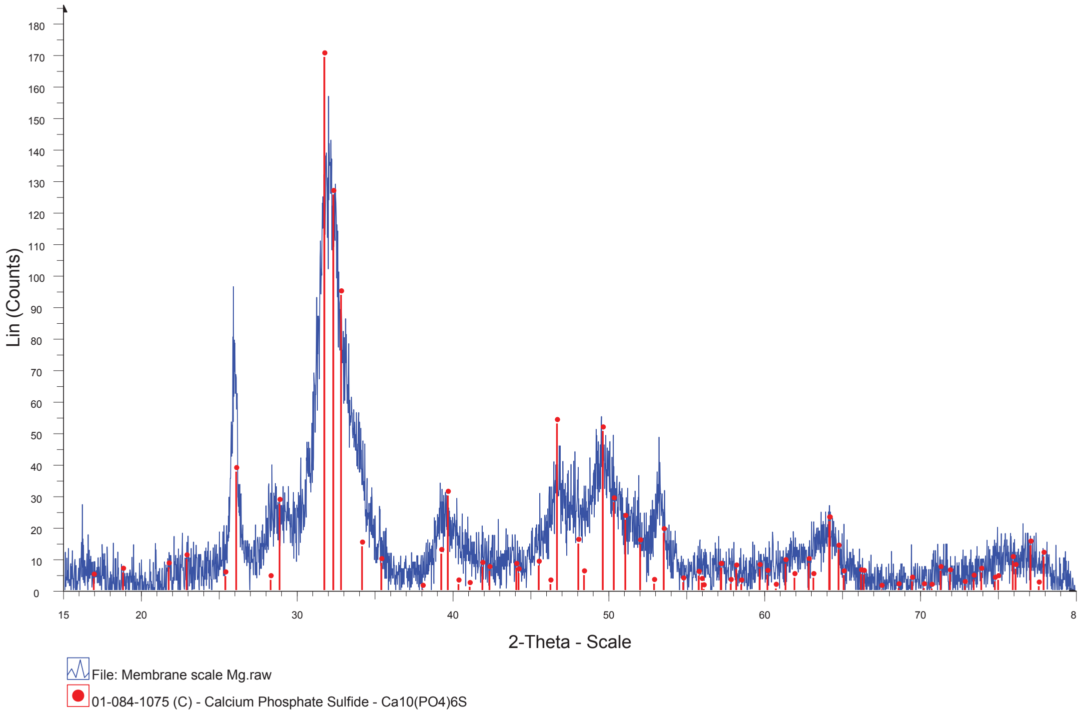
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2-Theta - Scale
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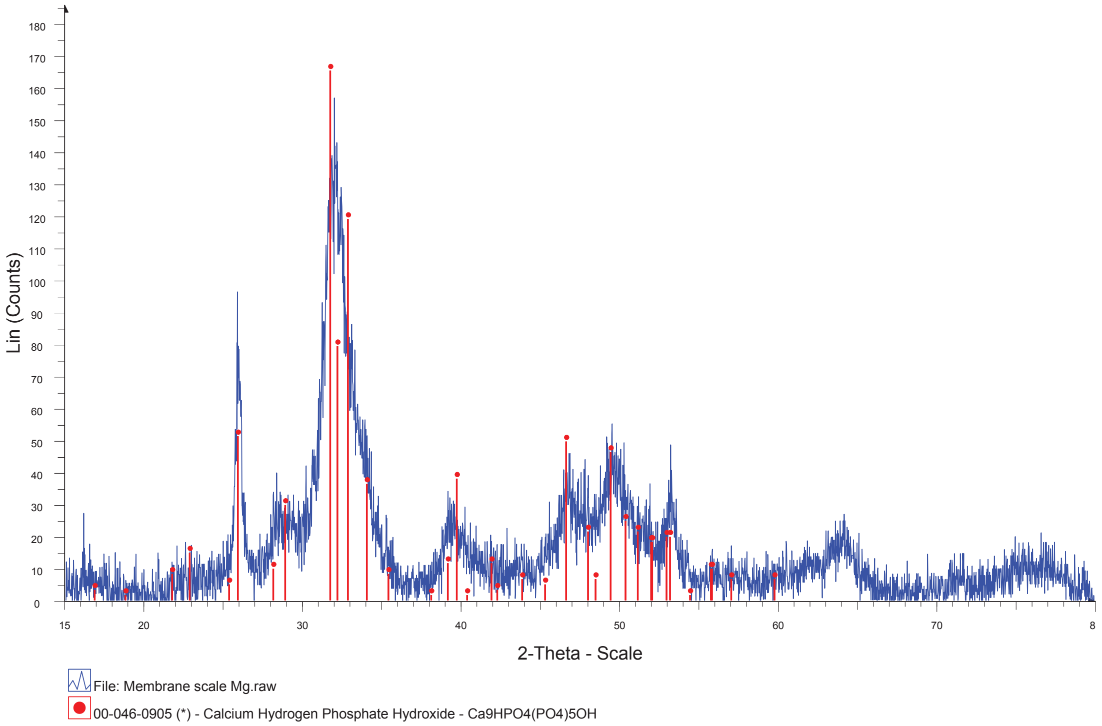


Figure 5.8: XRD analyses of deposition on the membranes after the specific duration of operation by employing DAP experiment and BGW without magnesium.

XRD analysis in Figure 5.7 and Figure 5.8 indicate that, the scaling layer is composed of hydroxylapatite or $Ca_{10}(PO_4)_5(OH)_3$ when magnesium is removed from the FS. Hydroxylapatite has very low solubility under alkaline pH which therefore promotes rapid scale formation and severe flux decline. Further, the increased presence of spectator ions such as Na^+ after replacing Mg^{2+} also probably leads to decreased solubility of hydroxylapatite and contributes to severer flux decline (Rootare et al., 1962). XRD analysis for scaling formed after removing Ca^{2+} ions from FS indicates the presence of both magnesium phosphate and struvite in the scales. Given that both hydroxylapatite and struvite have minimum solubility at a moderately alkaline pH (Harrison et al., 2011), it is difficult to correctly ascertain the actual cause for more severe flux decline with Ca than with Mg. It is likely that under an alkaline pH of the FS, calcium phosphate is less soluble than struvite and hence its scale formation is more rapid than magnesium phosphate or struvite scale.

Earlier, we have shown that Ca, Mg and P were responsible for the formation of the scaling layer on the membrane surface. While the P came from the DS due to reverse diffusion, Ca and Mg were already present in the FS and these ions have long been recognised as the scaling precursors in the salt rejecting membrane processes such as RO and NF (Antony et al., 2011, Chesters, 2009, Gilron and Hasson, 1987, Tang et al., 2011). Therefore, it is clear that the feed properties play a significant role in the formation of scales or the membrane fouling layer that contributes to scaling or fouling and consequently flux decline.

5.4.4 Effect of membrane material on water flux decline

At the present time, only a few membranes for osmotically driven processes are commercially available. Membranes for osmotically driven processes should have large water permeability and low reverse solute permeation. ICP and fouling are considerable problems in osmotically driven processes. Several novel membrane material choices and design strategies for FO membranes have emerged over the last few years including preparation of TFC membranes with a customized PSF support and TFC membranes on hydrophilic support (Thorsen, 2004). As explained earlier, the CTA membrane experienced severe water flux decline as a consequence of significant membrane scaling during FDFO desalination of the BGW process using DAP as DS. The objective of this part of study is to compare the CTA FO membrane and the PA FO membrane in terms of water flux decline and mass deposition during FDFO desalination of BGW. 3 M DAP and 35 g/l BGW were used as DS and FS respectively in the FDFO desalination process. To observe the influence of membrane material, the water flux decline for the CTA and the PA membranes was compared using DAP as DS. Interestingly for the similar experimental conditions, each membrane produced significantly different results in terms of water fluxes (Figure 5.9). In order to demonstrate the fouling mechanisms in the FDFO process, influence of membrane material in the water flux decline and membrane fouling have investigated that shows membrane–foulant interaction plays a key role in water flux decline and membrane fouling during FDFO process using DAP as DS. A severe flux decline was observed for the CTA membrane while for the PA membrane, the flux decline was gradual during the 20 hours of operation. A relatively noticeable scaling layer was observed on the CTA membrane but not on the PA membrane at the end of scaling experiment. The greater fouling propensity of the CTA FO membrane can be related to membrane characteristics. Experimental results thereby show that membrane properties play a vital role in the membrane scaling and flux decline in the FDFO desalination process using DAP as DS. Accordingly, an investigation into the correlation between different membrane materials and fouling property is really important during the fouling experiment with DAP DS and BGW FS.

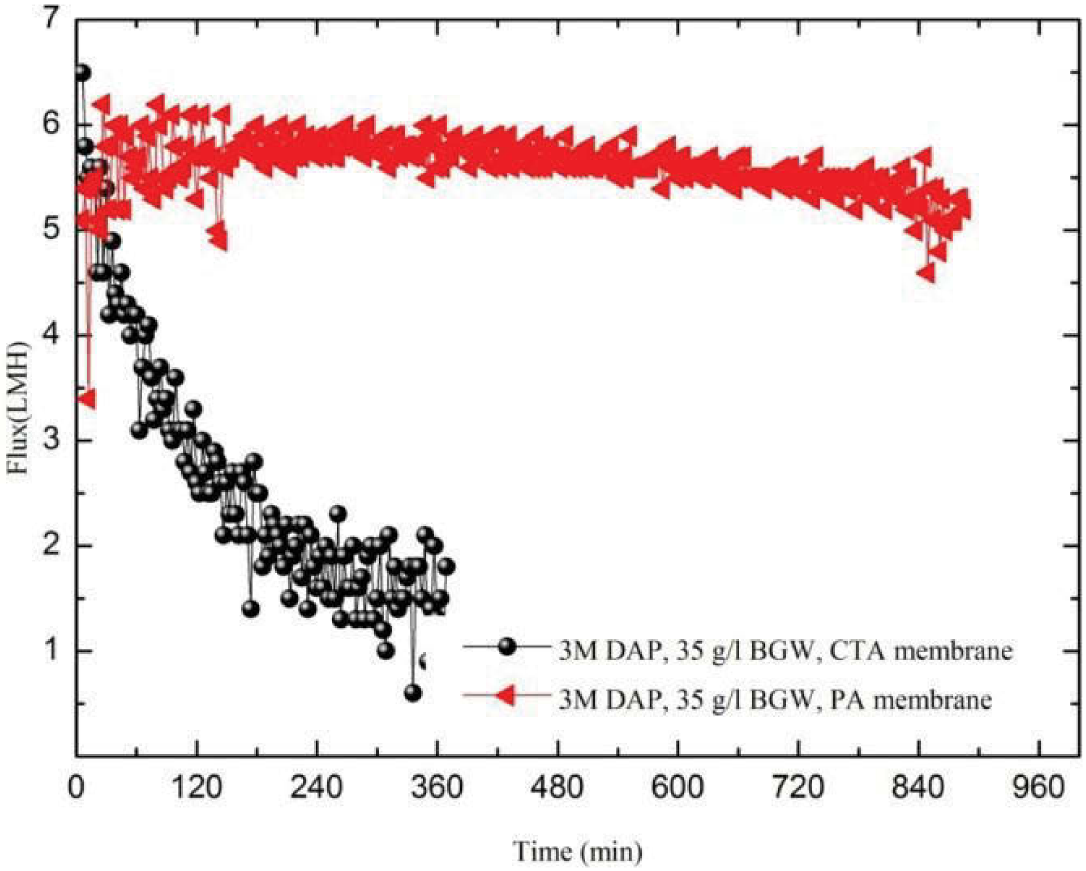


Figure 5.9: Effect of membrane material in water flux decline (Experimental conditions; DS: 3M DAP, FS: 35 g/l BGW, cross-flow velocity: 400 ml/min, CTA and PA membrane and a temperature: 25±1 °C)

In Chapter 4, the recently fabricated PA-2 membrane performed significantly better in terms of water flux compared to the PA-1 and the CTA membrane. The critical flux behavior during FDFO desalination of the BGW process using DAP as DS was compared between these three membranes.

Figure 5.10 shows the performances of the three membranes in terms of water fluxes in the FO mode of operation (active layer facing FS) at 3M DAP DS and 35 g/l BGW FS. Based on their characteristics (Table 5.1), the PA-2 membrane generated the highest water flux but also the most severe flux decline due to the thick scale layer which formed on the membrane surface. The PA-1 membrane generates high water flux with gradual flux decline behavior. The flux decline for the CTA membrane is less than the PA-2 membrane, nevertheless a thick scale layer was observed for the CTA membrane (Figure 5.10). The PA-2 membrane had a characteristically higher water flux and high salt permeability. In fact, at the commencement of the fouling experiment on the PA-2 membrane, the water flux rapidly declined and after 2 hours it had almost reached zero.

After selecting a suitable fertiliser as DS in the FDFO desalination process, using an appropriate membrane for the fertiliser is essential. This study indicates that the CTA and PA-2 membranes aren’t particularly suitable for the FDFO process especially using DAP as DS and BGW as FS.

This study confirmed that the membrane material of either property significantly influences the membrane scaling and fouling in the FDFO process.

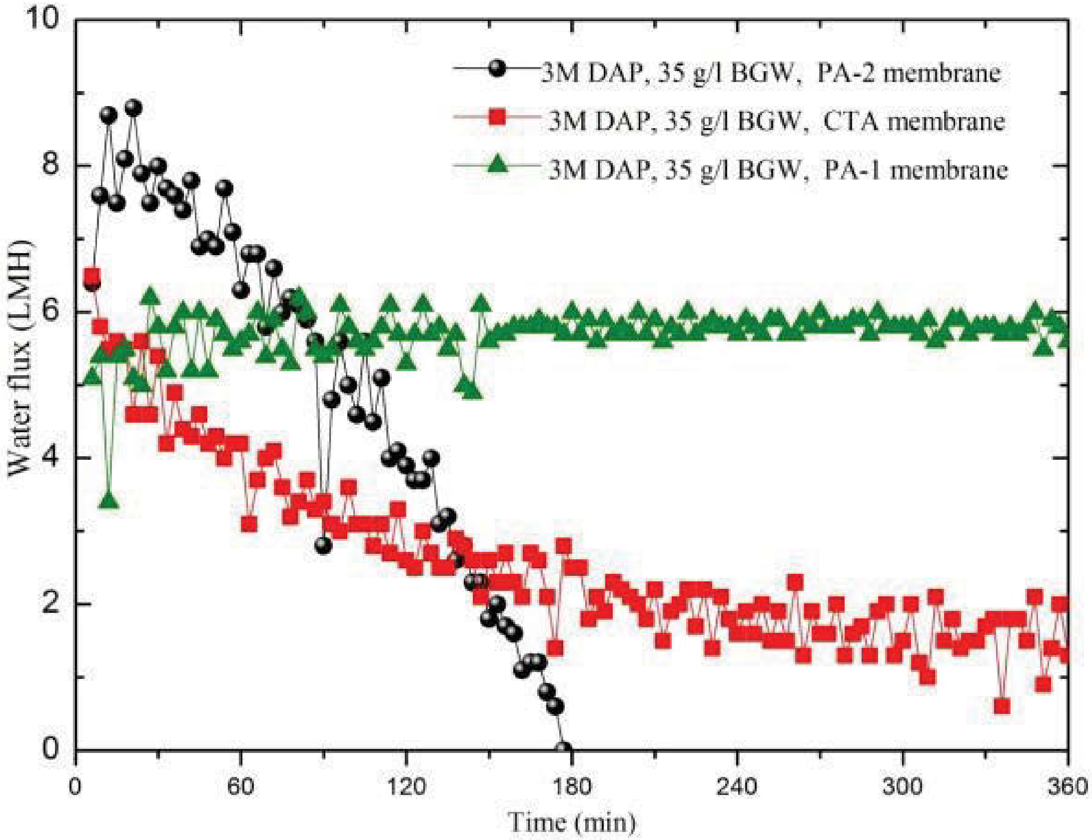


Figure 5.10: Effect of membrane material in water flux decline (Experimental conditions; DS: 3M DAP, FS: 35 g/l BGW, water cross-flow velocity: 400 ml/min, membrane: CTA, PA-1 and PA-2 and temperature: 25±1°C)

5.4.5 Influence of combined fouling (organic-inorganic) on water flux behavior

In real world situations, different types of foulants always coexist in natural waters. In order to identify the influence of combined organic-inorganic fouling, additional fouling experiments were conducted using a feed solution containing only the inorganic ionic species in the synthetic BGW (i.e., without organic foulants), and the flux decline was compared with that from the combined fouling experiment (i.e., inorganic compounds with organic foulants). Alginate, albumin (BSA), and humic acid (AHA) were chosen as model organic foulants in this study. In order to understand the effect of combined fouling on the water flux decline during FDFO desalination of BGW using DAP as DS, the water flux behavior of inorganic fouling was compared to combined fouling. The experimental condition was 3M solution of DAP as DS and 35 g/l BGW as FS using PA membrane was compared with similar experiments by adding 60 mg/l of each organic foulant in FS. From the results presented in Figure 5.11, there was no noticeable difference observed between membrane scaling and combined fouling with different foulant on the PA membrane. This shows the lower fouling potential of the FDFO desalination process using DAP or any other fertiliser solutions as DS on the PA membrane.

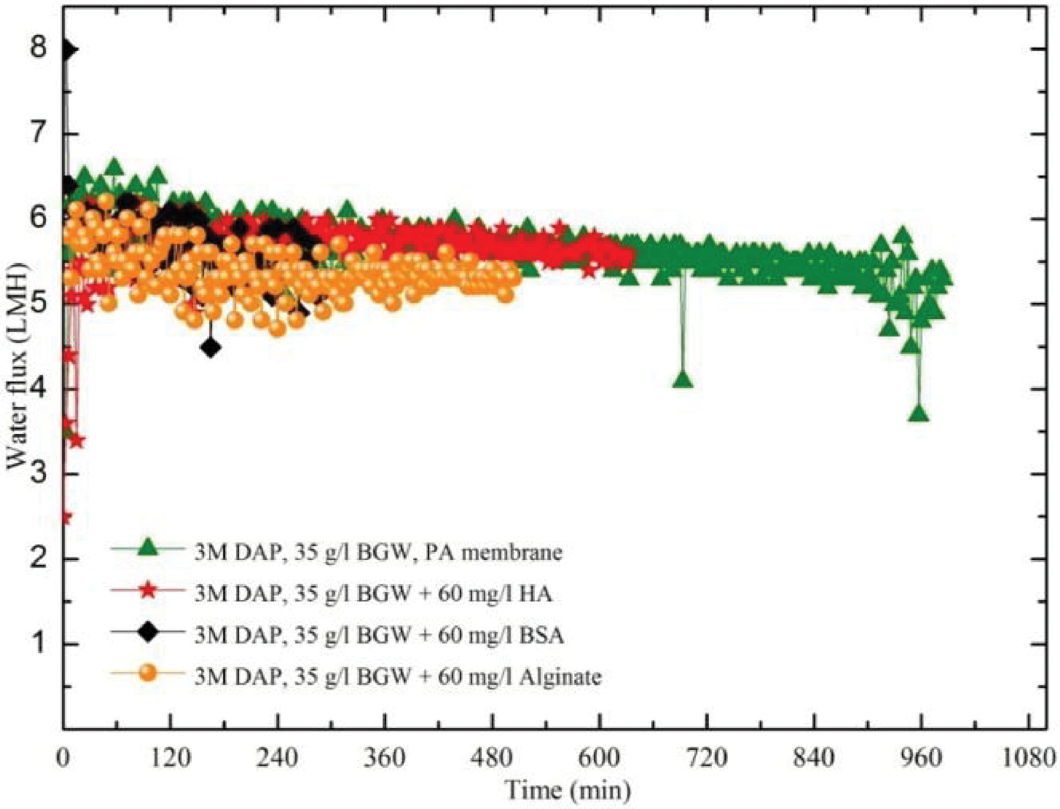


Figure 5.11: water flux behavior of combine fouling, (Experimental conditions; DS: 3M DAP, FS: 35 g/l BGW, 60 mg/l of each foulant, water cross-flow velocity: 400 ml/min, PA membrane and temperature: 25±1 °C)

In order to elucidate the dominating effect of combined organic-inorganic fouling on the CTA membrane, the flux declines and fouling layer from two fouling experiments were studied and compared. These experiments were inorganic scaling on a clean membrane (no organic foulant was added in BGW as FS), and combined fouling on a clean membrane (organic foulant was added in BGW as FS). Figure 5.12, compares the flux decline curves resulting from these two experiments by using alginate as organic foulant. It shows that the presence of alginate aggravated inorganic scaling and water flux decreased by around 35%. The relative permeability of sodium alginate decreased initial water flux to less than half and then continued with a gradual flux decline.

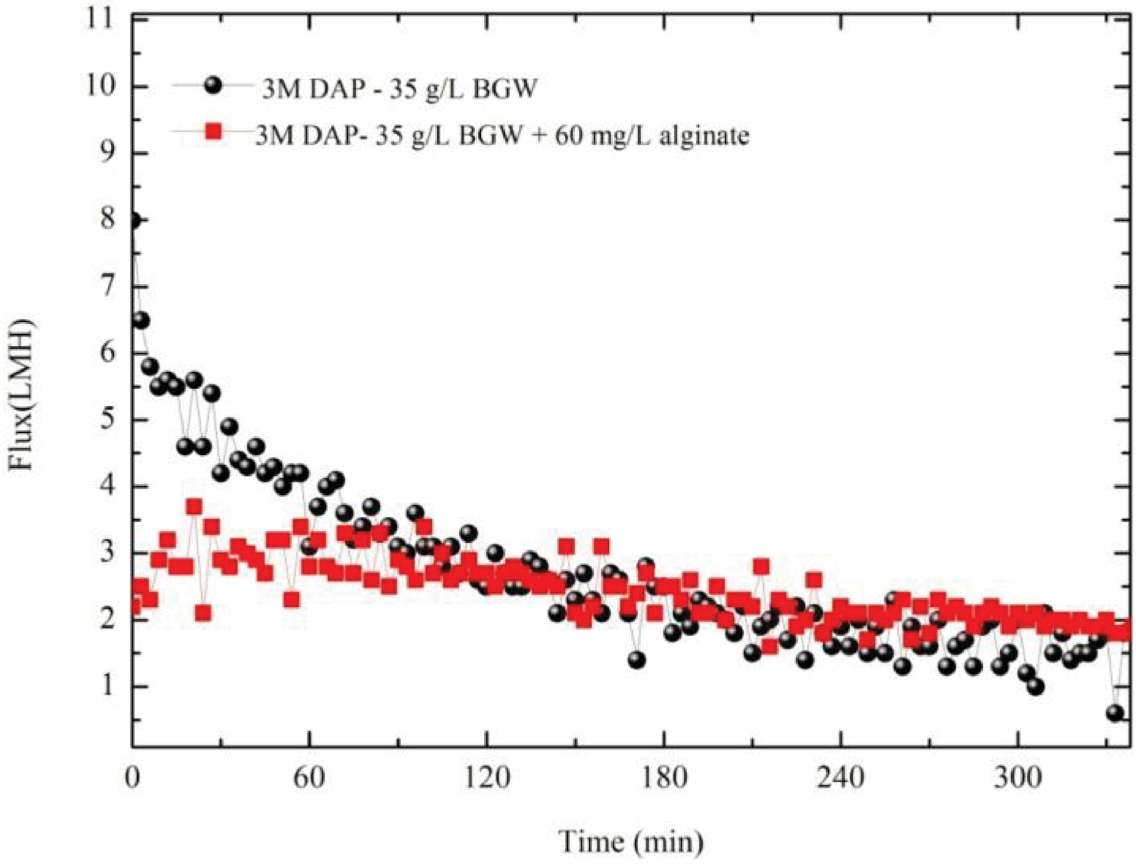


Figure 5.12: water flux behavior of combine fouling (Experimental conditions; DS: 3M DAP, FS: 35 g/l BGW, organic foulant: 60 mg/l alginate, water cross-flow velocity: 400 ml/min, CTA membrane and temperature: 25±1˚C)

5.4.6 Influence of membrane orientation on water flux behavior

Depending on the membrane orientation, the deposition of foulants occurs on different membrane surfaces. In FO (active layer facing FS) mode, foulant deposition occurs on the relatively smooth active layer. In PRO mode (active layer facing DS) foulant deposition takes place on the rough support layer side, or even within the support layer (Seidel and Elimelech, 2002). In order to elucidate the influence of membrane orientation on membrane scaling/fouling and water flux behavior, the flux declines during FO experiments with 3M DAP as DS and 35 g/l BGW as FS were comparatively observed under the FO mode and PRO mode using the CTA membrane. Figure 5.13 shows a comparison of these two experiments.

Water flux decline in the PRO mode was significantly less than in the FO mode. This was unexpected given that the effective concentration difference between the DS and the FS is usually higher under the PRO mode of membrane orientation and this generally results in a higher reverse draw solute flux and ultimately a higher scaling potential. However, the lower flux decline under the PRO mode of operation shows the likely lower reverse diffusion of phosphate ions through the membrane active layer. The higher rejection of phosphate ions (PO_4^{3+}, HPO_4^{2+}, $H_2PO_4^{+}$, etc.) could have been caused by the slightly higher pH under which the CTA membrane remains slightly negative in the surface charge.

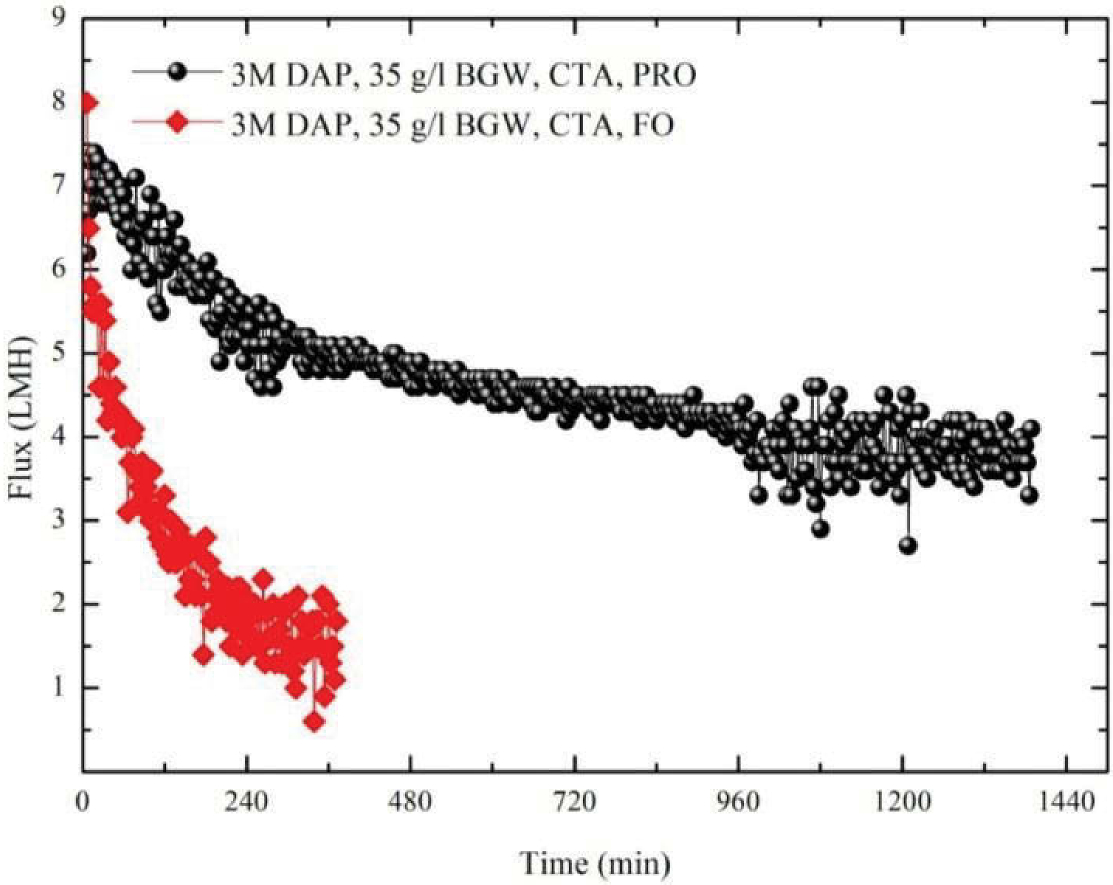


Figure 5.13: Influence of membrane orientation in water flux decline during the fouling experiment. Experimental conditions; DS: 3M DAP, FS: 35 g/l BGW, water cross-flow velocity 400 ml/min; CTA membrane and a temperature of 25±1˚C

5.4.7 Influence of physical cleaning of the water flux recovery

The effectiveness of physical cleaning on the recovery of water flux in the FO process after scaling or fouling was studied. Before the membrane was subjected to FDFO process, the baseline flux was obtained by using 1 M NaCl as DS and DI water as FS. After the FDFO experiments, the membranes were subjected to physical cleaning using DI water on both sides of the membrane at the same cross-flow velocity as the fouling experiment 400 ml/min in or (8.5 cm/s) for 20 mins. The baseline flux was again obtained using 1 M NaCl as DS and DI water as FS to study the restoration of water flux. The percentage of water flux restored was observed as a percentage ratio of the restored flux to the initial baseline flux (normalised) of the virgin membrane.

Figure 5.14 illustrates that the water flux recovery of fouled membrane in an experiment using 3M DAP as DS and 35 g/l BGW as FS after cleaning is 80% recovery for combined fouling (60 mg/l alginate as organic fouling) and 85% for individual foulant.

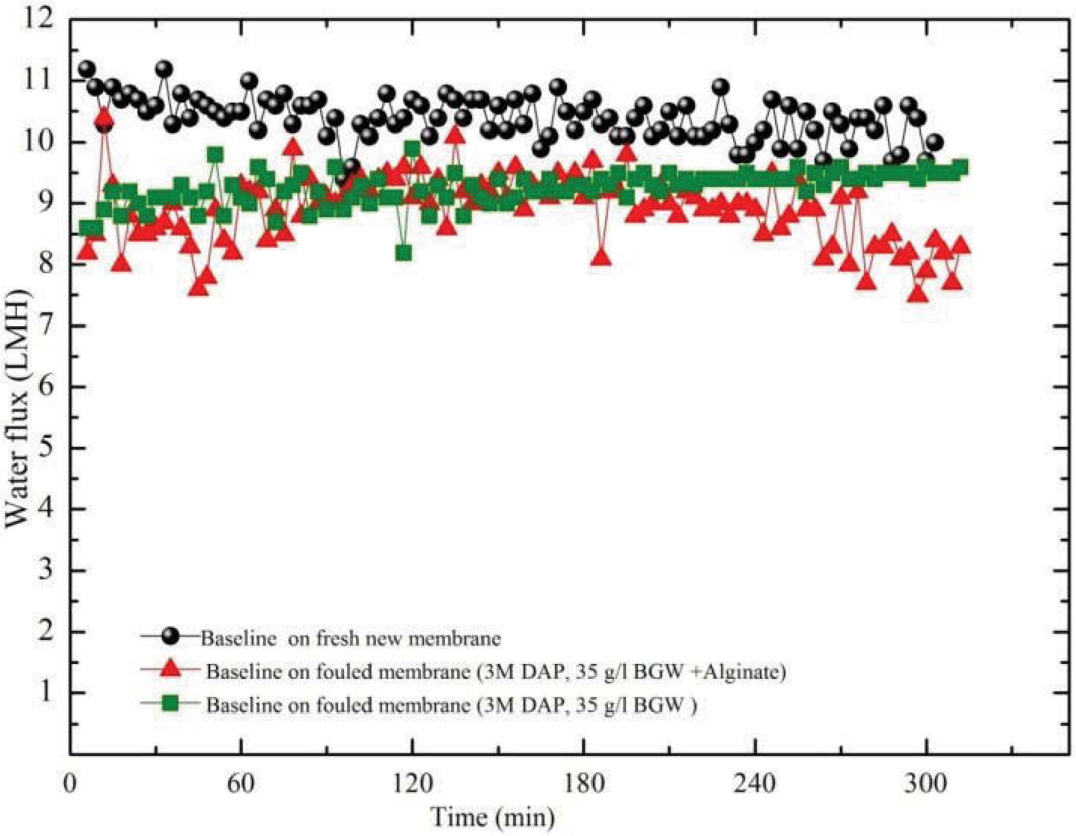


Figure 5.14: Comparison of baseline experiments before fouling experiment and after fouling experiment with membrane flushing to observe flux recovery rate (Experimental conditions: DS; 1M NaCl, FS: DI water, water cross-flow velocity 400 ml/min, CTA membrane and a temperature: 25±1 °C)

Although a noticeable flux decline was not observed with the other fertilisers as DS other than DAP, it was thought that nucleation to form surface crystals might start due to the long-term operation of the FDFO process. However, for DAP as DS, the water flux could only be restored to about 80% when the normal cleaning regime of 400 ml/min in for 20 min is applied. This shows that a higher cross-flow velocity or longer duration is required to clean the membrane more effectively. Therefore, a higher cross-flow velocity (1600 L/min) was adopted for physical cleaning of the membrane scaled during the FDFO process. Figure 5.15 shows that the flux recovery could increase significantly when a higher cross-flow velocity was adopted for physical cleaning. The water flux also nearly recovered completely when a higher cross-flow velocity was applied for cleaning within the same duration.

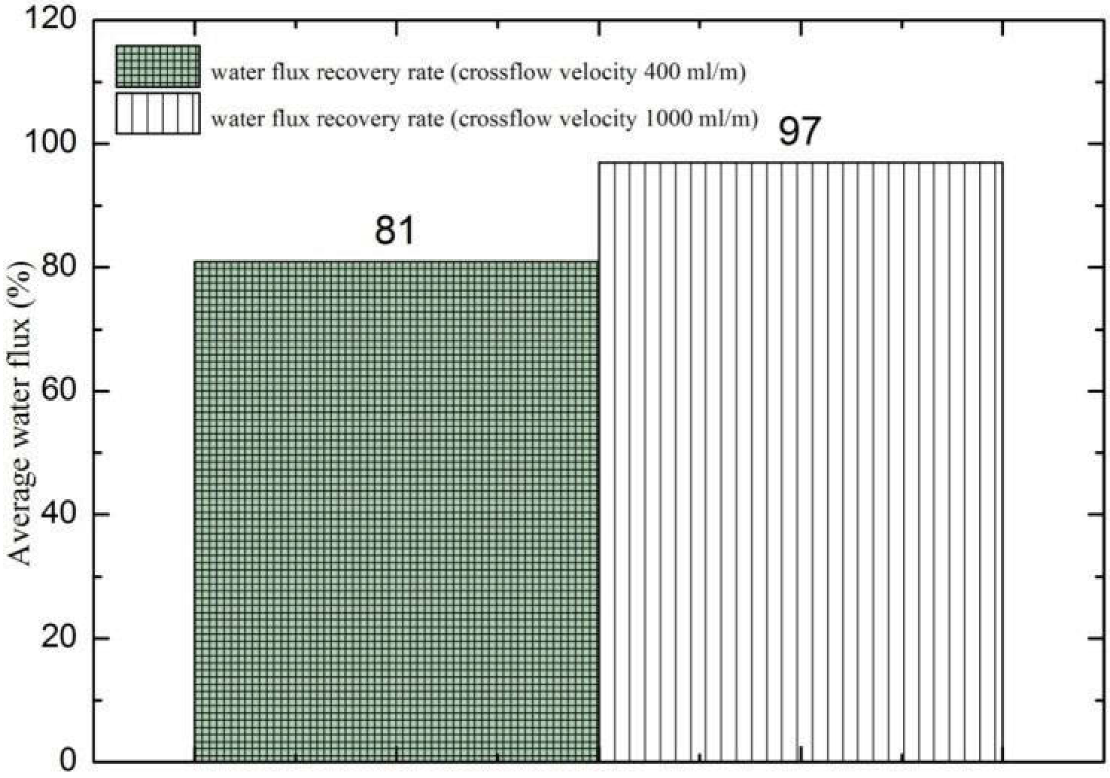


Figure 5.15: influence of cross-flow velocity in water flux recovery rate (Experimental conditions, baseline: DS; 1 M NaCl, FS: DI water, water cross-flow velocity: 400 ml/min, CTA membrane and a temperature: 25±1°C, FDFO operation: DS; 3 M DAP, FS: 35 g/l BGW, organic foulant: alginate)

One of the other observations that can be made from Figure 5.16 is that, when a higher DAP concentration is used, the water flux recovery is slightly lower than when a lower DAP concentration was used. This is consistent with our earlier observation that, when FO is operated at a high flux using higher DS concentrations, the cake layer formed can be more rapid, thicker and denser due to the convective force created by the water flux. Such a cake layer cannot easily be removed when a lower cross-flow cleaning procedure is adopted resulting in lower flux recovery rates. However, irrespective of the DAP concentrations, the flux recovery is almost full when a higher cross-flow rate is adopted. All the above results indicate that, the reverse diffusion of draw solute causes bulk crystallisation on the feed side which results in severe flux decline. Despite this, the flux can be fully recovered by adopting an appropriate physical cleaning regime.

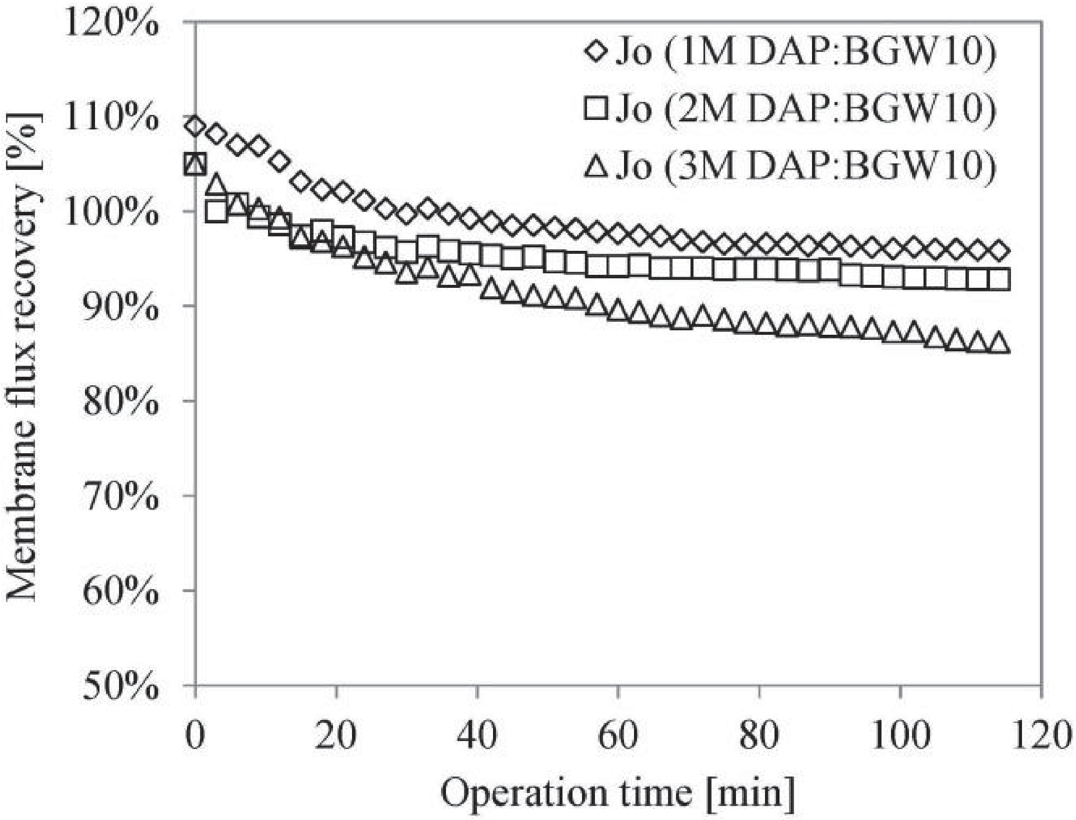


Figure 5.16: Flux recovery of the FO membrane after membrane has been fouled by inorganic foulant, using DAP as DS at different concentrations. All cleaning regimes were conducted at a cross-flow rate of 400 ml/min in for 20 minutes.

5.4.8 Influence of spacer on the scaling potential

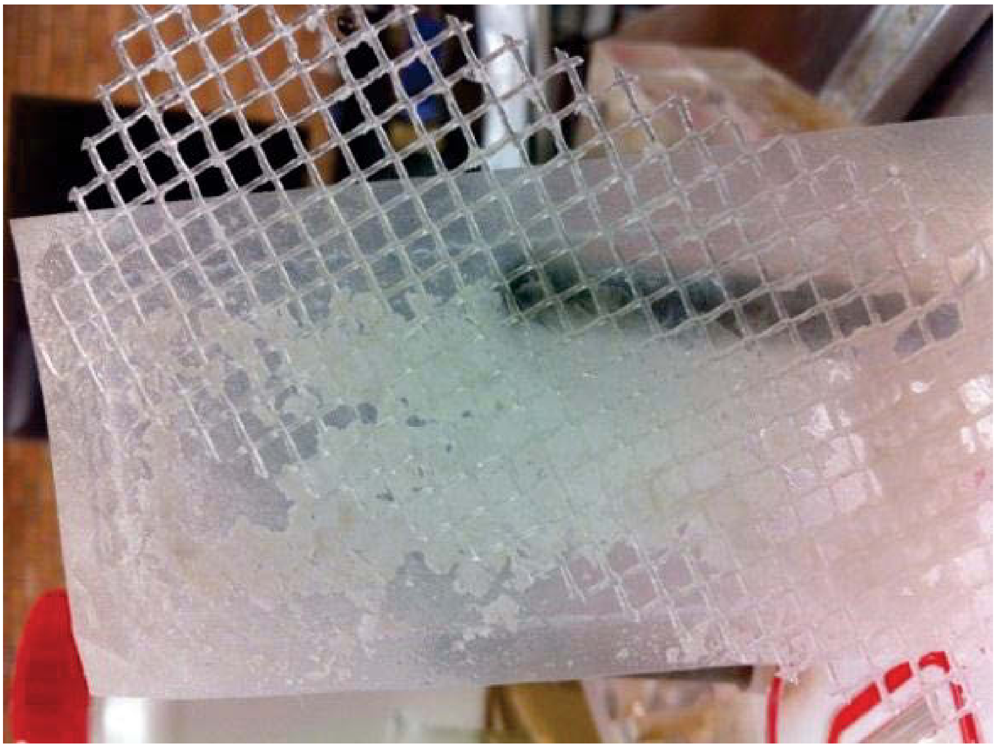
Optimising hydrodynamic conditions is a common approach for fouling control in various membrane separation processes (Goosen et al., 2005, Chan et al., 2011). Optimised hydrodynamic conditions provide better mixing and dispersion to the feed stream and impose additional shear force on the membrane surface, which results in a lower build-up of foulants near the membrane surface. Optimisation of hydrodynamic conditions also improves the efficiency of the membrane processes. However, fouling layers formed during the operation of pressure based membrane processes such as NF and RO are mostly irreversible and, hence, cannot be easily controlled by optimising hydrodynamic conditions (Ang et al., 2011). For this reason, hydraulic fouling control methods are more widely accepted for low pressure membrane systems, such as membrane bioreactors (Psoch and Schiewer, 2006).

In order to evaluate the influence of a spacer in reducing membrane scaling or fouling during the FDFO desalination process using DAP as DS, a feed channel spacer was employed as means to promote hydraulic mixing. A spacer was inserted in the feed channel to promote turbulence near the membrane on the feed side. Feed channel spacers improve mass transfer in the boundary layer near the membrane surface. Several studies have shown that feed spacers play an important role in the membrane system. Baker et al. (Baker et al., 1995) reported that initial fouling deposits were found accumulating alongside the membrane feed channel spacer; these deposits eventually encroached upon the remaining free membrane area.

In this study, fouling and flux decline tests were conducted with and without inserting polypropylene spacers that had diamond-shaped mesh in the feed channel (Figure 5.17).

Fouling experiments were conducted with 3M DAP as DS and 35 g/l BGW as FS using CTA FO membrane under FO mode with and without spacer on the feed side. The results in Figure 5.18 indicate that the presence of feed channel spacers caused more severe membrane scaling/fouling than without spacers. The higher flux decline during fouling runs with spacers (Figure 5.18) clearly demonstrates the enhanced accumulation of foulants on the membrane surface. The scales formed during the FO process probably could not move away from the membrane surface thereby resulting in an increased accumulation of foulant on the membrane surface.

(a)



(b)

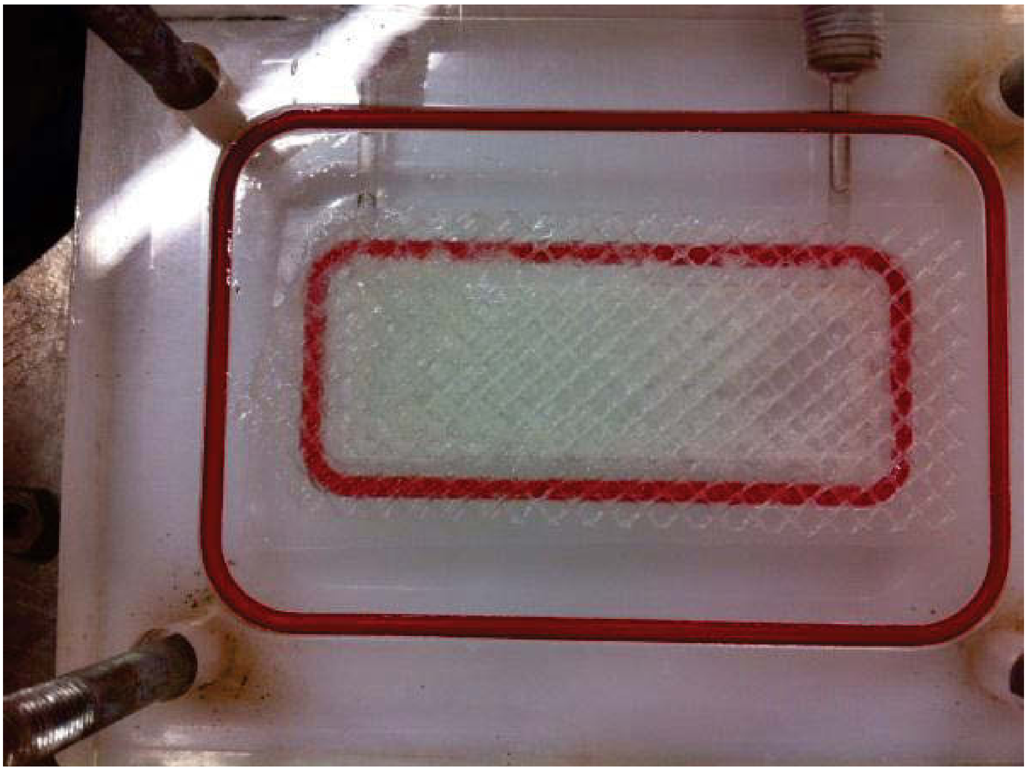


Figure 5.17: Feed spacer as a hydraulic fouling control method, a) membrane fouling with spacer b) spacer in feed side of membrane in membrane cell

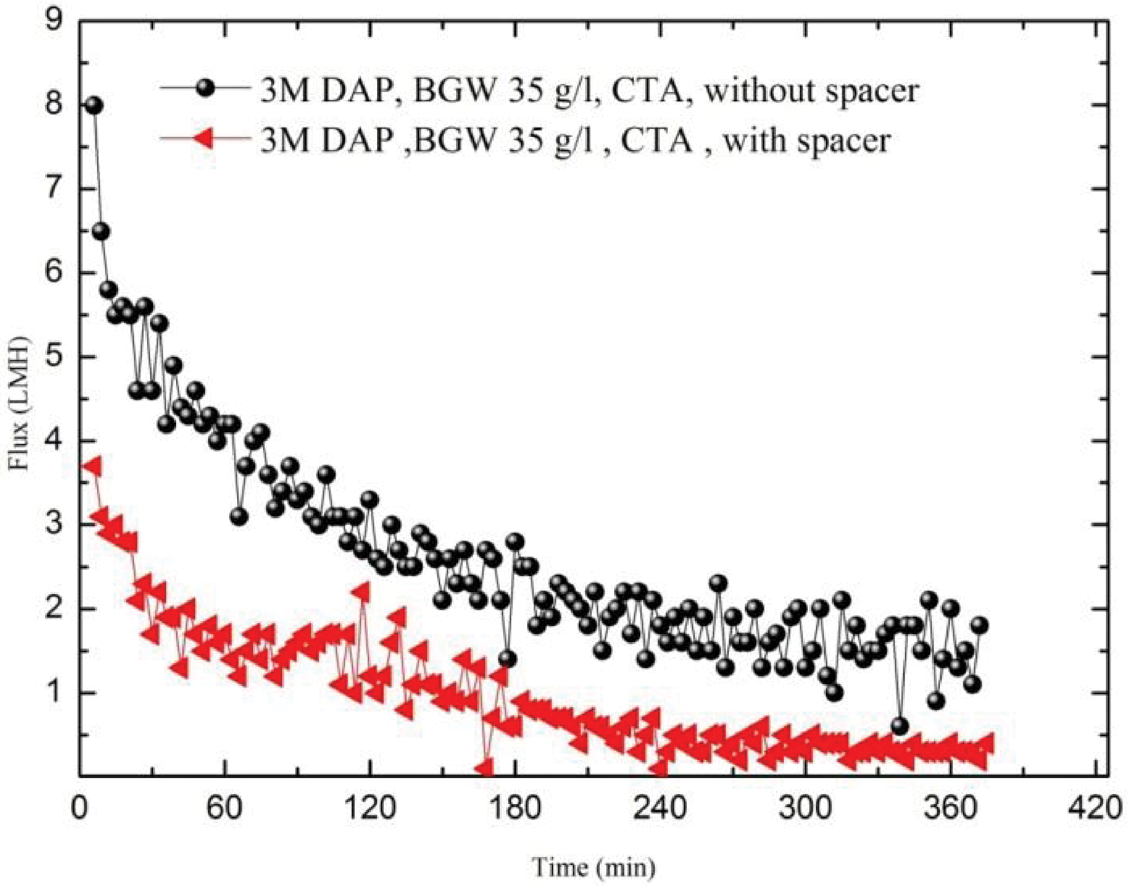


Figure 5.18: Impact of feed spacer on FO fouling ring FDFO process

5.5 Conclusions

In this study, the severe flux decline due to inorganic scaling in the FDFO process during the desalination of brackish groundwater using DAP as DS has been investigated. The study also evaluated the effectiveness of physical cleaning on the membrane flux recovery. The following inference has been drawn from this study:

- When FDFO is applied for the desalination of brackish groundwater containing multivalent ions, it is important to consider the influence of the reverse diffusion of draw solute on the scaling and flux decline potential.

- Reverse diffusion of draw solutes played a significant role on membrane scaling and flux decline during the FDFO desalination of BGW using DAP as DS.

- Membrane autopsy using SEM , EDS and XRD indicates that magnesium phosphate, magnesium ammonium phosphate or struvite, and calcium phosphate (hydroxylapatite) were mainly responsible for membrane scaling when DAP is used as DS with BGW

- The flux decline due to scaling was more severe for the FO process than in the PRO process. This is unexpected and is likely to be caused by the reduced reverse solute flux in the PRO process. This is because of the higher draw solute rejection as the membrane active layer is negatively charged under the alkaline pH offered by DAP DS.

- One interesting finding in this study is, the extent of fouling with Mg^{2+} in BGW was not as severe as the ones observed with Ca^{2+}, even though both were divalent ions. Also, the concentration of magnesium in FS is much higher than the concentration of calcium.

- The presence of feed spacer enhances scaling and leads to more flux decline. Physical cleaning was observed to be very effective in restoring the water flux although the cross-flow velocity played a significant role in the percentage of flux restored.

CHAPTER 6

University of Technology Sydney

Faculty of Engineering & Information Technology

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Fertiliser drawn forward osmosis desalination has recently been studied as one of the most feasible applications of the FO process for irrigation. This study has investigated the potential problems of membrane scaling and fouling in the FDFO process during the desalination of brackish groundwater. The major factors responsible for the performance of FDFO water flux behavior were thoroughly investigated and their implications for the overall process were discussed. The major factors assessed include membrane properties, DS properties and FS properties. The influences of all these factors were measured in terms of water flux decline. Six commercially available fertilisers (potassium chloride, potassium nitrate, ammonium sulphate, monoammonium phosphate or MAP, diammonium phosphate or DAP, calcium nitrate) were selected as DS to observe the effects of different fertilisers in water flux behavior during the FDFO process. A membrane autopsy was also conducted to identify the inorganic scaling formed on the membrane surface. Foulants were analysed using SEM, EDS and XRD.

Most fertilisers, with the exception of DAP, showed a gradual decrease in the water flux over time. This gradual decrease in the water flux is because of the decrease in the driving force (osmotic pressure difference) over time. However, a rapid decline in water flux observed for DAP as DS is quite in contrast to the other DS used. In fact, after about 4 hours of operation, the water flux rapidly declined to almost zero. These results indicate that, long-term observation of the performance of the fertiliser DS is important as some of the DS could promote membrane scaling and fouling of the membrane. Such significant flux decline was not observed during the short-term experiments in the laboratory experiments using BGW in previous studies.

DAP with one of the highest osmotic pressures amongst the six selected fertiliser solutions produced unexpected water flux behavior with severe flux decline and significant membrane scaling during the FDFO desalination process. EDS results of the scaled membrane show that the scaling layer is composed of a large components of Na, Ca, Mg and P. Other than P, all other elements shown are already present in the FS and are hence related to the feed properties. The presence of P in the scaling layer on the active layer side of the FO membrane shows that the reverse diffusion of DAP from the DS might have played a key role in the formation of scales. The XRD results indicate that the scales formed on the membrane surface are mainly composed of magnesium phosphate ($MgHPO_4$) and magnesium ammonium phosphate ($MgNH_4PO_4.6H_2O$) or struvite. These insoluble compounds are formed because of the reverse diffusion of DAP as DS towards the FS during the osmotic process which then reacts with the magnesium ions present in the FS.

This study confirms that Ca and Mg are mainly responsible for the formation of the scales during the FO process using DAP as DS and BGW as FS. When one of the ions Mg or Ca was removed from the FS, the water flux decline was still observed although the flux decline was more severe when the Mg ion was removed and only Ca was present as a precursor. This indicates that Ca is responsible for more severe fouling than Mg during the FDFO process with DAP even though both are divalent ions.

This work also reveals that besides the selection of a suitable fertiliser as DS during the long term FDFO process, selecting an appropriate membrane for the selected fertiliser is also essential. The interaction between fertiliser properties and membrane characteristics has a significant bearing on water flux behavior.

Alginate, albumin (BSA), and humic acid (HA) were chosen as model organic foulants to study the effect of combined fouling in water flux behavior during the long term operation of the FDFO desalination process. Alginate as organic foulant aggravates inorganic scaling and water flux decreases more than 30% on the CTA membrane during the FDFO desalination process using DAP as DS.

Physical cleaning with cross-flow rates similar to the normal FDFO process was adopted to evaluate the effectiveness of restoring the membrane flux after inorganic scaling. The flux recovery was about 80-97% depending on the type of the DS. However, when the cross-flow rate was increased, the water flux restored to almost full irrespective of the type of DS and DS concentration used.

6.2 Recommendations

Membrane fouling due to inorganic scaling becomes an issue that affects the performance of the FDFO desalination process. This fouling can influence the process by several factors including feed composition, the types of fertilisers used, and the operating conditions. As a result of this scaling and fouling study in the FDFO desalination process for the desalination of BGW, several recommendations for future studies can be outlined:

- Additional long term fouling experiments need to be performed on other fertilisers to confirm the results obtained from preliminary testing.
- More controlled experiments are required to clearly distinguish both the effects of organic and inorganic foulants on the membranes, as well as to develop possible relationships based on surface properties.
- Membrane properties including hydrophobicity and functional groups need to be further characterized and verified through various analytical techniques. A clear picture of the processes involved and more thorough study of surface properties using various sophisticated analytical techniques, specifically changes to functional groups, would greatly increase the level of understanding on the correlation between fouling potential and membrane surface chemistry.
- It is likely that scaling could occur within the membrane support structure. This phenomenon is possible when the feed rejection is lower and the diffusion of feed solutes towards the support layer meets the DS species that together may form precipitates that in turn form scaling compounds. The potential effects of such an occurrence also require further investigation, because there is a chance that the FDFO desalination process could result in an acceleration of ICP effects.

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