by

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Forward Osmosis in Reverse Osmosis Concentrate Management

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

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Certificate of Authorship

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

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Shahzad Jamil

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Table of Contents

Abstract

The production of fresh water and the disposal of wastewater are the major challenges of the last few decades. Reverse osmosis (RO) membrane plants are used extensively for brackish water desalination and industrial water purification. These plants operate at about 75% product water recovery so that about 25% of feed water is wasted as concentrated brine. The large quantities of concentrated brine generated has a disposal problem especially when the plants are located inland. Because of high disposal costs there is need to re-use and conserve water. RO reject concentrate (brine) is being increasingly processed to recover additional potable water. In order to achieve higher recoveries, therefore, alternate processes are used. Out of them forward osmosis is attractive.

FO water desalination technique uses the natural osmotic pressure of the draw solute to drive osmosis rather than hydraulic pressure. Fertilizer drawn forward osmosis (FDFO) has been applied as a low cost water desalination option for agriculture purposes. This technique is further investigated by applying pressure on feed solution to enhance water permeate flux, which is called pressure assisted fertilizer drawn forward osmosis (PAFDO). PAFDO can enhance final dilution of the fertiliser draw solution beyond osmotic equilibrium concentration. In simple terms, this technique can be considered combination of FO and low pressure reverse osmosis RO. Due to the low cost desalination potential, the FO and PAFO processes have gained attention of the research community.

Reverse osmosis concentrate (ROC) produced in water reclamation and desalination plants can endanger the environment if it is not treated before discharge. Volume minimisation of ROC can help in its easy disposal. The study examined the use of

forward osmosis (FO and PAFO) with and without granular activated carbon (GAC) fixed bed adsorption pretreatment for volume minimisation of ROC and removal of organic micropollutants.

In this study FO and PAFO were assessed in treating reverse osmosis concentrate using a low concentration of (KCl) as fertiliser DS. A low concentration of KCl (0.25 M) was chosen as DS and it was diluted to 0.14 M KCl during the FO operation due to transport of water permeate flux from feed solution. This diluted KCl solution can be used for direct fertigation, as the past studies showed successful use of 10 Kg/m^3 (≈0.13 M KCl) for fertigation.

Forward osmosis (FO) and nanofiltration (NF) membranes were tested to treat the ROC for possible water reuse. Due to very small pore sizes of FO membranes were used in nano-filtration mode to treat ROC from water reclamation plant. Commonly used NF membrane was good option for removing for organic compounds including micropollutants from wastewater however, most of inorganic compounds passed through the NF membrane. Since the FO membranes have pore size less than most of NF membranes, they also removed inorganic ions present in ROC. In this way the resultant permeate flux was able to be recycled back to RO unit to increase overall efficiency of the plant.

Fouling and scaling is an important and inevitable phenomenon in FO membranes as well. Lower membrane fouling and/scaling implies more product water, less cleaning and longer membrane life, thereby reducing operational and capital costs. It was observed that scaling and fouling were not fully reversed in FO/PAFO by physical cleaning. However, the physical cleaning followed by chemical cleaning could almost fully restore the activity of the membrane.

In this study, the membrane bioreactor (MBR) and granulated activated carbon were used as pretreatment methods to curtail organic fouling of the membrane. Both these pretreatment processes were proved to be successful to reduce total organic carbon of ROC including a majority of micropollutants. Moreover, inorganic carbon of ROC was reduced by acid pretreatment. These pretreatment processes resulted in high permeate water flux and less membrane fouling.

Keywords: Pressure assisted forward osmosis, Nano-filtration, chemical cleaning, membrane, Membrane bioreactor.

Journal Articles Published

1) **Jamil, S.,** Jeong, S. & Vigneswaran, S. 2016, 'Application of pressure assisted forward osmosis for water purification and reuse of reverse osmosis concentrate from a water reclamation plant', Separation and Purification Technology, vol. 171, pp. 182-90.
2) **Jamil, S**., Loganathan, P., Kazner, C. & Vigneswaran, S. 2015, 'Forward osmosis treatment for volume minimisation of reverse osmosis concentrate from a water reclamation plant and removal of organic micropollutants', Desalination, vol. 372, pp. 32-8.
3) Kazner, C., J**amil, S**., Phuntsho, S., Shon, H., Wintgens, T. & Vigneswaran, S. 2014, 'Forward osmosis for the treatment of reverse osmosis concentrate from water reclamation: process performance and fouling control', *Water Sci. Technol.* , vol. 69, no. 12, pp. 2431-7.

Conference papers and presentations

1. **Jamil S**., S.Jeong , and S. Vigneswaran Pressure Assisted Forward Osmosis for treating reverse osmosis concentrate from water reclamation plant, IWA World Water Congress & Exhibition 9-14 October 2016 Brisbane Australia.

2. **Shahzad Jamil**, P. Loganathan, S. Vigneswaran; Forward Osmosis and GAC adsorption hybrid system for RO concentrate volume minimisation and organic micropollutants removal, *Proceedings of the 9th IWA Micropol and Ecohazard Conference 22 - 25 November 2015, Singapore.*

3. ***Shahzad Jamil**, C. Kazner, S. Vigneswaran* Reverse osmosis concentrate treatment using forward osmosis for volume minimisation leading to zero liquid discharge *The 4th International Conference on Membrane Technology (3-6 Dec. 2014), HoChi Minh City Vietnam.*

4. **Shahzad Jamil**, Christian Kazner, Sherub Phuntsho, Hokyong Shon, Thomas Wintgens2 and Saravanamuth Vigneswaran, Forward Osmosis for the Treatment of RO Concentrate from Water Reclamation: Process Performance and Fouling Control, 7th IWA Specialized Membrane Technology Conference · Toronto, Canada · 25 – 29 August 2013.

5. Kazner, C., **Jamil, S**., Yapici, N., Fujioka, T., Listowski, A., Khan, S., Nghiem, L.D., Vigneswaran, S. & Wintgens, 'Behaviour of organic micropollutants in treatment of ROC from water reclamation towards zero liquid discharge', *Proceedings of the 8th IWA Micropol and Ecohazard Conference, EAWAG, Zurich, Switzerland*, pp. 114–5.

Nomenclature

ICP	:	Internal concentration polarization
FDS	:	fertilizer draw solution
TOC	:	Total organic carbon
GAC	:	Granulated activated carbon
MDL	:	Method detection limit
OMs	:	Organic micropollutants
ROC	:	Reverse osmosis concentrate
TIC	:	Total inorganic carbon
Jw	:	water flux (L/m^2 h)
P	:	hydraulic pressure (bar)
t	:	membrane thickness (µm)
PAFO	:	Pressure assisted forward osmosis
PAFDO	:	pressure assisted fertilizer drawn forward osmosis
TDS	:	Total dissolved solids
MF	:	Microfiltration
UF	:	Ultrafiltration
NF	:	Nanofiltration
RO	:	Reverse osmosis
FO	:	Forward osmosis
FS	:	Feed solution
DS	:	Draw solution
AL	:	Active layer
SL	:	Support layer
MBR	:	Membrane biological reactor
CP	:	Concentration polarization
ECP	:	External concentration polarization
ICP	:	Internal concentration polarization
RSF	:	Reverse solute flux
AL-DS	:	Active layer – draw solution
AL-FS	:	Active layer - feed solution
DI	:	Deionized
MD	:	Membrane distillation
PSf	:	Polysulfone
PES	:	Polyethersulfone
PA	:	Polyamide
CTA-ES	:	Cellulose triacetate with embedded polyester screen
TFC-ES	:	Thin flim composite with embedded polyester screen
PSF	:	Polysulphone
MWCO	:	Moleculor weight cut-off
Norm.	:	Normalized
VMD	:	Vacuum Membrane Distillation
ZLD	:	Zero liquid discharge

BSA	:	Bovine serum albumin
HA	:	Humic acid
TOC	:	Total organic carbon
SEM	:	Scanning electron microscope
LMH	:	$L/m^2/h$
HTI	:	Hydration Technology Innovations
DBPs	:	Disinfection By-Products
BTSE	:	Biological treated wastewater
WWTPs	:	Wastewater treatment plants

List of Symbols

A	:	Water permeability coefficient (L .m^{-2} .h^{-1}.bar^{-1})
B	:	Salt permeability coefficient (m.s^{-1})
C	:	Solute number density (L^{-1})
c	:	Solute concentration
D/Ds	:	Diffusion coefficient (m^2 s^{-1})
Dh	:	Hydraulic diameter (m)
D	:	Salt diffusion coefficient
I	:	Intrinsic membrane structural properties
J_s	:	Solute flux (g.m^{-2}.h^{-1})
J_w	:	Water flux (L m^{-2} h^{-1})
J_w, sp	:	Specific water flux (L m^{-2} h^{-1} bar^{-1})
k	:	Mass transfer coefficient
M	:	Solute molar concentration (mol. L^{-1})
M	:	Molar concentration of the solution
Mw	:	Molecular weight (g.mol^{-1})
N	:	Moles of solute (mol)
n	:	Van't Hoff factor
P	:	Applied hydraulic pressure (bar)
Re	:	Reynolds number
Sc	:	Schmidt number
T	:	Absolute temperature (in K)
t	:	Thickness of the membrane (m)
Δt	:	Time interval (h)
ΔV	:	Volume change (L)
ΔP	:	Pressure change (bar)
Sh	:	Sherwood number
μ	:	Conductivity (mS/cm)
S	:	Structural parameter
σ	:	rejection coefficient
π	:	Osmotic pressure

Superscripts/subscripts

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

Greek letters

π	:	Osmotic pressure (Pa)
φ	:	Osmotic pressure coefficient
σ	:	Reflection coefficient,
ε	:	membrane porosity
β	:	van't Hoff coefficient
τ	:	pore tortuosity

List of Figures

List of Tables

U T S

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Chapter 1

INTRODUCTION

1.1 Background

Throughout the world a trend to intensified use of desalination and water reuse as a means to reduce current or future water scarcity can be observed. Water scarcity, which occurs not only in arid regions, may be characterised as a mismatch between water supply and water demand: Pollution and exploitation of groundwater aquifers and surface water have led to a decrease of quantity and/or quality of available natural water resources in many regions. The ongoing growth of population, industry and agriculture further increases water demand. In addition, higher living standards, especially in industrialized countries, result in higher per capita water consumption and in intensified water scarcity.

1.2 Reverse osmosis

Water reuse systems based on dense membrane treatment such as reverse osmosis (RO) are being progressively applied to meet water quantity and quality requirements for a range of urban and environmental applications. For sustainable water reclamation, water reuse systems must address three issues: (1) the product water must be stable and high quality; (2) water production must be at relatively low cost; (3) the large volume of reverse osmosis concentrate (ROC) must be disposed in an ecologically friendly manner, which is of particular issue for inland plants. The ROC in wastewater reclamation plant usually represents approximately 10-20% of the feed water flow, depending upon the RO recovery ratio and contains the organic and inorganic contaminants at higher concentrations (Bagastyo et al., 2011a). The amount of ROC wastewater requiring disposal must be as minimum as possible (near zero-discharge); the recovery of high quality water should be as high as possible.

1.3 Reverse osmosis concentrate

Management issues related to proper treatment and disposal of ROC are an important aspect of sustainable water practice. The ROC is a significant component of the water treatment process and poorly managed treatment and disposal of ROC causes significant adverse consequences. In St Mary water recycling plant in New South Wales, the water inflow to RO plant is as high as 58 meglitres (ML) per day. This produces 7 ML (or

7000 m^3) of ROC per day. Even in a small to medium size water reclamation plant in Sydney, 2000 KL of water is treated by RO unit and around 300 kL of ROC is produced daily. The ROC consists of high level of organics (20-30 mg/L of DOC which is mainly refractory organics) and inorganic salts (Cl^-= 600-800 mg/L, Na^+= 400-500 mg/L, Ca^{+2}=100-200 mg/L, K^+= 100 mg/L). Among the organics, more than 60 % are humic compounds. The discharge of the ROC containing all the retained compounds into the natural water bodies threatens aquatic ecosystems. The most pronounced effects are eutrophication, pH value variation, accumulations of heavy metals and the acquisitions of the sterilizing properties of disinfectants (Perez-Gonzalez., 2012).

Treatments and sustainable management of ROC are still under development to increase the applicability of high quality water reuse systems, especially in inland plant locations. It has been shown to be technically feasible to achieve zero liquid discharge processes for ROC using processes such as thermal evaporators, brine concentrators, and spray dryers (Greelee et al., 2009). Other concepts involve eletrodialysis (ED) and eletrodialysis reversal (EDR) coupled with evaporation wind aided intensified evaporation (WAIV) (Korngold et al., 2005). However, further research is required to reduce capital and operational cost (Greenlee et al., 2009) and of these processes and make them applicable to a large scale scenario.

The cost of ROC waste disposal can be minimized and made valuable by reclaiming the ROC with the aim of producing salts from the solutes and recycling the water the treatment system (Khan et at., 2009). Suitable technologies for recovery of high salt concentration from the ROC include forward osmosis (FO) and membrane distillation (MD). They offer low complexity and sustainable energy consumption (Martinetti et al., 2009). In FO system, however, there are still challenges associated with the selection of an appropriate draw solution and its additional treatment (Chekli et al. 2012). On the other hand, MD has a high water recovery 80-90 % especially when coupled with crystallization (Ji et al., 2010). However, an industrial-scale application of MD technology has not yet been established (Guillen-Burrieza et al., 2012).

1.4 Research motivation and significance

The production of fresh water and disposal of wastewater are the major challenges of this century. Shortage of potable water supply and increasing demand in developing

countries due to rapid population growth and industrialization are among the major reasons for the worsening water situation (UN world water report 2006).

Reverse osmosis (RO) is an effective barrier in water production systems when the removal of dissolved contaminants or salts is needed to achieve high quality fresh water. RO plant leaves behind unwanted stream in the form of reverse osmosis concentrate (ROC). This stream usually consists of 10-30% of the influent for surface water and 50-75 % of the influent for seawater. While coastal communities have the opportunity to discharge ROC in the ocean, the inland facilities have to rely upon controversial alternatives, such as surface water or sanitary sewer discharge, evaporation ponds, deep well injection and land applications. These options are costly, not environmentally sustainable. Therefore, proper handling and disposal of the ROC have become critical issue, particularly for an inland community (Adam et al., 2007).

The main focus of this study is to investigate the effects of operating parameters/conditions for the smooth running of forward osmosis (FO) and pressure assisted forward osmosis (PAFO) operation as an emerging and novel technology. FO has significant advantage over the reverse osmosis (RO) desalination process especially in terms of energy consumption. Although FO and PAFO desalination is yet to be commercialized mainly due to the lack of suitable FO membranes and a suitable draw solution (DS), several significant research breakthroughs have recently been reported with to FO membrane fabrication from Hydration Technology Innovations (HTI) such as CTA-ES, CTA-NW and TFC-ES (www.htiwater.com). The separation and recovery of the DS still remains a significant challenge for drinking water applications. However, some researchers have tried blended fertilizers as solutions as DS so that it can be used for fertigation without the need for recovery of draw solute, however this study is still in trial phase (Phuntsho et al. 2012).

The FO process works on the principle of the natural osmotic gradient between two solutions being at different concentrations, where they are separated by a semi-permeable membrane. When saline feed water and the highly concentrated solution (referred to as draw solution or DS) are separated by a semi-permeable membrane, water moves from the saline water (lower solute concentration) to the concentrated DS (higher solute concentration), while retaining the solutes on both sides of the membrane. The main feature of the FO process is the transport of water across a semi-permeable

membrane which does not require hydraulic pressure. However, in PAFO a slightly elevated (200-400 kPa) pressure is applied on feed side leads to higher flux, thus higher water production but is significantly less than that in the RO process.

The separation and recovery of the DS requires an additional processing unit, which consumes energy and therefore still remains a significant challenge for high quality purposes such as drinking water applications. The success of FO desalination for potable purpose depends entirely on how easily and efficiently the draw solute can be separated from the water.

1.5 Research Objectives and Scope

In this study, an integrated reverse osmosis concentrate (ROC) treatment concept is implemented at minimal cost and minimum environmental impact. Here, the concentrate treatment combines the removal of bulk organics and organic micropollutants with desalination using FO (Figure 1.1).

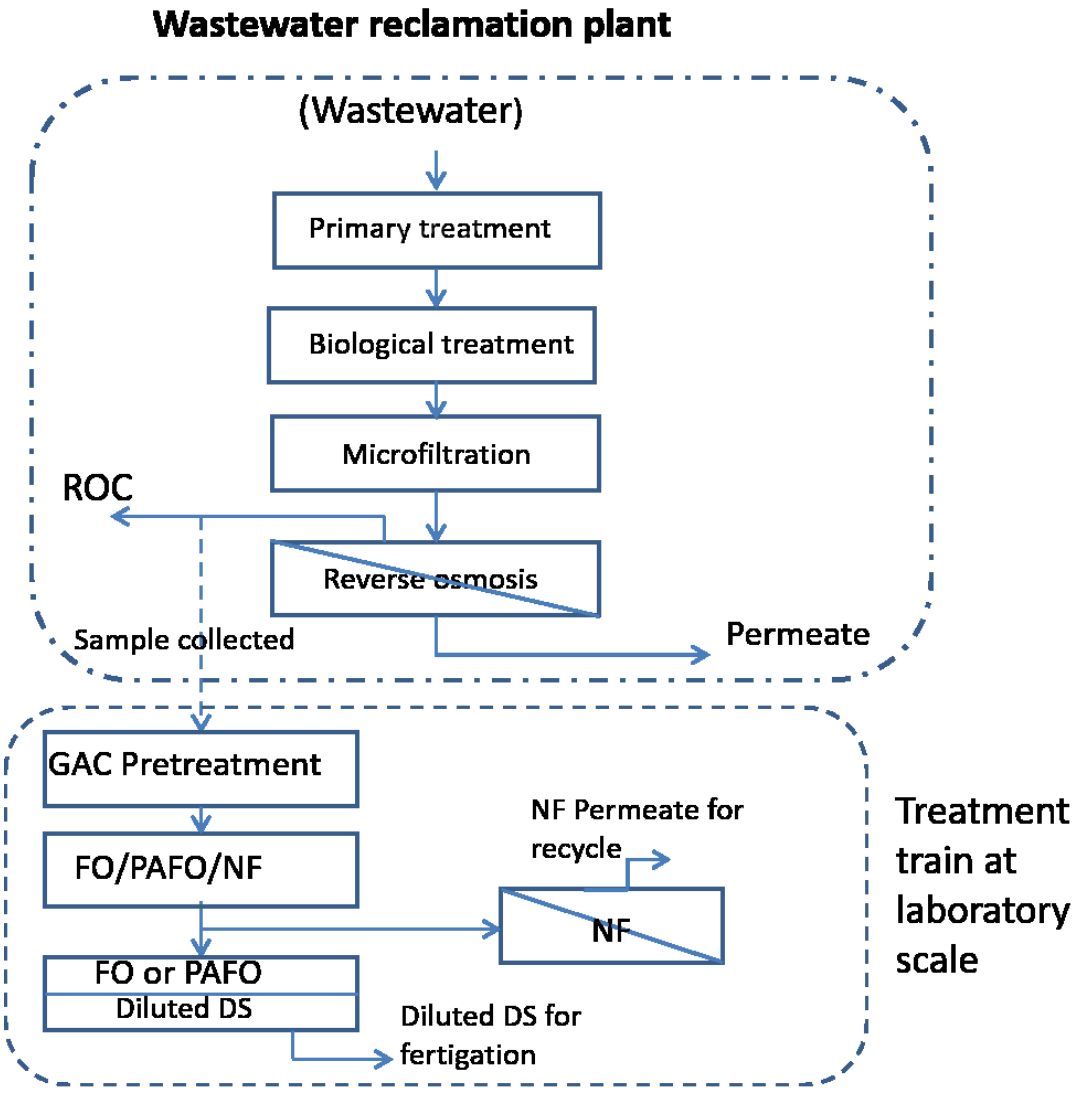

Fig.1. 1 Schematic of proposed integrated water reuse concepts for inland locations.

In this research work, Forward Osmosis (FO), pressure assisted forward osmosis (PAFO) and Nanofiltration (NF) treatment were experimented for the further

concentration of RO concentrate derived from the Sydney Olympic Park Authority's (SOPA) water Reclamation and Management Scheme (WRAMS). ROC from this plant is high in organic micropollutants, bulk organics besides salinity.

The present study aims to address four major questions concerning the application of FO membranes in the treatment of ROC:

- Identify the optimum operational conditions of forward osmosis, pressure assisted forward osmosis and nanofiltration to reconcentrate the ROC leading to near zero liquid discharge.
- Study the behaviour of different flat sheet FO membranes with respect to flux, fouling behaviour, reverse solute flow, rejection trend of inorganic and organic compounds.
- Investigate the removal of trace organic pollutants such as pharmaceuticals and personal care products (PPCPs) with FO membranes operation only and with pretreatment such as adsorption and membrane bioreactor. The effectiveness of pretreatment was studied in terms of FO membrane fouling reduction.

Following are the objectives of this study:

- To investigate FO as a promising technology to minimize the volume of ROC and produce near zero liquid discharge which is easy to handle for safe disposal

- To study the fouling behaviour of FO membranes with respect of organic fouling and inorganic scaling and study of membrane cleaning strategies

- To investigate the removal of organic micropollutants from ROC using FO with and without granular activated carbon (GAC) pretreatment

- To investigate the relative merits of PAFO over FO in increasing the production of permeate flux to further concentrate ROC to minimize its volume and optimize the concentration of draw solution (KCl) for direct utilization

- To investigate the relative merits of NF process using FO membranes in NF system in ROC treatment

1.6 The thesis is structured as follows:

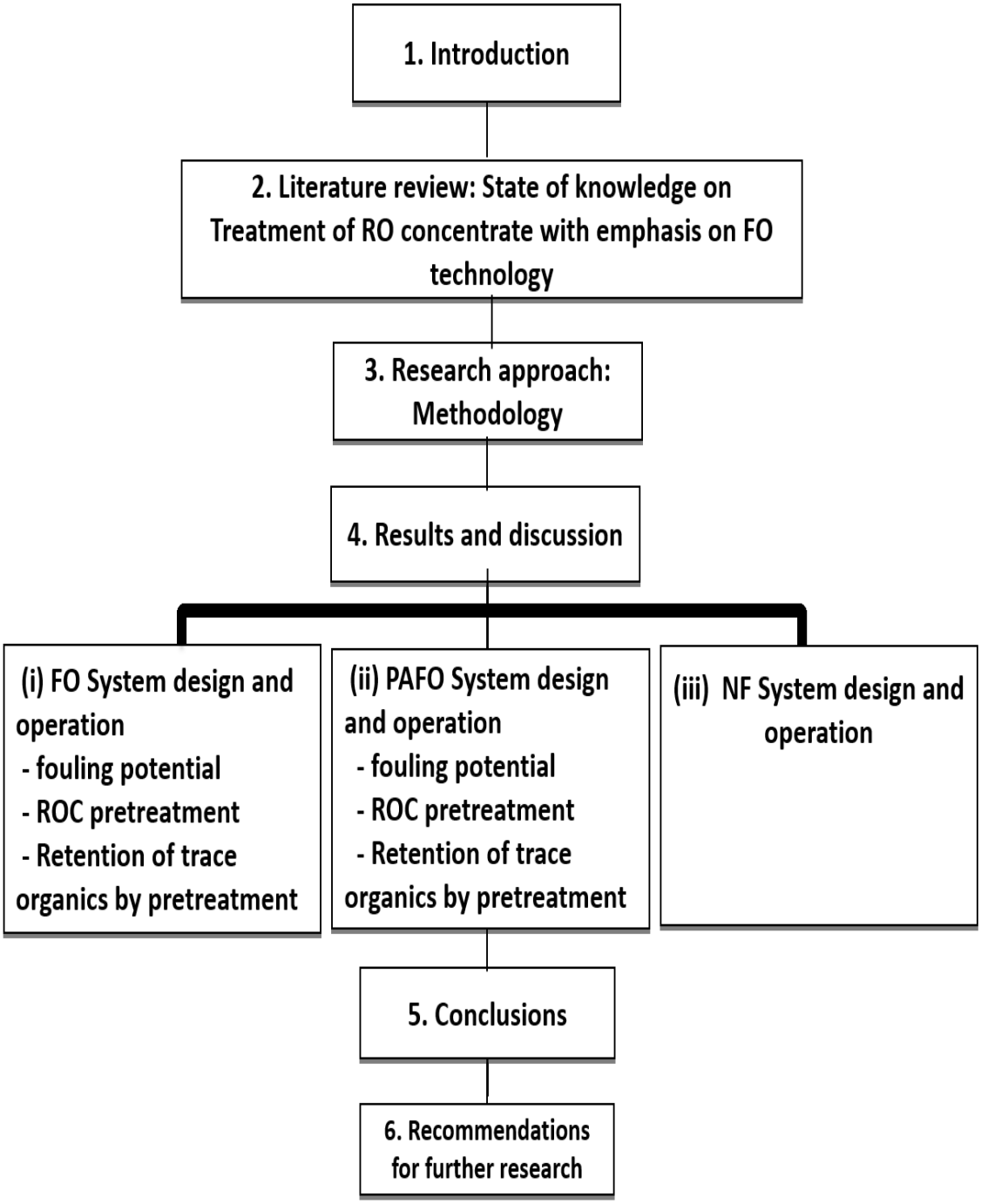

Fig.1. 2 Structure of the thesis

The study looks into main aspects: FO fundamental characteristics, comparison of the different flat sheet membrane performances in FO, PAFO and NF systems; effects of operating conditions; fouling potential and membrane cleaning strategies.

The structure of the thesis is as follows:

Chapter 1. Introduction

Chapter 2. Literature review: State of knowledge on Treatment of RO concentrate with emphasis on FO, PAFO and NF technologies

Chapter 3. Materials and methods used in this study.

Chapter 4. Forward Osmosis treatment for volume minimisation of reverse osmosis concentrate from a water reclamation plant and removal of organic micropollutants

Chapter 5. Application of pressure assisted forward osmosis for water purification and reuse of reverse osmosis concentrate from a water reclamation plant

Chapter 6. Use of forward osmosis membrane at nanofiltration mode for reverse osmosis concentrate treatment

Chapter 7. Membrane bioreactor as pretreatment to Pressure assisted Forward osmosis hybrid system for water purification of synthetic reverse osmosis concentrate

Chapter 8. Summarises of the main findings and general conclusions and recommendations for future research work.

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Chapter 2

LITERATURE REVIEW

2.1 What is reverse osmosis concentrate (ROC)

Reverse osmosis (RO) is widely used to convert seawater and wastewater into fresh water. However, the major drawback of this process is the generation of large amounts of highly concentrated brine as an unwanted by-product (Khan et al 2009). For example, 10–30% of surface water and 50–75% of seawater (based on feed stream) are produced as a wasted reverse osmosis concentrate (ROC). It has been known that ROC discharged can cause environmental problem, particularly for inland facilities (Adem et al 2007). In wastewater reclamation plants, RO is currently being used as a final treatment step after biological treatment followed by micro- filtration (MF) step to obtain high quality water for reuse (Lim et al. 2014). In this case, unwanted stream, ROC is also generated. This ROC is rich in dissolved organic compounds and comprised of significant amount of inorganic salts of Ca^{2+}, Mg^{2+} and SO_4^{2-}. The ROC also contains a broad range of organic micropollutants; such as pharmaceuticals, industrial chemicals and personal care products. This is a major concern in water recycling due to their potentially hazardous effects on human beings and the natural environment Amy et al (2011).

For example, an RO-based advanced water reclamation plant was planned for construction in Canberra, Australia in 2007. However, the sustainable management of ROC remains a major environmental and economic hurdle for the plant and has limited the implementation of the membrane process (Umar et al. 2013). In Queensland, Australia, the Bundamba advanced wastewater treatment plant which is part of Australia's largest water recycling scheme is required to treat its ROC and monitor the nutrients and metal concentration in the effluent prior to its discharge into Brisbane River (Vargas and Buchanan, 2011). The installation of proper systems for the

treatment and management of ROC produced from inland water treatment plants is mandatory in order to safeguard the ecology of receiving water bodies.

2.2 Treatment technologies for reverse osmosis concentrates

There are several conventional and emerging technologies for RO concentrate treatment as well as their process combinations aiming at Zero Liquid Discharge. Treatment technologies on ROC are mainly selected by the location of the plant. In inland plants the traditional options consist of reducing the concentrate volume prior to disposal while in coastal desalination plants RO concentrates could be discharged into the seawater (Tang & Ng. 2008).

The following technologies aim to reduce the concentrate volume to the highest point before disposal with the objective of achieving Zero Liquid Discharge (ZLD). ZLD is the highest point of reducing the concentrate volume and aims at maximum water recovery through several stages of treatment in order to avoid liquid effluent disposal. It recovers valuable compounds from the effluents.

A common solution for concentrate disposal especially for inland desalination plants in arid and semi – arid areas is solar evaporation (Ahmed et al. 2000). The RO concentrate is stored in shallow lined evaporation ponds where water can evaporate by using solar energy and leave behind the retained compounds like salts. The retained compounds are either left in the ponds or removed for disposal (Katzir et al. 2010). Evaporation ponds are easy to construct; surface area and pond depth are the main parameters for maximizing the rate of evaporation. The optimal pond depth ranges from 25 to 45 cm. However, evaporation ponds are not widely used because they require large land areas in places with low evaporation rates and furthermore these evaporation ponds can potentially contaminate groundwater coupled with the risk of leakage underneath the pond (Katzir et al. 2010). The evaporated water is not recovered and the process's productivity is quite poor, typically around 4 L/(m^2·d).

An alternative to natural evaporation is the technique known as Wind Aided Intensified Evaporation (WAIV), which was developed with a less land intensive method to reduce concentrate volumes. WAIV reduces the water volume through the utilization of the drying power of wind without generating small droplets that can cause salt drift. The

RO concentrate recirculates as falling films on vertical hydrophilic surfaces that are largely mounted parallel to the wind direction. The vapour pressure gradient between the wind and the wetted surface drives the evaporation mass transfer from the surface. Compared to solar evaporation, the evaporation rates can be improved by 50 - 90% with WAIV, but the applicability of this technique has been only demonstrated on a pilot scale (Perez-Gonzalez et al. 2012).

Due to conventional treatments like evaporation ponds having several disadvantages, there is a current demand for new alternatives to improve the management of RO concentrates. In the following section emerging technologies for RO concentrate treatment are presented with the focus on those aiming at ZLD.

Membrane distillation (MD) is an alternate technology for concentrate management with high water recovery rate (Ji et al., 2010). MD is an emerging technology, which is an integration of both thermal and distillation and membrane process. In an MD process, the feed water is heated (increasing the pressure) while the low pressure is created on the permeate side of the membrane through cooling system. This forms a vapour pressure difference across a hydrophobic membrane which is driving force of the process. Liquid is prevented from entering the pores of the membrane due to surface tension forces of the hydrophobic membrane. It is then condensed on the permeate side. As the water vapour pressure is not significantly reduced with high salt concentration, this technique is particularly useful for super concentration of ROC (Cath et al., 2004).

Industrial scale application of MD technology has not been established yet. There are only limited studied related to the usage of MD for the treatment of wastewater. ROC and a few related to MD studies have been carried out on ROC from saline wastewater and seawater desalination (Martinetti et al., 2009; Mericq et al., 2010). These studies showed that it was possible to achieve almost 80-90 % water recovery even with feed water containing high dissolved solids value of 7,500-17,500 mg/L.

The combination of Membrane Distillation with Crystallization (MDC) was also investigated with reference to ROC treatment. Carollo (2008) reports that for enhancing the recovery of the ROC chemical softening is applied in the primary RO plant. Conventional softening chemicals such as lime, sodium hydroxide and soda ash are used for the primary ROC to precipitate the hardness and other minerals. A softening

pre-treatment can remove up to 90% of some soluble salts and return the hardness and silica concentration to the original feed of the primary RO plant. The softened water is fed to the secondary desalting process where the total dissolved solids are higher than the primary RO. Consequently, higher feed pressures are required for the operation. Higher recoveries are possible in the secondary desalting step because the upstream softening may result in smaller concentrations of scaling precursors than the primary feed. The limiting factor is the production and disposal of large volumes of solids from chemical softening, the use of high dosages of chemicals and the presence of fine solids from the softening phase that can impact on downstream process performance.

Applying forward osmosis (FO) is an innovative technique that can reduce the concentrate volume. The main advantage of FO is lower energy requirement than RO. The driving force of FO is the osmotic pressure differential across the membrane, which transports water from the less concentrated feed stream to the highly concentrated draw solution. A concentrated and a diluted stream are generated because the membrane is permeable for water and rejects ions and most solute molecules. The draw solution is on the permeate side of the membrane and is diluted as water diffuses from the feed side into the permeate stream. The draw solution is highly concentrated and a wide range of draw solutions can be applied. The effectiveness of the driving force depends on the draw solution. The main criteria for the choice of draw solutions are: firstly, having a higher osmotic pressure than the feed solution; and secondly, easy separation of water from the solvent. Like Membrane Distillation, FO is restricted to laboratory scale to pilot scale. Large-scale applications showed the lack of available robust optimized membranes and also this technique has as inconvenience the need of a draw solute to create an effective driving force that allows water flux (Singh. 2009). The advantages of FO are presented in Figure 2.1.

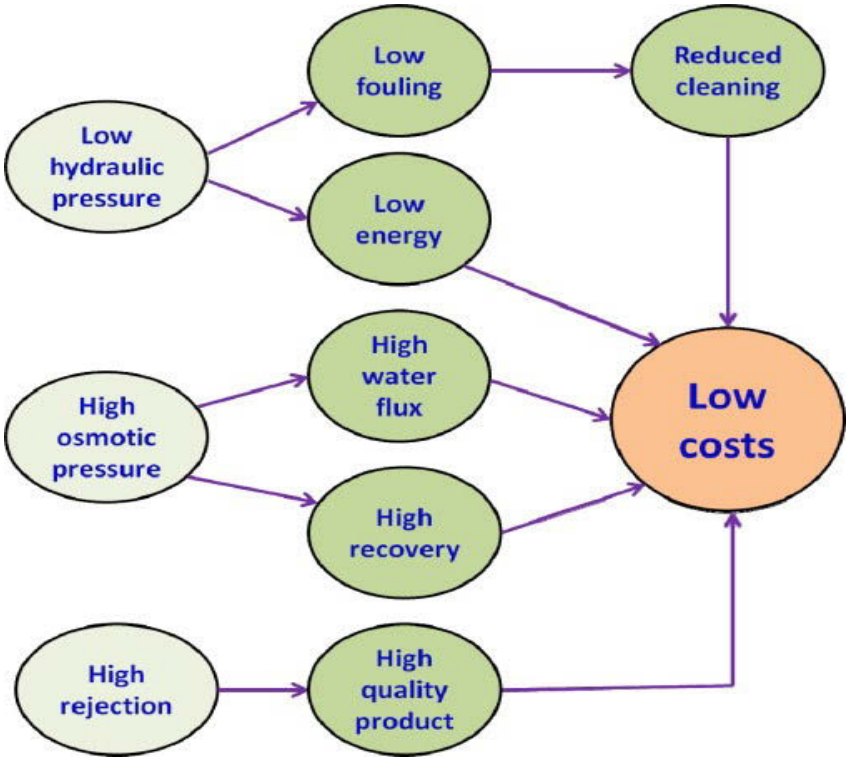

Fig.2. 1 Application of FO in water, energy and life science fields (Zhao et al., 2012)

2.3 Principles of forward osmosis

The FO process works on the principle of osmotic pressure differential between two solutions separated by a semipermeable membrane. The water naturally flows from lower solute concentration is called feed solution (FS) and then moves to a higher solute concentration, which is known as the draw solution (DS) (Fig. 2.2).

The general equation describing water transport in FO, RO, and pressure retarded osmosis (PRO) is described as follows (Zhao et al., 2012):

$$J_w = A\,(\sigma\,\Delta\pi - \Delta P) \qquad (2.1)$$

In this equation Jw is the water flux; A is the water permeability constant of the membrane, ΔP the applied pressure and σ the reflection coefficient. The difference (σ Δπ-ΔP) represents the effective driving force. The driving force in FO comes from the osmotic differential pressure of feed and draw solution so the water flux equation can be represented as follows by (Zhao et al., 2012).

$$J_w = A(\pi_{DS} - \pi_{FS}) \quad (2.2)$$

Here π_{DS} and π_{FS} are the osmotic pressures of feed solution and draw solution respectively.

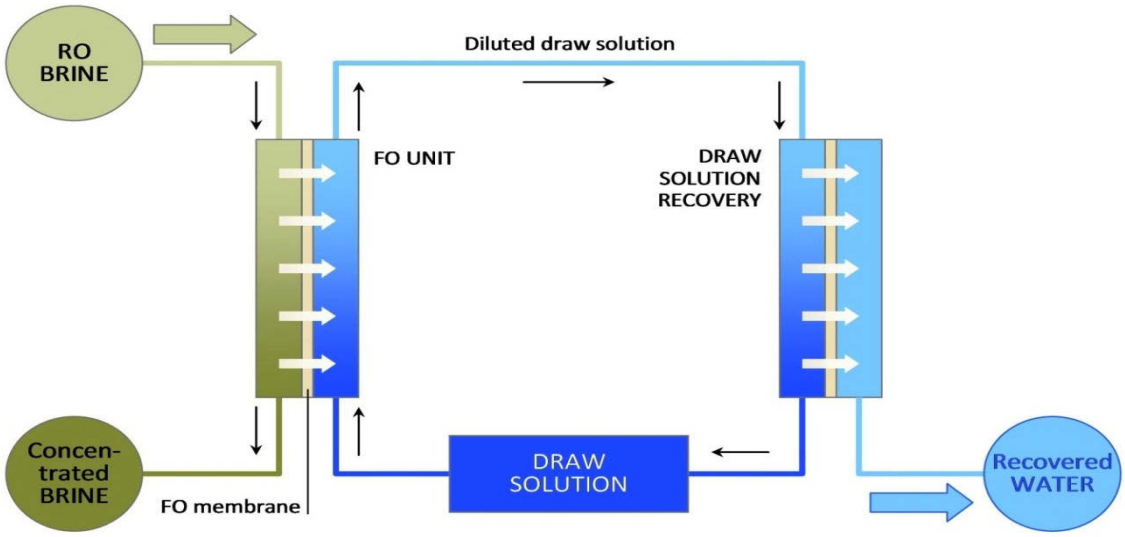

Fig.2.2 Forward osmosis for treating RO brine (Kazner et al., 2013; modified from Cath et al., 2006)

While solute is retained on both sides of the membrane, the salient feature of this process is that the transportation of water across the membrane does not require any additional force. Consequently, the energy consumption in this scenario is significantly less compared to RO (Zhao et al., 2012). Since no hydraulic pressure is required the severity of the fouling issue in the FO process is very less likely to be the major factor. Fouling in the FO process is observed to be reversible by water flushing so this process may not require chemical cleaning (Mi & Elimelech, 2010).

2.4 Principles of pressure assisted forward osmosis

In osmotic membrane processes, water flux is generally very much dependent on applied pressure, osmotic pressure of draw solution and the specific properties of the membrane. However, existing applications refer either on system without applied hydraulic pressure (FO) or systems where hydraulic and osmotic pressures are in opposite direction (RO and PRO). In those osmotic processes, the well-known general

equation governing water transport is based on the solution-diffusion theory (Zhao. et al., 2012; Lee et al., 1981).

$$J_w = A(\Delta P - \Delta \pi_m) \quad (2.3)$$

Where Jw is the water flux ($L/m^2.h$), A is the water permeability constant ($L/m^2.h.bar$), ΔP is the applied hydraulic pressure differential (bar) between the feed (P_F) and the draw solution (P_D) and $\Delta \pi_m$ is the osmotic pressure differential (bar) between feed and the draw solution across the membrane. Thus, it is expected that water flux through the membrane will be enhanced due to combined action of osmotic and hydraulic pressures. The newly developed concept, pressure assisted forward osmosis (PAFO) targets at pressurizing the low conductivity feed solution of FO to improve water permeation and therefore the overall efficiency of the system. As a result, PAFO presents the potential to limit membrane surface area or to further increase the recovery of FO system. For the PAFO concept to be sustainable, the additional energy required to pressurize the feed stream needs to be counterbalanced by significant increase in performances. The evaluation of the pressure impact on the PAFO system proposed in this study is a key element that will be used as the basis to determine if the extra energy due to pressurization could be counterbalanced by additional savings.

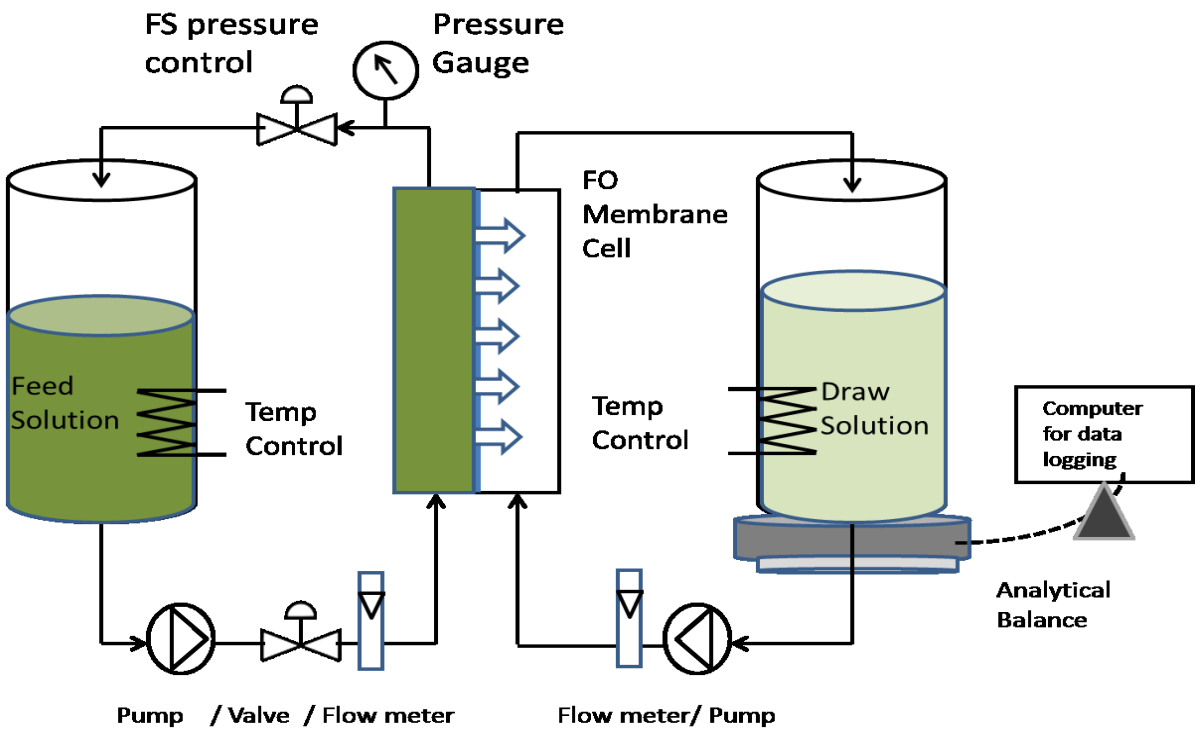

Fig.2.3 Flow diagram of an PAFO system

Not much work has been done in the context of PAFO. One research group considered the use of very moderate hydraulic pressure (up to 0.8 bar) to enhance fouling behaviour in the context of water extraction from sewage; a slight increase of water permeation was observed (Lutchmiah et al., 2011). In another study, the effect of transmembrane hydraulic pressure in FO was evaluated, confirming that FO industrial application requires pressurization for water circulation within spiral wound module. However, the applied pressure (up to 3.4 bar) remained very low in comparison to the osmotic pressure driving force (45 bar) and therefore no clear impact on flux have been observed for the membrane tested. Moreover, the tricot spacer used certainly helped supporting the membrane but may not be representative of industrial operation due to the important pressure loss generated (Coday et al., 2013).

The membrane water permeability constant (A) and solute permeabilities (B) are key elements in osmotic process performances. Following the earlier development of RO, their determination has been developed using procedure adapted to RO configuration (i.e. pre-compaction under high pressure operation). This procedure is commonly used for FO membrane characterization (She et al., 2012, Yip et al., 2010, Kim et al., 2012,

Wei et al., 2011) but its significance has already been controverted for FO/PRO configuration (Kim et al., 2012, Phillip et al., 2010). One recent study proposed a standardized test for osmotically-driven membrane processes using RO setup, but under limited applied pressure, so to be more representative of FO operating conditions (Cath et al., 2013). However, further systematic study on the impact of pressure on the membrane intrinsic characteristics as well as the significance of the used methodology is still needed. Membrane orientation is of key importance in FO and PRO operation. Conventionally, in FO operation, the active layer faces the feed solution leading to more ICP but limiting fouling, giving the best compromise for long term operation (Gray et al., 2006, Zhao et al., 2011a), while in PRO operations, the active layer faces the draw solution where hydraulic pressure is applied. Therefore, the impact of pressure for both membrane orientations has to be evaluated for PAFO regarding potential deformation as well as hydraulic performances. In PRO configuration, solute diffusion has been found to increase with pressure leading to enhanced ICP affecting the performances of the process. Membrane deformation was suspected to be responsible for the solute flux increase that was observed to be more important than calculated from the solution diffusion model (She et al., 2012).

2.4.1 Pressure assisted FO for volume minimization reverse osmosis concentrates

Pressure assisted FO (PAFO) technique was applied recently to reduce the volume of ROC (Jamil et al. 2016). The water flux in PAFO is the sum of two independent different flux components: an osmotic flux and a pressure-driven flux. However, PAFO flux is not as high as one may expect because the additional hydraulic pressure also increases the dilutive internal concentration polarization (ICP). As a result of increased ICP, the effective osmotic pressure is reduced and thus the PAFO water flux is not affected by the increase in draw solution concentration (or osmotic pressure).

The reason is explained as follows: Oh et al. 2014, calculated the water flux (J_W) in PAFO by the following equation.

$$Jw = A(\Delta P + \pi_{D,b}\exp(-Jw/k)) \qquad (2.4)$$

Here, A is the membrane pure water permeability, $\pi_{D,b}$ is the draw solution bulk osmotic pressure, and K is the solute resistance to diffusion within the porous support layer. The water flux is increased by the applied hydraulic pressure however, the effective osmotic pressure is decreased due to enhanced ICP as shown by the term: $\pi_{D,b}\exp(-Jw/k)$ in Eq. (2.4).

2.5 Nano filtration and Reverse Osmosis

A short introduction on NF is provided as NF may be able to be used with FO membranes to reduce the salinity in RO concentrate. More details are discussed in Chapter 6. Naonofiltration (NF) is the pressure driven membrane process for liquid-phase membrane separations. NF has replaced reverse osmosis (RO) in many applications due to lower energy consumption and higher flux rates (Raman, Cheryan, & Rajagopalan, 1994). The properties of NF membranes lie between those of non-porous RO membranes (where transport is governed by a solution diffusion mechanism) and porous ultrafiltration (UF) membranes (where separation is usually assumed to be due to size exclusion and, in some cases, charge effects). Commercial NF membranes possess a fixed charge developed by dissociation of surface groups such as sulphonated or carboxyl acids (Rautenbach & Groschl, 1990). The properties of NF membranes, therefore, allow ions to be separated by a combination of the size and electrical effects of UF and the ion interaction mechanisms of RO.

The pore size in NF membranes (normally ~ 1 nm) is such that small uncharged solutes may be highly rejected while the surface electrostatic properties allow monovalent ions to be reasonably well transmitted with multivalent ions mostly retained. These characteristics make NF membranes extremely useful in the fractionation and selective removal of solutes from complex process streams. This development of NF technology as a viable process has led to a marked increase in its adoption in a number of industries

such as treatment of pulp-bleaching effluents from the textile industry, separation of pharmaceuticals from fermentation broths, demineralisation in the dairy industry, metal recovery from wastewater and virus removal (Bowen et al., 2002).

Nanofiltration (NF) is one of promising technologies for the treatment of organic and inorganic pollutants in surface water. Because the surface water has low osmotic water treatment. The rejection behaviour by nanofiltration membranes is dependent on the molecular size as well as molecular charge of target solutes, because the membranes normally have charged properties, such as negative, positive or even neutral, in different pH condition. Moreover, the changing of nanofiltration performances caused by membrane fouling due to long-term operation is an important key for such application (Thanuttamavong et al. 2002).

The pore size of NF membranes is smaller than that of UF, typically around 1nm, which corresponds to dissolved compounds with a molecular weight of about 300 Da. This makes NF suitable for removing relatively small organics, e.g. organic micro pollutants (active compounds and endocrine disrupting compounds) and colour from surface water or groundwater, and degradation products from the effluent of biologically treated wastewater, dissolved organics and multivalent ions (Mohammad et al. 2013). Since they have the ability to remove multivalent ions, the NF membranes have found useful applications in water softening since the 1990s (Ang et al. 2014).

Apart from size exclusion, NF membranes are capable of rejecting charged compounds/ions by electrostatic forces. Polymeric NF membranes contain ionizable groups, e.g. carboxylic or sulfonic acid groups, which result in a surface charge in the presence of a feed solution. The equilibrium between the charged membrane and the bulk solution is characterized by an electric potential, the Donnan potential, which

retains ionic species. This mechanism (also known as ‘Donnan exclusion’) allows the removal of ions with a size below the pore size of the membrane. NF is an efficient system aiming to produce desirable quality of water for industrial, agricultural and indirect potable reuse applications from BTSE (Jacob et al. 2010). NF systems can provide a better quality of water compared to MF/UF. Different membranes characteristics are provided in Table 2.1.

Table 2.1 Overview of pressure-driven membrane processes and their characteristics - Van der Bruggen et al. (2003), (adapted from Shanmuganathan, 2015)

	MF	UF	NF	RO
Permeability (L/m^2.h.bar)	>1,000	10-1,000	1.5-30	0.05-1.5
Pressure (bar)	0.1-2	0.1-5	3-20	5-120
Pore size (nm)	100-10,000	2-100	0.5-2	<0.5
Rejection				
1. Monovalent ions	-	-	-	+
2. Multivalent ions	-	-	+	+
3. Small organic compounds	-	-	-/+	+
4. Macromolecules	-	+	+	+
5. Particles	+	+	+	+
Separation mechanism	Sieving	Sieving	Sieving/ Charge effects	Solution/ Diffusion
Applications	Clarification; pre-treatment; removal of bacteria	Removal of macromolecules, bacteria, viruses	Removal of (multivalent) ions and relatively small organics	Ultrapure water; desalination

Note: '+' denotes significant removal and '-' is insignificant removal

2.6 FO and PAFO performance parameters

2.6.1 Membrane performance

2.6.1.1 Concentration polarization

Concentration differential across osmotically-driven FO asymmetric membrane plays an important role in mass transfer (water permeate). Concentration polarization (CP) can be categorized as two types, external concentration polarization (ECP) and internal concentration polarization (ICP). ECP generally occurs at the dense active layer of the membrane while ICP happens inside the porous support layer.

2.6.1.2 External concentration polarization and modelling

The flow-through pressure-driven membranes cause a solute layer to build up at the membrane surface due to concentration polarization. To overcome this polarization a higher hydraulic pressure is required to transfer water to the permeate (Song & Elimelech, 1995). This phenomenon is not limited to pressure-driven membranes and also in osmotic- driven membranes when the feed solution comes into contact with the active layer where the solute layer builds up. Similarly, when the draw solution comes into contact with the permeate it is diluted at the permeate membrane interface. This reduction of the net effective osmotic driving force is called dilutive external CP (McCutcheon & Elimelech, 2006).

Both dilutive external CP and concentrative external CP reduce the net osmotic pressure across the membrane. In FO membrane the external CP has only a mild effect on water flux and is not the main cause of less flux (Achilli et al., 2009). The external CP can be minimized by increasing the flow velocity at the membrane surface.

McCutcheon and Elimelech (2006) have modelled ECP in FO using the boundary layer film theory. The general equation for concentration polarization modulus in pressure-driven membrane processes can be expressed as follows:(Zhao et al., 2012).

$$C_m/C_b = \exp(j_w/k) \qquad (2.5)$$

Where Jw is the water flux, k is the mass transfer coefficient, and C_m and C_b are the concentrations of the feed solution at the membrane and in the bulk solution

respectively. Furthermore, the mass transfer coefficient (k) is related to the Sherwood number (Sh) denoted as:

$$k = ShD/D_h \qquad (2.6)$$

D_h is the hydraulic diameter and D is the salt diffusion coefficient. When the feed concentration is low the concentration in eq (2.6) could be replaced by the osmotic pressures. So the concentration modulus can be shown as:

$$\Pi_{m\text{-}feed}/ \Pi_{b\text{-}feed} = \exp (j_w/k_{feed}) \qquad (2.7)$$

K_{feed} is the mass transfer coefficient on the feed side, $\Pi_{m\text{-}feed}$ and $\Pi_{b\text{-}feed}$ are the osmotic pressures of the feed solution at the membrane surface and in the bulk solution respectively.

As follows the dilutive ECP modulus in FO can be expressed as:

$$\Pi_{m\text{-}draw}/ \Pi_{b\text{-}draw} = \exp (j_w/k_{draw}) \qquad (2.8)$$

K_{draw} is the mass transfer coefficient on the draw side, and $\Pi_{m\text{-}draw}/ \Pi_{b\text{-}draw}$ are the osmotic pressures of the draw solution at the membrane surface and in the bulk solution, respectively.

The water transport phenomenon in RO, FO and PRO modes can be expressed by the general equation (2.1):

$$Jw = A (\sigma \Delta\Pi — \Delta P) \qquad (2.1)$$

A is the water permeability coefficient of the membrane, σ is the rejection coefficient, ΔΠ is the osmotic pressure difference across the membrane and ΔP is the applied hydraulic pressure. The difference (σ ΔΠ — ΔP) represents the effective driving force. In the FO system the driving force originates from the osmotic pressure difference between the draw solution and the feed solution so the water flux can be expressed as:

$$Jw = A (\Pi_{draw} — \Pi_{feed}) \qquad (2.2)$$

Where Π_{draw} and Π_{feed} are the osmotic pressures of the draw and feed solutions, respectively. Particularly both Π_{draw} and Π_{feed} should be effective osmotic pressures at the membrane surfaces:

By substituting equations (2.7) and (2.8) in equation (2.2)

$$Jw = A\,[\Pi_{b\text{-}draw} \exp(j_w/k_{draw}) - \Pi_{b\text{-}feed} \exp(j_w/k_{feed})] \quad (2.9)$$

Both concentrative and dilutive ECP are considered in eq (2.9). However, several important aspects of this equation should be recognized. Firstly, the mass transfer coefficients for the feed and draw solutions are not similar because of concentration differences on both sides. Secondly the solute permeability is assumed to be zero (i.e. the rejection coefficient σ=1), feed and draw solution concentrations are low because only then the concentration can be assumed equal to the osmotic pressure. Thirdly and finally this model is only suitable for dense symmetric films rather than asymmetric membranes. Thus the application of this model is relatively limited. We should consider that asymmetric FO membranes are in use, in which ICP effects are more important.

2.6.1.3 Internal concentration polarization and modelling

If the porous support layer of an asymmetric FO membrane faces the feed solution as in PRO, a polarized layer is established along the inside of the dense active layer. The water and solute propagating the porous layer is referred to as concentrative internal CP, and this phenomenon is very much similar to external concentrative CP, except it takes place within the porous layer and cannot be minimized by higher velocity. In FO applications like desalination and wastewater treatment, the active layer of the membrane faces the feed solution while the porous support layer faces the draw solution. As water permeates through the active layer, the draw solution within the porous structure becomes diluted. This is referred to as dilutive internal CP and it impacts on the net osmotic pressure of the system (McCutcheon & Elimelech, 2006).

It can be seen in Fig. 2.4 (b) that the osmotic pressure difference between the bulk feed and the bulk draw solution ($\Delta\pi_{bulk}$) is higher than the net effective osmotic pressure difference ($\Delta\pi_{eff}$), due to internal dilutive CP effect.

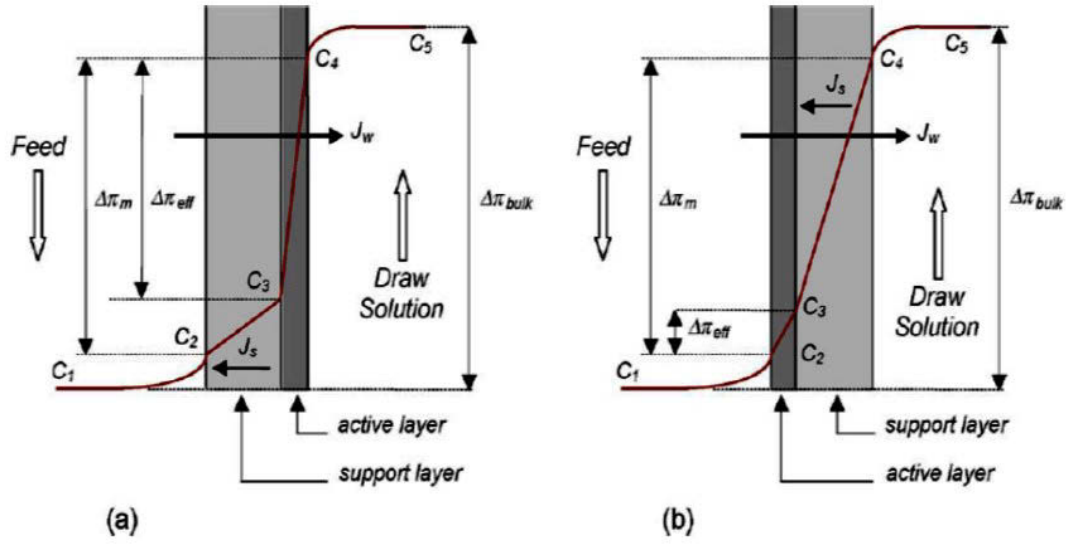

Fig.2. 4 (a) Concentrative internal CP and (b) dilutive internal CP across a composite or asymmetric membrane in FO (adapted from Cath et al., 2006)

2.7 Performance and optimization of the forward osmosis process

The following general criteria (Table 2.2) should be considered before selecting any FO membrane system.

Table 2.2 General FO design criteria

Performance criteria	Importance	Reference
Permeability and Membrane type	High density of the active layer for high solute rejection Minimum porosity of support layer for low internal CP	Cath et al., 2006
Flow mode	Should have good mechanical strength to withstand hydraulic pressure especially when used for PRO mode	Cath et al., 2006
Draw solution	The main criterion for selecting should be higher osmotic pressure compared to the feed solution	Cath et al., 2006
Resistance against cleaning agents	Both organic and inorganic fouling in FO operation are fully reversible, by water flushing which is attributed to less compact fouling layer formation.	Zou et al., 2012

2.7.1 Evaluation of draw solution

A number of draw solutions (DS) are used in this study. The identification of optimum draw solutions is currently one of the main commercial activities. The good DS should have following properties (Table 2.3).

Table 2. 3 Draw solutions

Draw solutions	Advantages / disadvantages	Reference
Monovalent inorganic solutions: NaCl, KCl	+ High osmotic pressure + Easily available and low cost + High solubility - Reverse osmosis required for DS recovery - Loss of DS by reverse salt diffusion	Cath et al., 2006
Bivalent inorganic solutions: $CaCl_2$	+ Very high osmotic pressure + DS recovery by nanofiltration - Loss of DS by reverse salt diffusion - Increased scaling risk on feed side	Phuntsho et al., 2012
Organic solutions	+ Large molecules + Recoverable by e.g. ultrafiltration and membrane distillation - Low diffusivity - Low osmotic pressure - Partly limited availability (patents) - Moderate to high costs - Risk of organic degradation/fouling	Adham et al., 2007

2.8 Membrane performance inhibitors

Membrane performance is inhibited similar way both in reverse and forward osmosis. However, in reverse osmosis high pressure is applied to move water molecules through the semi-permeable membrane contrary to forward osmosis. In both cases, care has to be taken to avoid accumulation of dissolved, colloidal or biological matter at the surface of the membrane, which inhibits the mass transfer across it. Both scaling and fouling

limit the membrane's performance and scaling leads to precipitation of inorganic material on the surface of membrane.

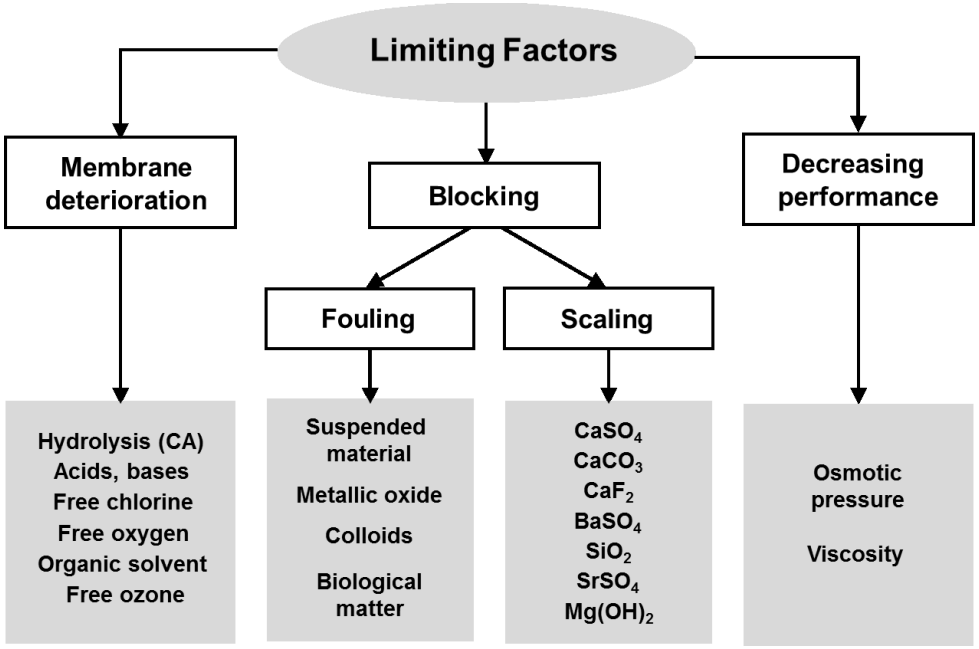

Fig.2.5 Limiting factors for membrane desalination by reverse osmosis
(adapted from Fritzmann et al., 2007)

2.8.1 Membrane fouling

The application of membrane technology has been successfully implemented to produce treated water of recyclable quality (Shon et al. 2004a). However, the performance of this technology is affected by 'membrane fouling' which is often caused by: i) the high levels of effluent organic matter (EfOM) in biologically treated sewage effluent (BTSE) (Qu et al. 2013; Park et al. 2006; Miao et al. 2014); ii) biological growth (biofouling); and iii) inorganic precipitates or particles (Kim and Dempsey, 2013).

Membrane fouling occurs due to the accumulation and deposition of the above mentioned substances such as organics/inorganics on the membrane surface and eventually they block membrane pores. This affects the performance of the membrane

in terms of permeability and rejection of organics (Speth et al. 1998). The flux decline in the membrane filtration is linked to the formation of the gel layer/surface cake layer material on the membrane surface, formed by colloidal/particulates. This ultimately affects the membrane pore structure (Fan et al. 2001) and in extreme cases it can result in membrane failure (Zularisam et al. 2006).

Membrane fouling is governed by several factors such as natural organic matter (NOM) (including its size, hydrophobicity, charge), the properties of membrane (hydrophobicity, charge, surface roughness), the characteristics of feed solution (pH, ionic strength, hardness ion concentration especially calcium ions) and the hydrodynamics of the membrane system (solution flux, surface shear) (Taniguchi et al. 2003). In previous studies, natural organic matter is found to be a major foulant that cause significant loss in membrane permeability (Yamamura et al. 2008; Yuan and Zydney 2000; Lee et al. 2006) and is the major limitation for the wide application of membrane technologies nowadays (Wintgens et al. 2005; Henderson et al. 2011).

2.8.1.1 Organic fouling on membrane surface

Many studies have focused on identifying the potential membrane foulants of EfOM in which the fractions of EfOM can be hydrophilic, hydrophobic and transphilic in character according to their functionality (Miao et al. 2014). Gray et al. (2007) found that the hydrophilic fractions of EfOM constituted the major foulant in MF membrane formed cake/gel layer on the membrane surface and subsequently led to rapid flux decline. The hydrophobic fractions showed a steady decline in flux and the formation of a gel/cake layer was not apparent.

Another, study concluding that membrane fouling was caused by hydrophilic fractions has received considerable attention (Yamamura et al. 2014). Hydrophilic fractions are composed of polysaccharides and proteins and the compounds' structure is rich in aliphatic carbons and hydroxyl groups (Ma et al. 2001). It has been found while comparing the Fourier transform infrared spectroscopy (FTIR) signals of clean and fouled membrane surfaces. The fouled membrane was covered with more polysaccharide substances (Kimura et al. 2004). Chemical analyses (excitation emission matrix (EEM and FTIR) confirmed that the substances such as protein-like, polysaccharide-like and humic-like substances are responsible for membrane fouling in the UF process (Zhou et al. 2014). The humic substances (humic and fulvic acids) are the major fraction of NOM comprising more than 50% of the dissolved organic carbon (DOC) that is mainly responsible for the colour in natural waters (Fan et al. 2001).

Xiao et al. (2013) investigated the membrane fouling using model foulants such as humics, bovine serum albumin (BSA) and sodium alginate as representative compounds of dissolved organic matter (DOMs) The adsorption of dissolved organics such as humic acid, fulvic acid and protein on the membrane surface is influenced by solution pH, ionic strength and calcium ions present in the feed water (Jones and O'Melia, 2000). Adsorption isotherm study (Jones and O'Melia, 2000) revealed the relationship between the adsorption of humics on the membrane as the function of solution pH. A continuous decrease in adsorption of humics and proteins was observed on the membrane with an increase in solution pH due to electrostatic interactions. Increased ionic strength shields some of the repulsive charges between the adsorbing molecules, resulting in increased adsorption.

In addition to organics, the presence of some inorganic ions was also collectively found to be aggravating the organic fouling. Combined membrane fouling (i.e. the organic

fouling associated with inorganic ions) has been studied especially in NF membranes and reported that membrane fouling caused by the mixtures of different organic foulants/inorganic ions is more complex than an individual foulant (Li and Elimelech 2006).

2.8.1.2 Membrane Scaling

In addition to membrane (organic) fouling, another issue associated with membrane technology is 'scaling' which is due to the deposition of inorganic salts on the membrane surface. Scaling is frequently encountered in NF/RO desalination plants as they have the capacity to reject such inorganic anions from feed water. Scaling can form through two major mechanisms, such as 'crystallization' and 'particulate fouling', on the membrane surface. Crystallization occurs when the salt concentrations exceed their solubility limit, and the ions crystallize on the membrane surface (Ang et al. 2014). In the meantime, particulate fouling occurs due to convective transportation of colloidal particulate matter from the bulk solution to the membrane surface (Guo et al. 2012).

Mostly, in pressure-driven membranes such as NF and RO systems, the dissolved inorganic salts are usually concentrated 4–10 times, and possibly precipitate on the surface of the membrane as a result of exceeding their solubility (Van de Lisdonk et al. 2000). Scaling causes a permeate flux decline during constant operating conditions and it is mainly formed by the precipitation of salts such as $CaCO_3$, $CaSO_4$, silicates and barium sulfates (Van de Lisdonk et al. 2000; Morillo et al. 2014) as these pressure-driven membranes retain such salts. The presence of especially the calcium ions in the feed solution was also found to cause irreversible fouling due to the aggregation of small molecules bound by calcium ions that formed larger complexes and often are deposited into the internal structures of the membrane (Zhou et al. 2014).

The higher the concentration of salt in feed water the greater the inorganic scaling. Scaling mitigations normally in practice are alterations of feed water characteristics, addition of antiscalants or acid, optimization of operation parameters and design, etc. (Ang et al. 2014). Fouling and flux decline are two of the most important factors affecting membrane treatment process costs. As such the lifespan of the membrane is obviously related to the feed water characteristics, hydraulic conditions of operation and frequency of membrane cleaning, and membrane fouling (Gwon et al. 2003).

2.8.1.3 Incomplete removal of organic micro pollutants

The focus of environmental research has been recently extended beyond classical environmental organic micro pollutants, and now considers at pharmaceuticals and personal care products (PPCPs) which enter the environment mainly through domestic use (Ternes et al. 2004). Pharmaceuticals are mainly prescribed drugs and over-the-counter therapeutic drugs and veterinary drugs. Personal care products refer to products used for personal and cosmetic reasons such as soaps, fragrances, and cosmetics (see the US EPA website).

The organic micro pollutants are also known as trace organics because of their presence in the environment ranging from nanogram to microgram (ng - µg). The occurrence of such pollutants has potential environmental risks in non-target species (Gunnarsson et al. 2008). The principle sources of such PPCPs are from the discharge of wastewater treatment plants (WWTP), hospital effluents, chemical manufacturing plants, livestock and agriculture, etc. (Pal et al. 2010). WWTPs are the main source that continuously releases PPCPs into water bodies such as small streams. No monitoring actions/precautions for micro-pollutants are defined in most of the WWTPs (Bolong et al. 2009) and WWTPs are not specifically designed to remove PPCPs. These contaminants can escape from the treatment system and may end up in aquatic

environments (Luo et al. 2014). Their peak concentrations can be more than 1 μg/L (Cleuvers, 2003). Concern for the need to remove such PPCPs has risen (Cleuvers, 2003; Kümmerer, 2009) and many studies have now been published on the topic (Pal et al. 2010; Cleuvers, 2003; Li, 2014). Published data on the occurrence of various pharmaceuticals in Australia is summarized below Table 2.4 (adopted from Pal et al. 2010).

Table 2.4 Occurrence of pharmaceuticals in Australia (Pal et al. 2010)

Compounds	Effluent, WWTP (ng/L)	Freshwater, rivers, canals (ng/L)
Anti-biotics		
Trimethoprim	58-321	4-150
Ciprofloxacin	42-720	23-1300
Sulfamethoxazole	3.8-1400	1.7-2000
Analgesics and anti-		
Naproxen	128-548	11-181
Ibuprofen	65-1758	28-360
Ketoprofen	-	<0.4 – 79.6
Diclofenac	8.8-127	1.1-6.8
Antiepileptic		
carbamazepine	152-226	25-34.7
Beta-blockers		
Propranolol	50	-
Atenolol	-	-
Blood lipid regulators		
Gemfibrozil	3.9-17	1.8-9.1

Conventional wastewater treatment plants are mainly designed to eliminate large suspended particles, pathogens and dissolved organics to some extent, however, the removal of pharmaceuticals by such treatment plants is not satisfactory (Heberer, 2002; Kimura et al. 2009). In primary treatment, these PPCPs are mainly removed by sorption onto sludge (Ternes et al. 2004), in which 28% removal of PPCPs and hormones can be achieved when wastewater passes through a sedimentation tank (Behera et al. 2011). Insignificant removal of naproxen and sulfamethoxazole was observed in the primary stage (Carballa et al. 2004). The secondary treatment associated with biological treatment can remove PPCPs through biodegradation/biotransformation and sorption (Carballa et al. 2004). However, in some circumstances, the effluent level of diclofenac, carbamazepine, erythromycin, and sulfamethoxazole can exceed their influent concentration. This happens due to the subsequent transformation of PPCPs back into parent compounds during biological treatment (Kasprzyk-Hordern et al. 2009).

Since the WWTPs are the main source that discharge PPCPS into the environment, the application or incorporation of advanced wastewater treatment techniques becomes important to eliminate such compounds in their discharge. In line with producing high quality recycled water, membranes are increasingly being used (Snyder et al. 2007; Urtiaga et al. 2013), in which pressure-driven RO membranes are proving to be effective in rejecting PPCPs (Bellona and Drewes, 2007; Radjenovic et al. 2011). This is despite the fact some PPCPs compounds were detected at trace levels in RO permeates (Snyder et al. 2007).

2.8.1 Membrane cleaning

In FO, organic foulants accumulate on the surface of the membrane only loosely due to a lack of hydraulic mechanical pressure (Lee et al., 2010). With this loose fouling layer, there may not be necessary to apply harsh chemical cleaning because fouling can be reversed by a simple physical cleaning facility such as hydraulic flushing. This is not likely the case for membranes in RO because the fouling layer is compact, dense and cross-linked, and therefore often cannot be reversed by water flushing.

In a comparison of fouling behaviour of FO and RO and flux recovery by flushing, both FO and RO fouled membrane underwent a high cross-velocity test for cleaning (Lee et al., 2010). After a 12-hour fouling run, the cross-velocity rose three-fold. Before running the flushing test, the FO membrane was more fouled than the RO membrane with respect to flux decline. The FO membrane was almost completely recovered while that of RO was not noticeable compared to the initial flux. This indicates that the structure of the fouling FO layer was loose and sparse enough to break down and removed hydraulic shear generated by rising flow-through. On the other hand, the shear rate itself is not enough to dislodge the compact and coherent fouling layer formed during the fouling RO run. Thus no change in the behaviour of the flow pattern was noticeable. Furthermore, it is interesting to note that the behaviour of low flow FO after increasing flow velocity across the membrane is completely different from initial flux drop behaviour.

This indicates that at higher cross-flow velocity the accumulation of foulant at the surface of membrane is far smaller, resulting in the much thinner layer formation of a foulant layer. Due to this thin fouling layer the acceleration of cake-enhanced osmotic pressure (CEOP) poses less of a threat due to reverse solute flow from the draw

solution. The reason is that concentration polarization within the fouling layer is dependent on the fouling layer thickness.

2.8.2 Pre-treatment of feed water

2.8.2.1 Pre-treatment: Conventional treatment

The application of conventional treatment techniques as pretreatment or coupled with membrane technologies would benefit the uninterrupted smooth operation of membrane processes with less fouling. Integrating different treatment strategies with membrane filtration in water treatment is a very important in improving the performance of membranes. Pre-treatment is commonly used for two major reasons: firstly, to enhance the removal efficiency of micro-pollutants and DBPs precursors; and secondly, to reduce membrane fouling (Huang et al. 2009).

a. Conventional pretreatment technologies

The advantages and disadvantages of several conventional treatments associated with membrane processes are summarized as follows (Table 2.5).

Table 2. 5 Merits and demerits of different pretreatment processes used (adapted from Shanmuganathan, 2015)

	Coagulation	Adsorption	Pre-oxidation	Pre-filtration
Chemicals applied	Coagulants/flocculants at proper chemical dose	Porous/nonporous adsorbents in suspension/fixed contractor	Gaseous/liquid oxidants	Granular media with/without coagulants, membranes
Physical mechanism	Increases the size of aquatic contaminants to filterable level	Binds small contaminants to adsorbents much better than membrane pores	May dissociate organic colloids into smaller sizes	Removes coarse materials that may cause cake/gel layer formation on downstream membranes
Chemical mechanism	Destabilizes contaminants to cause aggregation/adsorption on coagulants precipitates or membrane surface	Provides new interfaces to adsorb/accumulate substances detrimental to membrane performance	Oxidize/decompose NOM, possibly by mineralization if UV used	Selectively removes contaminants or other particles that are sticky to filter media and downstream membranes
Biological mechanism	Partially removes autochthonous NOM and hinders bacterial growth in feed water or on membrane	May adsorb organic contaminants relevant to biofouling	Suppress microbial growth	Partially remove microbes that can cause biofouling
Targeted contaminants	Viruses, humics/fulvics, proteins, polysaccharides with acidic groups, colloids smaller than membrane pores	Humics/fulvics, small NOM, DBPs, synthetic micro pollutants	Viruses and organic contaminants with ozonation	Particulate and colloidal organics/inorganics, microbiota

Advantages on the effect on membrane fouling	Reduces colloidal and NOM fouling Significantly improves MF/UF performance	May increase/decrease membrane fouling and increase the removal of DBPs and its precursors	May reduce biofouling and NOM fouling Reduces the occurrence of biofouling; increases organic removal	May reduce fouling to different extents May reduce biofouling, colloidal fouling/solids loading
Disadvantages	i. Difficult to use proper dose if feed water quality varies significantly ii. May exacerbate fouling iii. Produce solid wastes iv. Ineffective in mitigating the fouling caused by hydrophilic neutral organics	i. Possible exacerbation of membrane fouling ii. Difficult to remove PAC fine particles from treatment facilities	i. Formation of DBPs ii. May damage membranes, incompatible with oxidants iii. May be ineffective in suppressing the growth of some microbiota resistant to oxidation	i. Performance of pre-filters may deteriorate and be difficult to recover ii. May require pre-treatment (coagulation/pre-oxidation) to enhance the efficacy

There is a significant improvement of membrane technology when preteatment is used. The pretreatment makes the membrane process simple and cost effective by reducing fouling effects, extending membrane lifespan and replacements. The level of pre-treatment of feed water depends on the ultimate purpose of the end product water. The pre-treatments used can be carried out as follows.

(i.) Coagulation and flocculation

Biologically treated sewage effluent (BTSE) is a diluted form of ROC. The BTSE contains some particles (combination of biological organisms, bacteria, viruses, protozoans, colour-causing particles, organics and inorganics) that are not settled within a reasonable time frame. Coagulation/flocculation process normally accelerates the settling process of such particles with the help of specific flocculants. Coagulation of dissolved and colloidal substances in wastewater is explained by Derjaguin–Landau–Verwey–Overbeek theory (DLVO theory) (Lee et al. 2012).

The coagulation and flocculation process consist of several steps as listed below:

a. Coagulation: adding and rapid mixing of chemical coagulants into raw water. The water uniformly mixes with the coagulates and destabilise the charge on particles.

b. Flocculation: slow mixing of flocculants (aluminium sulfate, aluminium chlorohydrate, iron salts, etc.) with water to build up particles of floc.

c. Sedimentation: allowing the floc to settle out

Many studies have confirmed that coagulation as a pre-treatment to the membrane system improved the membrane's permeability and reduced fouling potential (Konieczny et al. 2006; Huang et al. 2011; Pikkarainen et al. 2004).

(ii.) Activated carbon (adsorption)

Numerous information is available on the topic of removing organics by activated carbon from wastewater for various experimental configurations and conditions (Löwenberg et al. 2014; Martin and Iwuco, 1982; Liyan et al. 2009; Jia et al. 2009; Kim et al. 2009a; Guo et al. 2005). Activated carbons are porous carbonaceous adsorbents, and a large variety of organic solutes can be removed from wastewater via adsorption into its pores. This has a high sorptive surface area (500-1500 m^2g^{-1}) and pore volume ranges 0.7 and 1.8 $cm^3\ g^{-1}$. Activated carbon is commercially available in the form of powdered activated carbon (PAC) and granular activated carbon (GAC).

Adsorption of organic constituents by activated carbon is the accumulation of substances at a surface of the carbon. The adsorbing phase is known as 'adsorbent' and the material being adsorbed is the 'adsorbate'. The adsorption induced by Van der Waals forces is generally referred to as 'physical adsorption' and is reversible, whilst adsorption involving an exchange of electrons between specific surface and solute molecules known as 'chemical adsorption' where chemical bonds are formed (Cecen and Aktas, 2011).

Removal of organic micro pollutants by GAC: The removal of pharmaceutically active compounds is growing due to their potential health risk to people and aquatic organisms when they are released into wastewater. Advanced oxidation processes such as UV-radiation and ozone treatment can be effective for the removal of these compounds, however, these techniques produce some unwanted newly-formed (toxic) by-products (Rossner et al. 2009). Adsorption processes do not add undesirable by-products to drinking water (Bonné et al. 2002; Quinlivan et al. 2005). As such, the

advanced oxidation techniques are often followed by activated carbon in order to reduce the excess organics and by-products produced (Bonné et al. 2002).

Activated carbon (both GAC and PAC) is found to be highly efficient in removing organic micro pollutants (Snyder et al. 2007; Verliefde et al. 2007). A dose of 10 mg/L coconut-shell-based activated carbon removed more than 98% of contaminants (Rossner et al. 2009). The performance of zeolites in the removal of such contaminants was less effective. A study done by Snyder et al. (2007) reported more than 90% removal of organic micro pollutants by PAC and GAC from drinking water.

In wastewater treatment it is recommended to use the PAC. Studies have been conducted on utilizing PAC in submerged membrane hybrid systems to facilitate the removal of organics and improve fouling control (Vigneswaran et al. 2003; Thiruvenkatachari et al. 2004; Shanmuganathan, et al., 2015).

(iii) Pre-treatment with porous membrane filtration

Ultrafiltration (UF) and microfiltration (MF) membranes have the ability to produce a feed water quality that is much better than conventional filtration processes such as media and cartridge filtration. MF can effectively remove suspended particles, organic colloids, turbidity and pathogens (Zularisam et al. 2006) whilst UF has slightly finer pores able to remove viruses, macromolecules, etc. MF and UF function at relatively low transmembrane pressure (TMP) of less than 2 bars (or 2.0 kPa), and as such are typically known as ‘low pressure membranes’ (LPM), requiring less energy (Huang et al. 2009). Pore sizes of low pressure membranes range from ~10 to 100 nm.

A major challenge for membrane technology is the inherent trade-offs between membrane selectivity and permeability and high energy consumption especially for pressure-driven membranes (Qu et al. 2013). An overview of the membranes processes, pore size, applied pressure, and rejection capability is presented in Table 2.5.

Advantage of MF/UF membranes as pre-treatment

Membrane filtration is found to be viable in terms of cost effectiveness and contaminant removal (Ang et al. 2014). In this context, MF/UF membranes are able to produce constant quality effluents from biologically treated wastewater irrespective of the performance of prior treatment of activated sludge treatments (Park et al. 2010). It is normally used as pre-treatment to NF/RO where high quality water is required. While comparing the cost of conventional and MF pre-treatment, the total cost of conventional pre-treatment was double of membrane filtration based on pretreatment (Won and Shields, 2001).

In terms of contaminant removal, MF and UF membranes are effective in removing suspended particles, macromolecules, etc., and using such membranes has become widespread as an alternative to conventional water treatment and filtration processes. It can meet stringent regulations particularly in removing pathogens such as *Giardia* and *Cryptosporidium* (Lebeau et al. 1998). The removal of colour, dissolved organics, organic micro pollutants, and inorganic ions by MF/UF membranes is still limited because their larger pore size (0.1-0.01 μm) (Kim et al. 2009a; Stoquart et al. 2012; Lebeau et al. 1998). The application of membrane pre-treatments such as MF and UF can significantly reduce the fouling potential more than conventional pre-treatment processes (Pearce, 2008).

(iv) Membrane Hybrid Systems

In order to improve treatment performance, the MF/UF membranes can be integrated/coupled with other processes such as coagulation, ozonation or adsorption. This is known as 'Membrane Hybrid Systems'. Different configurations of membrane hybrid systems are reported in the literature (Stoquart et al. 2012). Two such configurations are given below (Fig. 2.6 and 2.7)

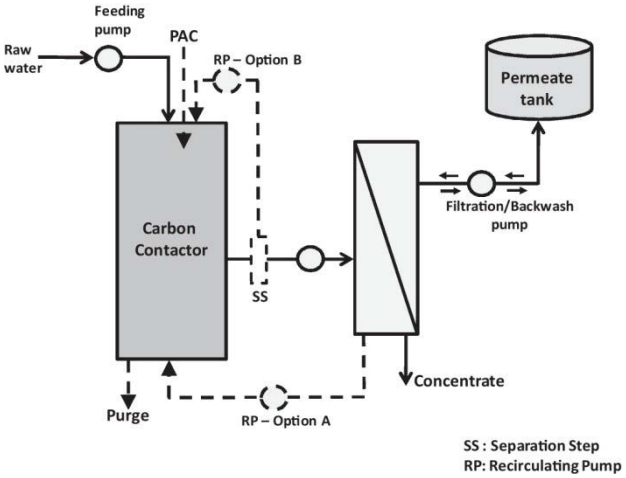

Fig.2. 6 Treatment prior to membrane filtration [pre-treatment]

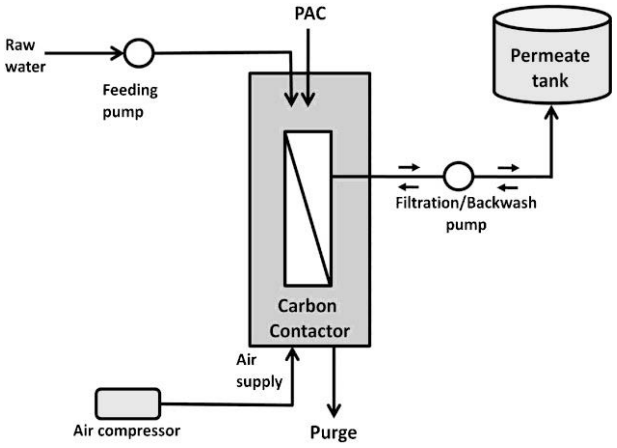

Fig.2.7 Treatment with membrane filtrations [integrated]

Development paths and benefits of Membrane-hybrid processes

The development paths from conventional treatment plants to a membrane-hybrid system are illustrated in Fig. 2.8. It shows the advances in terms of contaminant removal and system performance. The membrane hybrid system obviously produces enhanced quality of product water. It is environmentally friendly because there is less waste disposal and less chemical usage. Extensive research on this topic is needed to discover the best alternative systems whereby the water industry can manage water scarcity issues (Ang et al. 2014).

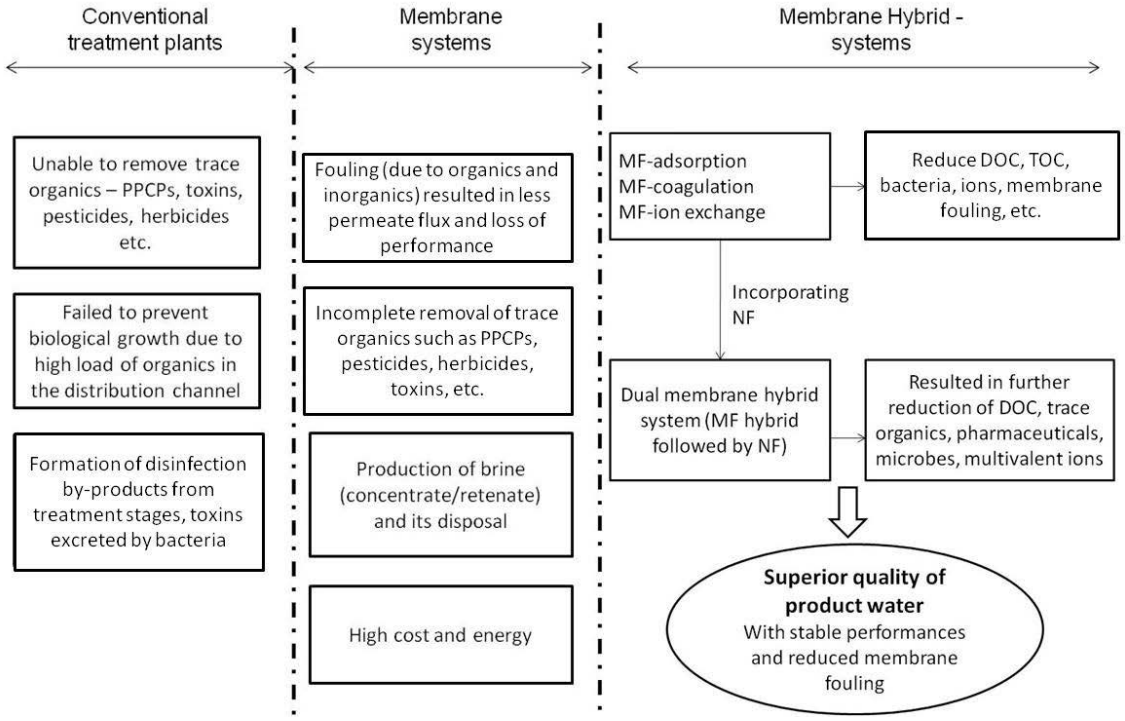

Fig.2. 8 Development of membrane hybrid systems (Ang et al. 2014; adapted from Shanmuganathan 2016).

(v) Biological pretreatment

The biological treatment significantly alters the characteristics of sewage effluent and reduces DOC from approximately 56-60 mg/L to 4.8-11 mg/L (Guo et al. 2011). The majority of this DOC left in the biologically treated sewage effluent (BTSE) is refractory organics which are resistant to biological degradation. BTSE contains a complex mixture of organic materials known as Effluent Organic Matter (EfOM) which mainly consists of: 1) refractory organics; 2) trace levels of synthetic organic compounds produced during disinfection process and 3) soluble microbial products (SMPs) derived during the biological treatment process of wastewater (Guo et al. 2011; Shon et al. 2006a).

EfOM in BTSE is mostly found in soluble form (86% of the chemical oxygen demand) (Shon et al. 2006a; Shon et al. 2006b) and these soluble/dissolved organics (DOC) are always difficult to remove (Guo et al. 2011). A UV chromatogram of BTSE showed several sub peaks in the range of 500–3000 Da. Stronger absorbance appeared at MW of 650 Da, 1000 Da, 1700 Da, and 2000 Da, demonstrating the presence of humic-like refractory substances. The weaker absorbance appeared at MW < 500 Da and MW > 10,000 Da shows the presence of high MW organics and SMPs, respectively (Guo et al. 2011).

The presence of EfOM not only affects the current discharge standards of BTSE, but also becomes a main constraint to wastewater reuse (Jarusutthirak and Amy, 2006). Different organic constituents found in BTSE is discussed below (Shon et al., 2006b).

i. Extracellular polymeric substances and soluble microbial products

This kind of organic matter is produced from bacterial metabolism during biological treatment and generally released during cell lysis, and diffusion through cell membrane/excretion (Barker and Stuckey, 1999). These products constitute the majority of the effluent COD (Shon et al. 2006b).

ii. Proteins

Protein is a complex structure and major constituent of living organisms and can decompose easily. Some forms of protein are soluble and others are not. Proteins contain carbon, hydrogen and nitrogen which is about 16% of protein. Urea and proteins are the main sources of protein in BTSE (Shon et al. 2006b). The organic nitrogen resulting to form nitrogenous DBPs is a potential cause of health problems (Bolto et al. 2004).

iii. Carbohydrates

Carbohydrates include starch, cellulose, sugars, etc. which can be degraded by enzymes of some bacteria and produce alcohols and carbon dioxide (Shon et al. 2006b). Carbohydrates provide a carbon source for microbes, and these are important for an effective biological treatment. However, such compounds are found to be major foulants in membrane processes (Jarusutthirak et al. 2002).

iv. Fat, oil and grease (fog)

These can be measured as fatty acids and their elimination during the biological treatment stage is 98-100%.

v. Surfactants

Surfactants normally lower the surface tension of a liquid and thus generally permit easier spreading. These are made up of organic compounds consisting of hydrophobic and hydrophilic groups and are known to be significant pollutants.

vi. Endocrine-disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs)

EDCs and PPCPs are found in trace amounts (µg-ng per Litre) in the aquatic environment. They are also known as trace organics which are considered to be potential threats to ecosystems. An EDC has been defined by the Organization of Economic and Cooperative Development (OECD), as "an exogenous substance or mixture that alters the function(s) of the endocrine systems and consequently causes adverse health effects in an intact organism, or its progeny or (sub) populations" (Lister and Van Der Kraak, 2001). EDCs can be pesticides, persistent organochlorines and organohalogens, heavy metals, phytoestrogens, synthetic and natural hormones, etc. (Daughton and Ternes, 1999). PPCPs are mainly medications used by humans and animals and these include a wide range of chemical contaminants originate from human use and excretion, veterinary applications of a variety of products, such as prescribed or non-prescribed medications, disinfectants, etc. The PPCPs found in an aquatic environment are analgesics, anti-inflammatory drugs, antibiotics, antiepileptic drugs, beta-blockers, blood lipid regulators, etc. (Daughton and Ternes, 1999). Pharmaceuticals are designed to be biologically active and may affect non-target organisms (Ying et al. 2004). The molecular weight of PPCPs ranges from 200 - 500 to 1000 Da.

Among the pharmaceuticals, non-steroidal anti-inflammatory drugs (NSAIDs), anticonvulsants, lipid regulators and antibiotics are considered to be a potential group of

environmental contaminants as these are often detected in aquatic environments. These NSAIDs are drugs with analgesic, antipyretic and anti-inflammatory effects, and drugs such as ibuprofen and diclofenac fall into this category. Anticonvulsants such as carbamazepine which is used in the treatment of epileptic seizures are often found in municipal sewage effluent. Lipid regulators such as gemfibrozil are used to lower the lipid levels in blood. Antibiotics are employed to treat infectious diseases and these include penicillins, tetracyclines, sulfonamides, and fluoroquinolones (Virkutyte et al. 2010).

Pharmaceuticals compounds are complex molecules and are developed and used due to their specific biological activity (Kümmerer, 2009). The pharmaceuticals taken by humans or other organisms are not completely metabolized by their body and residues can be excreted via urine and faeces as unchanged parent compounds, and as metobolites. Effluent from municipal WWTPs is the main source of discharging such compounds into the environment.

Toxicity experiments with a mixture of NSAIDs showed that combined toxicity of pharmaceuticals are much higher than the single compound due to synergistic effects (Cleuvers, 2004). Pharmaceuticals usually occur in aquatic environments as mixtures (Virkutyte et al. 2010).

Lee et al. (2011) studied the chronic effect of pharmaceuticals on fresh water crustaceans and on fish, in which both species were exposed to diclofenac for up to 3 months. There is a marked decrease in reproduction observed at 25 mg/L for Daphnia magna, whilst it was 50 mg/L for Moina macrocopa. A long-term (3 months) exposure of diclofenac at 25mg/L on Daphnia magna significantly reduced reproduction. Another study (Nassef et al. 2010) revealed that adult Japanese medaka fish (Oryzias latipes)

exposed to a mixture of PPCPs (composed of carbamazepine, dicofenac, triclosan) for 9 days affected their feeding behaviour and altered the swimming speed.

2.9 Concluding remarks

The production of fresh water and disposal of wastewater are major challenges of 21th century. Reverse osmosis (RO) membrane plants are used extensively for brackish water (total dissolved solids (TDS) range 1000–10,000 ppm) desalination and industrial water (TDS=100–1000 ppm) purification. These plants operate at about 75% product water recovery so that 25% of feed water is wasted as concentrated brine. The large quantities of concentrated brine generated has a disposal problem especially when the plants are located inland. Because of high disposal costs, there is a need to re-use and conserve this water. In order to achieve higher recoveries, therefore, alternate processes are required. Forward osmosis using natural osmotic pressure of DS is an option to treat this concentrated brine. But it generates another concentrated brine, which has to be treated to recover fresh water. That is not economical option. Pressure assisted forward osmosis (PAFO) technology using fertilizer draw solution (FDS) does not require regeneration and it can be used as such for any targeted application. NF is another option to treat this concentrated brine because it does not require any DS. Therefore, the final NF permeate can be recycled back to RO system.

U T S

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Chapter 3

MATERIALS AND METHODS

3.1 Introduction

In this chapter, the role of the various materials used and parameters is outlined. The methods used for different analyses are discussed. Three different experimental set ups were used. Each set up compared the performance of various FO and NF membranes performance by employing different DS and process conditions. Each plan has its own experimental protocols to obtain desired results. The general methods used are explained in this chapter. The specific information is given in chapers 4,5 and 6.

3.2 Chemicals used

In this study various types of feed solutions and draw solutions were employed. Because quality of permeate greatly depends upon membrane properties the quality of FS and DS used.

For standard data evaluation and performance testing, AR grade chemicals supplied by Sigma Aldrich, Australia were used, as received without any further treatment. Draw solutions (DS) and synthetic feed solution (FS) batches were prepared by dissolving measured quantities of these compounds in deionized water (DI).

3.2.1 Draw solutions (DS)

Potassium chloride with concentrations of 0.25 to 1 molar and sodium chloride 2-3 molar concentration were used as draw solutions.

3.2.2 Feed solution (FS)

Reverse osmosis (RO) concentrate samples were obtained from the Water Reclamation and Management Scheme (WRAMS) water recycling plant at Sydney Olympic Park, which is located at Homebush Bay in New South Wales. Its composition is given below (Table 3.1).

Brief description of Water Reclamation plant

The main operation in this treatment plant is mechanical pre-treatment by screening and grit removal followed by biological treatment comprising of a sequencing batch reactor (SBR) with two tanks. The biological treated wastewater (BTSE) is disinfected by UV disinfection, then the effluent was pumped to the water treatment plant. Water produced from the water reclamation plant or water from the brickpit reservoir receives its final processing at the Water Treatment Plant: water passes through continuous microfiltration to remove all particles larger than 0.2 microns (including parasites and bacteria). The MF unit has a total capacity of 7500 m^3/d and consists of 0.2 μm hollow fibre membranes (US Filter-Memcor), arranged in three blocks with 90 modules each (Chapman, 2006). The MF effluents then passes through reverse osmosis (RO) to reduce salinity. There are two RO treatment trains with a two-stage RO system. Each train has a capacity of 1000 m^3/d and is operated alternately on a daily basis.

Table 3. 1 General composition of ROC

Parameters	Units	Range
Total organic carbon (TOC)	mg/L	18.0-36.0
Total inorganic carbon (TIC)	mg/L	78.0-95.0
UV_{254}	1/m	0.7
pH		7.8
Conductivity	mS/cm	2.6-3.6
Alkalinity as $CaCO_3$	mg/L	380
Ca^{2+}	mg/L	73.0-108
Mg^{2+}	mg/L	63.0-84.0
K^{+}	mg/L	48.0-75.0
Na^{+}	mg/L	376.0-563.0
Silica as Si	mg/L	0.85
Br^{-}	mg/L	<5
Cl^{-}	mg/L	478.0-819.0
F^{-}	mg/L	4.8
SO_4^{2-} as S	mg/L	51.0-98.0
NO^{3-} as N	mg /L	5.5-17.0
Total P	mg /L	6.9

Synthetic ROC:

Synthetic ROC was prepared by mixing chemicals and its composition was comparable with real ROC. Chemical composition and properties of synthetic ROC is given in Table 3.2.

Table 3. 2 Chemical composition and properties of synthetic ROC

Parameters	Units	Chemical composition
$CaCl_2.2H_2O$	mg/L	292
NaCl	mg/L	750
KCl	mg/L	90
NaF	mg/L	7
$MgSO_43H_2O$	mg/L	450
$KH2PO4^-$	mg/L	15
$NaHCO_3$	mg/L	80
Glucose	mg/L	200
Yeast	mg/L	300
Total organic carbon (TOC)	mg/L	18.7
Total inorganic carbon (TIC)	mg/L	15.6
pH		5.5
Conductivity	mS/cm	2.65
TDS	mg/L	1569
NH4-N	mg/L	4.04
Phosphate	mg/L	18.2
COD	mg/L	440
Alkalinity as CaCO3	mg/L	150

3.3 Experimental set-up

3.3.1 Forward osmosis unit

The experimental set-up of the employed bench-scale forward osmosis (FO) unit is shown in Fig. 2.3 (Chapter 2). The specially designed cross-flow membrane cell is the core unit. It features a channel on each side of the membrane, which allows the feed and draw solutions to flow through separately. Each channel has a length of 77 mm, a width of 26 mm, and a height (thickness) of 3 mm; with an effective area of 20×10^{-3} cm^2 (Fig. 3.2). The flow through each channel was controlled by a variable speed drive (Cole-Parmer, Magnetic Pumps, USA). The targeted cross-flow rates for both the feed and draw solutions were adjusted manually using flow meters (Cole-Parmer Rotameters).

The temperature of both DS and FS was maintained through a water bath, in which stainless steel coiled pipes are immersed. The water bath's temperature is controlled using a temperature controller heater/chiller system (Thermoline BL-30, Australia). Photo of FO set-up and membrane test all are shown in Fig. 3.1.

Fig.3.1 Bench Scale FO set-up at the UTS laboratory

Fig.3.2 Overhead view of FO test cell with active flow cell of 2.6 x 7.7 x 0.3 cm on each side of the cell and double sealing

3.3.2 Forward osmosis membranes types

Three types of FO membranes obtained from Hydration Technologies Inc. (HTI), USA namely cellulose tri-acetate embedded polyester screen support (CTA-ES), Cellulose Triacetate non-woven support CTA-NW and Polyamide Thin–Film Composite embedded polyester screen support (TFC-PA-ES) were used in this study. Membrane properties are shown in Table 3.3.

Table 3.3 Properties of the FO membranes used (references provided by the vendor, otherwise specified)

	CTA	CTA-NW	TFC-PA-ES
Membrane supplier	HTI 97322 USA	HTI 97322 USA	HTI 97322 USA
Membrane type	HTI OsMem CTA –ES Membrane	HTI OsMem CTA – NW Membrane	HTI OsMem TFC–ES Membrane
Membrane material	Cellulose Triacetate embedded polyester screen support	Cellulose Triacetate non-woven support	Polyamide Thin–Film Composite (TFC) embedded polyester screen support
Water permeation (acc. to supplier)	9 LMH (FS: DI water, DS: 1M NaCl)	4 LMH (FS: DI water, DS: 1M NaCl)	17 LMH (FS: DI water, DS: 1M NaCl)
Contact angle	62	60	$\Theta = 100\ °$
Pore size	0.74 nm (Xie et al., 2012)	0.74 nm (Xie et al., 2012)	0.67–0.71 nm (Wei et al., 2011)
pH range	3 – 8	3 – 8	2 – 11
Cleaning recommendation	Cleaning chemicals approved for CA/CTA RO membranes	Cleaning chemicals approved for CA/CTA RO membranes	Cleaning chemicals approved for TFC RO membranes
Maximum operating temperature	71^0C	71^0C	71^0C
Maximum transmembrane pressure	-	10 psi	10 psi
Thickness	<50 µm (Cath et al., 2006)	40 µm (Yip et al., 2010)	

3.4 Experimental protocols

3.4.1 Performance measurements

Water flux was measured continuously by weighing the draw solution using a digital mass scale connected to a computer. The water flux (Jw) is calculated by using the following formula.

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

3.4.2 Reverse solute flow

Reverse draw solute flux for all experiments was monitored by measuring the electrical conductivity (EC) with a manual digital conductivity meter (Greisinger model GHM 3430, Germany). The initial and final conductivity of DS was measured to calculate the reverse solute flow using the following formula.

$$Js(\%) = [1 - C_{di}/C_{dfn}] \times 100 \quad (3.2)$$

Where Js is the reverse solute flow in percent (%) and C_{di} initial conductivity of DS and C_{dfn} is final normalized conductivity of DS.

3.4.3 Salt rejection

For flat sheet FO membranes were operated in the RO mode for feed water carrying 1000 ppm NaCl. The electrical conductivity of the feed water and the permeate collected was noted. Salt rejection was calculated by using the following formula:

$$R(\%) = \left[\frac{C_f - C_p}{C_f}\right] x100 \quad (3.3)$$

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

3.4.4 Influence of membrane properties

Three different types of membranes were studied in terms of their flux performance. One has a thick (non-woven) support layer compared to the other two which have a thin support layer (embedded polyester screen). Their properties are shown in Table 3.3. There is a large variation in the flux of the three types of FO membranes used. The membrane with thick support layer shows flux on the lower side. Membranes can be installed in two configurations - FO mode and PRO mode. In the FO mode the active layer faces FS while the support layer faces DS. In PRO mode, it is in other direction.

3.4.5 Fouling experiments

Two types of FS were used to study fouling of the membranes, and its impact on permeate flux:

- Study of real RO concentrate from SOPA's reclamation wastewater treatment plant to assess its effect on membrane fouling and resulting permeate flux (Chapters 4,5 and 6).
- Study of fouling employing synthetic ROC as the model compound and its influence on permeate flux (Chapter 7).

FO testing with model foulants: These tests were conducted to determine the specific fouling with model compounds, representing RO concentrate's major components. These tests were conducted for 40-70 hours for each type of membrane. Model foulants were used at elevated concentrations to accelerate the fouling affect and make clearer observations possible. Each fouling test was conducted with a new membrane and entailed an initial base line test with DI water at the respective DS concentration so that the flux decline and fouling impact could be identified.

FO testing with ROC: The FO system was then tested with real ROC from the wastewater reclamation plant. The RO concentrate was collected and then stored in glass bottles at 4^0C till consumption for testing. Conductivity of RO feed was monitored continuously. The concentrations of the organic and inorganic compounds were analysed for the initial and final solutions to identify organic and inorganic fouling. Since the ROC had a significant scaling potential, pH adjustment was examined as the method for reducing the risk of scaling.

3.4.6 Performance recovery

Membrane cleaning

After each experiment the membrane was flushed with DI water for about 20 minutes at higher cross-flow velocity of 27.8 cm/s to wash out loosely attached chemicals so that activity returned. DI water flushing was followed by chemical cleaning to recover rest of the fouling. However, after each experiment with the synthetic ROC or real ROC it lost some of its activity due to fouling.

3.5 Analytical techniques

3.5.1 Conductivity, pH and temperature

The electrical conductivity and pH of the FO feed solution and DS were measured at the beginning and end of the experiment using a manual pH meter (GMH 3430 Greisinger, Germany) and a manual conductivity meter (GMH 3530 Greisinger, Germany). The pH and conductivity meters were dipped until the meter reading was stabilized. The difference in conductivity indicates water transfer rate to DS and salt reverse flow to FS. Thermoline BL-30 (Australia) temperature controller heater/chiller system was used to maintain temperature conditions throughout the FO operation.

3.5.2 Inductively coupled plasma emission spectrometry

For the analysis of a wider range of anions and cations in the synthetic feed solutions and RO concentrates, an Inductively Coupled Plasma Optical Emission Spectrometry instrument (ICP-OES) was used (Perkin Elmer OPTIMA 7300 DV ICPOES Instruments, USA). This technology uses an ICP source which is made by heating

argon gas up to temperatures of 10,0000 degrees Kelvin. The dissolved samples dissociate in the plasma and excite thermally. By detecting the characteristic excitation of the elements or directing the ions into a mass spectrometer, the elements' variety and quantity can be screened.

3.5.3 Total organic carbon analysis

The concentrations of organic compounds in the samples were determined using a total organic carbon analyser (multi N/C 3100, Analytik Jena AG, Jena, Germany). The samples were stored at 4°C for analysis.

The TOC analyser combines the combustion of carbon substances with subsequent selective detection of the carbon dioxide generated by combustion. The combustion method for the aqueous samples is thermal oxidation. The basic principle of this method is the oxidation of the organic compounds with oxygen at temperatures of approximately 800 to 1000°C with copper oxide serving as the catalyst. The total organic carbon (TOC) is determined by the difference method which requires two measurements. At first, a part of the sample is transferred to the TIC reactor, where the carbonate–derived CO2 fraction is detected as total inorganic carbon (TIC) in phosphoric acid. In the next step total carbon (TC) is determined by inserting the untreated sample in the combustion unit of the analyser, which converts the organic and inorganic carbon compounds into carbon dioxide.

TOC is obtained by the following equitation:

$$TOC = TC - TIC \qquad (3.1)$$

Where TOC = Total organic carbon, mg/L

TC = Total carbon, mg/L

TIC = Total inorganic carbon, mg/L

3.5.4 UVA measurement

A photometer (Shimadzu Company), Model Iraffinity-1 FTIR (Fourier transform infrared) spectrophotometer was used to measure UVA 254 .

3.5.5 Contact angle tests

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

3.5.6 Liquid chromatography-organic carbon detection

Liquid Chromatography-Organic Carbon Detector (DOC-Labor Dr. Huber, Germany) was used for detecting the major fractions of organic matter in the samples (Fig. 3.6). LC-OCD is a size–exclusion chromatography combined with organic carbon detection to separate the pool of natural organic matter (NOM) into major fractions of different

sizes, based on the Graentzel thin–film UV-reactor. The size-exclusion chromatography is coupled with three detectors - OCD-OND-UVD (organic carbon, organic nitrogen and UV-absorbance) - which divide the natural organic matter in six major sub-fractions that can be assigned to specific classes of compounds: biopolymers, humic substances, building blocks, low molecular-weight (LMW), acids, low molecular-weight neutrals, and hydrophobic organic carbon (Huber et al., 2011).

3.5.7 Micropollutants measurement and selected micropollutants

Organic micropollutants including pharmaceuticals, personal care products, and industrial chemicals belong to the main classes of contaminants in water reuse applications. The properties of selected different compound classes and solute for the study are given in Table 3.4. Measurement is done using solid phase enrichment (SPE) prior to liquid-chromatography with mass spectrometry detection employing electrospray ionization (ESI) (HP-LC/MS-MS: Agilent 1200 HPLC with Applied Biosystems triple quadruple MS API 4000, Luna C18 column) (Fig. 3.7). The analytical method is based on that of (Vanderford et al. 2006).

Samples for the SPE were taken at the beginning and end of each test with RO concentrate without pre-treatment. 500 mL samples were extracted using 5 mL, 500 mg hydrophilic/lipophilic balance (HLB) cartridges (Waters, Millford, MA, USA). Cartridges were pre-conditioned with 5 mL of methanol and 5 mL of MQ water. Each sample was spiked with 50 µL of a surrogate standard containing 50 ng of an isotopically labelled version of each analysis. The sample was then loaded onto the cartridges at a flow rate of 10 mL/min, after which the cartridges were rinsed with 5 mL

of reagent water and dried with a stream of nitrogen for 30 min. Loaded cartridges were stored at 4°C in sealed bags under nitrogen until elution and analysis.

Table 3.4 Overview of selected and analysed trace organics

Analytes	Use	MW g/mol	pK_a	Log *D* at pH 8.0	Charge at pH 8.0
Atenolol	Beta blocker	266.37	9.5; 13.8	-1.87	positive
Trimethoprim	Antibiotic	290.32	7	0.94	positive
Verapamil	Ca channel blocker	454.6	8.7	2.97	positive
Caffeine	Stimulant	194.19	-	0.11	neutral
Primidone	Anticonvulsant	218.25	12.3	0.91	neutral
Paracetamol	Analgesic	236.27	0.37	2.45	neutral
Carbamazepine	Antiepileptic	236.27	0.37	2.45	neutral
DEET	Insect repellent	191.27	-0.4	2.46	neutral
Diazinon	Insecticide	304.35	1.6	3.46	neutral
Diuron	Herbicide	233.09	- 1.6; 13.8	2.7	neutral
TCEP	Flame retardant	285.49	4.4	-7.2	negative
Sulfamethoxazole	Antibiotic	253.28	0.89	-1.51	negative
Ketoprofen	Analgesic	254.28	4.1	-0.41	negative
Naproxen	Anti-inflammatory	230.26	4.4	0.16	negative
Ibuprofen	Analgesic	206.29	4.47	0.44	negative
Diclofenac	Analgesic	296.15	4.15	0.74	negative
Gemfibrozil	Lipid regulator	250.33	4.8	1.26	negative

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Chapter 4

FO treatment of ROC from water reclamation plant

4.1 Introduction

Biological treated wastewater contains different types of contaminants such as heavy metals, micropollutants, salinity and microorganisms, which need to be removed to make these waters suitable for potable uses. Membrane technologies such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) play a vital role in removing these contaminants. These technologies, however, generate large volumes of waste streams that require disposal with particular attention to minimising their environmental impact. Reducing the volume of waste streams aiming at zero liquid discharge is an attractive option for minimising the environmental impact and producing better quality product water.

Reverse osmosis is a popular method used worldwide to convert sea water and wastewater into fresh water (Fritzmann et al., 2007). However, the major drawback of this process is the generation of large amounts of highly concentrated brines as an unwanted by-product which can cause environmental problem if discharged untreated. Forward osmosis (FO) has been suggested as a low energy process which can be used to: firstly, extract water from the reverse osmosis concentrates (ROC); and secondly, reduce the volume of ROC for easy handling including the crystallisation of salts (Kazner et al., 2014; Adham et al., 2007). The FO of ROC produces FO permeate which can be used as high quality recycled water provided the major contaminants in ROC are removed. No convincing information is available on whether FO can remove micropollutants which are considered to be toxic to humans and aquatic organisms.

In this part of study, we investigated whether FO is a promising technology to minimize the volume of ROC for easy handling and for safe disposal, and the extent of removal of organic micropollutants from ROC using FO with and without granular activated carbon (GAC) pretreatment.

4.2 Experiment

4.2.1 Water and chemicals used

Reverse osmosis concentrate was obtained from the Sydney Olympic Park Authority's (SOPA) MF/RO water filtration plant, which operates with a volumetric feed flow of about 55 m^3/h. It has a water recovery of about 80% which leaves a reject stream (ROC) of about 20%. General characteristics of the ROC are presented in chapter 3, Table 3.1. Micropollutants detected in ROC and their properties are presented in Table 4.1. The ROC was sampled and stored in glass bottles at 4^{o}C until required for FO tests.

Analytical grade NaCl supplied by Sigma-Aldrich of minimum assay (99.7%) was employed to prepare the draw solution (DS). Sodium chloride with concentrations of 2 and 3 M was used in all the experiments. The main criteria for selecting NaCl are that it has a high solubility, osmolarity and is simple to reconcentrate with RO without any risk of scaling (Cath et al., 2013).

Table 4.1 Properties of the detected micropollutants and their initial concentration in ROC

Micropollutants	Class	MW[a] (g)	Charge[b] (pH 7.5)	Conc (ng/L)	Log D[b] (pH 7)	Log Kow[a] (pH 7)	pKa
Amtriptyline	Anti depressant	277	+	44	3.48	4.92	9.4[a]
Atenolol	Beta-blocker	266	+	325	-1.87	0.16	9.6[f]
Caffeine	Stimulant	194	0	1030	-0.11	-0.07	10.4[e]
Carbamazepine	Anti analgesics	236	0	1380	2.23	2.45	<1[c], <2[d]
Diclofenac	Analgesics	294	-	250	1.48	4.51	4.1 – 4.2[c]
Diuron	Herbicide	233	0	335	2.7	3.49	1.7[b] 13.8[b]
Fluoxetine	Anti depressant	309	+	27	2.6	4.05	10.1[c]
Gemfibrozil	Lipid regulator	250	-	816	1.26	4.77	4.7[d]
Ibuprofen	Analgesic	206	-	357	1.44	3.97	4.47[h]
Ketoprofen	Analgesics	254	-	165	-0.14	3.12	4.45[a]
Naproxen	Analgesics	230	-	1210	0.16	3.18	4.2[c]; 4.15[a]
Primidone	Therapeutic	218	0	234	0.55	0.91	11.7[b]
Simazine	Herbicide	202	0	61	2.2	2.18	1.62[a]
Sulfamethoxazole	Therapeutic	253	-	303	-0.77	0.89	2.1[d]; <2[d]
Triclocarban	Agricultural chemical	316	0	62	5.06	4.9	12.7[g]
Triclosan	Anti- infective	290	0	91	5.19	4.76	7.9 [c]
Trimethoprim	Anti-infective	290	0	618	0.94	0.91	6.6 – 7.2[c]; 7.12[a]
Verapamil	Hypertension	454	+	48	2.5	3.46	8.97[b]

[a]U.S. National library of medicine (http://chem.sis.nlm.nih.gov/chemidplus/rn/52-53-9); [b]Calculated with Advanced Chemistry Development (ACD/Labs) Software V9.04 for Solaris; [c] Serrano et al., (2011); [d]Westerhoff et al., (2005); [e]Yang et al., (2011); [f]Hapeshi et al., (2010); [g]Loftsson, Hreinsdóttir & Másson (2005); [h]Thomas (2006); [a]MW: molecular weight

4.2.2 Analytical methods

The electrical conductivity and pH of the feed solution (FS) and DS of the FO were measured at the beginning and end of the experiments using a manual pH meter (GMH 3430 Greisinger, Germany) and a manual conductivity meter (GMH 3530 Greisinger, Germany,) respectively. The quantitative analysis of anions (Cl^-) and cations (Na^+, Ca^{2+}) in the experimental samples was done using an ion chromatograph (Metrohm 790 Personal Ion Chromatograph, Herisau, Switzerland). Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES: Perkin Elmer OPTIMA 7300 DV, USA) was used for the analysis of a wider range of cationic and anionic contaminants. Total organic carbon (TOC) and total inorganic carbon (TIC) were measured using a total organic carbon analyser (multi N/C 3100, Analytik Jena AG, Jena, Germany). The details are given in chapter 3.

A Liquid Chromatography-Organic Carbon Detection unit (LC-OCD) (DOC-Labor Dr. Huber, Germany) helped to measure the major fractions of TOC in the samples. This unit is a size–exclusion chromatography combined with organic carbon detection which separates the pool of TOC into major fractions of different sizes, based on the Graentzel thin–film UV-reactor. The four major fractions of compounds are: biopolymers (>20,000 g/mol), humic substances (1200-500 g/mol), building blocks (weathering product of humic substances) (500-350 g/mol), and acids + low molecular weight (LMW) humics (<350 g/mol) (Amy et al., 2011).

The concentrations of organic micropollutants was determined by solid phase extraction (SPE) and analysis using liquid chromatograph with tandem mass spectroscopy. 5 mL analytes were extracted using 500 mg hydrophilic/lipophilic balance (HLB) cartridges (Waters, Milford, MA, USA). These analytes were separated using an Agilent (Palo Alto, CA, USA) 1200 series high performance liquid chromatography (HPLC) system equipped with a 150 x 4.6 mm, 5 µm particle size, Luna C18 (2) column (Phenomenex, Torrance, CA, USA). Mass spectrometry was done using an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) equipped with a turbo-V ion source employed in both positive and negative electro-spray modes. All calibration curves had a correlation coefficient of 0.99 or better.

4.2.3 Forward osmosis bench-scale unit

A bench-scale FO unit as shown in Fig. 3.1 was used for conducting the FO experiments. The FO cell (20 mm width x 3 mm height x 210 mm length) consists of a channel on both sides of the FO membrane which transport the feed solution from one side of the membrane to the DS on the other side of the membrane. The membrane consists of a cellulose triacetate material with embedded polyester screen support (CTA-ES Membrane 1401270) having a pore size of 0.74 nm obtained from Hydration Technology Innovations, USA (HTI 2012). The cross-flow velocity was maintained across the membrane by adjusting knobs manually using a variable speed drive (Magnetic drive pump 316 SS, Cole-Parmer, USA). The flow rate was monitored using rota-meters (Cole-Parmer) which were installed in a series with pumps along the draw solution and feed solution streams in the circuit. A new membrane was used for each test run. The temperature of feed solution and draw solution solutions was kept constant at 25.0 ± 0.2°C using a water bath, in which stainless steel coiled pipes were immersed. The water bath was connected to a temperature control system (Thermoline BL-30) to ensure the temperature remained constant.

4.2.4 Experimental protocols

The FO system was tested with real ROC from the Sydney Olympic Park WRAMS plant. The tests served to determine the specific fouling potential of the main components of ROC and their impact on the permeate flux. The tests were conducted for 15-16 h with ROC as the FS and different concentrations NaCl as the DS. Conductivity was monitored at the initial and final stages of the experiments. Concentrations of TIC and TOC in the initial and final solutions were analysed to determine the amount of these compounds adsorbed onto the membrane and to identify the compounds causing fouling. The amounts of TIC and TOC adsorbed were assumed to be the differences between the product of their respective initial and final concentrations and normalised volumes. As the ROC had a significant scaling potential, pH adjustment of ROC was studied as a method to reduce the risk of scaling (Kazner et al. 2014).

4.2.5 ROC volume reduction and rejection of organic micropollutants without GAC pretreatment using FO

The experiment consisted of five steps. In the first step, six litres of ROC were divided into three equal parts and FO was conducted using 2 M NaCl as the DS. In the second and third steps, the three portions of the treated ROC in the first step were combined and used as the feed solution to further concentrate and reduce the volume of ROC by means of two additional FO processes, one after the other, using again 2 M NaCl as the DS. The pH of the concentrated ROC in the third step was reduced to 5.0 to minimise the potential of scaling (Kazner et al. 2014) and the experiment was continued in a similar manner as the first three steps with two more FO treatments using 2 M and 3 M NaCl as the DS for the fourth and fifth FO steps, respectively. The volume of the ROC after each FO treatment was measured. The concentrations of organic micropollutants in the initial ROC and in the final FO permeate (fifth step) were also measured.

4.2.6 Removal of TOC by fixed-bed GAC column

TOC usually exists in wastewater as a complex mixture of organic compounds, humic acids and fulvic acids. Granular activated carbon is considered to be one of the common adsorbent employed for removing TOC, and has already been utilised as a medium in filter-adsorbents in many water treatment plants worldwide (Babi et al., 2007). An experiment was conducted using a fixed-bed column (23 cm height, 2.2 cm internal diameter) containing a coal-based GAC to reduce the concentrations of TOC and organic micropollutants in the ROC (Fig. 2). The GAC obtained from James Cummins P/L, Australia had a particle size of 8×30 mesh ASTM and surface area of 1000 ± 50 m^2/g. The ROC (8 L) was passed through the column at an upward flow velocity of 32 ml/min using a pump. The bed volume of the column was 87.4 cm^3.

4.2.7 ROC volume reduction and rejection of organic micropollutants using FO after GAC pretreatment

The experiment on volume reduction using FO without GAC pretreatment described earlier was repeated with GAC pretreatment in five steps as done previously. However, this time eight litres of the GAC treated ROC were divided into four parts and FO was

conducted using 2 M NaCl as the DS in the first step. To make the FO process more efficient by reducing potential fouling, the pH of the feed solution after the second step, instead of after the third step as done without GAC treatment, was reduced to 5.0. The volume of the ROC after each FO treatment was measured as before. The concentrations of organic micropollutants in the initial GAC pretreated ROC and in the final permeate (fifth step) were also measured.

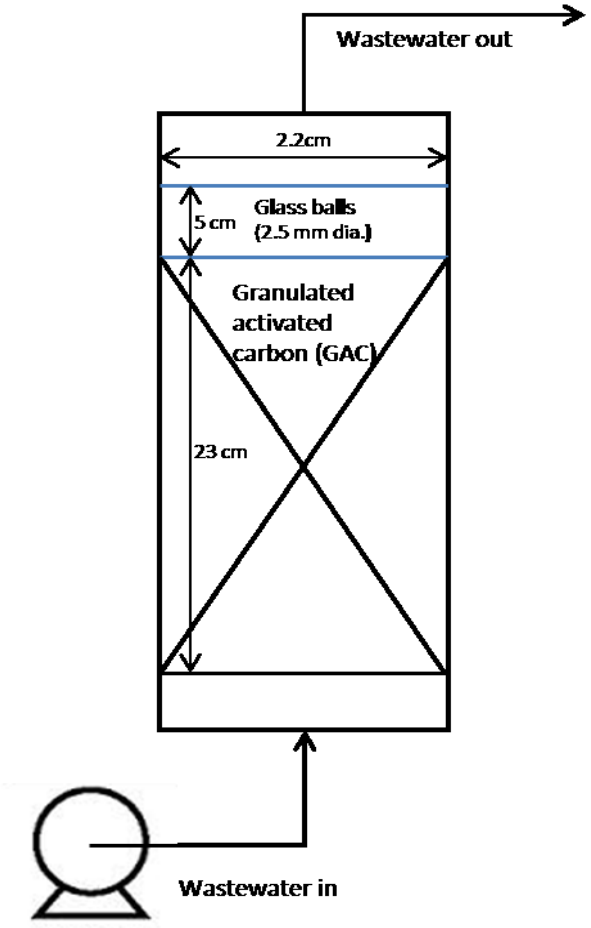

Fig. 4.1 Fixed-bed GAC adsorption column

4.3 Results and discussion

4.3.1 *FO without GAC pretreatment*

With each step of FO the volume of ROC decreased (Table 4.2). The final volume of ROC was 8% of the initial volume. This shows that FO can be effectively used to reduce the volume of ROC to a level of zero liquid discharge. As the final volume of

ROC is very small it can be easily handled for safe disposal or it can be used to crystallise the salts in ROC for beneficial use.

As the volume of ROC progressively declined with each step of FO, the flux of solution through the membrane was also reduced (Table 4.2). The decline of ROC flux as a percentage of baseline flux increased with each step until the pH was reduced at the end of the third step where the percentage decline abated. The flux decline was due to an increase in the concentration of the ROC as a result of volume reduction. The increased concentration of ROC caused fouling of the membrane due to the adsorption of inorganic and organic compounds. The results in Table 4.3 show that the amount of TIC adsorbed per unit area of membrane (0.45-1.71 mg/cm^2) was higher than the TOC adsorbed (0.29-0.76 mg/cm^2) during the first three FO steps. This is due to the higher initial TIC concentration in ROC compared to that of TOC. When the pH of the ROC was decreased to 5.0, the flux increased and flux decline as a percentage of the baseline solution decreased. This is due to the dissolution of the carbonate precipitates on the membrane and conversion of carbonates as CO_2 gas at the low pH.

Humic acids, building blocks, and acids + low molecular weight organics were the dominant foulants of the FO membrane (Fig. 4.2). Biopolymers such as polysaccharides contributed less to the fouling, particularly because the ROC had low polysaccharides concentration due to the MF pretreatment in the water filtration plant where the ROC was collected for the study. Due to the high molecular weights of polysaccharides they were easily removed in the MF treatment. The normalised concentrations (normalisation to the original volume of ROC) of the humic acids, building blocks, and acids + low molecular weight organics in solutions decreased compared to the initial concentration with each FO step showing they were adsorbed onto the membrane (Fig. 4.2).

Inorganic elemental analysis revealed a significant decrease in the normalised concentrations (normalisation to the original volume) of calcium, magnesium, potassium on the cation side and phosphate, carbonate sulphate on the anion side between the initial (FS of FO Step 1) and the final solution (FS of FO Step 5) (Fig. 4.3). The increase in concentration of sodium and chloride is probably due to diffusion of these ions from the DS containing high concentrations of NaCl to the FS. Modelling of the potential scaling from inorganic compounds at pH 7.5 with PHREEQC confirmed

the high risk of poorly soluble salts being formed, particularly calcite, dolomite, and aragonite.

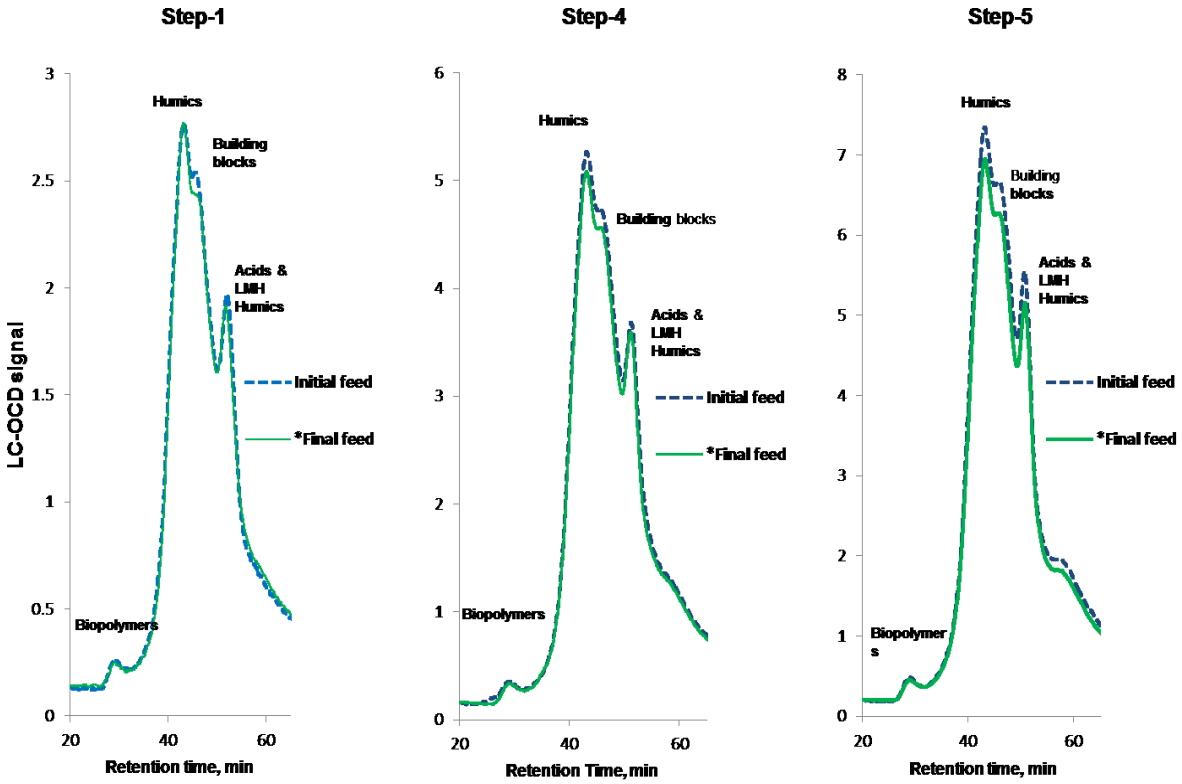

Fig. 4.2. LC-OCD chromatogram of the initial and final FO feed solution after the first, fourth, and fifth step of the FO process without GAC pretreatment (LMW-low molecular weight, *concentration normalised to the initial volume).

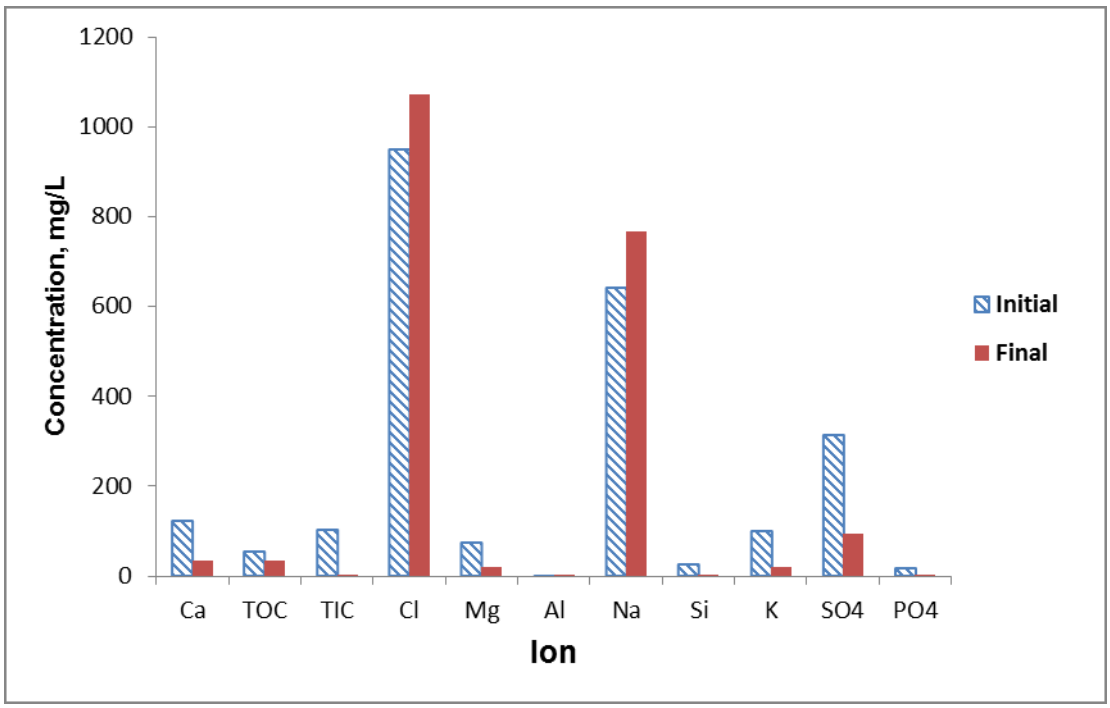

Fig. 4. 3 Concentration of ions in initial feed solution (FO Step 1) and final feed solution (FO Step 5) after the final volume was normalised to the original volume in FO without GAC pretreatment. The increase in Na and Cl ions is due to back diffusion from DS.

Table 4.2 Volume reduction of ROC and flux decline during FO without GAC pretreatment

FO step	FS	DS	ROC volume Initial/Final	Baseline flux (DI* water FS) avg.	Flux with ROC avg.	Flux decline
		mg/L	L	L/m^2·h	L/m^2·h	%
	Unadjusted pH 7.5					
1	ROC	2 M NaCl	6.00/3.54	19.2	12.6	34.0
2	ROC	2 M NaCl	3.54/2.75	19.2	9.7	49.5
3	ROC	2 M NaCl	2.75/2.10	19.2	9.1	52.6
	Adjusted pH 5					
4	ROC	2 M NaCl	2.10/1.14	19.2	13.5	29.7
5	ROC	3 M NaCl	1.14/0.47	22.4	12.7	43.3

Table 4.3 Inorganic (I)) and organic (O) carbon (C) adsorption on membrane during FO without GAC pretreatment (IC adsorbed at steps 4 and 5 cannot be calculated because part of the IC was lost to atmosphere as CO2)

FO step	FS	DS	TOC, Initial/final	TIC Initial/final	TOC adsorbed	TIC adsorbed	TOC adsorbed	TIC adsorbed
			mg/L	mg/L	mg/cm^2	mg/cm^2	%	%
Unadjusted pH 7.5								
1	ROC	2 M NaCl	50.6/76.7	103.4/155	0.76	1.71	11.0	12.0
2	ROC	2 M NaCl	76.7/94.9	155.0/185.6	0.29	0.90	5.0	7.0
3	ROC	2 M NaCl	94.9/115.2	177.0/212.5	0.45	0.45	7.0	4.0
Adjusted pH 5								
4	ROC	2 M NaCl	115.2/196.8	48.0/39.7	0.43	-	7.0	-
5	ROC	3 M NaCl	196.8/439.5	15.0/10.2	0.43	-	8.0	-

4.3.2 *FO with GAC pretreatment*

With each step of FO the volume of ROC was decreased (Table 5) as observed in the case of FO without GAC pretreatment. The final volume of ROC was 8% of the initial volume which is same as for FO without GAC pretreatment. This shows that FO can be effectively used to reduce the volume of ROC to a level of zero liquid discharge even with GAC pretreatment. As the volume of ROC progressively fell with each step of FO, the flux of solution through the membrane also declined (Table 4.5). The increased concentration of ROC caused fouling of the membrane via the adsorption of inorganic and organic compounds. The results in Table 6 show that the amount of TIC adsorbed per unit area of membrane (1.36-2.10 mg/cm^2) was higher than the TOC adsorbed per unit area of membrane (0.12-0.31 mg/cm^2) during the first two FO steps as observed in the case of FO without GAC pretreatment. GAC pretreatment greatly reduced TOC in the ROC by adsorption. This is evident in the TOC concentration decreasing from 50.6 mg/L in ROC before GAC treatment to 5.5 mg/L after GAC treatment (Tables 4.4 and 4.6).

4.3.3 *Removal of organic micropollutants*

Organic micropollutants occur at elevated concentrations in ROC and therefore they have to be removed if the ROC is to be safely disposed of without any adverse environmental impacts. Furthermore, removal of organic micropollutants will reduce FO membrane fouling which would allow the membrane to be effectively used for a longer period. Table 4.6 shows the removal of the micropollutants by adsorption onto GAC, and rejection by the FO membrane with and without GAC pretreatment. Only data for the draw solution concentrations of organic micropollutants at the last step of the FO process are presented. The concentrations obtained for the other steps are similar and therefore they are not presented. The rejection of the micropollutants was calculated as the difference in the amounts of micropollutants in ROC before and after FO using normalised volumes of ROC (i.e. normalising the actual concentrations in the reduced volumes of ROC after FO to the original volume of 2 L of ROC). GAC pretreatment alone removed 15 of the 18 micropollutants tested from the ROC at > 82%. FO without GAC pretreatment rejected 9 micropollutants at >82%.

Table 4.4. Volume and flux decline during FO with GAC pretreatment

FO step	FS	DS	ROC volume (L)-Initial/Final	Baseline flux (DI* water FS avg.	Flux with ROC avg.	Flux decline
		mg/L	L	$L/m^2 \cdot h$	$L/m^2 \cdot h$	%
Unadjusted pH 7.5						
1	ROC	2 M NaCl	8.0/5.0	19.2	9.4	51.0
2	ROC	2 M NaCl	5.0/4.3	18.0	11.0	39.0
Adjusted pH 5						
3	ROC	2 M NaCl	4.3/2.8	18.2	15.1	17.0
4	ROC	2 M NaCl	2.8/1.6	18.5	13.0	31.0
5	ROC	3 M NaCl	1.6/0.6	22.4	12.0	46.0

Table 4.5 Inorganic (I) and organic (O) carbon (C) adsorption on membrane during FO with GAC pre-treatment (IC adsorbed at steps 3, 4 and 5 cannot be calculated because part of the IC was lost to atmosphere as CO2)

FO step	FS	DS	TIC initial/final	TOC, initial/final	TIC adsorbed	TOC adsorbed	TIC adsorbed	TOC adsorbed
			mg/L	mg/L	mg/cm^2	mg/cm^2	%	%
	Unadjusted pH 7.5							
1	ROC	2 M NaCl	104.0/149	5.5/7.0	2.10	0.12	10.0	11.0
2	ROC	2 M NaCl	149.0/160	8.0/9.0	1.36	0.14	8.0	15.0
Adjusted pH 5								
3	ROC	2 M NaCl	47.0/46.0	9.0/11.2	-	0.17	-	18.0
4	ROC	2 M NaCl	6.2/7.3	11.2/16	-	0.14	-	19.0
5	ROC	3 M NaCl	7.3/5.3	16.0/21.3	-	0.31	-	51.0

The three micropollutants which were least removed by GAC were caffeine, trimethoprim, and verapamil at 79.2%, 65.4%, and 58.3 %, respectively. The reason for GAC not being able to remove a very high percentage of caffeine is probably due to its hydrophilic character (negative log D value) (Table 4.2). GAC being hydrophobic has a preference for the adsorption of hydrophobic compounds (Nguyen et al., 2012)). Trimethoprim and verapamil have high molecular weights (Table 4.2) and therefore they might have not sufficiently penetrated into the pores and cavities in GAC to be adsorbed (Margot et al., 2013). The low hydrophobicity of trimethoprim (log D = 0.94, Table 4.2) may be an additional reason for only a small percentage being removed. Many micropollutants (gemfibrozil, ibuprofen, ketoprofen, and naproxen) are negatively charged and have low log D values (hydrophilic) (Table 4.2) but have high adsorption capacity (>97% removal). The reason for this could be that these compounds are adsorbed by other mechanisms such as π-π interaction, specific polar interaction (H-bonding), van der Waals forces (Löwenberg et al., 2014; Margot et al. 2013; Nguyen et al., 2013)

The rejection of micropollutants by FO is poor, especially that of caffeine (44.1%), carbamazepine (52.3%), and diclofenac (52%). The reason for the low rejection of caffeine and carbamazepine may be that their concentrations in ROC were very high (Table 4.2). Additionally, caffeine has a very low molecular weight which may have helped it to pass through the FO membrane. The low rejection of diclofenac in spite of its negative charge may be because of its strong H-bond donor characteristic which attracted it to the membrane (Nguyen et al. 2013).

The FO membrane kept rejecting the micropollutants thus making the ROC more concentrated with micropollutants. This means that only small percentages of the micropollutants entered the DS. However, GAC pretreatment followed by FO reduced the concentrations of the micropollutants both in the ROC and DS. Seventeen out of the 18 micropollutants had concentrations in the DS below the detection limit (Table 4.7). Therefore, the DS was largely free from contamination with micropollutants. However, the DS was highly concentrated with NaCl and therefore it cannot be directly used for human consumption or irrigation of crops. There are, however, two ways in which it can be utilised advantageously. One is to use it as a DS for a future FO process. The other is to treat it by RO to remove the salts so that the RO permeate can be blended with the main stream RO permeate. The ROC resulting from this treatment can be mixed with other

ROCs and treated via the FO process. This concept of coupling RO and FO processes has been proposed by Chekli et al., (2012).

Table 4.6 Concentrations of organic micropollutants in initial ROC, in DS after Step 5 FO, in ROC after GAC treatment only and in DS after Step 5 FO with GAC pretreatment.

	Reporting level (ng/L)	Initial conc. in ROC (ng/L)	Final conc. in DS after FO only (ng/L)	Rejection by FO only %	Final conc. after GAC treatment only (ng/L)	Removal after GAC treatment %	Final conc. in DS after GAC and FO (ng/L)
Amtriptyline	5	44	<5	>88.6	<5	>88.6	<5
Atenolol	5	325	45	86.2	<5	>98.4	<5
Caffeine	10	1030	576	44.1	214	79.2	158
Carbamazepine	5	1380	658	52.3	<5	>99.6	<5
Diclofenac	5	250	120	52	<5	>98	<5
Diuron	10	335	33	90.1	<10	>97	<10
Fluxetine	5	27	<5	>81.5	<5	>81.5	<5
Gemfibrozil	5	816	260	68.1	<5	>99.4	<5
Ibuprofen	5	357	<5	>98.6	<5	>98.6	<5
Ketoprofen	5	165	<5	>97	<5	>97	<5
Naproxen	5	1210	308	74.5	9	99.3	<5
Primidone	5	234	75	67.9	<5	>97.9	<5
Simazine	5	61	<5	>91.8	<5	>91.8	<5
Sulfamethoxazole	5	303	84	72.2	<5	>98.3	<5
Triclocarbon	10	62	<10	>83.8	<10	>83.9	<10
Triclosan	5	91	18	80.2	17	90.8	<5
Trimethoprim	5	618	212	65.7	214	65.4	<10
Verapamil	5	48	<5	>89.6	20	58.3	<5

Forward osmosis treatment of ROC as FS was successful in rejecting most of the organic micropollutants from ROC due to the membrane operation restricting them going to the DS. However, GAC fixed-bed adsorption pretreatment removed most of the micropollutants from the ROC. GAC pretreatment followed by FO treatment restricted almost all the organic micropollutants from the ROC going to the DS. The removal of individual organic micropollutants varied widely and depended on many factors, such as their molecular weight, charge, hydrophobicity, and H-bonding. Used DS can be reused in subsequent FO treatment processes. Alternatively, after salts have been partially recovered from the used DS by RO treatment, the resultant RO permeate can be blended with the main RO permeate.

4.4 Conclusion

The study showed that FO is a promising technology for reducing the volume of ROC leading to zero liquid discharge. Five repeated FO steps using 2 or 3 M NaCl as the DS reduced the volume of 6 or 8 litres of ROC to 8%. With each successive step the flux decreased due to increased concentrations of organics and inorganics caused by the volume reduction of ROC which led to membrane fouling and scaling. Humic acids, building blocks, and acids + low molecular weight organics and carbonates of calcium and magnesium were found to have accumulated in the membrane. However, the flux decline was controlled by reducing the ROC pH from 7.0 to 5.0.

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Chapter 5

Application of pressure assisted forward osmosis for water purification and reuse of reverse osmosis concentrate from a water reclamation plant

5.1 Introduction

In wastewater reclamation plants, RO is currently being used as a final treatment step after biological treatment followed by microfiltration (MF) step to obtain high quality water for reuse (Lim et al., 2014). In this case, unwanted stream, ROC is also generated. This ROC is rich in dissolved organic compounds with average concentration of 27 mg/L in terms of (DOC) and comprised of significant amount of inorganic salts of Ca^{2+}, Mg^{2+} and SO_4^{2-}. The ROC also contains a broad range of organic micropollutants; such as pharmaceuticals, industrial chemicals and personal care products. This is a major concern in water recycling due to their potentially hazardous effects on human beings and the natural environment (Amy et al 2011).

Forward osmosis (FO) or pressure assisted forward osmosis (PAFO) can be used to minimise the volume of ROC for its safe discharge and reuse (Cath et al., 2006). In FO processes, there are two solutions; feed solution (FS) and draw solution (DS), which are separated by semipermeable membrane. FS has low osmotic pressure normally faces to active layer of the membrane and is called FO mode, on the contrary if FS faces to support layer of the membrane the system is called PRO mode (Cath et al., 2006).

If pressure is applied on FS side (PAFO), the permeate flux would be increased. The advantage of PAFO is getting a higher permeate water flux (J_w) even with relatively less concentrated draw solution (DS) (Blandin et al., 2013). Some studies have tested PAFO by at pressurising the feed solution to enhance water permeation through synergising osmotic and hydraulic driving forces (Blandin et al., 2013, & Oh et al., 2014). They showed the impact of hydraulic pressure on the FO membrane properties and the overall performances of the system. The increase in membrane water

permeability was mainly due to the membrane deformation against the spacers. They also observed that reverse salt diffusion was significantly lower than expected by the solution diffusion model, confirming the interest of PAFO in tackling current limitations of FO technology. However, more severe concentration polarization (CP) was observed in PAFO. To solve this problem, ultrasound was applied to the PAFO process (Choi et al., 2014). It showed improvement of flux and reduction of the decline in flux by scaling and colloidal fouling, which increased CP in FO process. Their study also highlighted the benefit of reducing the membrane fouling by scales and colloids.

FO and PAFO have a range of potential advantages due to low hydraulic pressure needed by this osmotically driven operations. These operations hold the promise of helping to achieve low energy utilisation, thereby lowering the operational cost, if suitable draw solutes and regeneration methods can be developed. Furthermore, the membrane fouling in FO and PAFO is relatively low and reversible. Moreover, a variety of contaminants can be rejected through these membrane operations (Zhao et al., 2012). Fouling rates were high not only in FO but also in PAFO especially in the treating high organic containing water. In order to reduce the organic fouling in FO process, our previous study was conducted with a pretreatment the granular activated carbon (GAC) adsorption (Jamil et al 2015). GAC was effective in controlling organic fouling. In addition, inorganic scaling of the feed solution could be addressed by pH adjustment.

Regeneration of draw solution can be energy intensive. However, if low concentration of fertiliser such as (KCl) is used as a draw solution, the diluted draw solution during FO process can directly be used for fertigation. Potassium chloride (KCl) is well known

fertiliser. For example, it was reported that 10 Kg KCl/m^3 (around 0.13 M KCl) is usually effective in planting of rice at panicle initiation, boot leaf and flowers to increase the seed yield and improve the quality (Jayaraj et al., 1997).

The objectives of this study were: (i) to investigate the relative merits of PAFO over FO to further concentrate ROC to minimize its volume for water purification and reuse the draw solution as fertilizer with low concentration of KCl (DS); (ii) to remove organic compounds and micropollutants from ROC using GAC pretreatment to reduce the organic fouling on membrane in PAFO, and (iii) to control the membrane scaling by softening the ROC with acid treatment.

5.2 Materials and methods

5.2.1 Reverse osmosis concentrate (ROC)

Reverse osmosis concentrate (ROC) obtained from a water reclamation plant in Sydney, Australia was used in this study. RO in this water reclamation plant has a water recovery of about 80%, which leaves a reject stream of about 20%. Water quality of the ROC is presented in **Table 3.1**. Micropollutants detected in ROC and their properties are presented in **Table 5.1**

Table 5.1 Properties of the detected micropollutants in ROC and their initial concentration.

Micropollutants	Class	MW* (g)	Charge[b] (pH 7.5)	Conc. (ng/L)	Log D[b] (pH 7)	Log Kow[a] (pH 7)	pKa
Benzophenone	Personal care product	182	n.a	56	n.a	3.18	n.a[a]
Caffeine	Stimulant	194	0	164	-0.11	-0.07	10.4[e]
Carbamazepine	Anti analgesics	236	0	474	2.23	2.45	<1[c], <2[d]
Diazinon	Insecticide	304		7			
Diclofenac	Analgesic	294	-	142	1.48	4.51	4.1 4.2[c]
Diuron	Herbicide	233	0	182	2.7	3.49	1.7[b] 13.8[b]
Naproxen	Analgesic	230	-	34	0.16	3.18	4.15[a]
4-n-nonylphenol	Detergent	220	n.a	30	n.a	5.76	n.a[a]
Primidone	Therapeutic	218	0	14	0.55	0.91	11.7[b]
Simazine	Herbicide	202	0	59	2.2	2.18	1.62[a]
Sulfamethoxazole	Therapeutic	253	-	737	-0.77	0.89	2.1[d]; <2[d]
Triclocarban	Agricultural chemical	316	0	13	5.06	4.9	12.7[f]
Triclosan	Anti- infective	290	0	55	5.19	4.76	7.9[c]
Verapamil	Hypertension	454	+	9	2.5	3.46	8.97[b]

[a]: U.S. National library of medicine (http://chem.sis.nlm.nih.gov/chemidplus/rn/52-53-9).
[b]: Calculated with Advanced Chemistry Development (ACD/Labs) Software V9.04 for Solaris.
[c]: (Serrano et al. 2011)
[d]:(Westerhoff et al. 2005).
[e]: (Yang et al. 2011).
[f]: (Loftsson, Hreinsdóttir & Másson 2005). *MW: molecular weight; **n.a: not available.

5.2.2 Chemicals and reagents

Commercial grade potassium chloride (KCl) of minimum assay (99.0%) was employed. KCl at a concentration of 0.25 M (mole) was used as draw solution (DS) in all the experiments. The following are the main reasons for selecting KCl; it is a fertiliser with high solubility (4.6 M) and two molar KCl solution has a high osmotic pressure of 89.3 atm at 25°C. Moreover, it has the highest pure water flux (6.34 m/s) among the fertilisers tested in a previous study (Phuntsho et al., 2011).

5.2.3 Bench-scale pressure assisted forward osmosis (PAFO)

A bench-scale PAFO unit was used for conducting the PAFO experiments as shown in Fig. 2.3. The lab-scale PAFO membrane cell used was 77 mm length x 26 mm width x 3 mm height. It consists of a channel one each side of the FO membrane, which transport the FS from one side of the membrane to the DS on the other side of the membrane. The PAFO used a flat sheet membrane of cellulose triacetate with embedded screen support (CTA-ES) (obtained from Hydration Technologies Inc. (HTI)). In this study, different pressures (0, 2, 3, and 4 bar) were applied on FS side and two different concentrations of DS (0.25 and 0.40 M of KCl) were used. As FO membrane is designed for low-pressure operation, a maximum pressure employed in this study was 4 bar. Spacers were used on both sides of the membrane, which provided additional support for the FO membrane. Pressure on the feed side of the membrane was regulated manually using the valve located at the outlet of the membrane cell (Fig. 2.3). A cross-flow velocity of 10.7 cm/s was maintained across the membrane by adjusting knobs manually using a variable speed drive (Magnetic drive pump 316 SS, Cole-Parmer, USA). The flow rates were monitored using rota-meters (Cole-Parmer, USA), which were installed in a series with pumps along the FS and DS streams in the

circuit. The temperature of FS and DS was kept constant at 25.0 ± 0.2°C using a cooling water bath, in which stainless steel coiled pipes were immersed. The water bath was connected to a temperature control system (Thermoline BL-30) to ensure constant temperature condition.

5.2.4 Experimental protocols

The PAFO system was tested with real ROC collected from a water reclamation plant. First series of experiments were conducted to determine the specific fouling potential of the main components of ROC and their impact on the permeate flux. The tests were conducted for 90 h with ROC as the FS and 0.25 M of KCl as the DS. Conductivity was monitored at the initial and final stages of the experiments. Concentrations of total inorganic carbon (TIC) and total organic carbon (TOC) in the initial and final solutions were analysed to determine the amount of these compounds adsorbed onto the membrane surface to identify the compounds causing fouling. The amounts of TIC and TOC retained were assumed to be the differences between the product of their respective initial and final concentrations (C_0 and Ce) and normalised volumes (Vn) i.e. (C_0- Ce)*Vn.

Secondly, as the ROC had a significant scaling potential as shown in Table 3.1 pH adjustment of ROC was studied as a method to reduce the scaling on the membrane (Jamil et al., 2015).

The ROC was then pretreated with GAC fixed bed column to reduce the organic carbon in the FS, which had significant organic fouling potential on the membrane. Details on the GAC pretreatment procedure is described in the following section.

5.2.5 Fixed-bed GAC column

ROC is a complex mixture of organic compounds humic acids and low molecular weight acids and neutrals, biopolymers and organic micropollutants (OMs). Granular activated carbon (GAC) is considered to be suitable and practical for removing TOC, and is been utilized in several water treatment plants worldwide to remove dissolved compounds (Babi et al., 2007). An experiment was conducted using a fixed-bed column (35 cm height and 2.2 cm of internal diameter) packed with coal-based GAC (MDW4050CB supplied by James Cumming & Sons Pty Ltd. Sydney, Australia) to reduce the concentrations of TOC in the ROC. The GAC had a particle size of 12×40 mesh (ASTM) and surface area of 1000 ± 50 m^2/g. More details of GAC can be found elsewhere (Shanmuganathan et al., 2015). The ROC was passed through the column at filtration velocity of 6.3 m/h using a pump. The bed volume of the adsorption column was 133 cm^3.

5.2.6 Analytical methods

The analytical methods to measure pH, conductivity, inorganic ions, total organic and inorganic carbon (TIC and TOC) are explained in sections 3.5.1, 3.5.2 and 3.5.3 (chapter 3) respectively.

Methods for liquid chromatography-organic carbon detection (LC-OCD) and micropollutants are explained in sections 3.5.6 and 3.5.7 respectively in chaper 3.

5.3 Results and discussion

5.3.1 PAFO performance indicators

5.3.1.1 Water permeation with different applied pressures and DS concentrations

In osmotic membrane processes, water flux is greatly dependant on (i) differential applied pressure (ΔP), (ii) osmotic differential pressure between feed and draw solutions ($\Delta\pi$), and (iii) specific properties of the membrane. As shown in Fig. 5.1, the permeate water flux (Jw) in PAFO is proportional to the applied pressure to FS, and DS (KCl) concentrations. The difference in flux was not significant between two DS concentrations (0.40M and 0.25 M) used and, as such, lower concentration of DS of 0.25M KCl was chosen for the subsequent experiments. Here, deionised (DI) water was used as FS. The osmotic pressure (π= iCRT) of 1M KCl is 49.5 bar at 25^0C and it is proportional to concentration (M). The ratio of osmotic pressure of 0.40M KCl and 0.25M KCl is 1.6. The increase in average flux in FO was expected to be 1.6. However, the increase in average flux was in the ratio of 1.4 as the DS concentration was decreased with the time and feed solution concentration was increased, accordingly the net osmotic pressure decreased.

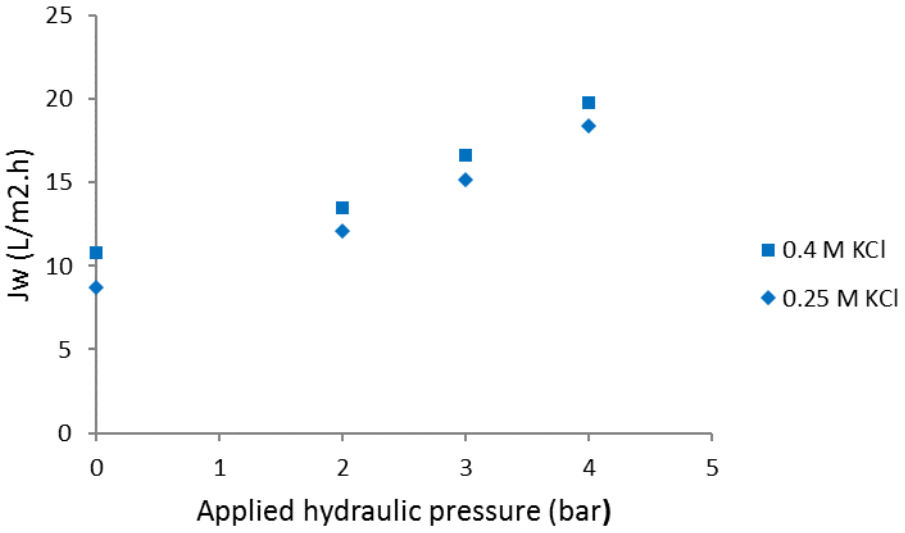

Fig. 5.1 Water permeate flux (Jw) profile at different applied pressures (0, 2, 3 and 4 bar) (Feed solution = DI water, and DS = 0.25 and 0.40 M KCl)

5.3.1.2 Reverse solute diffusion

The reverse solute diffusion or flux (Js) from the draw solution to the feed solution leads to the loss of draw solutes requiring additional cost for replacement of the draw solution. It was expected that applied pressure on FS would restrict reverse solute flow. However, the reverse solute flux was very similar of about 0.63 and 1.0 g/L both in FO (without any pressure) and PAFO operations at applied pressure of 2, 3 and 4 bar with 0.25M and 0.40M KCl, respectively (Fig. 5.2). This indicates that although the pressure applied at FS could reduce the possibility of reverse solute flow, the membrane properties might have changed with applied pressure (Bladin et al., 2013). This may have resulted in the same reverse solute flow even with the pressure applied at opposite direction of revere flow. There are other possible mechanisms of reverse salt flux in

PAFO process. It was reported that the reverse solute flux (RSF) was lower and feed solute rejection was higher in the PAFO (Sahebi et al., 2015). As any osmotic process, PAFO is associated with two independent solutions on each side of the membrane and hence there is a bidirectional movement of solutes. The solute fluxes are usually assessed in terms of salt rejection for feed solutes and the RSF for draw solutes. The RSF is measured as a ratio of reverse draw solute flux (Js) and the water flux (Jw) while Js (where Js = BΔC) is given as a function of solute permeability coefficient B and the concentration difference ΔC between draw solution (CD) and feed solution (CF) (where ΔC= CD-CF). Sahebi et al. (2015) showed the SRSF for FO process (DP = 0) is 0.77 g/L and 0.60 g/L for NaCl and KCl, respectively, however, it decreases to 0.49 g/L and 0.45 g/L, in PAFO process. As mentioned earlier, the decline in the SRSF in the PAFO process is likely due to either change in the B value or change in the CD or both. This study however, observed a decrease in the reverse diffusion of the draw solutes with applied pressure indicating that the increased water permeability likely limits the diffusivity of the draw solutes through the membrane due to enhanced convective water flux that drives the draw solutes away from the membrane due to back diffusion. The alternative explanation is that, the increase in the applied pressure increases the water flux, which in turn alters the solute concentrations at the membrane boundary layer on both sides of the membrane due to enhanced CP effects. This reduces the concentration difference (ΔC=CD-CF) between the DS and FS that determines the rate of reverse diffusion of the draw solutes. The DS concentration decreases due to increased dilution while FS concentration increases due to more feed solute rejection thereby reducing the ΔC and ultimately the RSF (Coday et al., 2013).

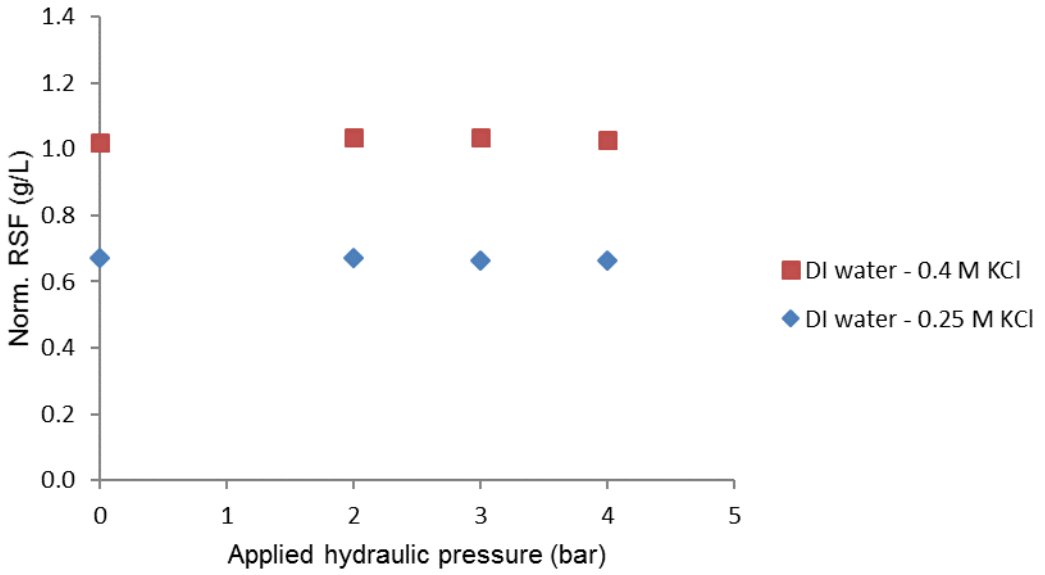

Fig. 5.2 Reverse solute flow with CTA-ES membrane using DI water as FS and 0.25 and 0.4 M KCl as DS.

5.3.2 Fluxes with different applied pressures with ROC

PAFO was then tested with real ROC as FS and 0.25M KCl as DS. Different pressures (0, 2 3 and 4 bar) were applied on FS. As can be seen from **Fig. 5.3**, the initial water permeate flux was proportional to the applied pressure. When the 2 bar of pressure was applied on FS, flux was improved by approximately 20%, from 6.9 (no pressure; 1 bar) to 8.7 L/m^{2}h (LMH). There was decline in flux with time and this was more significant with higher applied pressure. During 90 h of PAFO operation with 4 bar pressure, 70% of flux decline was observed while FO mode resulted in a lower decrease in flux (by 50%). This is probably due to the compact fouling on the membrane surface and high flux that increased the loading at higher applied pressure (Roig et al., 2010 & Nguyen 2012). The overall total water production during 90 h was 915 mL (44%) for FO (without pressure). However, this amount increased in PAFO application with applied pressure of 2 bar 1033 mL (53%). The flux conversion further increased with 3 and 4

bars applied pressure to 1235 mL (63%) and 1470 mL (73 %), respectively. Here the water production is the amount (or %) moved to DS from FS. It should be noted the values are based on small FO membrane area of 22.0 cm^2 and this is the reason why, only small quantity is noticed. Nevertheless, a 1 bar increase in applied pressure resulted in 10% water production improvement.

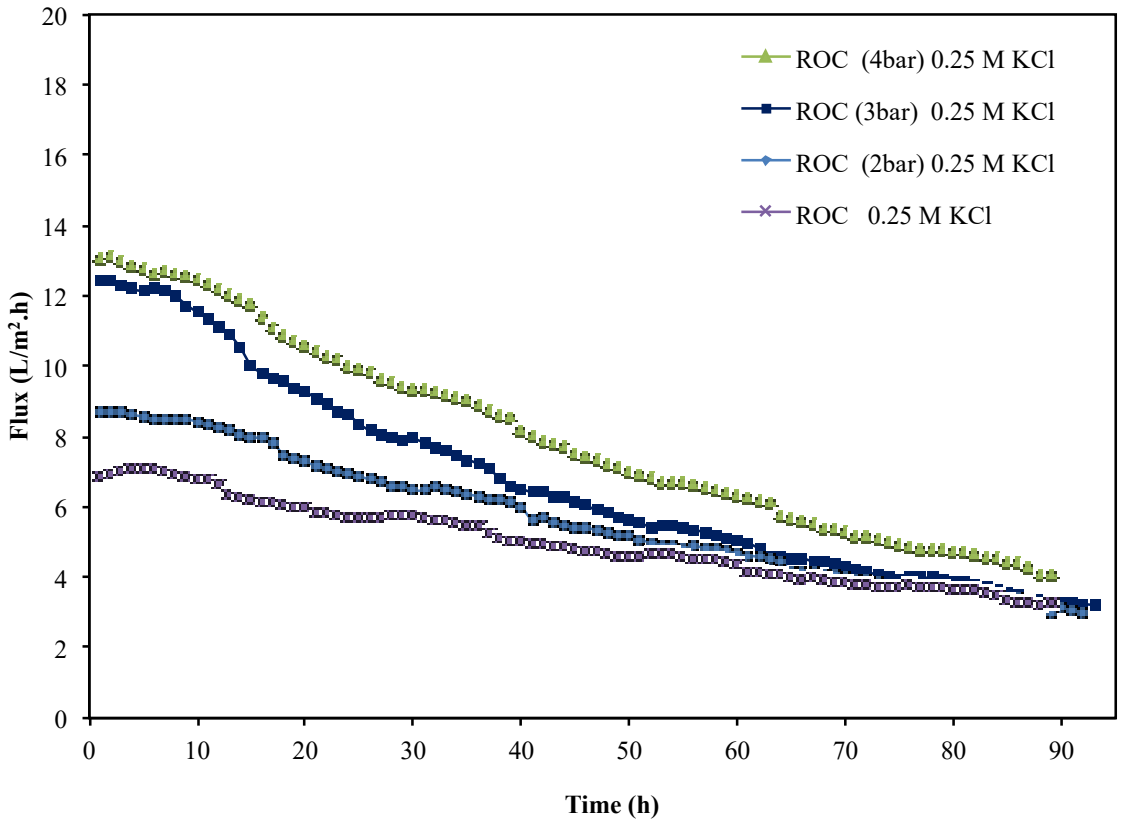

Fig. 5.3 Water permeate flux (Jw) profile at (0), 2, 3 and 4 bar applied pressures (FS = real ROC, and DS = 0.25 M KCl).

Note: Pressure 0 bar = FO mode without any additional applied pressure

5.3.3 Fouling and its mitigation

Flux decline and fouling pattern were studied with ROC and pretreated ROC as feed solution: i) ROC without any treatment; ii) Pre-softened ROC, and iii) ROC pretreated by GAC adsorption and pre-softening.

The (pre)-softening of ROC was done by adding the predetermined quantity of HCl to ROC to adjust pH to 5.0 for scaling control. The ROC was also pretreated by passing it through the fixed GAC adsorption column to reduce organic fouling on the membrane. The volume conversion (i.e. as permeate volume or productivity) of PAFO operated with 3 bar of applied pressure was low of about 44 % (**Table 5.2** and **Fig. 5.4**), when there was no pretreatment. This low volume conversion was probably due to the fouling by organic and inorganic compounds.

Table 5.2 ROC volume reduction with PAFO at 3 bar pressure and 0.25M KCl as DS.

PAFO (Operation for 90 h)	ROC without any treatment (pH 8)	ROC (pH adjusted) (pH 5)	ROC (GAC pretreated and pH adjusted)
Initial/final volumes of FS (Vi/Vf)	1.79	3.17	4.35
Flux conversion of ROC* (%)	44	68	77

In the second experiment, ROC solution was softened by adding HCl and the softened solution was used as feed to PAFO experiment. The softening (pretreatment) increased

the volume conversion significantly from 44 % to 68 %. The alkalinity (as $CaCO_3$) of the ROC was high of 380 mg/L and the addition of HCl reduced the inorganic carbon by the release of CO_2. This helped to reduce the inorganic scaling of the membrane and it was confirmed by TIC analysis.

In the third experiment, the softened ROC solution further underwent GAC adsorption prior to PAFO experiment. The resultant volume conversion was increased further from 68 % to 77 %.

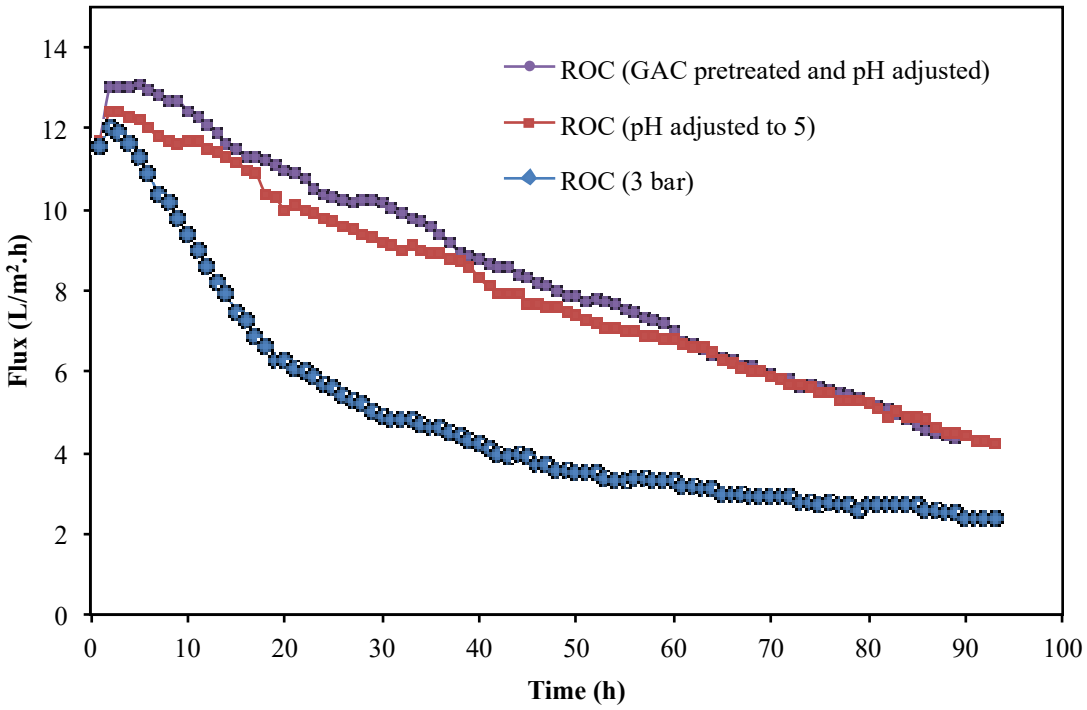

Fig. 5.4 Comparison of flux in PAFO with and without pretreatment of ROC (Pressure = 3 bar, DS= 0.25 M KCl, and CTA-ES, HTI membrane in FO mode at 25 °C)

5.3.3.1 Fouling recovery

The fouling recovery of fouled membrane by ROC was studied by washing with two different solutions: DI water and acidic water. A baseline test was first conducted with DI water with 3 bar of pressure as FS and 0.25 M KCl was used as DS (Fig. 5.5A). PAFO was then operated with real ROC as FS for 16 h (with 0.25 M KCl as DS) (Fig. 5.5B), in order to study the combined effect of inorganic scaling and organic fouling by ROC on CTA-ES membrane. The membrane was then flushed with DI water for 30 min at a cross flow velocity of 21.4 cm/s after 16 h of PAFO operation with ROC. The PAFO run was continued after flushing fouled membrane with DI water (Fig. 5.5C). Finally, the membrane was washed with DI water followed by acidic water of pH 4.5 (Fig. 5.5D).

As shown in **Fig. 5.6** and **Table 5.4**, the average baseline water flux (Jw) was 14.9 LMH. The resultant flux with ROC as FS was decreased to 11.4 LMH (by 23.5%) due to fouling (scaling and organic fouling). Both sides of the membrane were then washed with DI water. This water flush improved the membrane flux by only 7.5%. Again the same membrane was flushed with acidic water (pH 4.5) and the PAFO experiment was continued with DI water as FS. The membrane flux was increased by 14.0% and almost restored to its original baseline flux (98.0%). This indicated that most of the fouling by ROC on the CTA-ES membrane was removed by DI water flushing followed by acidic water cleaning.

Table 5.3 Effectiveness of membrane cleaning with DI water wash and acidic water (pH 4.5) flushing after ROC fouling experiment (DS = 0.25 M; Pressure = 3bar; and Experiment duration = 16 h).

PAFO steps	FS	Average flux (Jw) ($L/m^2.h$)	Fouling (%)	Fouling recovery (%)	Average flux comparison (%)
Baseline test	DI water	14.9	-	-	100
ROC	ROC	11.4	23.5	-	76.5
Membrane flushed with DI water	DI water	12.5	16.0	7.5	84.0
Membrane flushed with diluted HCl of pH 4.5	DI water	14.6	2.0	14.0	98.0

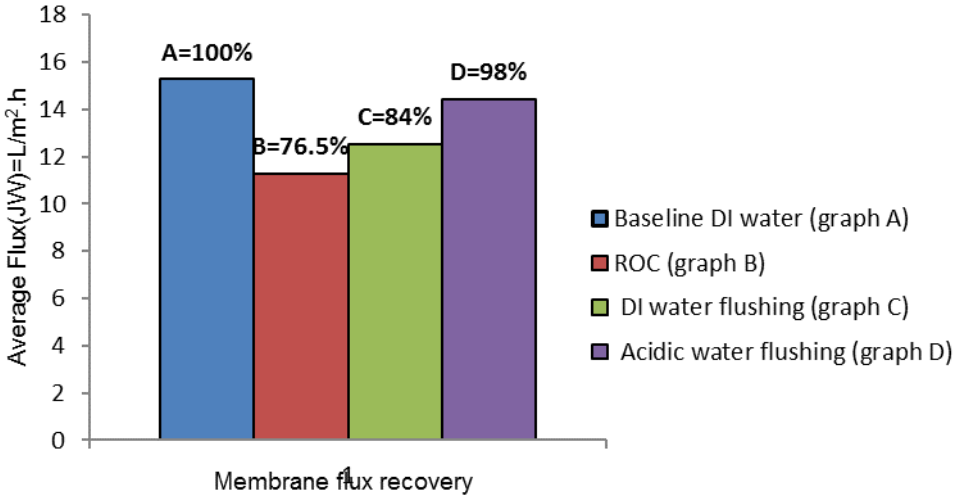

Fig. 5.5 ROC fouled membrane recovery after DI water and acid flushing experiment (0.25 M KCl as DS and Pressure 3 bar at FS).

5.3.3.2 Inorganic and organic fouling

As shown in Table 5.4, organic and inorganic carbon fouling on the membrane was studied with ROC with and without pretreatment. The experiments were run for 90 h. For each test using different FSs, new membrane (CTA-ES from HTI) was used. Firstly, real ROC without any treatment was used as FS. In this case, the inorganic scaling was 22% (in terms of TIC), while organic fouling (in terms of TOC) was 13.5% on the membrane (Table 5.4). However, when ROC solution was softened by the addition of HCl, the TIC of the solution was reduced from 78.4 to 5.8 mg/L. However, the TOC remained the same at 17 mg/L. Lastly, the pretreatment with softening followed by GAC adsorption column reduced the TOC from 17 mg/L to 2.2 mg/L. In this case both TOC and TIC were reduced and resulted in less organic fouling and

scaling on the membrane. This shows that PAFO can effectively be used to reduce the volume of ROC with minimal fouling and scaling by pretreatment with GAC adsorption and softening with acid.

Xie et al. (2015) compared the fouling behaviour of alginate on FO and PAFO processes. They demonstrated that hydraulic pressure played an important role in membrane organic fouling behaviour, particularly in fouling reversibility in FO and PAFO. The fouling layer thickness in FO was lower than PAFO while the alginate foulant volume of PAFO was larger than FO. The alginate fouling reversibility in FO process was higher than PAFO. Such fouling layer characteristics indicated that the large hydraulic pressure induced significant compression and compaction of the alginate fouling layer, which led to irreversible fouling layer formation. Their study proposed two possible compaction mechanisms, namely permeate drag force and compression of foulants. Fouling layers in FO and PAFO membrane processes investigated undergo similar extent of compaction due to the permeate drag force as identical initial water fluxes were employed. However, the compressibility of foulants under hydraulic pressure may contribute to compression of fouling layers to a significant extent.

In a previous study (Kim et al., 2014) the propensity and reversibility of combined organic–colloidal fouling in PAFO were systematically investigated. Alginate, silica colloids, and their mixture (i.e., combined organic–colloidal) were used as model foulants. Their findings demonstrate that combined organic–colloidal foulants caused more rapid flux decline than the individual foulants due to the synergistic effect of alginate and silica colloids. As a result, much lower flux recovery was achieved by

physical cleaning induced by increasing the cross-flow rate, in contrast to single foulants where the fouling layer was easily removed under all solution conditions. The role of applied hydraulic pressure in PAFO was examined to elucidate the mechanism of fouling layer formation, fouling reversibility, and water flux recovery. Higher fouling propensity and lower fouling reversibility of combined organic– colloidal fouling were observed in the PAFO. As ROC was rich in both inorganics (colloidal) and organics, it can be seen a rapid decline in flux with ROC feed (Fig. 5.3). However, the fouling was partially recovered by DI water flushing and the rest by acidic water circulation

Table 5.4 Total inorganic carbon (TIC) and total organic carbon (TOC) adsorbed on the membrane in PAFO: i) ROC without any treatment; ii) Softened ROC; and iii) Pre-treated ROC (by GAC and softening). (DS= 0.25 M KCl; applied pressure= 3 bar).

FS	TOC Initial/final mg/L	TIC Initial/final mg/L	TOC adsorbed mg/cm^2 of membrane	TIC adsorbed mg/cm^2 of membrane	TOC adsorbed at membrane %	TIC adsorbed at membrane %
i) ROC without any treatment	17/14.7	78.4/61.1	0.11	0.86	13.5	22
ii) Softened ROC	17.2/13.2	5.8/1.4	0.2	-	23	-
iii) Pretreated ROC (by GAC and softening)	2.2/2.1	5.4/1.4	-	-	-	-

5.3.4 Removed dissolved organic carbon fractions

A detailed organic fraction study by LC-OCD showed that ROC is mainly composed of hydrophilic compounds (92.4 %) (**Table 5.5**). The hydrophilic DOC fraction is further subdivided into humic substances (HS; 77.0% out of hydrophilic DOC fraction) lower molecular weight neutrals (LMW-N; 12.6 %) and the rest are biopolymers (BP) and building blocks (BB). BP was probably removed by MF used in the reclamation plant prior to RO. Some of the LMW-N and BB would have been biologically oxidized during the biological treatment used upstream of MF and RO. Thus, HS and remaining LMW-N are the major contributors for membrane organic fouling. HS was reported as a main organic foulant in FO process (Sahebi et al., 2015). The permeation of solutes decreased as the deposition of HS increased. It was hypothesized that the hydrated HS fouling layer reduced solute diffusion through the membrane pore and increased solute rejection by steric hindrance, but not the permeation of water molecules. However, GAC adsorption column removed about 78 % of DOC mainly HS as presented in **Table 5.5**. This clearly increased the flux in PAFO as shown in **Fig. 5.4.** More than 50 % of the LMW-N was also removed by GAC.

Table 5.5 Organic fractions of ROC before and after GAC pretreatment (analysed by LC-OCD).

	DOC	Hydrophobic DOC	Hydrophilic DOC				
				BP	HS	BB	LMW-N
ROC (mg/L)	19.8	1.5	18.3	0.9	14.1	1.0	2.3
Composition (%)	100	7.6	92.4	4.9	77.0	5.5	12.6
GAC treated ROC (mg/L)	4.4	0.8	3.6	0.7	1.5	0.4	1.0
Removal eff. (%)	78	48	80	13	89	63	59

5.3.5 Inorganic ion concentration

Inorganic ion analysis revealed a significant decrease in the normalised concentrations of calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na) on the cation side and chloride (Cl), nitrate (NO_3) phosphate (PO_4), carbonate (CO_3), and sulphate (SO_4) on the anion side between the initial FS and the final FS (**Fig. 5.6**). For example, the initial concentration of SO_4 in FS was 150 mg/L. After PAFO operation the final concentration of SO_4 in FS was reduced to 112 mg/L. The difference between initial and final normalized concentrations of FS was deposited on the surface of membrane. (**Fig. 5.6A**). It was revealed that DS contained some of the ionic species, which were not rejected by the membrane. The rejection was mainly governed by size of the molecule and charge on it and initial concentrations in FS. The SO_4, PO_4 and NO_3 were completely rejected by membrane. However, Ca, Mg and Na were partially rejected and the rest passed through membrane by about 11, 6 and 27 %, respectively (**Table 5.6**). The concentrations of K

and Cl ions could not be quantified in DS because they were present in both FS and DS. However, the increase in concentrations of K and Cl in FS was due to reverse diffusion of these ions from the DS containing high concentrations of KCl. Moreover, in second and third sets of experiment, the Cl concentration was increased further in FS because HCl was added for softening the ROC (**Fig. 5.6B & 5.6C**).

Table 5.6 Ionic species passed through the membrane from FS to DS.

	Ca	Mg	Na	NO_3	SO_4	PO_4
ROC initial conc. (FS)mg/L	73.1	63	369	27.4	149.8	9.36
DS final normalized conc.mg/L	8.6	4	100	0	0	0
Ions passed to DS (%)	11.8	6.3	27.1	0	0	0

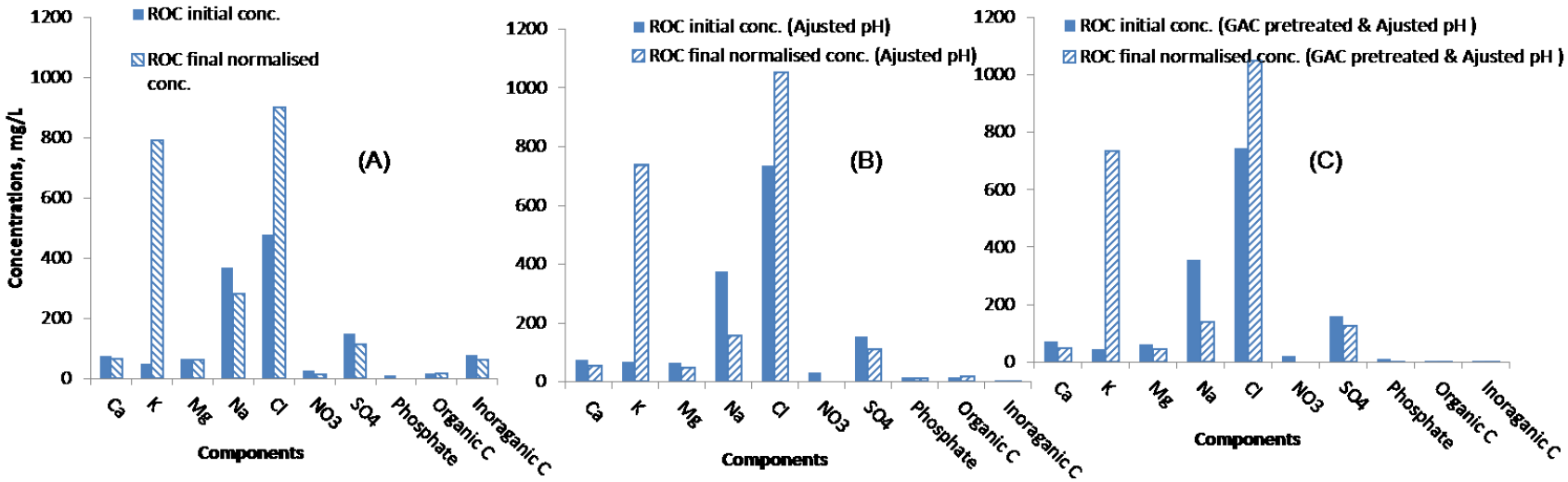

Fig. 5.6 Concentration of components in initial and final FS volume normalised to the original volume in PAFO with three different FSs: (A) ROC without any treatment; (B) ROC pH adjusted to 5; and (C) ROC - GAC pre-treated and adjusted pH 5.

5.3.6 Removal of organic micropollutants

Organic micropollutants are found in ROC and these compounds can have potential hazardous effects on environment if discharged untreated (Blandin et al., 2015 & 2016). Moreover, the removal of organic micropollutants and humic substances will reduce FO membrane fouling and this would enhance membrane efficiency. **Table 5.7** shows the removal of the micropollutants by GAC adsorption. GAC pretreatment removed 12 of the 14 micropollutants tested from the ROC below detection limit.

The two micropollutants, which were not removed by GAC, were caffeine and 4-n-nonylphenol and their removal efficiencies were at 91.5 % and 43.3 %, respectively. The possible cause for GAC not being able to remove a very high percentage of caffeine is due to its hydrophilic character (negative log D value; **Table 5.1**). GAC has an affinity for the adsorption of hydrophobic compounds (She et al., 2013). Whereas, naproxen is also negatively charged and have low log D values (**Table 5.1**) but it has high adsorption capacity (below detection limit). The reason for this could be that this compound is adsorbed by other mechanisms such as π-π interaction, specific polar interaction (H-bonding), and van der Waals forces (She et al 2013, Xie et al., 2015 & Kim et al., 2014).

Table 5.7 Concentrations of organic micropollutants in untreated ROC, in ROC after GAC treatment only, and in DS after GAC pretreatment and PAFO

	Detection limit (ng/L)	Conc. in untreated ROC (ng/L)	Conc. in ROC after GAC treatment (ng/L)	Removal eff. by GAC treatment (%)	Final conc. in DS after GAC pretreatment and PAFO (ng/L)
Benzophenone	20	56	<20	*	<20
Caffeine	10	164	14	91.5	14
Carbamazepine	5	474	<5	*	<5
Diazinon	<5	7	<5	*	<5
Diclofenac	5	142	<5	*	<5
Diuron	5	182	<5	*	<5
Naproxen	5	34	<5	*	<5*
4-n-nonylphenol	<5	30	17	43.3	17
Primidone	5	14	<5	*	<5
Simazine	5	59	<5	*	<5
Sulfamethoxazole	5	737	<5	*	<5
Triclocarbon	10	13	<10	*	<10
Triclosan	5	55	<5	*	<5
Verapamil	5	9	<5	*	<5

*Below detection limit.

5.4 Conclusions

The water production was higher in PAFO by 9 % and 29 % at moderate applied pressure of 2 and 4 bars during the 90 h of experiments with ROC. The study examined the need for GAC adsorption and pH adjustment as pretreatment to reduce organic fouling and softening to reduce the scaling on FO membrane. The GAC adsorption reduced TOC by about 90 % and softening of ROC by acid reduced the inorganic carbon by about 85 %, which helped to control membrane fouling and scaling. GAC pretreatment also adsorbed 12 out of 14 organic micropollutants (studied in the present study) from the ROC to below detection limit. This study confirmed that GAC pretreated ROC can safely be discharged into the environment. In this study, a low concentration of 0.25 M KCl solution chosen as DS. It was diluted to 0.14 M KCl due to transport of water permeate flux (J_w) from feed solution during the PAFO experiments. This diluted KCl solution can be used for direct fertigation, as the past studies showed successful use of 10 Kg/m^3 (≈0.13 M KCl) for fertigation.

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Chapter 6

Use of forward osmosis membrane at nanofiltration mode for reverse osmosis concentrate treatment

6.1 Introduction

The real challenge for RO used in water reclamation plants is the generation of brine (or concentrate) stream, which contains high dissolved contaminants and salts. Advanced oxidation processes and membrane distillation (MD), (Martinetti et al 2009., & Zhou et al., 2011b) have been applied for ROC treatment; however, this option is not cost-effective for wider application. Pressure assisted forward osmosis (PAFO) was investigated with simple pretreatment in this study in chapter 5 (Jamil at. el., 2016).

Ren and McCutcheon (2014) study has indicated that support layer of FO membrane imparts a resistance to solute diffusion and causes internal concentration polarization (ICP). If one uses nanofiltration (NF) instead of FO, one does not need DS. Xie et al. (2012) investigated a FO membrane (HTI type CTA-ES) which is cellulose triacetate embedded in a polyester mesh for mechanical support. They estimated the mean effective pore as 0.74 nm diameter through membrane transport model. However, using the same transport model the average pore diameter of "tight" NF membrane (type NF 90) was estimated to be 0.68 and 0.78 nm according to Nghiem et al. (2008) and Lopez-Munoz et al (2009), respectively. In further comparison, the FO membrane has a considerably smaller pore diameter than "loose" NF membranes like NF 270 with a pore diameter (0.88 and of 0.84-nm) (Nghiem et al.,2008 & López-Muñoz 2009) and BQ01 with a pore diameter of 1.6 nm (Seidel et al. 2001). Hence, the rejection of trace organic contaminants by the FO membrane is expected to be higher than that of a normal NF membrane, if FO membranes such (HTI type CTA-ES) are used as normal cross flow NF mode.

Xie et al. (2012) described that the active layer of the HTI FO membrane is mostly made of cellulose triacetate (CTA), however, the skin layer of mostly available commercially available NF and RO membranes is made of polyamide (PA) or its derivatives. It was further noted that HTI FO membranes has lower permeability but much higher NaCl rejection compared to most of NF membranes. The pure water permeability and NaCl salt rejection of the HTI FO membrane in the reverse osmosis (RO) mode were 1.1 L/m^2.h.bar and 92.8%, respectively. However, it was reported that pure water permeability and NaCl salt rejection by NF membrane NF90, which is a tight NF membrane, were 6.4 L/m^2.h.bar and 85%, respectively (Xie et al., 2012). Thus the rejection of inorganics by FO membranes would be better than the NF membranes, even though the flux is less. Thus one could use FO membranes in small water reclamation plants where the quantity of ROC is small in quantity. For example, the amount of ROC is in the water reclamation plant, where the ROC is collected for this study is only 300 m^3/d.

The objectives of this study are (i) to analyse the factors affecting the NF and FO membranes in cross flow NF system in treating wastewater ROC and (ii) to study the behaviour of NF and FO membranes with ROC and pretreated ROC. The schematic of the use of nanofiltration in the ROC treatment is presented in Fig. 6.1.

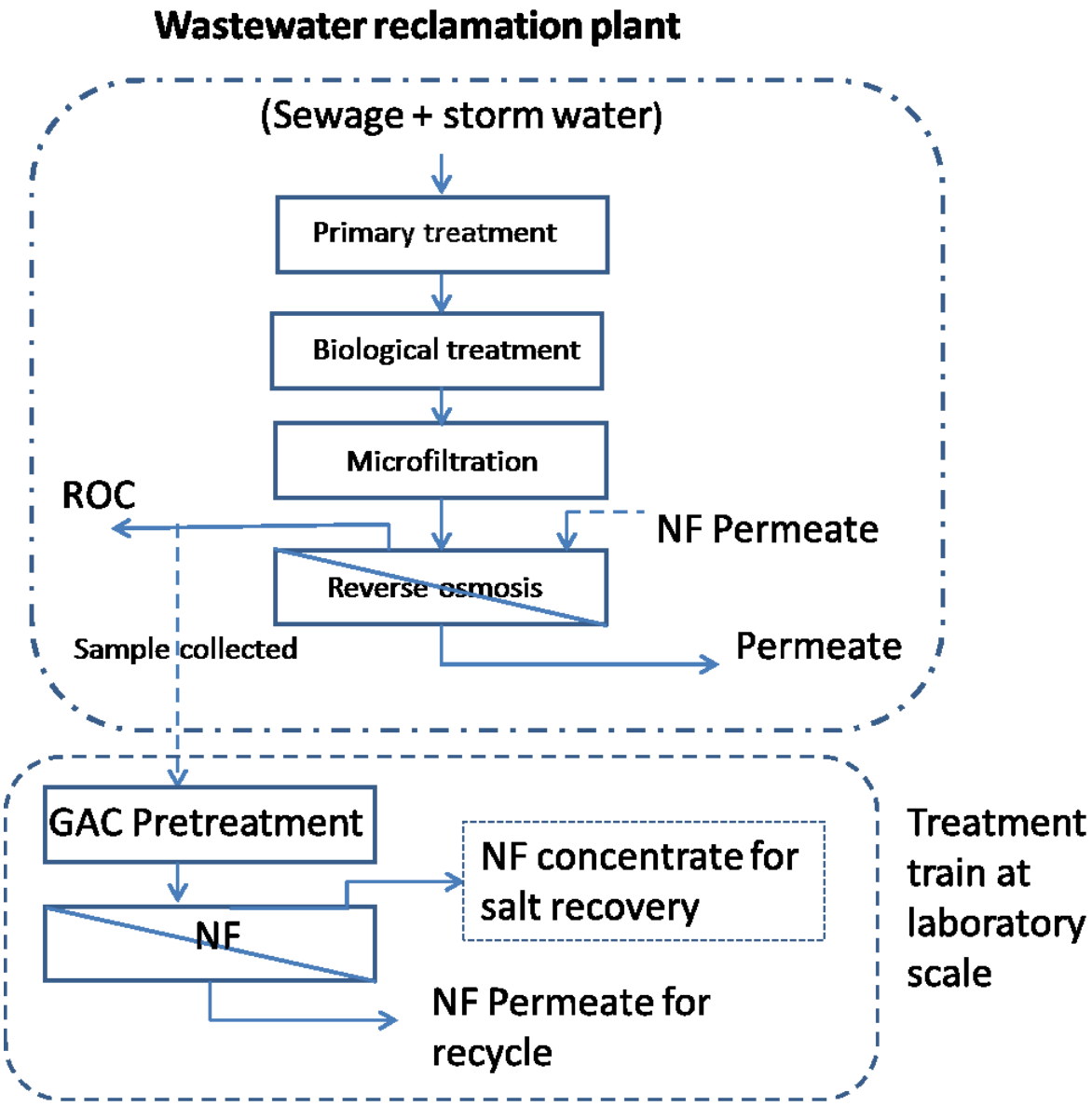

Fig. 6.1 Schematic diagram of NF for ROC treatment with pretreatment.

6.2 Materials and methods

6.2.1 ROC characteristics

ROC was collected from a water reclamation plant in Sydney, Australia. RO was operated at a water recovery of about 72%, which generated a reject stream (ROC) of about 28%. Water quality of the ROC is summarised in **Table 6.1.**

Table 6.1 Characteristics of ROC

Parameters	**Units**	**Value**	Sample for the present study
RO recovery	%	-	72
Total organic carbon (TOC)	mg/L	18.0-45.0	44.3
Total inorganic carbon (TIC)	mg/L	30.0-95.0	33.0
UV_{254}	1/m	0.7	0.7
pH		7.8	7.8
Conductivity	mS/cm	2.6-3.6	2.5
Alkalinity as $CaCO_3$	mg/L	380	-
Ca^{2+}	mg/L	70.0-108	70.7
Mg^{2+}	mg/L	55.0-84.0	57.5
K^+	mg/L	40.0-75.0	44.0
Na^+	mg/L	376.0-563.0	359.0
Silica as Si	mg/L	0.6-0.9	0.7
Br^-	mg/L	<5.0	<5.0
Cl^-	mg/L	478.0-819.0	491.0
F^-	mg/L	4.8	<5.0
SO_4^{2-} as S	mg/L	5.0-200	186.0
NO_3^- as N	mg /L	5.5-17.0	9.4
Total P	mg /L	6.5-6.9	6.8

6.2.2 Membranes used

Three types of membranes; one NF type NP 030 Microdyn-Nadir (Xiamen Co., Ltd) and two FO membranes HTI type cellulose triacetate with embedded polyester screen support (CTA-ES) and thin-film composite with embedded polyester screen support (TFC-ES) were used in a cross flow NF apparatus to compare their effectiveness in removing organic and inorganic compounds. The properties of these membranes are given in Table 6.2.

Table 6.2 Properties of NF and FO membranes (provided by vendor, otherwise specified).

	CTA–ES	**TFC–ES**	**NP 030**
Membrane supplier	HTI 97322 USA	HTI 97322 USA	Microdyn-Nadir (Xiamen) Co., Ltd
Membrane type	HTI OsMem CTA–ES Membrane (FO)	HTI OsMem TFC–ES Membrane (FO)	NP 030 (NF)
Membrane material	Cellulose Triacetate (CTA) embedded polyester screen support	Polyamide Thin–Film Composite (TFC) embedded polyester screen support	Polyethersulfone (PES)
Average Pore diameter	0.74 nm [a] 0.5-0.6 nm[c]	----	------
pH range	3 – 8	2 – 11	
Membrane property	Hydrophilic	Hydrophilic[b]	Hydrophilic
Thickness inclusive support layer	210 µm	126 µm	
MWCO	-	-	400 Da

[a] Xie et al., 2012

[b] Ren and McCutcheon 2014

[c] Fang et al. 2014

6.2.3 Analytical techniques

The pH and electrical conductivity of the FS and DS were measured at the beginning and end of experiment by using a manual Multi Portable pH and conductivity meter (HQ 40d, HACH USA). For the analyses of a wider range of anions and cations in the ROC, an Inductively Coupled Plasma Optical Emission Spectrometry instrument (ICP-OES, Perkin Elmer OPTIMA 7300 DV ICPOES Instruments, USA) was used. The samples were diluted with deionised (DI) water by a dilution factor of 1:10 and 1:20. Total organic carbon (TOC) and total inorganic carbon (TIC) were measured using a total organic carbon analyser (multi N/C 3100, Analytic Jena AG, Jena, Germany). Concentrations of TIC and TOC in the initial and final solutions were analysed to determine the amount of these compounds retained onto the membrane surface and hence to identify the compounds causing fouling. In other words, the amount of TIC and TOC retained on the membrane was assumed to be the difference between the product of their respective initial and final concentrations in FS and permeate. A spectrophotometer was used for the UV measurement. The details of the analyses are presented in chapter 3.

6.2.4 Bench-scale Nanofiltration unit

. A bench-scale NF unit was used (**Fig. 6.2**). The NF filtration unit was equipped with rectangular (108 mm length x 63 mm width) cross-flow cell having a membrane effective surface area of 68 cm^2. The tests were conducted on this lab-scale membrane cell using flat sheet NF and FO membranes. In this study, only a small pressure of 4 to 5 bar was applied. Pressure on FS side of the membrane was regulated manually using the valve located at the outlet of the membrane cell. The flow rate of FS was maintained at 500 cm^3/min across the membrane by adjusting knobs manually using a variable

speed drive (Magnetic drive pump 316 SS, Cole-Parmer, USA). The flow rate was monitored using rota-meters (Cole-Parmer, USA), which were installed in a series with pumps along the FS streams in the circuit. The temperature of FS was kept constantly at 25.0 ± 0.2°C using a water bath, in which stainless steel coiled pipes were immersed. The water bath was connected to a temperature control system (Thermoline BL-30) to ensure the temperature remained constant. The water flux was calculated by measuring the mass of permeate over time, recording the data with computer fitted with software. Each reading was recorded at 3 min interval and the permeate flux was calculated with moving average of 2 h basis. Experiments were started with 2 L of FS.

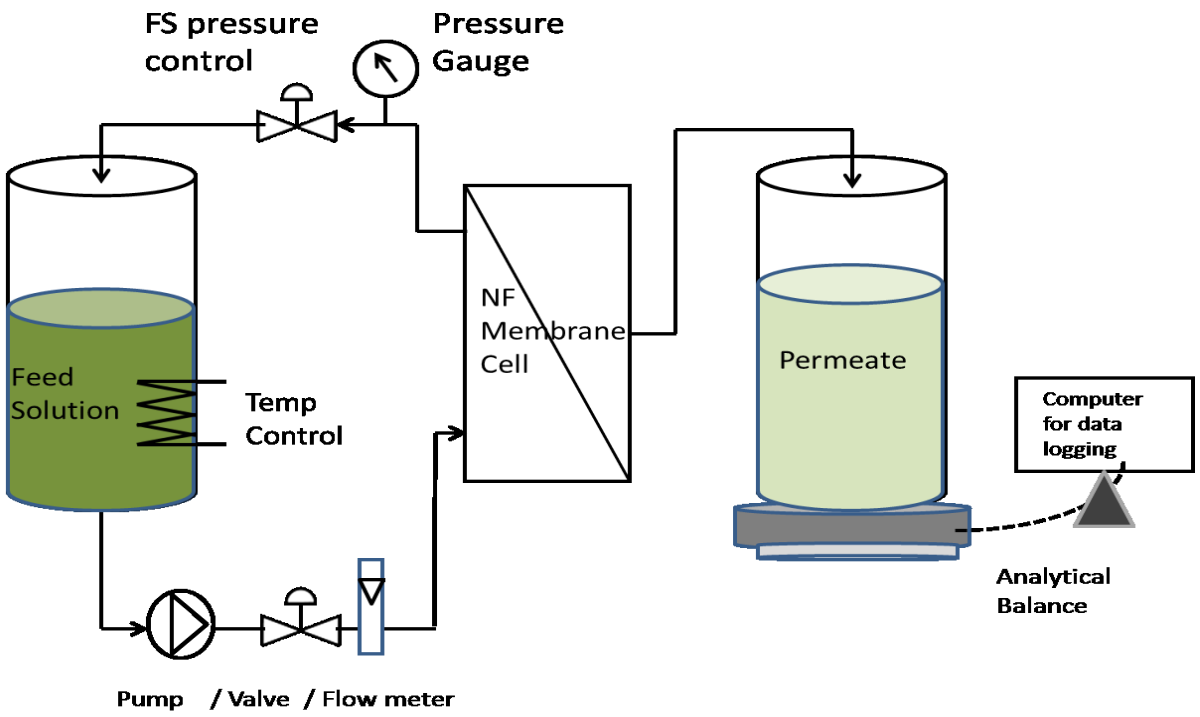

Fig. 6.2 Flow diagram of a bench-scale NF set-up used in this study.

6.2.5 TOC removal using fixed-bed GAC column

ROC is a complex mixture of organic compounds consisting of humic substances and LMW acids and neutrals, biopolymers and organic micropollutants (OMs). GAC adsorption column was used as pretreatment to remove TOC to minimize organic fouling on the membranes.

6.3 Results

6.3.1 Flux and fouling study with ROC with NF membrane

NF was tested at 4 bar applied pressure. The average flux was about 6.5±0.1 L/m^2.h as shown in **Fig. 6.3a**. The flux remained almost constant during the 17.5 h of operation. The initial conductivity of FS was 2.5 mS/cm and final conductivity of permeate was 2.15 mS/cm; which shows that most of the ionic species were passed through the membrane. Analysis made on NF permeate showed that main cations, calcium (Ca^{2+}), magnesium (Mg^{2+}) and sodium (Na^{+}) were rejected by only less than 10% (**Table 6.3**). However, among anions only phosphate (PO_4^{3-}) with initial concentration of 6.8 mg/L was rejected to method detection limit (MDL=5) and the rest passed through the membrane. As shown in **Table 6.2**, MWCO of this membrane is 400 (Da) which indicates the main reason for passing inorganics through the membrane. On the other hand, almost all the organics in terms of TOC (about 92%) was retained by this membrane (**Table 6.4**). Thus, this membrane was efficient to restrict organic compounds but rejections of inorganic species were not good.

Table 6. 3 Rejection behaviour of NF and FO membranes with respect to ionic species present in ROC

	Ca^{2+}	K^{+}	Mg^{2+}	Na^{+}	Cl^{-}	NO_3^{-}	PO_4^{3-}	SO_4^{2-}
ROC (mg/L)	70.7	44.0	57.5	359.0	491.0	41.7	6.8	186.0
% removed by NP030	8.8	2.2	6.0	6.0	0.0	0.0	*	3.0
% removed by TFC-ES	27.9	27.9	26.9	26.7	20.0	14.2	*	24.4
% removed by CTA-ES	46.6	29.7	40.8	29.8	20.0	25.5	*	65.0

Table 6.4 Behaviour of NF and FO membranes when ROC is used as FS.

Membrane type	NP 030	TFC-ES	CTA-ES
Applied pressure (bar)	4	4	4
Initial/final volume of FS (mL)	2000/1260	2000/1370	2000/850
Permeate (mL)	740	630	1150
Initial conc. of TOC in FS (mg/L)	43.9	43.2	43.2
Final conc. of TOC In Permeate (mg/L)	3.7	9.9	8.9
Initial conc. of TIC in FS (mg/L)	33.2	32.9	32.9
Total TOC in the system (mg)	87.7	86.4	86.4
Total TOC on the membrane surface (mg)	32.6	21.6	21.6
TOC on the membrane surface (mg/cm^2)	0.40	0.32	0.32
Initial cond. of FS (mS/cm)	2.5	2.3	2.5
Final cond. of FS (mS/cm)	2.1	2.6	4.5
Final cond. Permeate (mS/cm)	2.2	1.9	1.1
Membrane surface area (cm^2)	68	68	68
Operation time (h)	17.5*	6.0*	90.0*

* Operation time is chosen on the basis of permeate flux.

6.3.2 Flux and fouling study with ROC with FO membranes

6.3.2.1 TFC-ES

FO membrane from HTI (TFC-ES) was tested in NF cross flow experimental set-up. The average flux was about 15.2±0.1 L/m^2.h as shown in **Fig. 6.2b**. The flux decreased marginally from 15.6 to 15.1 L/m^2.h during 6 h of operation. The initial concentration of TOC in FS was 43 mg/L and final concentration of permeate was about 10 mg/L (**Table 6.4**) which indicated that about 16 % on the basis of mass balance passed through the membrane. Similarly, the initial conductivity FS was 2.34 mg/L and final

conductivity of permeate was 1.94 mg/L. This indicates that about 83 % ionic species were passed through the membrane during the 6 h of operation.

Table 6.3 shows that it rejected about 28 % of cation species and 14-24 % anions. On the other hand, it rejected about 77 % of organic compounds (**Table 6.4**). This indicates that the membrane is good to reject organic compounds but the rejection of inorganic species was only14 -28 %. However, this rejection was higher than NF membrane. As mentioned in section 6.1 there are two reasons why FO membrane could behave better in NF system: firstly, most FO membranes are tight compared to NF membranes; secondly, FO membranes have support layer that can restrict solute due to ICP effect.

6.3.2.2 CTA- ES

CT A-ES FO membrane from HTI was also tested with real ROC as FS at 4 bar applied pressure. The NF operation was conducted for 90 h of operation. The initial flux was low at about 2.3 L/m^2.h and after 90 h of operation it was reduced to about 1.5 L/m^2.h (**Fig. 6.2c**). The initial concentrations of TOC and TIC were 43.2 and 32.9 mg/L, respectively (**Table 6.4**). The decrease in flux was due to organic fouling and inorganic scaling of the membrane. The organic fouling was 0.32 mg/cm^2during the 90 h of operation. However, TOC flux in permeate solution was 1.9 mg/m^2.h. The initial conductivity of FS was 2.5 mS/cm and it was increased to 4.5 mS/cm during 90 h of operation. This indicated about 55 % of ionic species were rejected by this membrane. It rejected about 79 % of dissolved organic compounds (**Table 6.4**) and the rejection of the ionic species was 20-65 % of the initial concentrations (**Table 6.3**). This agrees with the findings of previous studies. The rejection of inorganics was better than NF030 and TFC-ES membrane, even for a long run time of 90 h (**Tables 6.3**).

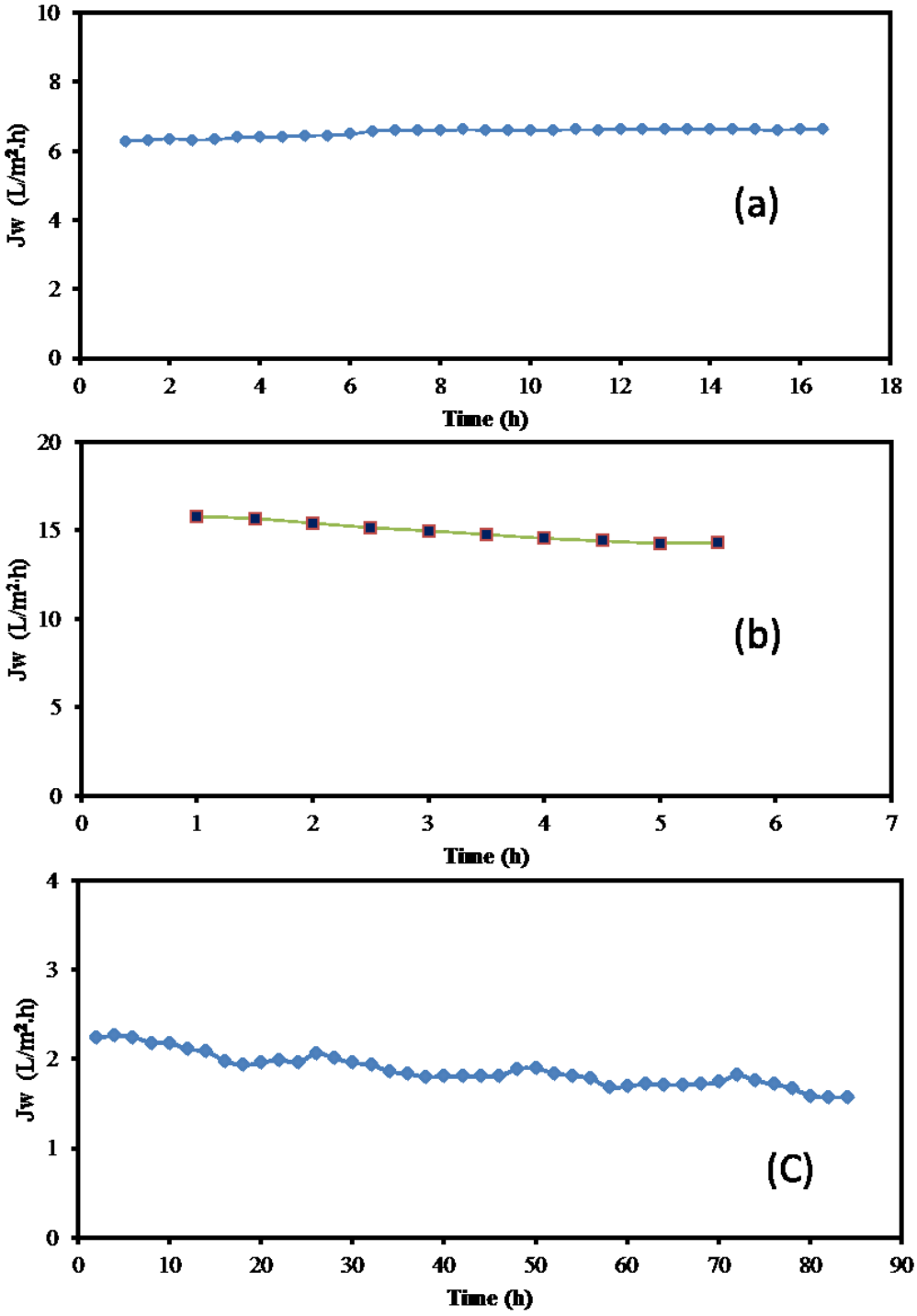

Fig. 6.3 Water permeate flux (Jw) profile of (a) NF030, (b) TFC-ES and (c) CTA- ES at 4 bar applied pressure (Feed solution = ROC from water reclamation plant).

6.3.3 Performance of FO membrane in NF operation ROC with pretreatment

The permeate volume increase was only 2 % with GAC adsorption pretreatment while the permeate volume was increased by 17% with GAC and acid pretreatment (Table 6.5). This indicates the inorganic scaling was the main cause for the decrease in flux. Another parameter to check the membrane performance is conductivity of the FS. If the conductivity of FS increases with membrane operation, it means that inorganics components in the FS are rejected or adsorbed on the surface of the membrane. In this study, the conductivity of FS was increased from 2.5 to 4.5 mS/cm with no pretreatment. However, when the pH of the ROC was reduced from 8.9 to 5.0 with acid treatment and this acidic environment increased the conductivity of the FS from 3.0 to 6.8 mS/cm (Table 6.5). However, some part of increase in conductivity was due to acid addition and rest was due to rejection of membrane. This indicates that in acidic environment, the rejection of ionic species was increased from 43 to 56 %. They may have followed other mechanism like electrostatic interactions between ions and membrane surface, which is based on the Donnan exclusion. By this mechanism, the cations are repulsed by the membrane surface and equal number of counter-ions are retained that results in salt retention (Teixeira et al 2005).

Table 6.6 shows that with GAC pretreatment, the rejection of Ca, Mg, NO_3, and SO_4 was increased. The reason could be the organic carbon would have taken free spaces for adsorption of ionic species (donnan exclusion) on the membrane.

However, with GAC and acid treatment the Donnan exclusion seems more pronounced and most of the mentioned ionic species including Na^+, K^+, Cl^- were rejected by this membrane.

Table 6.5 Behaviour of FO membrane (CTA-ES) in NF operation: i) ROC without any treatment; ii) ROC (GAC pretratment) and iii) ROC (GAC pretreated and softening).

	ROC	ROC-GAC	ROC-GAC and acid treatment
Applied pressure (bar)	5	5	5
Initial/final volume of FS (mL)	2000/850	2000/825	2000/610
Permeate (ml)	1150	1175	1390
Initial conc. Of (TOC) in FS (mg/L)	43.22	4.3	0.553
Final conc. Of TOC In Permeate (mg/L)	9.91	0.12	0.45
Initial cond. of FS (mS/cm)	2.54	2.44	2.97
Final cond. Of FS (mS/cm)	4.48	4.27	6.82
Final cond. Permeate (mS/cm)	1.14	1.57	1.25
Membrane surface area (cm^2)	68	68	68
Operation time (h)	90	90	76

Table 6.6 Rejection of inorganics by FO membrane (CTA-ES) in NF operation with GAC pretreatment and GAC along with acid pretreatment.

		Ca^{2+}	**K^{+}**	**Mg^{2+}**	**Na^{+}**	**Cl^{-}**	**NO_3^{-}**	**PO_4^{3-}**	**SO_4^{2-}**
ROC (mg/L)		70.7	44.0	57.5	359.0	491.0	41.7	6.8	186.0
CTA-ES	% removed	46.0	29.7	38.8	28.8	19.0	24.5	*	65.0
CTA-ES (GAC Pretreatment)	% removed	71.8	30.2	69.9	31.5	22.6	65.0	*	81.7
CTA-ES (GAC and acid treatment))	% removed	89.6	32.01	90.2	52.1	33.9	79.1	*	94.9

6.4 Conclusion

This study showed that NF membrane is a good option for pretreatment for organic compounds from wastewater however, most of inorganic compounds were passed through the membrane. This study investigated the use of FO membranes in cross flow NF mode. The FO membranes have pore size of less than most of NF membranes, so they can also remove inorganic ions present in ROC. The support layer of FO membrane can create ICP but permeate exiting membrane would help to prevent inorganics from going to permeate side. Although CTA-ES has lower flux as compared to NF030 and TFC-ES membrane, CTA-ES (FO membrane) removed inorganic compounds better than other two membranes for longer duration of 90 h operation. The net water permeate flux was improved by 17%, with (CTA-ES) FO membrane when GAC and acid pretreatments were applied. The final NF permeate from CTA-ES membrane can be recycled.

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Chapter 7

Membrane bioreactor as a pretreatment to Pressure assisted Forward osmosis hybrid system for water purification of synthetic reverse osmosis concentrate

7.1 Introduction

In chapters 4, 5 and 6 Granulated Activated Carbon (GAC) was as pretreatment to FO in treating Reverse osmosis concentrate (ROC). This was mainly to remove total organic compounds (TOC), which mainly consists of organic micropollutants (OMPs), personal care products (PCPs) and natural organic matter (NOM). GAC pretreatment is a physio chemical process. In this chapter membrane bioreactor (MBR) was used as pretreatment to curtail TOC of synthetic ROC. The presence of TOC affects the FO membrane in two ways; i) It passes through the membrane and affects the quality of permeate water ii) It is also the main cause of membrane fouling which affects its performance in terms of permeate flux and efficiency.

The objectives of this study were: (i) to control the membrane fouling and quality of permeate water by MBR pretreatment of synthetic ROC. The synthetic ROC was used as a feed to MBR to maintain the feed concentration of ROC constant.

(ii) to investigate the relative merits of PAFO over FO in concentrating the synthetic ROC to minimise its volume for safe discharge and water purification. The MBR pretreatment was compared with GAC pretreatment.

7.2 Materials and methods

7.2.1 Synthetic Reverse osmosis concentrate (ROC)

The chemical composition of synthetic ROC and its properties are shown in table 7.1.

Table7. 1 Water quality of Synthetic ROC.

Parameters	Units	Chemical composition	
Chemicals used to prepare synthetic ROC			
$CaCl_2.2H_2O$	mg/L	292	
NaCl	mg/L	750	
KCl	mg/L	90	
NaF	mg/L	7	
$MgSO_43H_2O$	mg/L	450	
$KH2PO4^-$	mg/L	15	
$NaHCO_3$	mg/L	80	
Glucose	mg/L	200	
Yeast	mg/L	300	
Properties of Synthetic ROC		**Synthetic ROC**	**MBR treated ROC**
Total organic carbon (TOC)	mg/L	18.7	7.67
pH		5.5	6.52
Conductivity	mS/cm	2.65	2.53
TDS	mg/L	1569	
NH4-N	mg/L	4.04	0.036
Phosphate	mg/L	18.2	18.1
COD	mg/L	440	20
Alkalinity as CaCO3	mg/L	150	20

7.2.2 Membrane Bioreactor Set-up

The schematic diagram of MBR system is shown in Fig. 7.1. The MBR consists of aerobic sludge tank with a working volume of 10L containing hollow fibre membrane module. Hollow fibre made of HF Polyninylidene fluoride (PVDF) membranes with a total effective membrane filtration area of 0.01m² was used. The pore size of hollow fibre membrane is 0.1μm and the length of each fibre is 17.5cm with an outer fibre diameter of 2.0mm and an inner fibre diameter of 0.8mm. The braid-reinforced hollow fibre MF (Cleanfil-S, Kolon, South Korea) used comprised of three different materials which are Polysulfone, Polyethersulfone and Polyvinlidene Fluoride as a coating layer. One end of the hollow fibre membrane was sealed up with a high-strength adhesive into aerobic sludge tank and the other end was tied together with acrylic tube that is connected to a suction pump to withdraw effluent. The MBR was operated at a flux of 20 L/m²h (20LMH). Trans membrane pressure (TMP) was monitored by an electronic pressure gauge each time before and after the cleaning procedure.

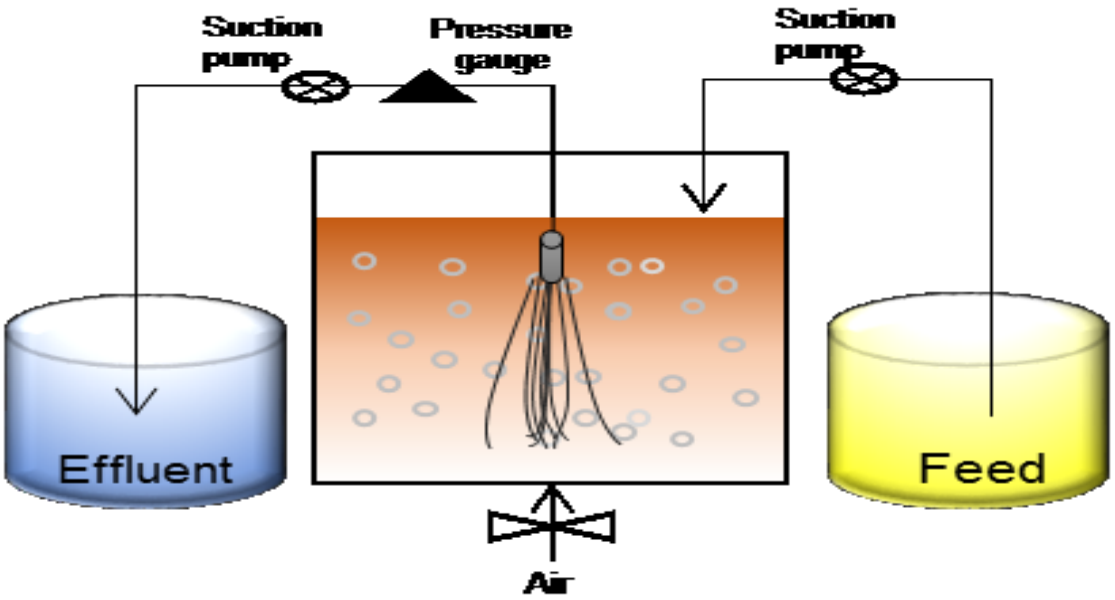

Fig. 7. 1 Submerged MBR set-up

7.2.3 Experimental protocols

The FO/PAFO system was tested with synthetic ROC. The chemical composition of the synthetic ROC and properties are given in Table 7.1. A series of experiments were conducted to determine the specific fouling potential of the main components of synthetic ROC and their impact on the permeate flux. The tests were conducted for 40-72 hours with synthetic ROC as the FS and 0.25/0.5 M of KCl as the DS. Commercial grade potassium chloride (KCl) of minimum assay (99.0%) was employed. KCl at a concentration of 0.25 and/or 0.5 M (mole) was used as draw solution (DS) in all the experiments. The main reason for selecting KCl; it has high osmotic pressure of 44.0 atm. at 25°C for one molar solution. Moreover, it exhibited the highest pure water flux (2.57 m/s) among the fertilisers tested in a previous study (Phuntsho et al., 2012).

Conductivity was monitored at the initial and final stages of the experiments. Concentrations of TOC in the initial and final solutions were analysed to determine the

amount of these compounds adsorbed onto the membrane surface to identify the compounds causing fouling. The amounts of TOC retained were assumed to be the differences between the product of their respective initial and final concentrations (C_0 and Ce) and normalised volumes (Vn) i.e. (C_0- Ce) $*$Vn.

MBR was used as pretreatment of synthetic ROC to reduce mainly organic fouling of the membrane. As shown in Table. 7.1 the MBR pretreatment reduced TOC and COD by 60 and 95.5 percent respectively.

7.2.4 Analytical methods

The pH, conductivity, TOC, LC-OCD and cations, anions were measured and the details on the measurement methods are given in chapter 3.

Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were measured using standard method as follows: The mixed liquor was filtered through 1.2µm filter paper. Filtered paper was kept in the desiccator at 100°C during 1 h for MLSS, and then it was placed in the furnace at 550°C for 30min for the measurement of volatile suspended solids (which is MLVSS). It was measured twice a week.

7.2.5 Bench-scale forward osmosis unit

A bench-scale FO and PAFO and their details are explained in Chapters 4 and 5. The schematic diagrams are shown in Chapter 2; figures, 2.2 and 2.3 respectively.

7.3 Results and Discussion

7.3.1 MBR pretreatment of Synthetic ROC

MBR pretreatment reduced the total organic carbon of synthetic ROC by 60 % (Table 7.1). The chemical oxygen demand (COD) was reduced to 95.5 %. This indicates that MBR treated ROC reduces the organic fouling of the membrane in FO and PAFO. Table 7.2 shows the LC-OCD analysis of synthetic ROC before and after MBR treatment. The biopolymer compounds were reduced by 93.2 % followed by Low molecular weight neutrals (LMN) and hydrophilic compounds.

Table7. 2 LC-OCD analysis of Synthetic ROC and MBR treated ROC

	Hydrophilic	Biopolymers	Hemic substances	Building Blocks	LMW Neutrals
M.W*		>20,000	~1000	300-500	<350
Syn. ROC (DOC) ppb	18714	5409	6963	2025	4346
MBR treated ROC (DOC) ppb	7578	369	4105	1620	1484
% Reduction DOC**	59.5	93.2	41.0	20.0	65.9

* M.W Molecular weight

** Dissolved organic carbon

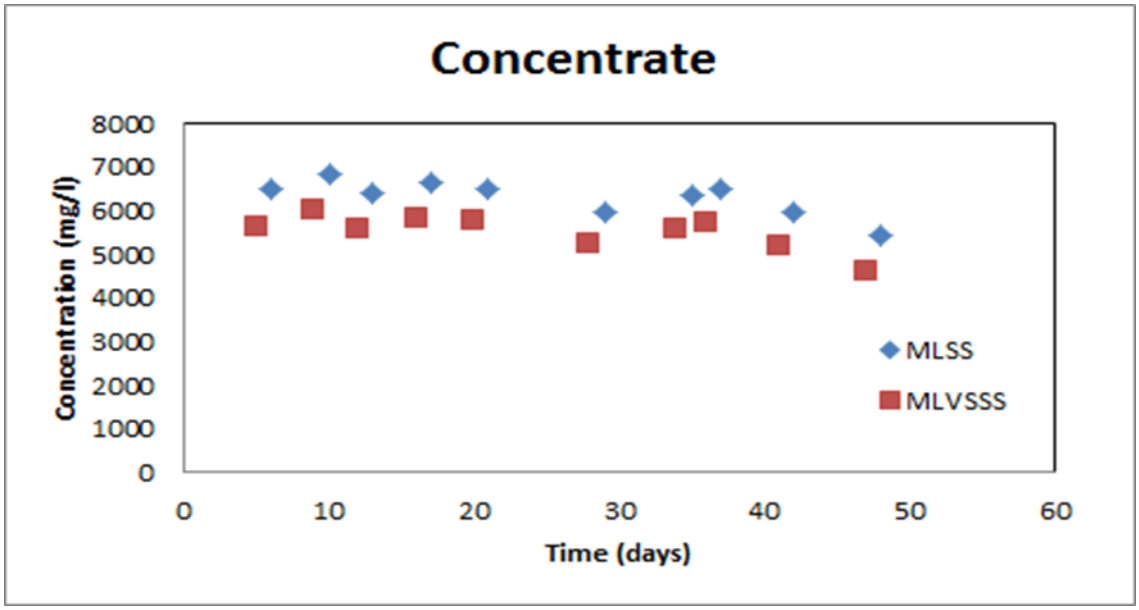

Fig. 7. 2 Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS).

The biomass was measured in terms of MLSS concentration and it was maintained around from 5.5g/l to 6.5g/l (Fig. 7.2) after an acclimation period of 40 days of MBR operation. The pH was in the range from 6.5 to 7.0. The MBR was trialled at 5,10,20 and 23 L/m^2.h (LMH) and the flux of 20 LMH was found to be sustainable. Thus, only the results at 20 LMH is reported. The details can be found elsewhere (Yunju, 2017). The TMP was increased from 5 to 22 kPa (Fig. 7.3) during the 33 days of operation (after an acclimation period of 40 days). After 33 days, a chemical backwashing was conducted for 1hr with sodium hypochlorite solution. Backwashing with chemical was found to be effective in removing fouling. Membrane clogging was caused by biomass from the activated sludge attached to the hollow fibre membranes. This was the primary reason for the rapid increase in the TMP.

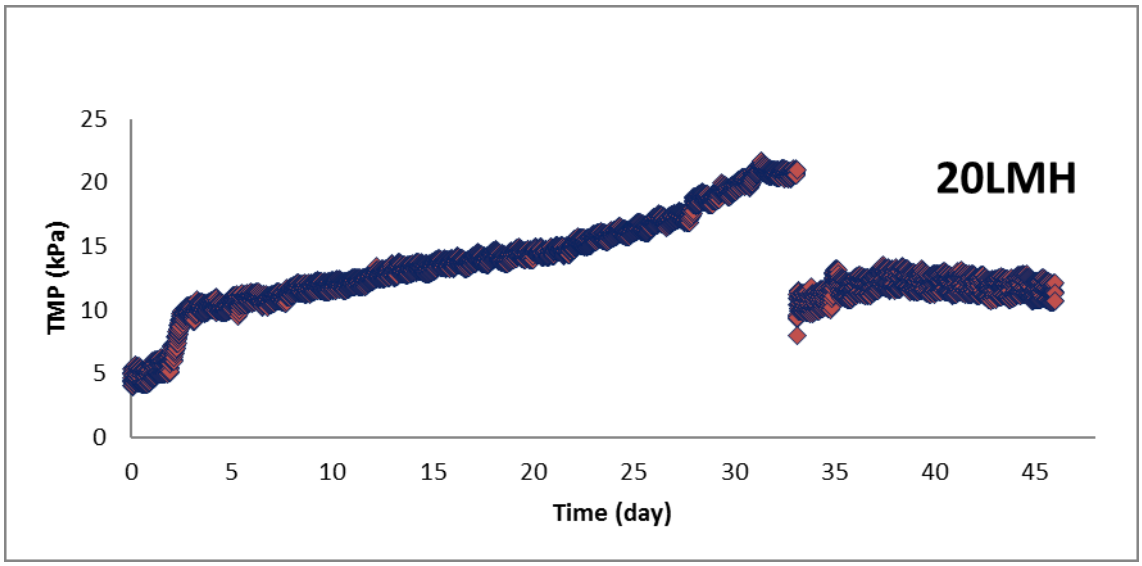

Fig. 7. 3 Trans membrane pressure (TMP) with time; (Jw = 20 L/m².h)

7.3.2 Effect on water flux in PAFO with applied pressure

FO was tested at applied pressures 0-4 bar with MBR treated effluent collected after 40 days of operation. Here the FS was DI water and 0.25 M KCl was draw solution. As expected, the water flux increased with the applied pressure at feed solution (Fig.7.4). The active layer of FO membrane (AL-FS) was facing feed solution and the support layer was facing draw solution (SL-DS). During FO operation, although no pressure (0 bar) was applied, the system pressure was around 1.0 bar. However, in PAFO with the application of 3 bar pressure at FS, the resultant average permeate flux (Jw) was increased by 42 %; and when the pressure was increased to 4 bar, the resultant flux was further increased to about 56% in comparison to no applied pressure. The average flux was calculated based on 5 hours of FO operation.

The percentage of increase in flux by the application of pressure was calculated using the equation, (1-Jw0/Jwp)*100

Where, Jw0=water flux at no applied pressure (FO mode)

Jwp=water flux at applied pressure (PAFO mode)

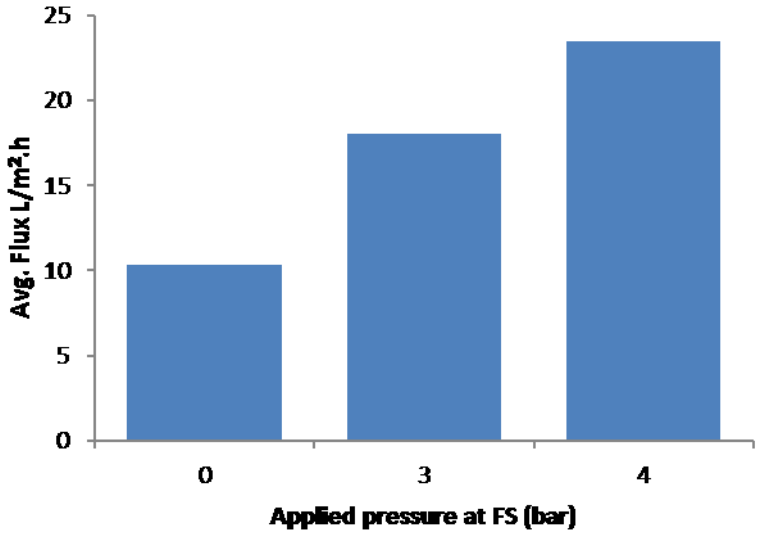

Fig. 7. 4 FO/PAFO flux with deionized water (DI) as feed solution at different applied pressures and 0.25 M KCl of draw solution

7.3.3 Water flux with synthetic ROC in FO with and without MBR treatment

Figure 7.5 (A, B & C) shows the flux and fouling propensity of synthetic ROC and MBR pretreated ROC. Although the initial flux was higher, as the pressure is increased the resultant flux was decreased with time with untreated ROC due to inorganic carbon scaling and organic carbon fouling on the surface of membrane. The fouling behaviour is complex particularly when inorganic carbon and organic carbon fouling happens simultaneously (Zhao et al., 2012). However, the decrease in flux with time was less for the MBR pretreated ROC (Fig 7.5).

The average flux of FO with synthetic ROC as FS with and without MBR treatment is shown in (Fig. 7.5 A). The average flux was increased to 7.1 from 6.2 LMH respectively

With the application of 4 bar pressure, the average net flux was increased from 8.5 to 13.3 LMH (Fig.4 C) with MBR pretreatment. The average flux was calculated based on 40 hours of membrane operation. This indicates that MBR pretreatment of synthetic ROC can improve membrane performance by controlling organic fouling.

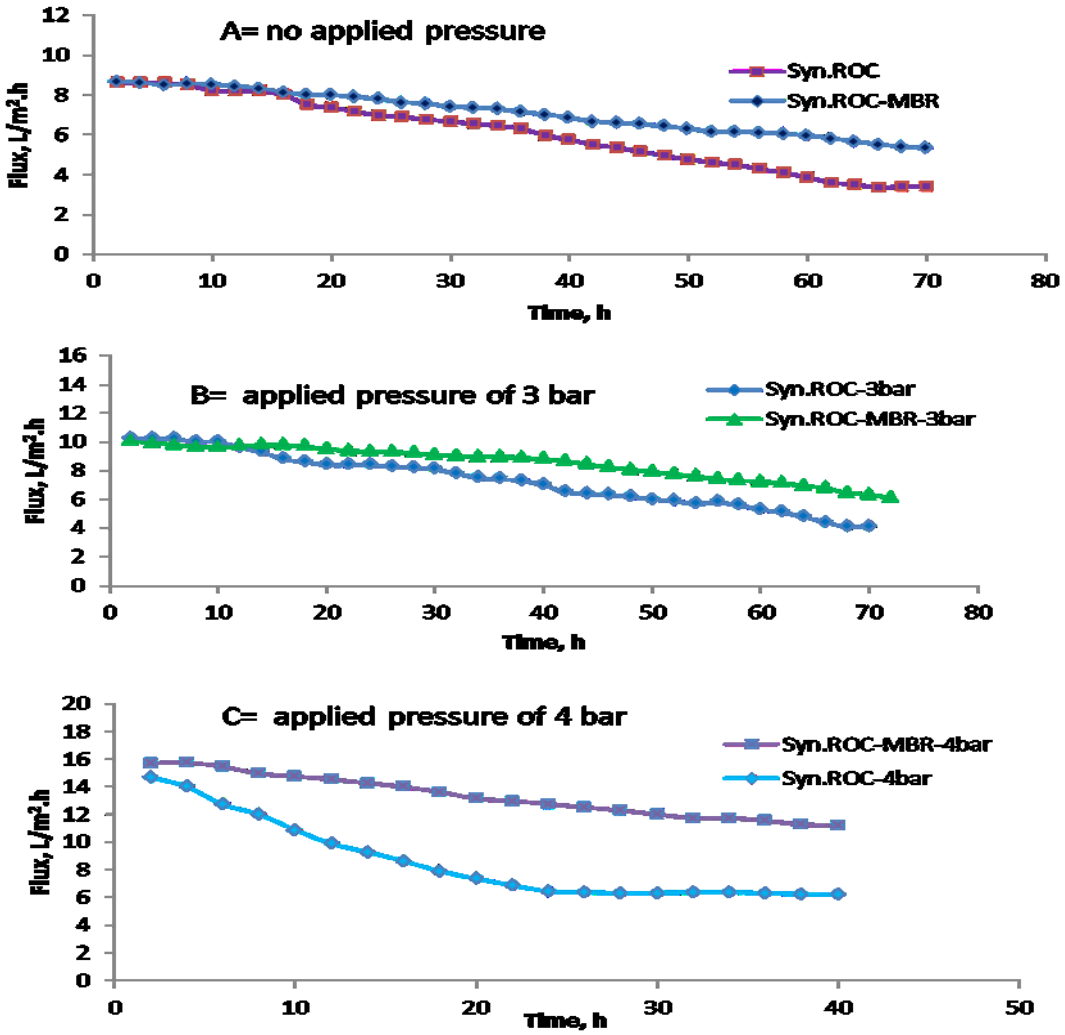

Fig. 7. 5 Comparison of flux and flux decline with and without MBR pretreatment at applied pressures (0, 3 & 4 bar and 0.25KCl as DS (TFC-ES membrane, 25^0C).

7.3.4 Fouling recovery

Most of the previously studies with PAFO have been conducted with DI water or dilute NaCl as feed solution (Choi et al., 2009; Bladian et al., 2013; & Sahebi et al., 2015). But with wastewater, the results on the permeate flux are different (Fig. 7.5). The factors such as ionic species and organic matter present in ROC that cause inorganic scaling and organic fouling are important and needs to be considered. Moreover, some of the inorganic and organic compounds would pass through the membrane and contaminate the permeate. So feed solution recovery is another important factor which has to be considered for treating any concentrate stream. Higher feed recovery leads to decrease in resultant permeate flux due to increase in TDS of FS and some sparingly soluble salt that may precipitate causing cake formation on the surface of membrane. The recovery of ROC may be set on the basis of TDS or conductivity of FS depending upon the quality of RO concentrate.

The fouling recovery of fouled membrane by synthetic ROC was studied by washing with two different solutions: DI water and acidic water. A baseline test was first conducted with DI water as FS and 0.5 M KCl as DS prior to the use of synthetic ROC fouling test (Fig. 7.6a). FO was then operated with synthetic ROC as FS for 72 h of operation (0.5 M KCl was used as DS) (Fig. 7.6b), in order to study the synergistic effect of inorganic scaling and organic fouling by synthetic ROC on TFC-ES membrane. Combined organic- colloidal foulants cause more rapid water flux decline than individual foulants due to their synergistic effect (Kim et al., 2014). After 72 h of FO operation with synthetic ROC the membrane was then flushed with DI water for 30 min at high flow velocity of 21.4 cm/s after 72 h of FO operation with ROC. The FO run was then continued with DI water after flushing fouled membrane with DI water

(Fig. 7.6c). Finally, DI water run was made after the membrane was washed with DI water followed by acidic water of pH 4.5 (Fig. 7.6d). The acid wash was conducted to remove the inorganic scalants.

As shown in Fig. 7.5 the average baseline water flux (J_w) was 13.9 LMH. The resultant flux with synthetic ROC as FS was decreased to 7.1 LMH (by 49 %) due to fouling (scaling and organic fouling). However, the flux did not decrease only by fouling. Other factors such as FS concentration and external concentrative polarization were also involved. With the increase in FS concentration, the net osmotic pressure decreases. Another phenomenon which takes place at the membrane surface was external concentration polarization (ECP) due to high FS concentration at the surface of the membrane; particularly when the pressure is applied on feed side (Zhao et al., 2012). Both sides of the membrane were then washed with DI water. This water flush improved the membrane activity back to 85.6% by defouling.

Finally, the same DI water washed membrane was flushed with acidic water (pH 4.5) and the FO experiment was repeated with DI water as FS. The membrane activity was restored back to almost normal (97%). This indicates that FO fouling is reversible, the fouled membrane can be recovered with DI water flushing following by chemical cleaning (Lee et al., 2010; Katzir et al., 2010; Paugam et al., 2004); Jamil et al., 2016).

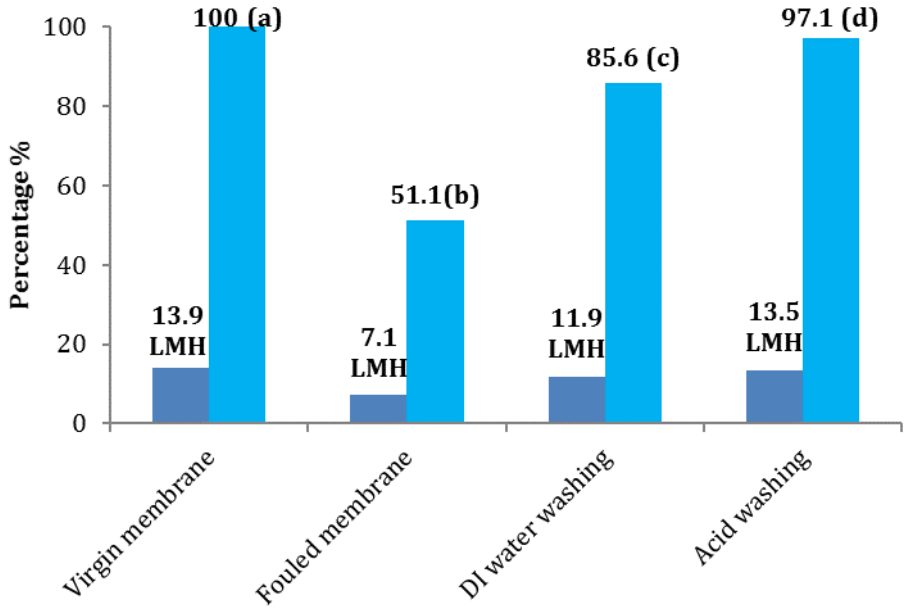

Fig. 7. 6 Fouling recovery of TFC-ES membrane by flushing with DI water and acidic water of pH 4.5 (Water used for the experiments is DI water)

7.3.5 Inorganic and organic fouling

In this study two solutions were studied as FS. First was with synthetic ROC having dissolved organic carbon (DOC) about 19 mg/L and the second was MBR treated ROC having DOC about 7.7 mg/L. Table 7.3 shows rejection of inorganic species with untreated synthetic ROC. It was noted that divalent or trivalent cations and anions are mostly rejected by this membrane however, monovalent such as sodium was rejected only by 53.5 %. However, scaling of membrane was depended upon the initial concentration, charge of the molecule and the properties of the membrane such as pore size (Jamil et al., 2016).

Table 7.4 shows the behaviour of inorganic ions with MBR treated ROC. Cations Ca^{+2} and Mg^{+2} were rejected by about 78 and 80 %. However, the rejection of $SO4^{-2}$ and $PO4^{-3}$ was 100% of the initial concentration. It was explained higher negative charge of

the radical/ion leads to greater electrostatic interaction and Donnan effect and higher hydration energy of the radical/ion is more difficult for it to penetrate into the membrane (Zhao et al., 2012). That's why the rejection of $SO4^{-2}$ and $PO4^{-3}$ were 100 % of the initial concentration [Table 7.3]. The monovalent Na^{+} was rejected by about 43. However, rejection of K^{+} and the Cl^{-} can't be calculated because they were present in both FS and DS.

It was also noted that the presence of organic fouling restricted more ionic species going into draw solution than alone inorganic compounds [Table 7.3 and 7.4]. So membrane fouling is a complex phenomenon particularly when both inorganic and organic compounds are present in feed solution (Kim et al., 2014).

Table7. 3 Inorganic scaling with synthetic ROC (FS), 0.25 M KCl (DS)

Component	Initial conc. FS	Final Conc. (Norm.) FS	Final Conc.(Norm) DS	Restricted by membrane	Membrane Scaling
	mg/L	mg/L	mg/L	%	$mg/cm^{2}.h$
Ca^{+2}	88.9	83	5.9	92.9	0.00
Mg^{+2}	50.3	46.4	1.04	98	0.004
Na^{+}	355	165	165	53.5	0.035
$PO4^{-3}$	18	12	n.a	100	0.008
$SO4^{-2}$	196	180	n.a	100	0.022

Concentration factor (C.F) = Initial volume/final volume

Dilution factor (D.F) = final volume/initial volume

Normalized concentration (For FS) = final conc./C.F

Normalized concentration (For DS) = final conc.*D.F

Norm. Normalized

Table7. 4 Inorganic scaling with MBR treated synthetic ROC (FS), 0.25 M KCl (DS)

Component	Initial conc. FS	Final Conc. (Norm.) FS	Final Conc.(Norm) DS	Restricted by membrane	Membrane Scaling
	mg/L	mg/L	mg/L	%	$mg/cm^2.h$
Ca^{+2}	88.9	69	5.1	77.6	0.021
Mg^{+2}	50.3	40.2	2.43	79.9	0.011
Na^{+}	355	154	177	43.4	0.033
$PO4^{-3}$	18	12	n.a	100	0.00
$SO4^{-2}$	196	157	n.a	100	0.054

7.4 Concluding remarks

In this study, the membrane bioreactor (MBR) was used as pretreatment to synthetic concentrated brine. MBR treatment was able to curtail organic carbon by 59 % of the original concentration. Organics in terms of the chemical oxygen demand was reduced by about 96 %. Thus MBR pretreatment was able to reduce the membrane fouling. As a result, the resultant permeate water flux was improved. Among the DOC, the higher reduction was observed for biopolymers followed by LMW neutrals.

Fouling of the membrane with untreated synthetic concentrated brine was recovered partially by flushing membrane with DI water at higher velocity. However, the membrane fouling was almost fully recovered by water flushing followed by acidic water cleaning of pH4.

The FO membrane performance was evaluated with respect to inorganic compounds in both untreated and treated synthetic brine. The divalent/trivalent molecules were mostly rejected and monovalent was rejected only partially.

PAFO has an additional advantage of increased flux with an applied pressure of 4 bar pressure and DS concentration of 0.25M KCl. The water permeate flux was increased by 56 % with an applied pressure of 4 bar as compared to FO.

Recovery of draw solution is energy extensive. However, application of low applied pressure in PAFO and by use of low concentration of fertilizer such as 0.25 M KCl as DS, makes this process sustainable. Further, one can use diluted draw solution (0.14 M KCl) free from organic and inorganic pollutants for agriculture use.

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Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

The specific conclusions are presented under each chapter (Chapter 4 to 7). This section gives the general summary of the work.

Forward osmosis (FO) water desalination technique uses the natural osmotic pressure of the draw solute to drive osmosis rather than hydraulic pressure. In this study KCl was draw solution. This technique is further developed by applying pressure on feed solution to enhance water permeate flux which is termed as pressure assisted fertilizer drawn forward osmosis (PAFDO). PAFDO can enhance final dilution of the fertiliser draw solution beyond osmotic equilibrium. For its low cost desalination potential, the FO and PAFO process which has gained attention of the research community.

This study provides further insight into the FO and PAFO processes to clarify the issues that are directly contributing towards enhanced FDFO performance. This study explores important findings as to how various issues can affect the FO and PAFO performance and shows how short comings with these techniques can be minimized by using different types of membranes in order to improve the overall FO and PAFO performance. This study recommends possible future work directions that can help to improve the performance of FO and PAFO in order to gain real benefits in terms of low carbon foot prints and sustainability. Some important operational issues of membrane based systems such as membrane fouling and scaling are evaluated in detail. Additionally, the advantages of pretreatment of wastewater was evaluated in order to improve FO performance. Granulated activated carbon and membrane bioreactor were used as pretreatment to reduce organic fouling of the membrane. Another, important

problem namely, membrane scaling was addressed by softening the FS with acid pretreatment.

This study also revealed that WWTPs are one of the main sources that discharge PPCPs into the environment. PPCPs are found in ROC and these compounds can have potential hazardous effects on environment. The removal of PPCPs with membrane technology and GAC pretreatment has been studied.

A new idea is presented in this study, using FO membranes in cross flow nano-filtration system to treat ROC from water reclamation plant. In this way, the resultant permeate can be recycled back to RO unit to increase the overall efficiency of the plant.

8.1 Pretreatment of ROC

Pre-treatment is commonly used for two major reasons: firstly, to enhance the removal efficiency of micro-pollutants and secondly, to reduce membrane fouling. In this study GAC adsorption and MBR pretreatments were used, which are described below.

8.1.1 GAC pretreatment

Organic micropollutants are found in ROC and these compounds can have potential hazardous effects on environment if discharged untreated. Moreover, the removal of organic micropollutants and humic substances reduced FO membrane fouling and enhanced the membrane efficiency. GAC pretreatment removed the majority of the micropollutants from the ROC to below detection limit. The GAC adsorption reduced TOC by about 90 % and softening of ROC by acid reduced the inorganic carbon by about 85 %, which helped to control membrane fouling and scaling. GAC pretreatment also adsorbed 12 out of 14 organic micropollutants (studied in the present study) from

the ROC to below detection limit. This study confirmed that GAC pretreated ROC can safely be discharged into the environment.

8.1.2 MBR pretreatment

In this study, the membrane bioreactor (MBR) was used as pretreatment of synthetic concentrated brine. MBR treatment was able to curtail organic and inorganic carbon by 60 % of the original concentration.

The higher reduction was observed in biopolymers followed by LMW neutrals. MBR pretreatment reduced the membrane fouling and the resultant permeate flux of FO was improved.

8.2 Main findings of FO and PAFO system

8.2.1 Flux performances

The water production was higher in PAFO by 9 % and 29 % at moderate applied pressure of 2 and 4 bars during the 90 h of experiments with ROC. It was noted that the higher feed TDS severely affected the FO/PAFO flux. A small increase in the TDS of the FS resulted in a sharp decline in the FO flux. Concentration polarization (CP) effects seem to contribute towards delivering these lower flux performances. Experimental results further indicated that besides possessing higher $\Delta\pi$, the FO/PAFO flux decreased comparatively more sharply with the rise in FS concentration and even for the higher DS concentration. As FO/PAFO operation progressed the TDS in feed solution increased. This resulted in rapid decline in flux and it reached a low level for osmotic equilibrium.

8.2.2 Use of final diluted DS

The FO and PAFO were assessed with low concentration of potassium chloride (KCl) as fertilizer DS. In this study, a low concentration (0.25 M KCl) fertiliser solution was

chosen as DS and it was diluted to 0.14 M KCl during the FO operation due to transport of water permeate flux (J_w) from feed solution. This diluted KCl solution can be used for direct fertigation. Past studies showed successful use of 10 Kg/m^3 (≈0.13 M KCl) for fertigation.

8.2.3 Reverse and forward solute performances

Unlike the RO/NF membranes, the FO/PAFO deals with two types of solute movements a) Forward solute flux (FSF); FS solutes towards the DS side and b) Reverse solute flux (RSF); DS solutes towards the FS side. Thus FO membranes deliver poor outcome with inferior salt rejection properties. Most of the research for FO membranes development has been focused on developing membranes which show a higher flux performance. No serious effort has been made to enhance salt rejection and to reduce FSF/RSF.

FS/DS carrying higher valency cations or anions such as Ca^{2+}, Mg^{2+}, SO_4^{2-}, PO_4^{3-} components comparatively showed less solute flux as compared to monovalent ions such as Na^+, K^+, Cl^- which reflects the importance of the size of the FS/DS solutes for specific FSF and RSF.

8.2.4 Concentration polarization

It was observed that net osmotic pressure difference across the active layer of the membrane was much lower than the theoretical bulk osmotic pressure difference of FS and DS, which resulted in much lower water flux than expected. This lower than expected water flux is attributed to concentration polarization (CP). In either membrane orientation mode i.e., AL-FS or AL-DS, the CP phenomenon developed on both sides of the membrane. This study showed that flux started to decline sharply from the start

which indicated that CP quickly builds up on the membrane surface and results in flux decline.

The blank tests which were conducted with DI water as FS showed the highest possible flux and remained almost constant for longer period of time as compared to compared to experiments with ROC. This was due to no solute concentration development from feed side at the membrane surface. However, in actual tests with ROC the sharp flux decline in the initial stages of the FO run indicated that CP was developed due to FS and DS solute associated with AL and SL of the membrane, which in turn cause a rise in the solute concentration at the membrane interface. We also believe that the FS solute particles develop loose bond with functional groups of the membrane polymer responsible for osmosis and affect the resultant permeate flux.

8.2.5 Membrane fouling and cleaning

FO membranes were evaluated for their behaviour for inorganic scaling and organic fouling risks and it was found that the FO, like the RO membrane, also poses potential operational risks of scaling and fouling. It was noticed during FO fouling studies that the commonly used FO fouling protocol may not be similar to the RO fouling protocol to evaluate FO fouling. The RO fouling was evaluated against a fixed driving force (hydraulic pressure) and any changes in the flux performance may be referred to the fouling impact. However, in FO, as the driving force (net osmotic pressure difference between the FS and DS) keeps on changing constantly, due to change in concentrations of FS and DS. Thus, it is really difficult to predict any flux changes associated particularly with the scaling or fouling. For any two tests, at any particular time, FO

does not show the same driving force and hence for the evaluation of fouling and scaling, on the basis the flux comparison for two different curves may not be useful.

The FO membrane indicated varying degree of fouling potential for membrane use in AL-FS and AL-DS orientations. The FO membranes showed a lower risk of fouling in AL-FS orientation as compared to AL-DS. However, it was found that fouling variations are not related to membrane properties, instead the hydrodynamic conditions employed for the process affects the fouling potential. However, the change in concentrations of FS and DS with passage of time alters the flow pattern of RSF/FSF and permeate flux and could play a major role in the development of fouling and scaling on the membrane surface.

It was observed that scaling and fouling are not fully reversed for the FO membranes by physical cleaning in AL-FS and AL-DS orientations even at higher cross flowrates. It was found physical cleaning with DI water at a cross flow velocity of 21.4 cm/s for 30 minutes followed by chemical cleaning with HCl (pH 3) for 45 minutes at same cross flow velocity almost fully restored the activity of the membrane.

8.3 Main findings of NF system

In this study, a cross flow NF system was used for water purification of ROC. It was revealed that NF membrane is a good option for pretreatment for organic compounds from wastewater however, most of inorganic compounds were passed through the membrane. This study investigated the use of FO membranes in a cross flow NF system. The FO membranes have pore size of less than most of NF membranes, so they can also remove inorganic ions present in ROC. The support layer of FO membrane can create ICP but permeate exiting membrane would help to prevent inorganics from

going to permeate side. Although CTA-ES has lower flux as compared to NF030 and TFC-ES membrane, CTA-ES (FO membrane) removed inorganic compounds better than other two membranes during an operation of 90 h duration. The net water permeate flux was improved by 17%, with (CTA-ES) FO membrane when GAC and acid pretreatments were applied. The final NF permeate from CTA-ES membrane can also be recycled.

8.4 Recommendations for future study

The study indicated some practical limitations of FO such as lower flux with high TDS feed limiting the osmotic equilibrium and resultant permeate flux. However, this issue was partially overcome with application PAFO. However, higher RSF and FSF are still challenges particularly the movements of monovalent ions present in FS to DS and vice versa.

Various studies have indicated the role of various membrane properties such as pore size, zeta potential, and the surface charge of the membrane. However, that no clear theory on the mechanism of actual water movement through any membrane is documented. So it is really difficult to describe through which mechanism the water molecules actually transport through the membrane pores. The two types of membrane used in this study showed varying performances which indicates the active role of the membrane characteristic in terms of delivering resultant permeate flux performance. Thus detail study should be conducted in this area.

FO and PAFO operations are far from its commercialization due to RSF and FSF. It is suggested there is an urgent need for the development of membrane which would have 100 % rejection of salts on both side of the membrane. This would help for quick commercialization of FO and PAFO operations.

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