Forward Osmosis for the Treatment of Reverse Osmosis Concentrate from Water Reclamation: Process Performance and Fouling Control

by

Shahzad Jamil

A thesis submitted in fulfilment of the requirements for the degree of
Master by Research

Principal Supervisor
Dr. Christian Kazner

Co-supervisor
Prof. Saravanamuth Vigneswaran

University of Technology Sydney
School of Civil and Environmental Engineering
Faculty of Engineering and Information Technology

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ABSTRACT

Reverse osmosis concentrate (ROC) is considered to be an obstacle in the production of high quality water from water reclamation and desalination plants using dense membrane systems. It normally comprises 10-30% of the feed water of water reclamation plants and 50-75% of the feed water from sea water desalination plants. While coastal water reclamation plants have the opportunity to discharge the RO concentrate directly into the ocean, inland facilities depend on controversial options such as surface water discharge, evaporation ponds, deep well injection and land applications. However, all these options are not sustainable or environmentally friendly. Therefore methods for proper disposal of RO concentrate especially for inland plants are urgently required.

Various integrated concentrate treatment concepts have been proposed to minimise waste and maximise water recovery. A key issue in applying the Zero Liquid Discharge principle is the impact of foulants on the concentrate desalinating system, consisting of forward osmosis (FO) and a subsequent crystalliser.

This study investigates forward osmosis, which appears to be a promising technology that represents a step towards zero liquid discharge. Organic fouling and inorganic scaling are hypothesised to be the main membrane foulants in FO. Furthermore FO is analysed in the context of removing organic micropollutants from RO concentrate.

The following methodology was applied to this study. Two types of flat sheet membranes Cellulose Tricacetate (CTA) and Thin-Film Composite polyamide (TFC-PA) supplied by Hydration Technology Innovation for FO were used. Two model foulants - alginate and humic acid - were used to examine organic fouling of FO membrane. Real RO concentrate from the Sydney Olympic Park Authority's water recycling plant was used to study fouling and its impact on water flux. Both membranes showed similar trends but permeate flux was higher with the TFC-PA membrane compared to the CTA-NW membrane. Forward osmosis was studied in two ways: FO mode (active layer facing feed solution); and pressure retarded mode (PRO) modes (support layer facing feed solution).

The results indicate that alginate is a strong foulant of the PA membrane in PRO mode, and the resulting flux decreased sharply. On the other hand, however, in FO mode only moderate fouling was observed.

CTA and TFC (PA) membranes were checked for fouling by humic acid. Approximately 7% TOC was adsorbed on the membrane's surface resulting in a minor flux decline of 2-4%.

Real RO concentrate was tested in concentrations of 38 mg/L (TOC equivalent) with both membranes in FO mode. The TOC adsorption at the membrane surface was low between 2-9%, however a high flux decline was observed with increasing draw solution concentrations. The observed flux decline was about 10-26% for the CTA membrane and 5-55% for the TFC-PA membrane, depending on the DS concentration of 1-4 M NaCl in both cases.

Analysis of the inorganics revealed that inorganic scalants were the major contributor to the flux decline. Phosphates, carbonates and silicates were detected as the main scaling compounds. Reducing the pH meant that membrane scaling was significantly reduced.

Organic micropollutants were not fully retained by the FO membrane. Size exclusion was identified as the main retaining process. In a comparison of the two membrane types, CTA removed the trace organics to a smaller degree than the TFC membrane. Removal ratio ranged from 40 to 97% (CTA) and 70 to 99% (TFC). Rejection depended on the DS concentration with increasing retention at higher fluxes.

The study showed that forward osmosis is a promising technology for RO concentrate treatment and opens new avenues for further research work:

- Recovery of nutrients and salts from RO concentrates in water reclamation
- Recovery of draw solution and its reuse, thus making FO operation continuous
- Post-treatment of permeate to produce high quality recycled water

Acknowledgments

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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.

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

Signature of Candidate

Shahzad Jamil

Sydney, October 2013

ACRONYMS AND ABBREVIATIONS

Avg.	Average
CFV	Cross-flow velocity
CTA	Cellulose tri-acetate
DS	Draw solution
DI	Deionised
ECP	External concentration polarization
FO	Forward osmosis
FS	Feed solution
HA	Humic acid
ICP	Internal concentration polarization
LMH	$L/(m^2{\cdot}h)$
M	Molar
MF	Microfiltration
MWCO	Molecular weight cut-off
NaCl	Sodium chloride
NF	Nanofiltration
NOM	Normal organic matter
PA	Polyamide

RO	Reverse osmosis
SEM	Scanning electron microscopy
SOPA	Sydney Olympic Park Authority
T	Temperature
TDS	Total dissolved solids
TFC	Thin film composite
TOC	Total organic matter
UF	Ultrafiltration
UV_{254}	UV absorbance at 254 nm
WAIV	Wind Aided Intensified Evaporation
WWTP	Wastewater treatment plant
ZLD	Zero liquid discharge

Introduction

1.1   Research motivation and significance

For centuries most countries around the world have enjoyed clean fresh water as an abundant and inexpensive resource. Now due to climate change and on-going population growth one third of the world's population is facing water shortages. In fact 1.2 billion people live without clean drinking water while 2.6 billion lack adequate sanitation (Shannan et al., 2008).

High quality water reuse based on dense membrane treatment is expected to be progressively applied in many regions of the world (GWI, 2009), yet treatment and sustainable management of the produced reverse osmosis (RO) concentrates are still a critical issue in dual membrane treatment and limit the application, especially in inland locations. Various concentrate treatment concepts have been proposed to minimise waste and maximise water recovery (Khan et al., 2009; Pérez-González et al., 2012). A key issue in applying the Zero Liquid Discharge principle is the fate of organic compounds and for instance their impact as foulants on the concentrate desalinating system, consisting of forward osmosis (FO) and a subsequent crystalliser (Adham et al., 2007).

Khan et al. (2009) stated that new sources of integrated water supplies systems like seawater, brackish groundwater, and even recycled water are still relatively new ways to produce drinking water. Membrane technologies such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) play a vital role in these circumstances for removing chemical substances, salinity and microorganisms. These technologies, however, generate waste streams that require disposal with particular attention to minimizing their environmental impact. Seawater desalination plants, surface and groundwater softening, as well as brackish water desalination plants have an impact on the environment through their wastewater discharges with high salinity. However, water reclamation plants generate waste streams consisting of high salinity, high nutrient content and anthropogenic pollutants such as endocrine

disruptors, carcinogenic chemicals and metals. Thus managing these concentrate streams must be regarded as a major issue that needs to be resolved.

The focus of most studies was to address the reduction of organic contamination (Pérez-González et al., 2012). Initially nitrogen was considered to be a minor issue, but in some WWTPs the ammonia concentration in RO concentrates was as high as 120 mg/L. Ersever et al. (2007a, b) investigated the separation of nitrogen compounds from RO brines by biological nitrification-denitrification and sulphate control through a fluidized bioactive absorber reactor (FBAR) process and granular activated carbon (GAC). These tests were conducted at different nitrate concentrations and retention times. It was indicated that the FBAR process could prove to be an efficient technology for the removal of nitrogen from RO concentrates.

The potential solutions for concentrate treatment and management rely on evaporation ponds, falling film evaporators, crystallization, spray dryers, membrane distillation, and discharge to the wastewater collection system, land application, deep well injection or disposal to surface waters (Khan et al., 2009). All of the above described methods have serious implications for the environment and economic factors to be considered. For example eco-friendly solar evaporation leads to heavy loss of water, which later has to be made up by other freshwater sources (e.g. from seawater desalination), and consumes large areas of land.

Pérez-González et al. (2012) published a review on the treatment of RO concentrate including applications in water reclamation. They reported that the majority of research focuses on the reduction of pollutants and micropollutants that did a lot damage to the environment. Promising results have been achieved through advanced oxidation technologies and one of them is electrochemical oxidation with boron-doped diamond anodes for removing micropollutants and persistent compounds. However, the generation of oxidation by-products has been identified as a critical issue.

To meet the growing global water demand, available alternative water sources such as seawater and brackish water are being increasingly targeted. Although these desalination technologies are now being used all over the world to provide water for

urban and industrial applications and significant improvements in membrane technology during the last few decades, these options are still energy intensive and leave a large carbon footprint. Wastewater effluents as sources for water recycling can reduce the environmental footprint, particularly the energy demand (Yüce et al., 2012). However, they produce the aforementioned waste streams which might require further treatment depending on the local conditions.

The main focus of this study is to investigate various operating parameters/conditions for the smooth running of FO operation as an emerging and novel technology, which has significant advantages over the reverse osmosis (RO) desalination process especially in terms of energy consumption. Although FO 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 (TFC-ES, HTI 2013). The separation and recovery of the DS still remains a significant challenge for drinking water applications.

Forward osmosis (FO), is considered to be a new and clean process due to its low energy requirements. The FO process works on the principle of the natural osmotic gradient between two solutions being at different concentrations, when 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 that transporting water across a semi-permeable membrane does not require hydraulic pressure. Consequently, the energy consumption is significantly less than that in the RO process (see Figures 2.2 and 2.3).

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.

1.2   Research Objectives and Scope

The research work presented here is part of the European-Australian research project known as "ACTIWATE - Advanced concentrate treatment for integrated membrane based water reuse systems". An integrated reverse osmosis concentrate (ROC) treatment concept aimed to be implemented at minimal cost and with as small an environmental impact as possible, is investigated (see Figure 1.1). Applying the Zero Liquid Discharge (ZLD) approach, the concentrate treatment combines the removal of bulk organics and organic micropollutants with desalination stages. The further concentration of the ROC to supersaturated concentrations leads to precipitation of the salts and the removed water enhances either: firstly, the recovery ratio by blending the high quality FO permeate with the mainstream RO permeate; or secondly, the overall water recycling by conveying the desalinated water of poorer quality back to the main treatment train.
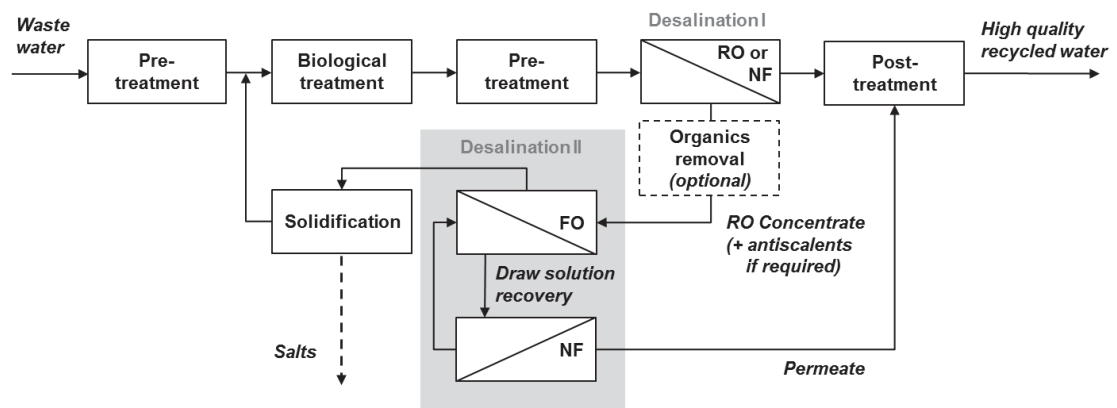
Fig. 2.1   Schematic of proposed integrated water reuse concepts for inland locations (adapted and modified from Kazner, 2012)

The FO process can be used in many applications, due to its versatility such as wastewater treatment (Cath et al., 2006; Cornelissen et al., 2008), seawater and brackish water desalination (McCutcheon et al., 2005, 2006), power generation (Loeb, 2002), food processing (Petrotos et al., 1998; Petrotos & Lazarides, 2001).

In this research work Forward Osmosis treatment is applied for the further concentration of RO concentrate derived from the Sydney Olympic Park Authority's (SOPA) Water Reclamation and Management Scheme (WRAMS) water recycling plant. RO concentrate from this plant is full of organic micropollutants, bulk organics besides more variation in the salinity. The research objective is to study FO operation for treating reverse osmosis concentrate (ROC). The particular emphasis is put on membrane fouling issues and trends that affect the performance of the FO system - and developing strategies for reinforcing the membrane's performance either by flushing or chemical cleaning. The studies are conducted in laboratory scale and from these the criteria are established for designing a pilot plant that tests real RO concentrate on a continuous mode.

The present study aims to address three major questions concerning the application of FO membranes in the treatment of RO concentrate:

- Identify the optimum operational conditions of forward osmosis for concentration of RO concentrate Desalination kinetics
- Determination of critical flux
- Study different membrane types (CTA and TFC)

1. Study and control the fouling and scaling behavior of different FO membranes through model foulants and real RO concentrate using
   - model solutions (alginate and humic acids)
   - real RO concentrate (Sydney Olympic Park water filtration plant) with and without pre-treatment
2. Investigate the removal of trace organic pollutants such as pharmaceuticals using the selected FO membranes to allow for a blending of the FO permeate with the RO permeate as water produced by the reclamation process and increase the overall water recovery.

The conclusion should comprise optimum working parameters for the FO plant's operation (pilot test) and design. Figure 1.2 provides an overview of how this thesis is structured.

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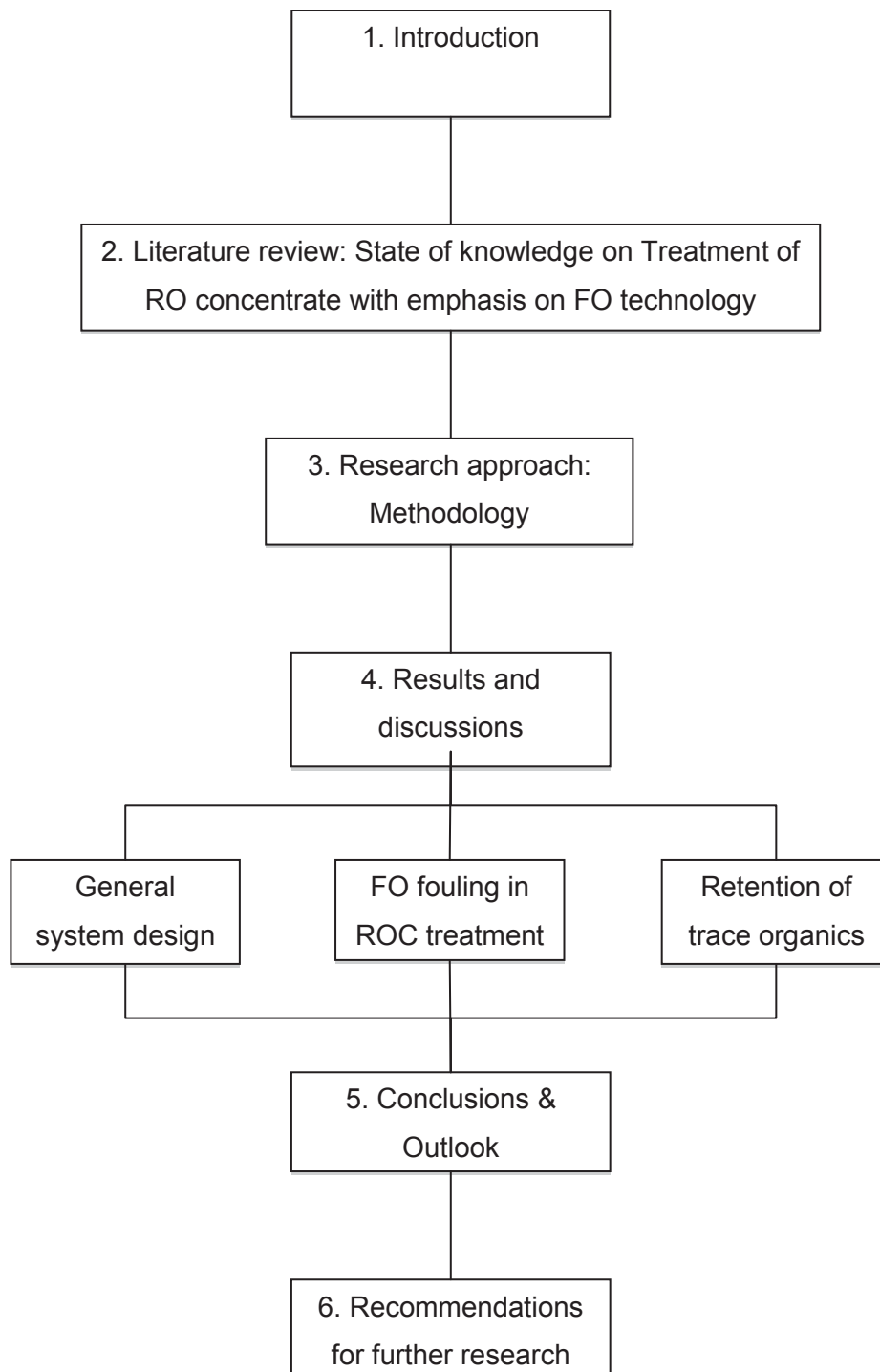
Fig. 2.2   Structure   of   the   thesis

2 Literature review

2.1 Management and treatment of reject streams from reverse osmosis

2.1.1 Management of concentrate from dense membrane processes

With the rapid increase in global demand for water, membrane technology is increasingly filling the water deficits through reverse osmosis treatment in seawater desalination plants, water reclamation plants and brackish water treatment plants. However, these plants generate large amounts of concentrates containing all types of compounds. Currently these concentrates are discharged into surface, groundwater and marine water bodies, posing a threat to these ecosystems; hence there is an urgent need to address this problem and to find environmentally friendly solutions for the disposal of these RO concentrates (Perez-Gonzalez et al., 2012).

While coastal plants have the opportunity to discharge effluents directly into the sea, inland communities have to discharge them into open channels, evaporation ponds or deep well injection sites. These methods are not considered safe and environmentally sustainable. Safe disposal of RO concentrate is thus a particular issue for inland plants (Adam et al., 2007)

2.1.2 State-of-the-art technologies for the treatment of reverse osmosis concentrates

In this section several conventional and emerging technologies for RO concentrate treatment as well as their process combinations aiming at Zero Liquid Discharge are presented.

Treatment technologies on reverse osmosis concentrates are mainly conditioned 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 are directly 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 and recover 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 components 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 availability of this technique has been only demonstrated on a laboratory scale (Perez-Gonzalez et al., 2011).

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 is a alternative process for highly concentrated aqueous solutions. The modification Vacuum Membrane Distillation (VMD) is an evaporative technology that uses a membrane to support the liquid vapour interface (Urtiaga et al., 2001). The driving force is the vapour pressure gradient, which is generated by the temperature differential across the membrane. Neither organic fouling nor biofouling were observed in experiments with real RO concentrates for an operational time of a few hours. However, due to high salt concentrations calcium scaling occurred. Scaling reduced the transmembrane permeate flux but it was reversible after appropriate washing and chemical cleaning. Advantages over conventional distillation are: firstly, the high contact area per unit of equipment volume provided by the membrane, allowing very compact installations; and secondly, reduced footprint. Despite these advantages Vacuum Membrane Distillation is not yet available on an industrial scale.

The combination of Membrane Distillation with Crystallization (MDC) was also investigated with reference to RO concentrate treatment. Carollo Engineers (2008) report that for enhancing the recovery of the RO concentrate chemical softening is applied in the primary RO plant. Conventional softening chemicals like lime, sodium hydroxide and soda ash are used for the primary RO concentrate 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 (Carollo, 2006). 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. Its main advantage is that of requiring less energy than RO. The driving force of FO is the osmotic pressure differential across the membrane, which the transport of 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).

2.2 Forward Osmosis
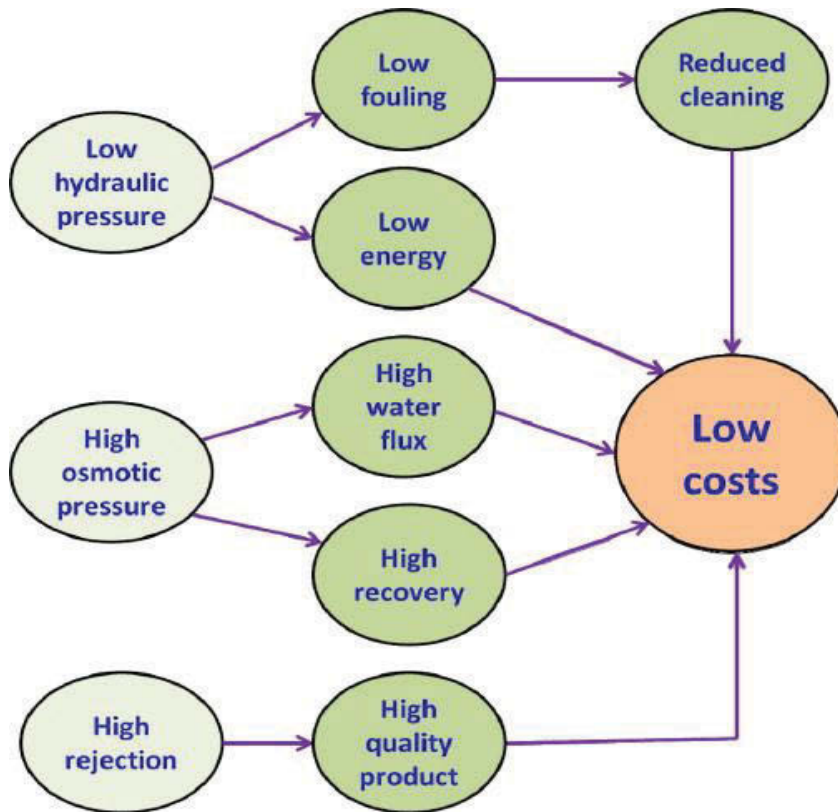
Fig. 2.1 Application of FO in water, energy and life science fields (Zhao et al., 2012)

2.2.1 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).

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

$$J_w = A \, (\sigma \, \Delta\pi - \Delta P) \qquad (1)$$

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 $\Delta\pi$-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).

$$J_w = A (\Delta\pi draw - \Delta\pi feed) \qquad (2)$$
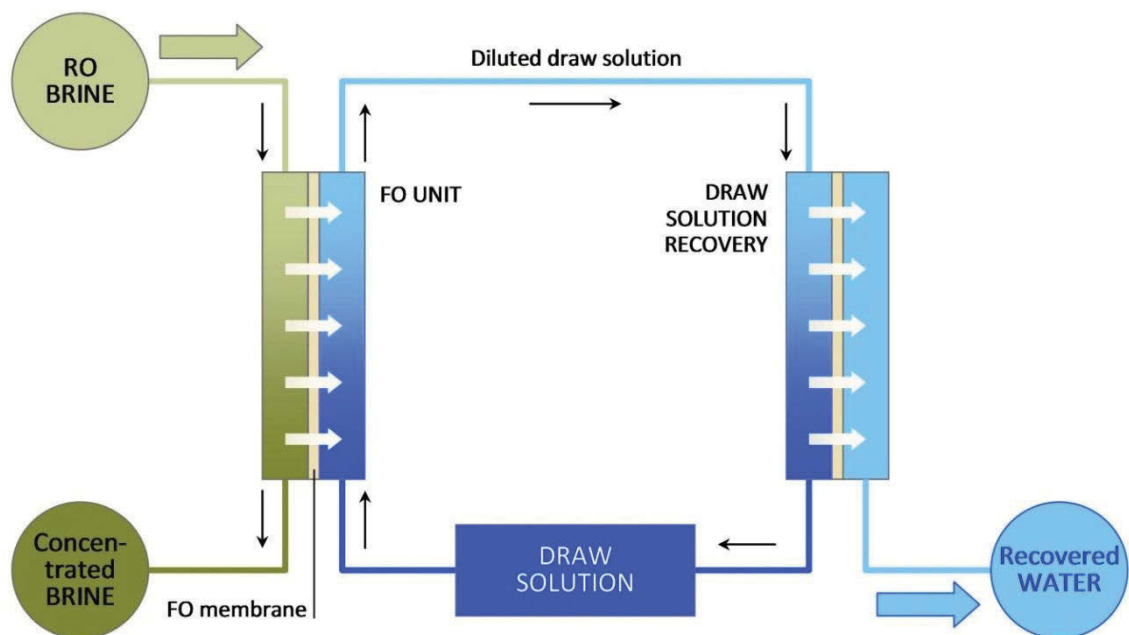
Fig. 2.2   Forward osmosis for treating RO brine (Kazner et al., 2013; modified from Cath et al., 2006)

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).
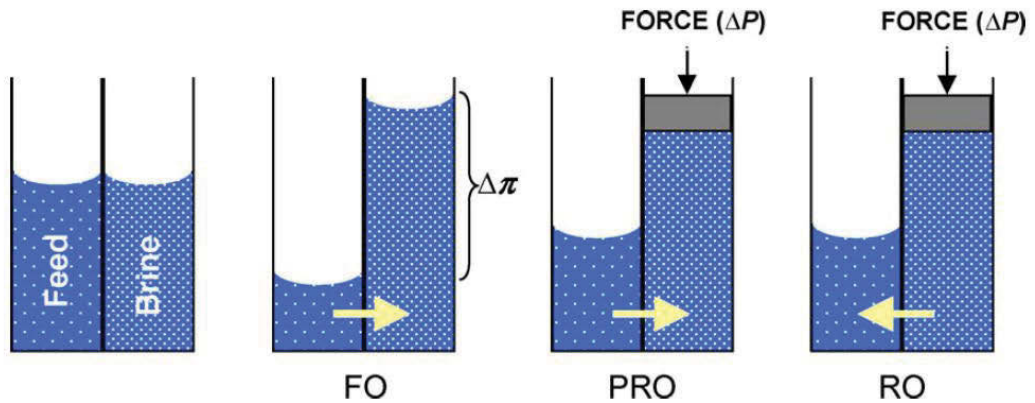
Fig. 2.3 Solvent flows in FO, PRO and RO. For FO, ΔP is zero and the water diffuses to the higher concentration side of the membrane. Regarding PRO mode water diffuses to the higher concentration side under positive pressure ($\Delta\pi > \Delta P$). For RO, water diffuses to the less concentrated side due to hydraulic side ($\Delta P > \Delta\pi$) (adapted from Cath et al., 2006)

2.2.2 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.

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 since it occurs in osmotic- driven membranes as well 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 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:

$C_m/C_b = \exp(j_w/k)$ (1) (Zhao et al., 2012 ; Mulder, 1996)

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:

$k = ShD/D_h$ (2)

D_h is denoted as hydraulic diameter and D is the salt diffusion coefficient. When the feed concentration is low the concentration in eq (1) could be replaced by the osmotic pressures. So the concentration modulus can be shown as:

$\Pi_{m\text{-feed}}/ \Pi_{b\text{-feed}} = \exp (j_w/k_{feed})$ (3)

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:

$\Pi_{m\text{-draw}}/ \Pi_{b\text{-draw}} = \exp (j_w/k_{draw})$ (4)

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.

Theoretical backgrounds

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

$$Jw = A (\sigma \Delta\Pi - \Delta P) \quad (5)$$

A is the water permeability coefficient of the membrane, σ is the rejection coefficient, $\Delta\Pi$ is the osmotic pressure difference across the membrane and ΔP is the applied hydraulic pressure. The difference ($\sigma \Delta\Pi - \Delta P$) 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:

$$Jw = A (\Pi_{draw} - \Pi_{feed}) \quad (6)$$

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:

$$Jw = A (\Pi_{m\text{-}draw} - \Pi_{m\text{-}feed}) \quad (7)$$

By substituting equations (3) and (4) in equation (7)

$$Jw = A [\Pi_{b\text{-}draw} \exp (j_w/k_{draw}) - \Pi_{b\text{-}feed} \exp (j_w/k_{feed})] \quad (8)$$

Both concentrative and dilutive ECP are considered in eq-(8). 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 assumed to be zero (i.e. the rejection coefficient $\sigma=1$) and feed and draw solution concentrations are low because only then can the concentration be assumed to be 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.

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Internal concentration polarization and modeling

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.
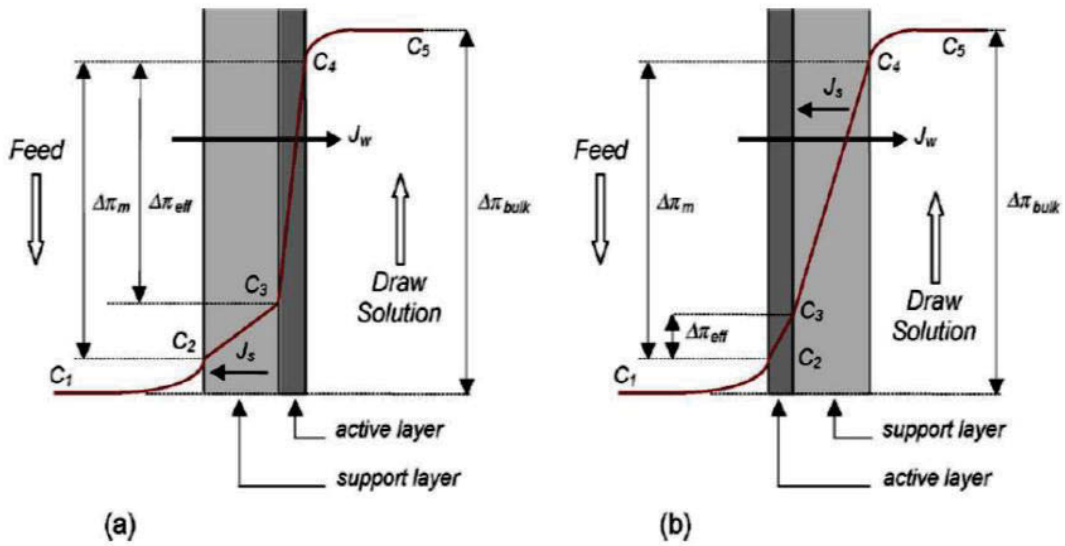
Fig. 2.4 (a) Concentrative internal CP and (b) dilutive internal CP across a composite or asymmetric membrane in FO (adapted from Cath et al., 2006)

2.3   Performance and optimization of the forward osmosis process

The following general criteria should be considered before selecting any FO membrane system.

Table 2.1   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. This is due to a	Zou et al., 2012

2.3.1   Evaluation of draw solution

In this study sodium chloride was used as the draw solution because it has excellent properties such as high osmolality (Cath et al., 2006) and low viscosity. DI water as feed solution (FS) and NaCl as draw solution (DS) were used as a baseline to compare permeate flux drawn from real RO concentrate and model compounds. The results of permeate flux are shown in Figures 4.2 and 4.3. Table 4.2 presents an overview of different organic and inorganic draw solutions as alternative solutions for RO concentrate as feed solution All draw solutions have advantages as well as major disadvantages for treatment of RO concentrate, which would prevent full-scale application. The identification of optimum draw solutions is currently one of the main commercial activities.

Table 2.2   Draw solutions

Draw solutions	Advantages / disadvantages	Reference
Monovalent inorganic solutions: NaCl	+ 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 (EST) Achilli et al., 2010 JMS
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	Yen et al., 2010; Adham et al., 2007

2.3.2   Influence of draw solution concentration on permeate flux and permeability

The filtration experiments were conducted with sodium chloride as draw solution to compare them with what the literature results. The draw solution concentrations were studied in the range of 1 to 4 molar equivalent to 58.44 to 233.76 g/L NaCl. Given an osmotic pressure of 1 M NaCl solution of around 50 bar (see Fig. 4.4) this is equal to a pressure range of 50 to 200 bar. The two investigated membrane types (CTA and PA) were installed in FO mode as well as in PRO mode (PA only) using DI water as the feed solution.
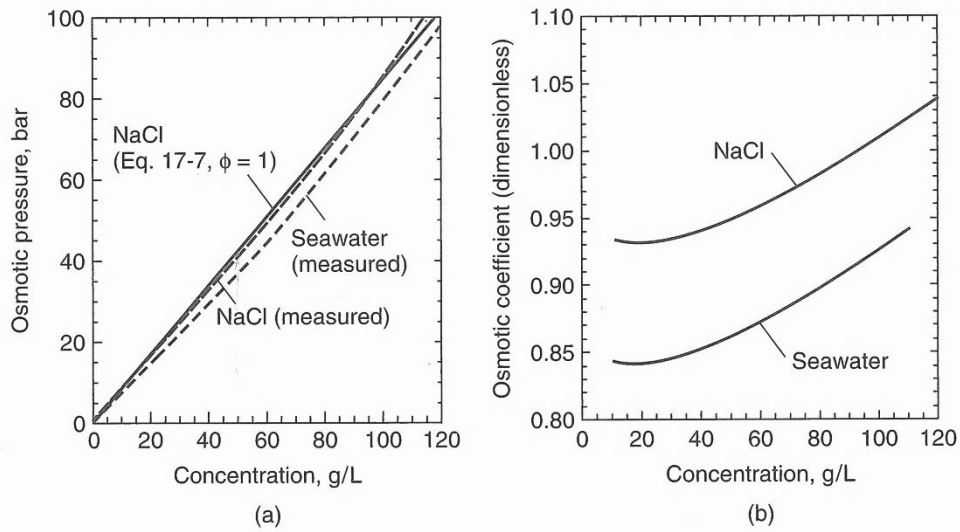
Fig. 2.5   (a) Osmotic pressure of aqueous solutions of sodium chloride. (b) Osmotic coefficients for sodium chloride and seawater (osmotic coefficient for seawater with the van't Hoff equation is based on a concentration of NaCl equal to the TDS of the seawater) (adapted from Crittenden et al., 2005, Fig. 17-9, p. 1356)

2.4   Membrane performance inhibitors

Membrane performance is inhibited similarly in both 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 and fouling. This is due to the transport of particulate matter to the surface or biological growth on the surface (Fritzmann et al., 2007).
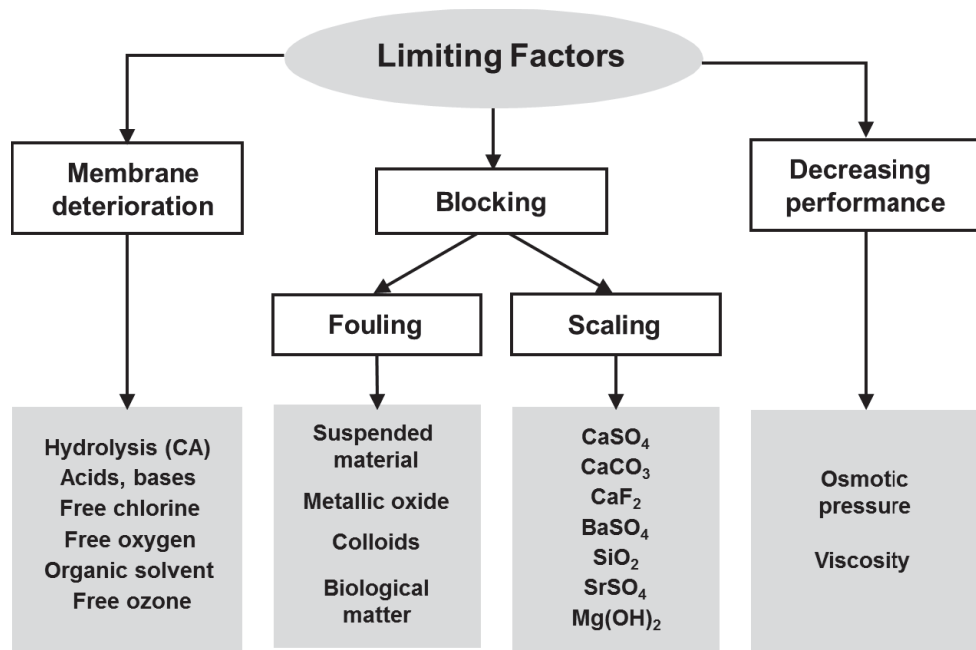
Fig. 2.6   Limiting factors for membrane desalination by reverse osmosis (adapted from Fritzmann et al., 2007)

2.4.1   Membrane fouling

Membrane fouling is a major disadvantage of membrane filtration processes, in that it results in a loss of membrane permeability. Membrane fouling is generally categorized into four areas (Pontie et al., 2005): inorganic fouling, particle/colloidal fouling, organic fouling and biofouling.

2.4.2   Membrane scaling

Scaling is caused by exceeding the solubility of soluble salts at the surface of the membrane which can lead to precipitation. A thin layer of precipitates is formed that hinders the mass transfer through the membrane and this normally happens on the feed side. The membrane surface is the most sensitive for salt deposition caused by concentration polarization. Some of the important scaling agents are $CaCO_3$, $CaSO_4$, $BaSO_4$ and silica. Scaling can dramatically reduce permeate flux, and has to be controlled by all means (Fritzmann et al., 2007).

The downstream part of the FO stage is most susceptible to scaling, where concentration in the feed solution is the highest. Although scaling for some compounds can be removed by flushing the membrane with deionized water and acid, in practice it is often not possible to transport the crystalline mud out of the module. Therefore, pre-treatment is recommended for stabilization of substances that could cause scaling. Precipitation can be prevented by pH adjustment and using anti-scalants. Crystal growth is usually divided into three stages as shown in Fig. 2.6.

Inorganic fouling is normally caused by carbonates and metal hydroxides on the membranes due to changes in water chemistry (Pontie et al., 2005). Scaling is caused by exceeding the solubility of soluble salts like $CaSO_4$, $CaCO_3$, calcium phosphate, and aluminium hydroxides, etc. Chemical and physical parameters which are responsible for precipitation are pH, flow velocity, temperature, permeation rate, salt concentration and concentration polarization (Al-Amoudi |& Lovitt, 2007). Furthermore scaling normally results in a decline in permeate flow and high concentration of salts can cause denaturation of proteins. This situation can become more problematic.
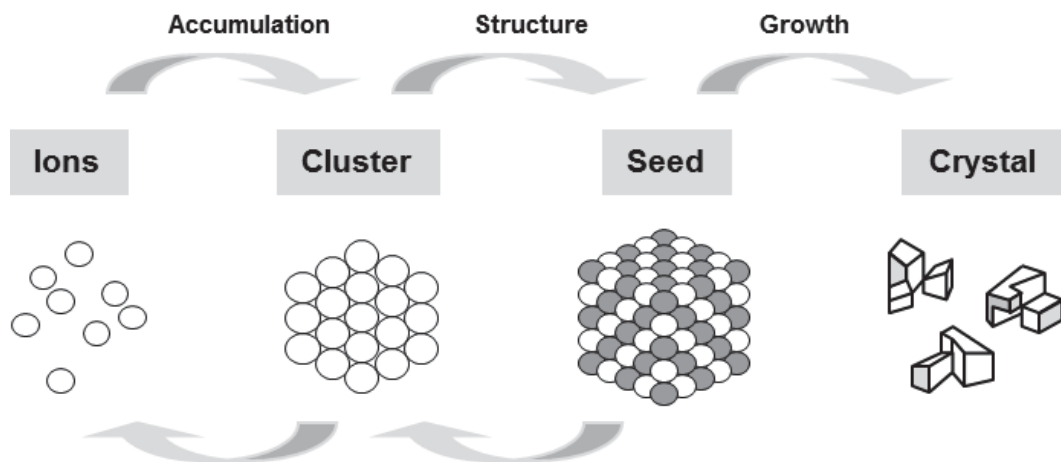
Fig. 2.7   Scaling stages (Fritzmann et al., 2007)

Silica scaling and reversibility in Forward Osmosis

Mi and Elimelech (2013) compared silica scaling and its reversibility in forward osmosis to reverse osmosis. The flux decline in FO and RO is observed to be very

similar under silica scaling in the two modes. However, the flux recovery is close to 100% in the FO mode while it is around 80% in the RO mode. Polyamide (PA) and cellulose acetate (CA) membranes materials were employed for the test run to study silica scaling and cleaning. It is observed that the flux decline rates for both the cases are similar, but the recovery of flux in the CA membrane is 30-40% higher than that of the PA membrane. AFM force measurements specify that the surface roughness of the membrane increases the adhesion force between the PA membrane and a silica gel layer, thus decreasing the cleaning efficiency of the said membrane. Dynamic light scattering and energy-dispersive X-ray spectroscopy results indicate that silica scaling starts as a monosilicic acid deposition on the membrane's surface, followed by polymerization/condensation that forms an amorphous silica gel layer at the interface between the membrane and the silica particles (Mi & Elimelech, 2013).

2.4.3 Organic fouling

Organic fouling

Organic fouling has been most poorly understood compared to other fouling agents (Amy, 2008). The foulants in this case are polysaccharides and proteins but these components occur in both abiotic macromolecular and colloidal forms. There is some degree of hydraulic reversibility during backwashing of low pressure membranes but this option does not exist for high pressure membranes; the chemical cleaning may be constrained by the compatibility of membrane material with the cleaning agent. Pre-treatment through coagulation can improve the situation but there is little consensus on the attributes of powdered activated carbon pre-treatment (Amy, 2008).

Natural organic matter (NOM) is a very common organic foulant present in surface water or wastewater. Organic matter normally consists of fulvic acid, humic acid, polysaccharides, and aromatic compounds; in addition, there are lower molecular weight compounds like phenols, pesticides, trihalomethanes (THM) and a variety of

toxic chemicals (Potts, Ahlert & Wang, 1981). These are sources of energy for microorganisms and may cause reversible or irreversible flux decline. The factors that impact on natural organic matter fouling are ionic strength, concentration, pH, divalent cations, NOM fraction (hydrophilic/hydrophobic), molecule or membrane charge, surface morphology, concentration polarization and permeate flux. Al-Amoudi and Lovitt (2007) indicated that the major occurrence of flux decline is caused by the hydrophobic fraction while the hydrophilic fraction had a smaller effect. The hydrophobic part of NOM tends to adsorb more than the hydrophilic to the membrane surface. Moreover, the hydrophilicity of the NOM increases as molecular weight also increases. It was further noticed that the fouling effect of divalent ions of higher molecular weight than lower molecular weight NOM was more evident. Thus hydrophilicity and molecular size play an important role in retention of dissolved organic compounds.

Organic matter such as plants degrade into a matrix of macromolecules called humic acids. Natural waters usually contain humic substances concentrations in the range of 0.5-20 mg/L and up to 100 mg/L in surface sea water (Fritzmann et al., 2007). Humic acids are polymeric phenolic structure compounds and have the ability to form chelates with metal ions. Specifically with iron ions, a gel-like fouling layer is formed by complexation of multivalent ions. These organics are able to adsorb at the surface of the membrane and it can be an irreversible process. At high values of pH>9 fouling can be prevented since membrane and organics assume the same negative charge. The resulting repulsion is used for cleaning the membranes.

Due to calcium complexation highly irreversible fouling is formed. Calcium complexes form a highly compactable flock-like structure which also causes highest flux decline compared to other chelates. The hydrophobic humic substances are deposited on the membrane surface and the adsorption is favoured with positively charged, higher molecular weight compounds (Fritzmann et al., 2007).

Valladares Linares et al. (2012) focused on characterization of the natural organic matter (NOM) fraction that caused fouling on the active layer of a FO membrane in a

novel plate and frame configuration, using secondary wastewater effluent as a feed solution (FS) and seawater as the draw solution (DS). Additionally, transparent exopolymer particles (TEP) were observed on the support layer (SL) of the membrane's contact with the DS. The NOM fouling layer was composed of biopolymers and protein-like substances, which badly affect the flux of water through the membrane. However, the reversibility of NOM is found to be up to 90%, when air scouring for 15 minutes is used as a cleaning technique. After chemical cleaning the irreversible fouling was 8.2% in this study. TEP formed clusters clearly identifiable with an optical microscope and TEP-specific dye. Chemical cleaning with 1% NaOCl for 10 minutes proved to be the most effective method for removing TEP.

Sangyoup Lee et al. (2010) noticed that the tendency for flux decline in FO changed dramatically according to the type of organic foulant and draw solution used as driving force. Reverse solute diffusion played an important role in cake formation. The permeate flux in FO during organic fouling is fully recoverable by increasing the cross flow velocity, while no noticeable change was observed in RO. They concluded that organic fouling in FO could be controlled by optimizing hydrodynamics of the feed stream without utilizing chemical cleaning.

2.5 Countermeasures

2.5.1 Pre-treatment of feed water

The pre-treatment of dense membrane processes can be divided into two parts: conventional pre-treatment and membrane filtration such as microfiltration and ultrafiltration.

The conventional pre-treatment process

The main objective of any pre-treatment is to reduce the concentration of fouling agents in the feed water to the level that would provide smooth, long-term performance of membrane elements. Seawater RO system membrane fouling can develop due to the presence of impurities in feed water like colloidal and particulate matter, and dissolved organics as a result of biological growth in the RO system. Scaling is not considered to

be a major issue in most seawater feeds. Precipitation of sparingly soluble salts is less likely to occur in RO concentrate due to the relatively low recovery rate and low concentration of bicarbonate ion (Wilf & Schierach, 2001). The most likely cause of fouling in membranes is particulate matter, organics and biogrowth. Recent research work on membrane fouling processes has claimed that colloidal fouling is enhanced by ionic strength and permeate flux. The high ionic strength of treated water reduces mutual double layer repulsion between colloidal particles and the membrane surface. The foulant layer on the membrane surface is the result of permeate flux, which results in drag forces perpendicular to the membrane surface forces colloidal particles and organic macromolecules into the membrane surface. The fouling phenomenon affects the membrane surface's water flux and salt passage. High pressure is required under high fouling conditions to achieve design flow across the membrane. There is increase in salt passage, resulting in the permeate becoming more saline. Later stages of biological and particulate fouling will result in choking of feed channels and increased pressure drop.

The Silt Density Index (SDI) test is used to predict and then prevent the particulate fouling on the membrane surface. The SDI is a measure of filterability of RO feed through a membrane filter with a pore size of 0.45 micron. Silt is composed of suspended particulates all types that accumulate on the membrane surface. Sources of silt are organic colloids, iron corrosion products, precipitated iron hydroxide, microorganisms such as algae, and fine particulate matter. SDI testing is a widely accepted method for estimating the rate at which colloidal and particle fouling will occur in water purification systems, especially using reverse osmosis (RO) or nanofiltration membranes. SDI measures the fouling potential of suspended solids. It does not measure the quantity of particulate matter, since its size and shape vary. On the other hand turbidity estimates the amount of suspended solids. They are not the same and there is no direct correlation between them. In practical terms, however, the membrane show very little fouling when the feed water has a turbidity of <1 NTU. Correspondingly the membranes show very low fouling at a feed SDI less than 5. However, for the long-term stable membrane performance the average value of SDI should be <3 (Wilf & Klinko, 1998).

2.5.2 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 treatment processes depending on media and cartridge filtration. However, traditional spiral wound ultrafiltration membrane elements were suitable for treating high fouling surface water. The elements of the UF could not work at high flow rates without severe fouling in the membrane surfaces and fills feed channels. High cross-velocities are required through filter elements to reduce concentration polarization, and necessitates an increase in energy consumption. Membrane cleaning, often required, is very stressful and not effective in restoring the flow of permeate. Recently, new microfiltration and ultrafiltration technologies were introduced on the basis of large inner diameter capillary 0.7 to 0.9 mm (Wilf & Klinko, 1998). Membrane materials consist of polypropylene, polyethylene sulphonated sulfone or cellulose acetate.

There are two common characteristics of novel commercial equipment:

1.   A frequent short duration, automatically cleaning sequence of capillary fibre, which makes it possible to maintain stable permeate flow with minimum off-line operation of the system.

2.   The ability to work in a very low cross-flow velocity, or even in direct flow (dead end) mode.

Off-line cleaning time is very short due to pulse cleaning and is comparable to the time out, off line conventional filters due to filter backwashing. This frequent pulse cleaning leads to stable permeate flow rates. The feed pressure is in the range of 1 to 2 bars; operation at low pressure and low cross-flow or direct filtration situation results in high recovery rates and very low energy consumption of about 0.1 kWh/m^3 of filtrate.

2.5.3   Membrane cleaning

In FO, organic foulants accumulate on the surface of the membrane only loosely due to a lack of hydraulic mechanical pressure (Sangyoup <u>Lee</u> 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 behavior of FO and RO and flux recovery by flushing, both FO and RO fouled membrane underwent a high cross-velocity test for cleaning (Sangyoup 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 behavior of the flow pattern was noticeable. Furthermore, it is interesting to note that the behavior of low flow FO after increasing flow velocity across the membrane is completely different from initial flux drop behavior.

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.

2.6   Conclusion

Membrane technology, especially osmotically-driven processes technologies have shown great potential in many applications like desalination, water purification and wastewater treatment. However they are facing numerous challenges in terms of membrane performance such as fouling and concentration polarization, and ideal draw solute. Specifically, internal concentration polarization (ICP) happening at the porous support layer side of the membrane is a critical issue. It is therefore vital to develop both novel FO membranes and draw solutes. Fouling is a complex phenomenon influenced by the physicochemical properties of the membrane, the module or test cell configuration, solute properties, pre-treatment process and operating conditions are critical variables. For the best performance all these factors have to be considered.

3 Materials and methods

3.1 Chemicals, reagents and employed solutions

In this chapter the materials employed (chemicals, inorganic and organic solutes, types of membranes and FO apparatus) are described. Solution preparation, analytical methods and experimental protocols are explained. A detailed description of the FO bench-scale system (system schematics and operation modes) and the properties of the membranes are elaborated in detail.

For standard data evaluation and performance testing, AR grade sodium chloride (NaCl) was supplied by Sigma Aldrich, Australia and 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) as described below.

3.1.1 Draw solutions

Sodium chloride with 1, 2, 3, and 4 Molar concentrations respectively was used as the draw solution in all the experiments.

3.1.2 Feed solutions

Humic acid (HA) was obtained as a commercial technical grade solid from Fluka (ash content 20%). 4g/L concentration stock solution was prepared and filtered with Whatman filter paper 4 (Cat. No. 1004-240) to remove all insoluble materials. Following this its total organic carbon (TOC) was measured as described in section 3.4.4, and diluted to the targeted experimental concentration with deionized (DI) water.

Alginate (alginic acid sodium salt from brown algae) was obtained from Sigma-Aldrich Australia. A 200 mg/L bulk stock solution was prepared in DI water, the TOC of solution was subsequently determined and finally the targeted TOC concentrations of the feed solutions were adjusted by adding DI water.

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 and full analysis is given below (Table 3.2).

3.1.3 Synthetic FO feed solutions

The synthetic feed solution was prepared on the basis of DOC values of real RO concentrate. Two model foulants were chosen, i.e. sodium alginate (ALG) and humic acid (HA) to study the fouling propensity on membrane and resultant flux. The properties of these two model compounds - alginate and humic acid - are shown in Table 3.1.

Table 3.1   Properties of the model foulants

Foulant	Representing	Category	Origin	Molecular Formula*	Molecular weight*, g/mol	$\dfrac{gTOC}{gComp}$
ALG	SMP	Poly-saccharide	Brown seaweed, algae	$[C_6H_7NaO_6]_n$	12000 - 180000	0.36
HA	NOM	Humic acids	Soil	$C_9H_8Na_2O_4$	226.14	0.65

* Literature data (Johnson et al., 1997), (Sigma Aldrich, 2012, Chemical Book, 2012); (adapted from Yapici, 2012)

3.1.4 Concentrate from reverse osmosis

Fig. 3.1 Sydney Olympic Park Authority's Water Reclamation and Management
Scheme (WRAMS)

As mentioned earlier, Sydney Olympic Park Authority's (SOPA) Water Reclamation
and Management Scheme (WRAMS) water recycling plant is located at Homebush Bay.
This plant receives water from sewage and a surrounding catchment area of 7.6 km^2.
The water reuse plant saves more than 800000 m^3 of drinking water per year and the
recycled water is supplied to domestic users, irrigators, Sydney Olympic Park and the
suburb of Newington (SOPA, 2006). Recycled water is clear and odourless (just like
drinking water from the main supply) after using treatment processes and is used where
drinking water quality is not required, such as for irrigation of public landscapes, home
toilets, washing machines, etc. The WRAMS consists of the water reclamation plant

(WRP), water treatment plant (WTP), storm water collection, clean water storage and recycled water delivery systems as shown in Fig. 3.2.
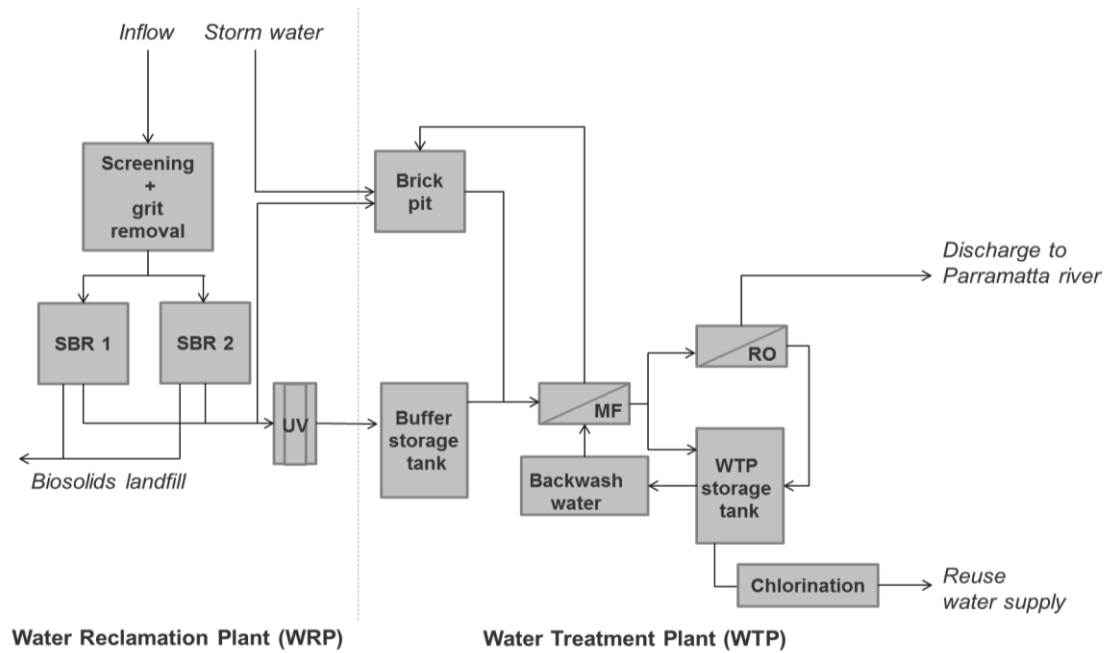
Fig. 3.2   Flow chart of the SOPA Water Reclamation and Management Scheme (Yapici, 2012)

Fig. 3.3   Microfiltration and Reverse Osmosis Elements

First of all the domestic sewage is treated in the water reclamation plant which functions mainly to remove solid materials, organics, ammonia and phosphorous. The main operation here is mechanical pre-treatment by screening and grit removal followed by biological treatment comprising of a sequencing batch reactor (SBR) with two tanks. After finishing UV disinfection the effluents are then 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, viruses 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) and then through reverse osmosis 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.

A summary of the analysis concerning the basic water and salinity of the MF feed and RO feed, permeate, and concentrate between November 2011 and October 2012 is shown in Table 3.2.

Table 3.2   Average concentrations of water samples from SOPA's water treatment plant (n = 3, Kazner et al., 2012) and RO concentrate used in this study (sampled in March 2013)

		Typical concentrations in 2012				Sample for study
		MF Feed	RO Feed	RO Perm.	RO Conc.	RO Conc.
Recovery of RO					80%	82%
DOC	mg/L	6.58 ±2	6.32 ±0.6	0.19 ±0.1	27.8 ±1.5	38.0
UV254	1/m	0.17 ±0.05	0.17 ±0.01	0.01 ±0.01	0.69 ±0.02	0.78
pH	unit	6.8 ±0.15	7.2 ±0.34	5.6 ±0.13	7.6 ±0.16	7.8
El. conductivity	μS/cm	771 ±273	723 ±72	10.6 ±3	3053 ±673	3050
Calcium	mg/L	20.5 ±0.8	22.2 ±0.6	0.2 ±0.1	95.2 ±4.6	113
Magnesium	mg/L	7.3 ±0.5	10.1 ±0.4	0.08	44.6 ±0.2	52.5
Potassium	mg/L	15.6 ±0.7	15.6 ±0.6	1.1 ±0.1	64.3 ±3.2	73.6
Sodium	mg/L	77.4 ±2.2	88.1 ±1.8	2.6 ±0.2	372.5 ±4.9	424
Iron	mg/L	0.13 ±0.13	0.04 ±0.03	< LOQ	0.15 ±0.08	0.07
Silica as Si	mg/L	2.9 ±0.1	2.7 ±0.2	0.05	11.75 ±0.6	11.6
Fluoride	mg/L	0.73 ±0.1	0.85 ±0.1	< LOQ	3.48 ±0.7	5.8
Chloride	mg/L	116.8 ±6.8	142.5 ±5.7	1.31 ±0.2	604 ±13.6	710
Bromide	mg/L	0.38 ±0.2	0.48 ±0.1	< LOQ	1.57 ±0.2	1.53
Nitrate as N	mg/L	1.91 ±0.14	1.40 ±0.08	0.09 ±0.02	5.25 ±0.37	10.8
Phosphate as P	mg/L	0.39 ±0.26	0.52 ±0.09	0.03 ±0.03	2.79 ±0.18	7.3
Sulphate	mg/L	38.4 ±1.1	43.0 ±1	0.3 ±0.1	180.8 ±1	251

3.2   Experimental set-up

3.2.1   Forward osmosis unit

The experimental set-up of the employed bench-scale forward osmosis (FO) unit is shown in Figure 3.4. The bench-scale unit was used for conducting all the subsequently described FO experiments. 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 210 mm, a width of 20 mm, and a height of 3 mm; with an effective area of 4.2×10^{-3} m^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).
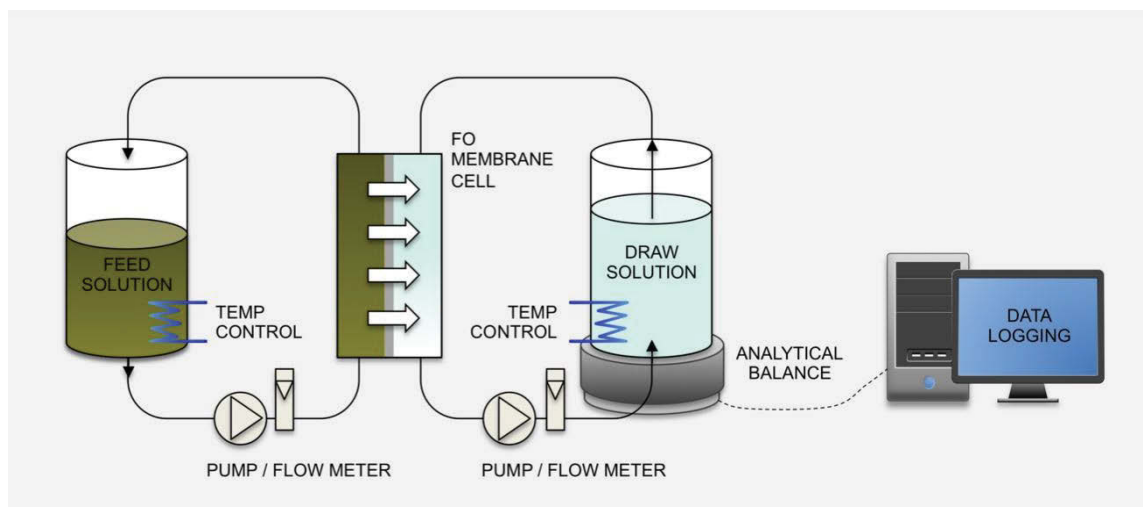
Fig. 3.4   Flow schematic of the lab-scale FO set-up (Kazner et al., 2013)

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).

Fig. 3.5   Bench Scale FO set-up at the UTS laboratory

Fig. 3.6   Overhead view of FO test cell with active flow cell of 2 x 21 x 0.3 cm on each side of the cell and double sealing

3.2.2 Forward osmosis membranes types

Two types of FO membranes were obtained from Hydration Technologies Inc. (HTI) which is based in the United States, i.e. cellulose tri-acetate (CTA) and thin film composite polyamide membrane (TFC) for all the tests. Membrane properties are shown in Table 3.3.

CTA-NW Membrane (support layer side)

TFC-ES Membrane (active layer side)

Fig. 3.7   CTA-NW and TFC-ES Membrane

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

	CTA 2013	CTA-NW 2013	TFC-PA 2013
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	-	-	$\Theta = 105\,°$ (Tiraferri et al., 2012)
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)	

3.3 Experimental protocols

3.3.1 Performance measurements

Water flux was measured continuously by weighing the draw solution using a digital mass scale connected to a computer.

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 and final volume of FS was measured to calculate the reverse solute flow towards the feed side.

3.3.2 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 three types of FO membranes. 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 and vice versa.

3.3.3 Fouling experiments

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

- Study of fouling employing humic acid as the model compound and its influence on permeate flux
- Study of alginate (polysaccharide) as the model compound and its effect 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

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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 run for 15 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 RO concentrate: The FO system was then tested with real RO concentrate from the wastewater reclamation plant. The RO concentrate was collected for same day 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 analyzed for the initial and final solutions to identify organic and inorganic fouling. Since the RO concentrate had a significant scaling potential, pH adjustment was examined as the method for reducing the risk of scaling.

3.3.4 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. However, after each experiment with the model foulant or real RO concentrate it lost some of its activity due to fouling.

3.4 Analytical techniques

3.4.1 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.

3.4.2 Ion chromatography

The quantitative analysis of anions (Cl^-) and cations (Na^+, Ca^{2+}) in the experimental samples was done using an ion chromatograph (IC-Metrohm 790 Personal IC, Herisau, Switzerland) at the UTS laboratories. Samples were diluted with DI water by a dilution factor of 1:10 and 1:20. The chromatographic process separates the different ions by using an analytical column Metrosep C4–150/4.0 and a mobile phase composed of 3.2 mmol/L sodium bicarbonate ($NaHCO_3$) and 1.0 mmol/L sodium carbonate (Na_2CO_3) delivered at a flow rate of 0.7 mL/min. The ions' concentration is measured by the change in conductivity of the mobile phase. The mobile phase (eluent) carries the samples' ions through the system. The conductivity of the mobile phase is measured continuously by an EC detector at the end of the column to determine the quantity of the eluting ions as a function of time. These measurements are compiled into a plot of ion abundance versus time. The position of a peak in the chromatogram belongs to a specific ion and the peak size is a function of the concentration for the corresponding ion (Mee-Inc, 2012; adapted from Yapici, 2012).
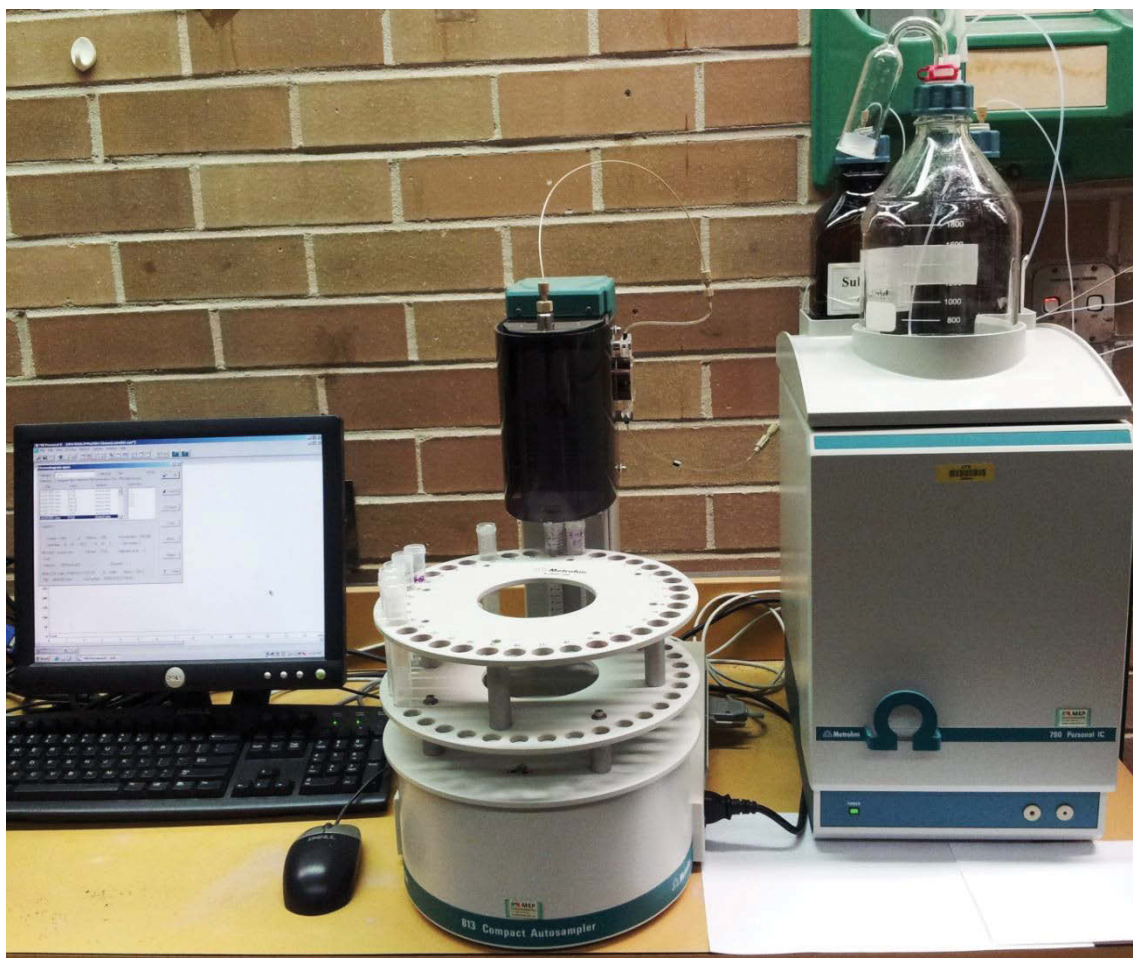
Fig. 3.8   IC instrument at the UTS laboratory

3.4.3   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) at the chemical laboratories of University of New South Wales (UNSW) 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 <u>excite</u> 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 (UNSW, 2012; adapted from Yapici, 2012).
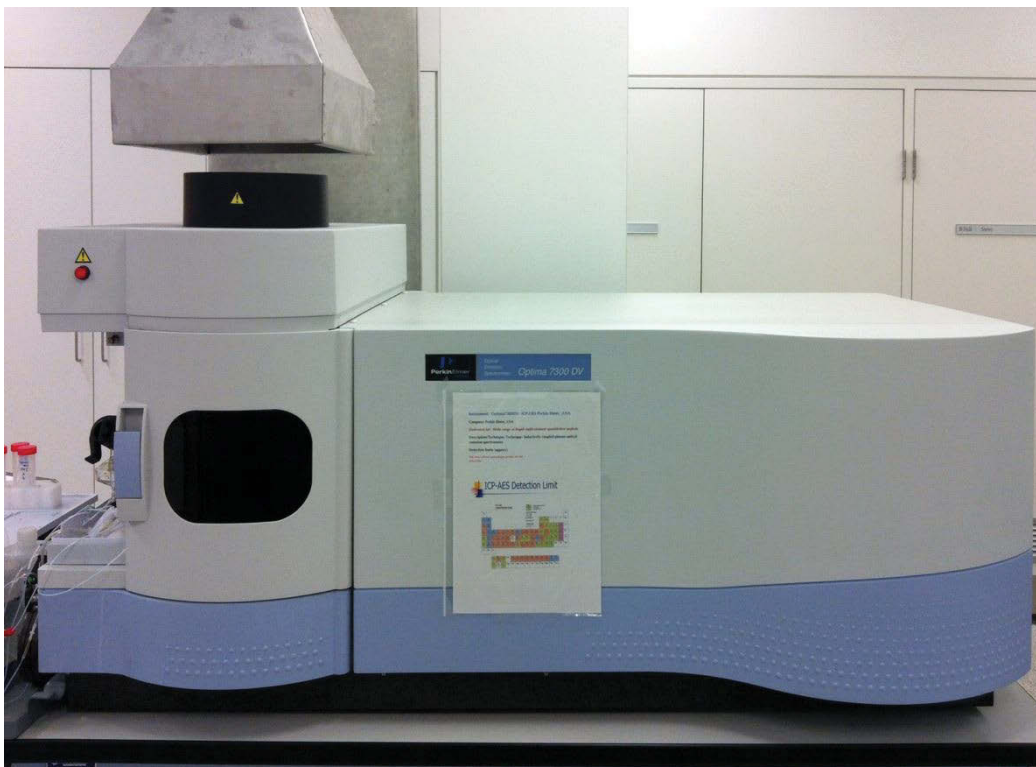
Fig. 3.9   ICP-OES instrument at UNSW laboratory (adapted from Yapici, 2012)

3.4.4   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) at UTS. 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 CO_2 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:

$$TOC = TC - TIC \tag{3.1}$$

Where   TOC = Total organic carbon, mg/L

TC =   Total carbon, mg/L

TIC = Total inorganic carbon, mg/L

3.4.5   UVA measurement

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

Fig. 3.10   Spectrophotometer at UTS laboratory

3.4.6 FEEM

Fluorescence Excitation–Emission Matrix (FEEM) spectrophotometer was used to determine the fluorogenic nature of DOM. Fluorescence analysis was undertaken with a Varian Cary eclipse fluorescence spectrophotometer, using a sealed quartz cell of 4 mL, 1 cm path length. The method was applied as described by Anthony et al. (2012). Samples were diluted by a factor of 10.

3.4.7 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 at the University of New South Wales (UNSW). 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., 2010).
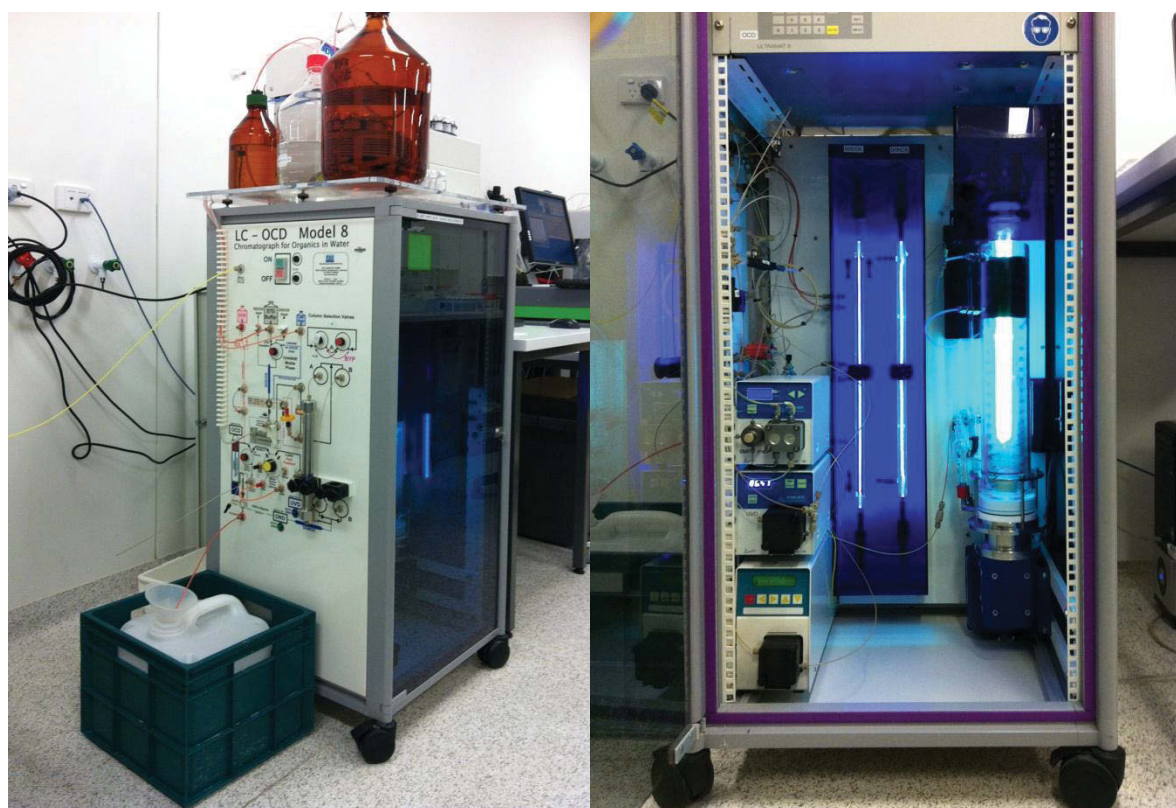
Fig. 3.11   LC-OCD instrument at UNSW laboratory

3.4.8   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 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) at the UNSW lab (Dr. James McDonald, Dr. Stuart Khan). The analytical method is based on that of Vanderford et al. (2006).
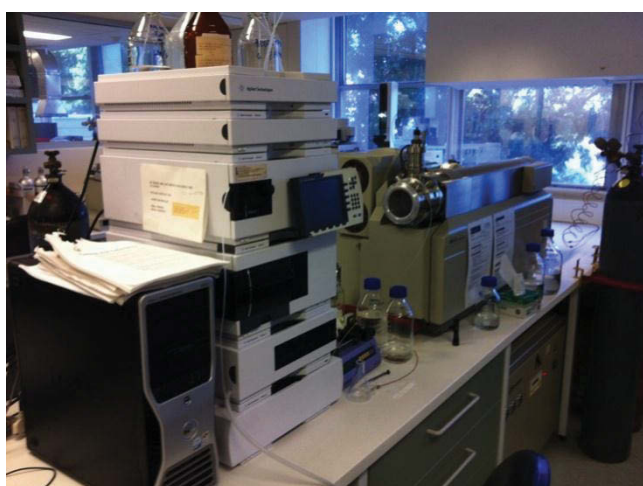
Fig. 3.12   SPE sample enrichment and LC-MS instrument at UNSW laboratory

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 analyzed trace organics (Kazner et al., 2013)

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

4 Results and discussions

4.1 This section highlights the results from the bench scale FO system as described in section 3.2. The following issues have been studied:

- General performance and optimum operation of the bench scale set-up

- Organic fouling of the FO membrane using model foulants

- Organic fouling and scaling of the FO membrane when treating RO concentrate

- Removal of organic micropollutants in FO treatment of RO concentrate

The test results are given in Figures 4.1 and 4.2. The observed fluxes ranged from 6 to 13 LMH for the CTA membrane and 16 to 25 LMH for the PA membrane (FO mode). In PRO mode (with the active layer facing the draw solution suppressing internal concentration polarization) the pure water flux increased from 25 to 47 LMH.

While the flux generally increased significantly with increasing DS concentration, it was observed that the water permeability dropped as osmotic pressure increased (Fig. 4.6). The water permeability ranged between 0.12 to 0.065 L/(m2·h·bar) for the CTA membrane and 0.32 to 0.13 L/(m2·h·bar) for the PA membrane (both in FO mode). Switching to PRO mode increased the water permeability by 56 to 88%, ranging from 0.5 to 0.24 L/(m2·h·bar).
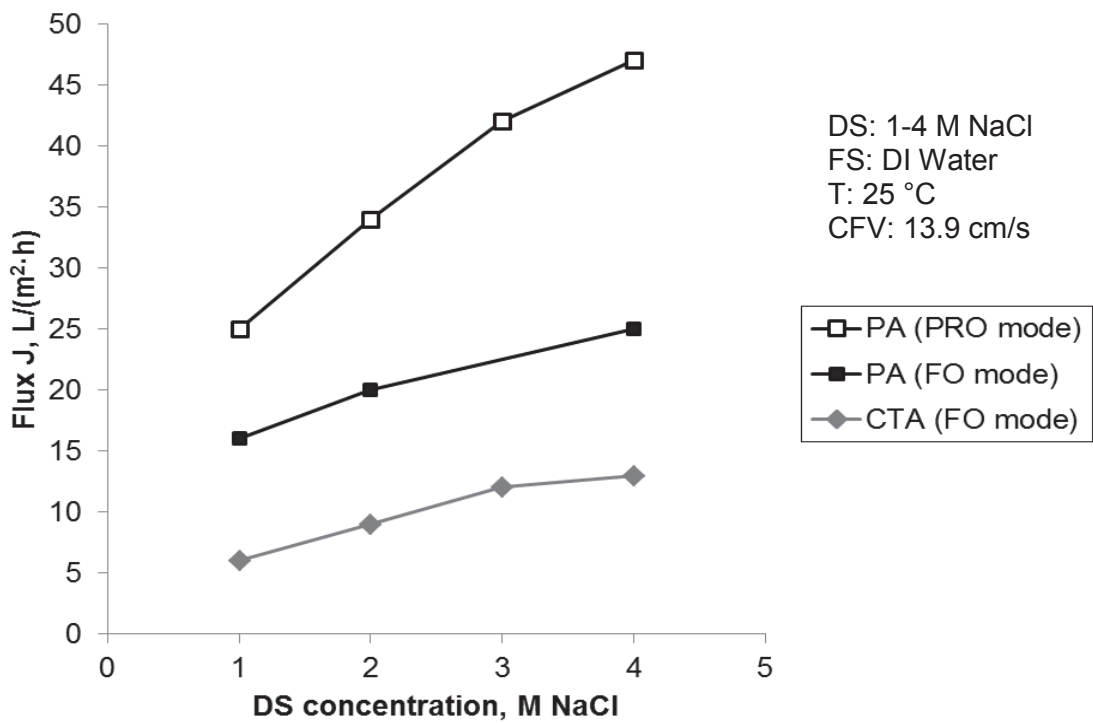
Fig. 4.1 Water flux of tested FO membranes (FS: DI water, DS: NaCl; membrane in FO mode; T = 25°C)

Setiawan et al. (2012) reviewed the pure water permeability (A) of a broad range of various membranes used in FO studies. Most of these studies used slightly different process conditions, which do not allow for a direct comparison. However, it can be concluded that the commercially available membranes used in our study achieve a water permeability at the lower end of the range of different membrane types and materials as reported by Setiawan et al. (2012). The maximum pure water permeability of their own novel hollow fibre membrane was around 4 L/(m^2·h·bar) in FO mode. This suggests that novel membrane materials as well as different membrane types offer significant optimization potential to reduce the osmotic pressure demand. They may also increase permeability resulting in less demand for membrane areas.
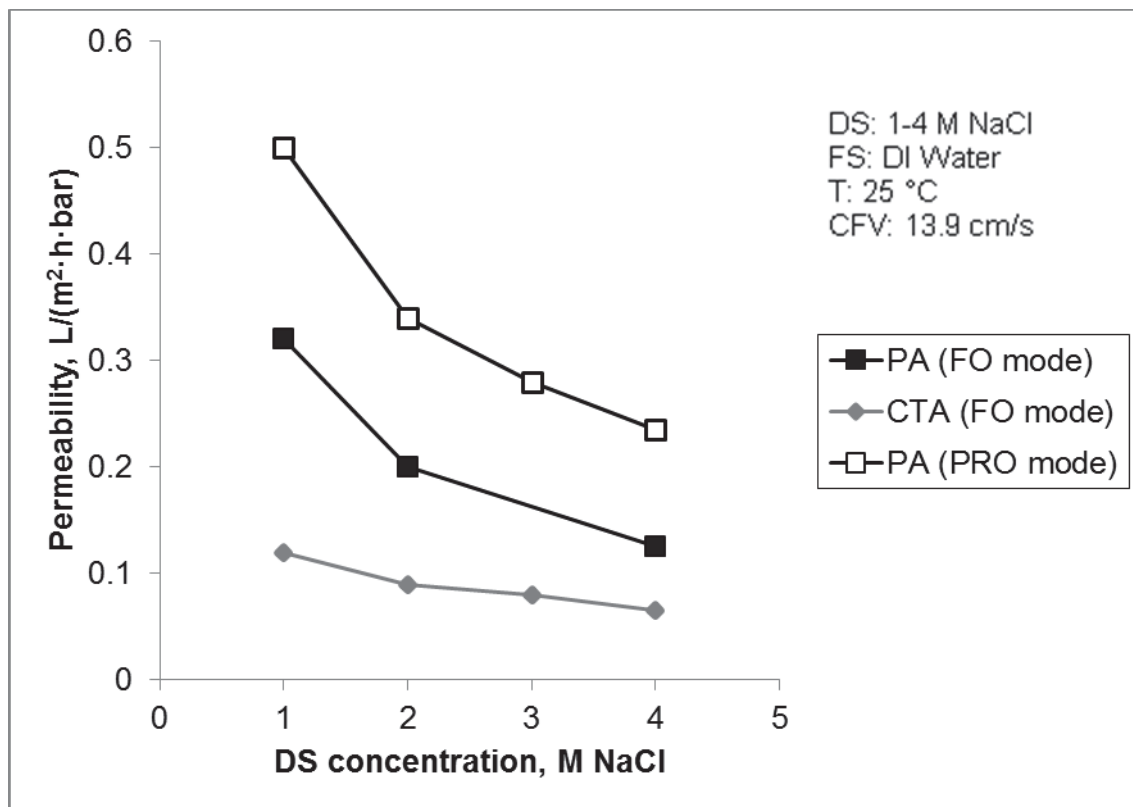
Fig. 4.2 Water permeability of tested FO membranes (FS: DI water, DS: NaCl; membrane in FO mode; T = 25°C)

4.1.1 Evaluation of membranes

Two types of membranes, polyamide (PA) and cellulose triacetate (CTA), were selected for all the lab scale tests and their properties are given in Table 4.3. Membranes can be characterized on the basis of permeate flux, reverse solute flow, resistance to chemical cleaning and flux recovery with hydraulic flushing.

Table 4.1   Osmotic permeability and reverse solute flow of four flat-sheet membranes were tested (FS: DI water and DS: 1M-NaCl)

Membranes used	Specific flux FO mode	Specific flux PRO mode	Average Reverse solute flow FO mode	Average Reverse solute flow PRO mode	Operation time
	$L/m^2{\cdot}h{\cdot}bar$	$L/m^2{\cdot}h{\cdot}bar$	%	%	h
CTA-2012	0.12	-	0.80	-	4.35
PA-2012	0.32	-	0.92	-	4.35
CTA-2013	0.12	-	0.80	-	15
PA-2013	0.32	0.50	1.03	1.10	15*, 5**

* FO mode, ** PRO mode

Four flat sheet membranes were received from the same vendor, two in 2012 and two in 2013 for this project. All four membrane coupons were shipped soaked in glycerine to make them wet. It is recommended the coupons should be soaked in water for 30 minutes prior to use. After glycerine extraction the membranes must be kept moist at all times and not allowed to freeze. The CTA and PA membrane coupons showed very similar osmotic permeability - 0.12 and 0.32 $L/m^2{\cdot}h{\cdot}bar$, respectively. Furthermore the reverse solute flow is very similar that shown in Table 4.3.

The PA-2013 membrane was tested in PRO mode (membrane active layer facing the draw solution). It has a higher osmotic permeability of 0.5 $L/m^2{\cdot}h{\cdot}bar$ but reverse solute flow proved to be high (3.8%), while in FO mode it was 2.21%. The probable cause could be ICP.

4.1.2   Influence of membrane orientation
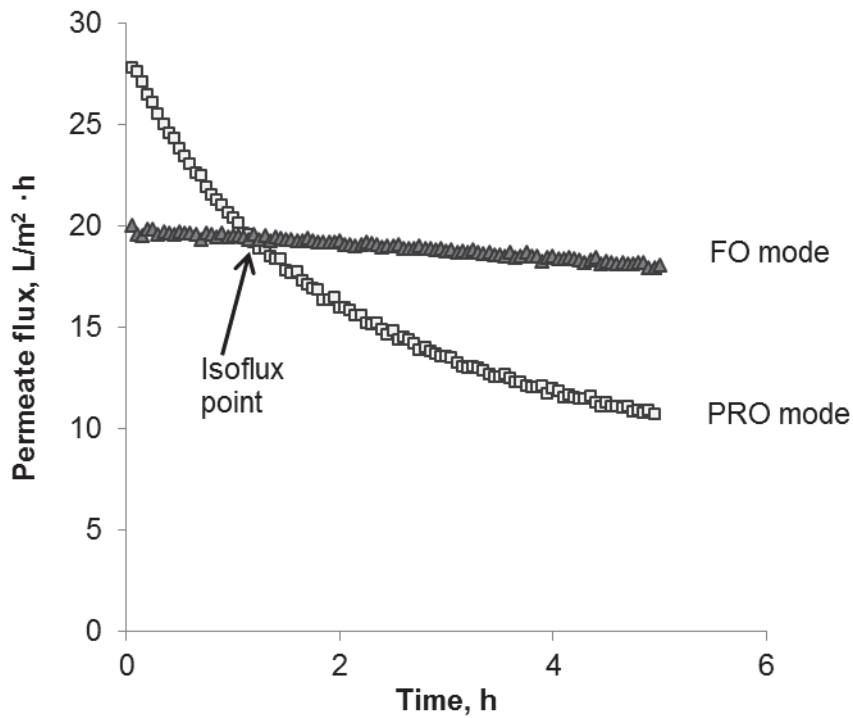
Fig. 4.3   Comparison of permeate flux in PRO and FO modes (PA membrane, 25°C, FS: Alginate 30 mg/L, DS: 2M NaCl, chemical cleaning after ROC treatment)

Zou et al. (2012) pointed out that flux decline in PRO and FO modes under membrane fouling was a function of the feed concentration. If the feed solution has a higher fouling tendency, the flux decline in PRO mode could be significant and isoflux point happens relatively early (in comparison with low foulant concentration).

A synthetic foulant solution (30 mg/L alginate) was used as feed with PA membrane in PRO and FO mode, and 2M NaCl as draw solution. It can be seen in Fig. 4.3 that alginate with this concentration was a strong foulant so the isoflux point happened just after one hour of membrane operation.

4.1.3 Effect of feed cross-flow velocity on permeate flux

The FO system was studied at different cross-flow velocities (CFV) to identify the influence of the CFV on the permeate flux. 1M NaCl was used as the draw solute and DI water as FS running the experiment at three different CFV of 8.3, 13.9, and 19.4 cm/s, respectively at 25^0C. A CFV of 13.9 cm/s gave the optimum flux of 15.5 LMH while with the other two velocities the resultant flux was lower at around 12 to 14 LMH as shown in Fig. 4.4.
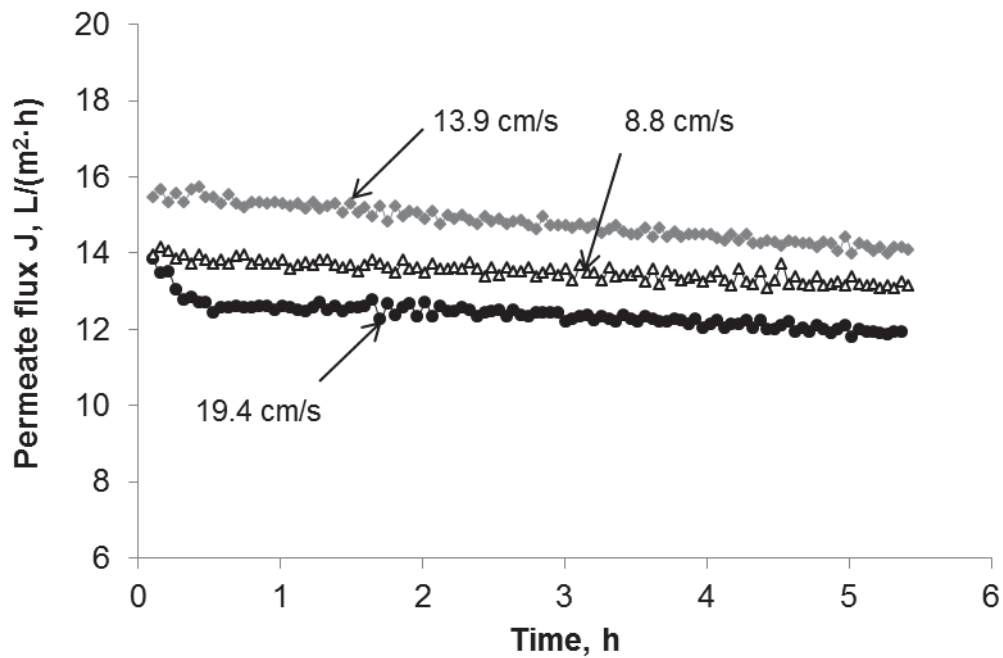
Fig. 4.4   Effect of cross-flow velocity (CFV) on permeate flux (DS: 1M NaCl, FS: DI water, T: 25°C, Mode: FO, Membrane: CTA, CFV: 8.8, 13.9, and 19.4 cm/s)

4.1.4   Influence of flow directions on FO membrane flux

Under otherwise identical operating conditions the flow direction of the feed and draw solutions was changed from counter-current flow to co-current flow. With co-current flow the permeate flux decreased by about 2 LMH as shown in Fig. 4.5. This indicates that counter-current flow has an overall larger osmotic gradient resulting in higher permeate flux.

With reference to the findings the FO experiments are still limited to bench scale and small apparatuses are being used so the benefits of counter-current over co-current are yet to be investigated in a full-scale scenario. However, McCutcheon and Elimelech (2006) used a custom-built FO apparatus with counter-current flow and introduced mesh spacers in both channels to improve support of the membrane and to create turbulence for mass transfer. McCutcheon et al. (2005) in another FO set-up used co-current flow pattern to reduce strain on the suspended membrane.
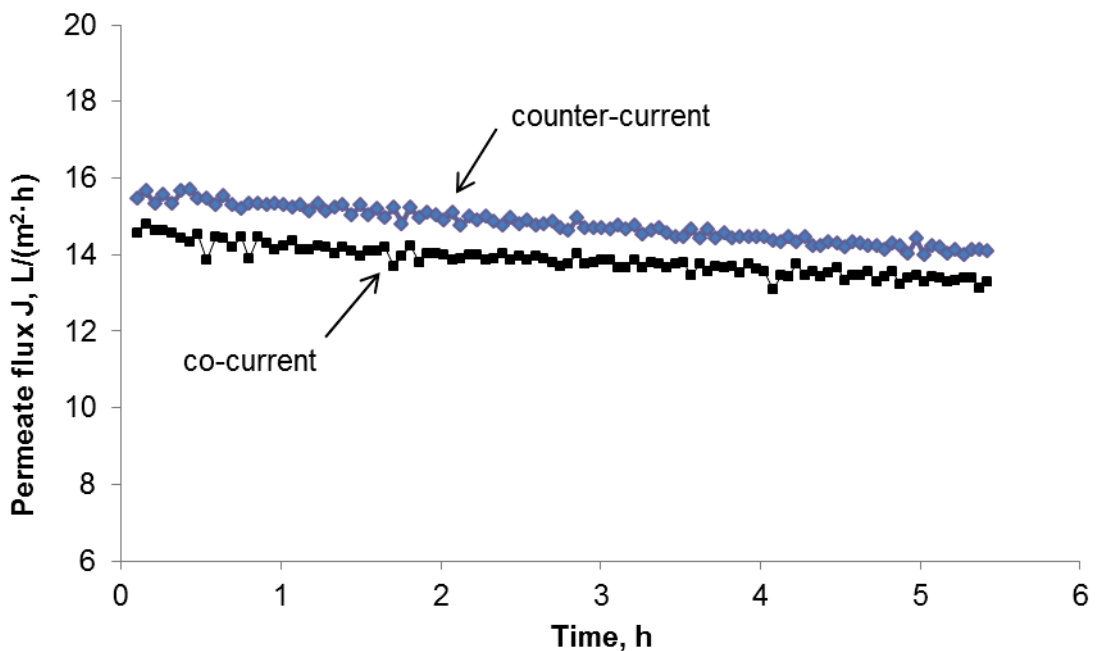
Fig. 4.5   Influence of co-current vs. counter-current flow on permeate flux (DS: 1M NaCl, FS: DI water, T: 25°C, CFV: 13.8 cm/s, Membrane: PA)

4.1.5   Flux recovery with hydraulic flushing of PA membrane

A baseline test with virgin PA membrane was conducted using DI water (FS) and 1M NaCl (DS) for 15 hours of operation. The average flux 12.8 LMH was obtained and then the same test was conducted with RO concentrate as FS. The average flux in this case fell to 11.4 LMH due to fouling. After the test the fouled membrane was flushed at a high CFV of 27.8 cm/s for 20 minutes. The first test was then repeated and about 19% flux decline was observed Table 4.4 and Fig. 4.7) probably due to organic and inorganic fouling. This means flushing was not effective in this case.

Table 4.2   Flux recovery test: DI water vs. RO concentrate (DS: 1M-NaCl)

Membrane used	Average Flux (DI water)	Average flux with RO concentrate	Flux, after flushing	Reduction in permeate flux
	$L/m^2 \cdot h$	$L/m^2 \cdot h$	$L/m^2 \cdot h$	%
PA-2013	12.8	11.4	10.4	19
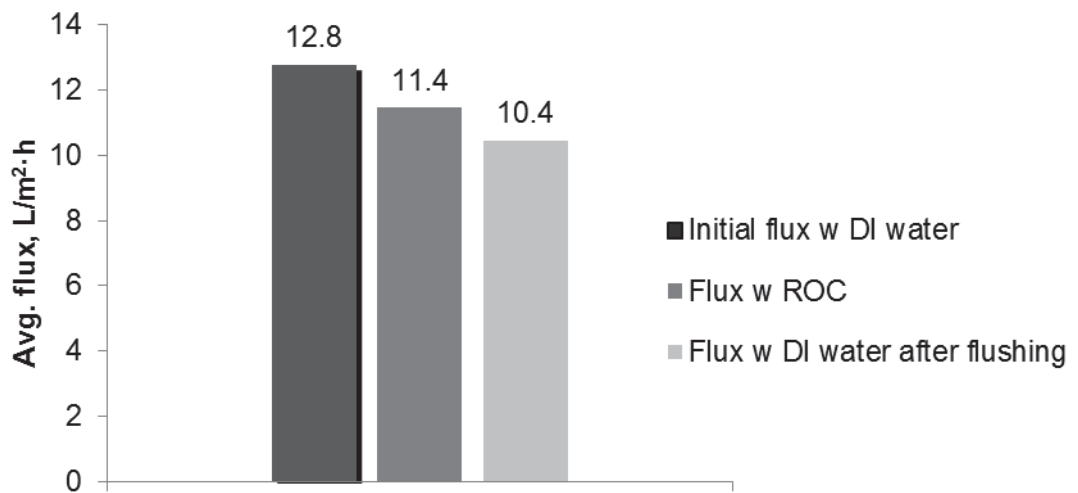
Fig. 4.6   Membrane flux recovery after flushing (PA membrane, 25°C, DS: 1M NaCl, 20' hydraulic flushing after ROC treatment)

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4.1.6   Flux recovery with chemical cleaning of PA membrane

A fouled membrane was chemically cleaned by adopting following procedure:

- 20 minutes hydraulic flushing

- 20 minutes acid cleaning with HCl at pH of 2.5

- 20 minutes flushing with DI water

- 20 chemical cleaning with NaOH at pH of 11.0

- 20 minutes flushing with DI water

Before chemically cleaning a baseline test, DI water as FS and 2M NaCl as DS was conducted and the same test was repeated afterwards. After chemical cleaning the resultant average flux decreased from 16.4 to 13.3 LMH as shown in Fig. 4.8. The reason behind this could be the membrane structure changed and the reverse solute flow increased from 3.36 mS/cm to 15.1 mS/cm, about 4.5-fold.
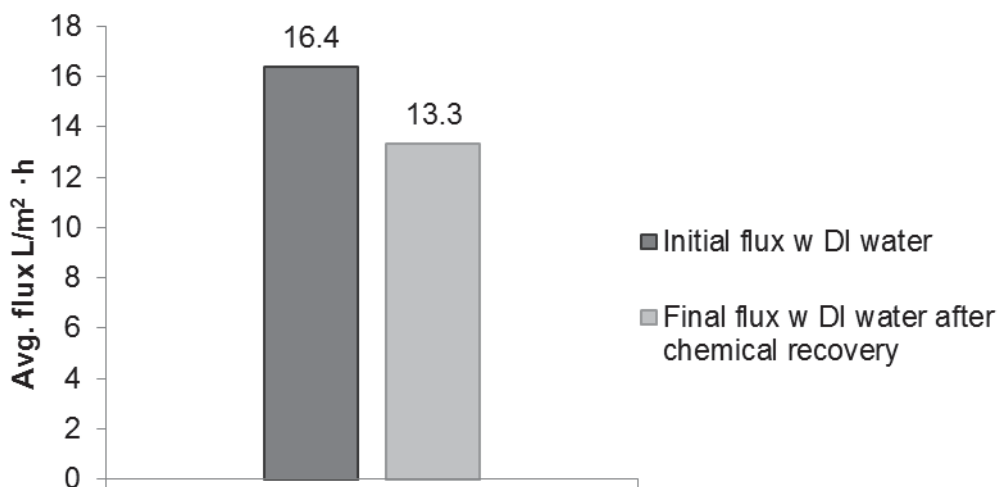
Fig. 4.7   Membrane flux recovery with chemical cleaning (PA membrane, 25°C, DS: 2M NaCl, chemical cleaning after ROC treatment)

Cath et al. (2006) summarized the properties of a good FO membrane as having high density of the active layer for high solute rejection, and minimum porosity of the

support layer for low internal CP. Therefore, higher permeate flux - hydrophilicity for enhanced permeate flux and reduced membrane fouling, and having good mechanical strength – are necessary to withstand hydraulic pressure especially when used for PRO mode. Furthermore a good membrane should be chemically resistant and allow for flux recovery either with hydraulic flushing or chemical cleaning. Our tests revealed that after hydraulic flushing a 19% activity loss of the membrane occurred and with chemical cleaning the membrane was negatively impacted, leading to an increase of reverse solute flow 4.5-fold over the original.

Zou et al. (2012) indicated both inorganic and organic fouling in FO operation are fully reversible, by water flushing that leads to less compact fouling layer formation due to low pressure system. It may not require chemical cleaning but in our case 19% membrane activity was lost due to inorganic and organic fouling. Hydraulic flushing was not fully helpful and moreover, the FO system appears to operate at low pressure. In reality, however, with 1M NaCl as draw solution this results in an osmotic pressure of 50 bar.

Chung et al. (2011) pointed out that deterioration of the thin, non-robust polymer layers in certain membrane technologies results in the formation of cracks and pin-holes, which can badly affect the membrane's performance. So a full range is needed in order to understand the changing properties of these types of thin layers.

Table 4.3 Chemical cleaning results of TFC (PA) membrane

	DI (FS); 2 M NaCl Before Chemical Cleaning	DI (FS); 2 M NaCl After Chemical Cleaning
Initial Conductivity of FS	12.5 µS/cm	13.8 µS/cm
Final Conductivity of FS mS/cm	3.36	15.1
Operation time, h	15	15.8

4.1.7   Summary of results and discussions

Comparison of membranes

- Thin film composite (TFC) PA membrane has a higher flux than CTA membrane in FO modes and even higher in PRO mode under the same test conditions. PA membrane: clean water flux of 12 to 16 LMH in FO mode and 25 LMH in PRO mode (both with 1M NaCl, DS)
- CTA membrane: clean water flux 7-8 LMH (1M NaCl, DS) in FO mode.

Effect of draw solution concentration

- The draw solution concentration is directly proportional to the permeate flux. With 1, 2 and 4M NaCl the resultant flux increased from 6 to 13 LMH using the CTA membrane.
- This indicates osmolality had a high impact of the draw solution.

Effect of cross-flow velocity (CFV)

The impact of the cross-flow velocity was tested in this bench scale set-up. Three velocities were applied to FS and DS sides to study the resultant effect on flux with CFV of 8.8, 13.9, and 19.4 cm/s. The optimum velocity was 13.9 cm/s.

- Minimum CFV required to counteract ECP was 13.9 cm/s in this set-up.

Influence of DS/FS flow directions

When comparing co-current and counter-current flow pattern, in the latter the flow was slightly higher than the former.

- Minor influence of flow direction in lab scale unit.

4.2 Fouling of forward osmosis membranes in RO concentrate treatment – model foulant study

4.2.1 Introduction

Wastewater effluents mainly consist of natural organic matter (NOM), soluble microbial products (SMPs), and trace organic compounds (Shon et al., 2005). As described in Chapter 2, membrane fouling is a highly complex phenomenon. In this study the focus is on organic fouling which was investigated with model foulants (section 4.2) and real RO concentrate (section 4.3). Alginate, bovine serum albumin (BSA) and humic acid are typically chosen as model foulants (Mi & Elimlech, 2008) representing certain compounds or groups in effluent organic matter. Humic acid normally represents NOM while alginate represents polysaccharides, which form an important group of biopolymers derived from SMPs.
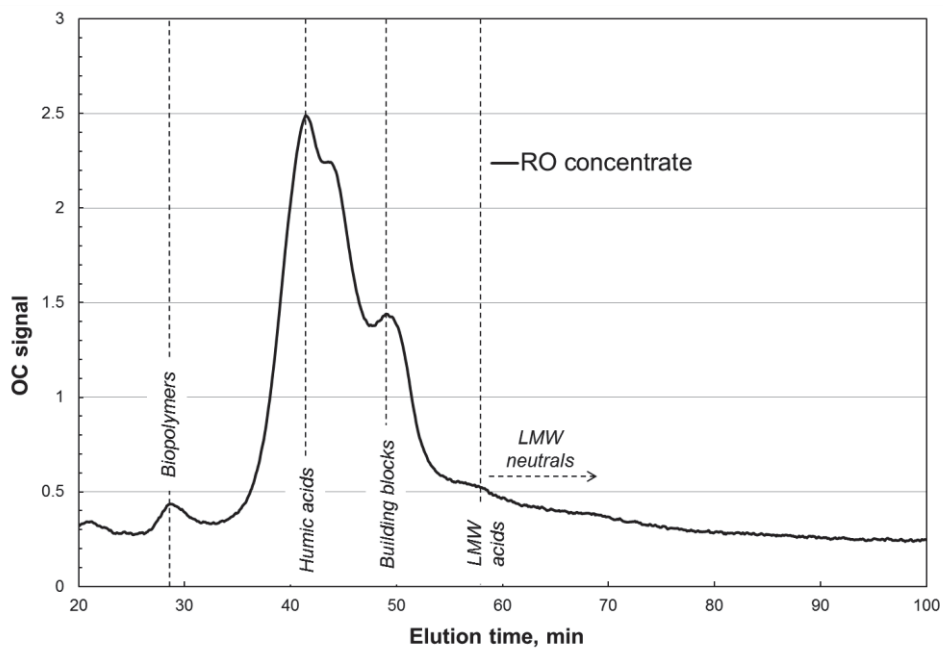
Fig. 4.8 Typical LC-OCD chromatogram of RO concentrate from water reclamation

The chosen test solutions

Alginate and humic acid were chosen for this study. As shown in Figure 4.9, RO concentrate is typically mainly composed of humic acid and building blocks, while the

biopolymers containing polysaccharides are relatively small due to their prior removal in microfiltration.

Sodium alginate from brown algae was used in elevated concentrations of 30-75 mg/L total organic carbon (TOC) as feed solution to study fouling effects which may occur in full scale systems with real ROC only after longer operating periods. Likewise humic acid from soil was used in higher concentrations of about 30-40 mg/L total organic carbon. The real RO concentrate from SOPA typically contained between 25-45 mg/L, however, covering the full range of EfOM.

All tests employed sodium chloride in 1-4M molar concentrations as draw solutions with CTA-NW or TFC (PA) membrane as filter media.

Baseline experiments

All fouling tests were conducted in batch mode and the osmotic pressure of the draw solution decreased continuously due to its dilution by FS permeate. To differentiate between fouling effects and loss in osmotic driving force due to permeate flux, baseline tests were done to quantify the flux decline and evaluate the fouling impacts (Mi & Elimelech., 2008).

Objective

This chapter investigates the impact of organic fouling by model foulants on FO performance using the most recent specimen of the main commercially available FO membranes provided by HTI. The study re-applies foulants used in earlier studies (Mi & Elimelech, 2008) to identify potential improvements in the FO membranes in terms of increased anti-fouling properties.

4.2.2 Tests with alginate

Table 4.6 and Fig. 4.10 show the results from the alginate fouling tests. Initially alginate was tested in concentrations of about 25 mg/L (TOC equivalent) with the TFC membrane in FO mode. The observed flux decline was 3-8% in a rather moderate range. The corresponding TOC adsorption was between 8-13%. To study the potential long-term impact of low concentrations, elevated alginate concentrations of about 75 mg/L were applied. Under these conditions the effect of flux decline was more pronounced with a decrease of 3-15% depending on the DS concentration (1-4 M NaCl) and TOC

adsorption ranging from 28-34%. Finally the TFC-ES membrane was studied in pressure retarded mode (PRO) with the active layer facing the draw solution and the support layer facing the model foulant containing feed solution. The flux decline is very prominent ranging from 38-47% while the TOC adsorption was similar to the adsorption in FO mode (10-19%). Obviously the fouling impact of the absorbed TOC was much more severe, presumably due to blocking of the support layer.

Table 4.4   Flux decline and TOC adsorption with Alginate (CTA NW and TFC membranes, FO and PRO mode)

Foulant	Foulant	TOC	DS, initial conc.	Baseline flux avg.	Flux with foulant avg.	Flux decline	TOC adsorbed	TOC adsorbed
	mg/L	mg/L		$L/m^2·h$	$L/m^2·h$	%	mg	%
CTANW								
FO mode								
Alginate	200	74.42	1M NaCl	5.79	5.65	2.4	20.63	27.8
Alginate	200	74.42	2M NaCl	8.34	7.77	6.8	25.19	33.9
Alginate	200	74.42	3M NaCl	10.18	8.93	12.3	24.2	32.7
Alginate	200	74.42	4M NaCl	11.45	9.76	14.8	21.1	28.4
TFC-ES								
FO mode								
Alginate		25.3	2M NaCl	19.6	18.9	3.6	2.23	8.8
Alginate		25.4	4M NaCl	25.4	23.5	7.5	3.17	12.9
PRO mode								
Alginate		27.9	1M NaCl	22.4	13.7	38.8	5.5	18.6
Alginate		24.9 9	2M NaCl	29.7	16.0	47.1	2.5	10.0
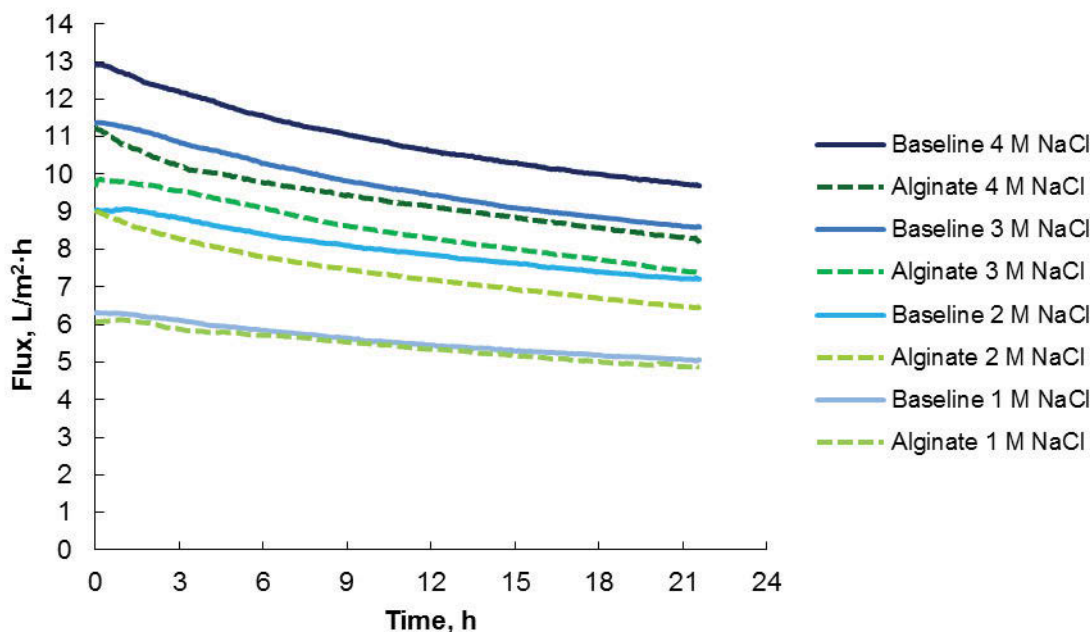
Fig. 4.9 Fouling of TFC membrane by alginate: Flux versus time (Mode: FO, CFV = 13.9 cm/s, Mode= FO, Membrane= CTA 2012, T=25°C)
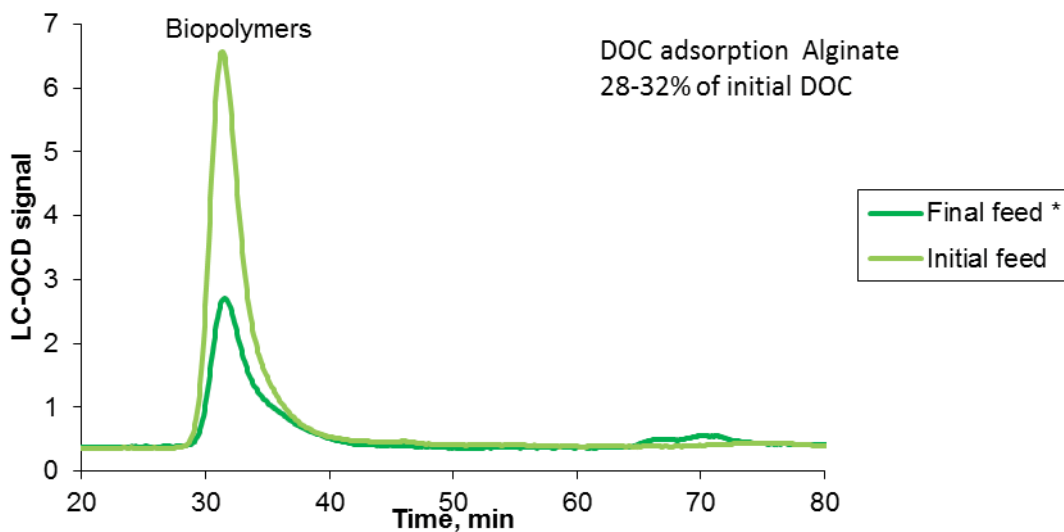
Fig. 4.10 **Alginate test:** LC-OCD chromatogram of the FS at the begin and the end (*normalized concentration) of 15-h-lab test (CTA membrane, T = 25°C, FS: ALG, DS: 2M NaCl, initial DOC = 74.42 mg/L

Alginate adsorption was monitored with Liquid chromatography – organic carbon detection as shown in Fig. 4.11. It shows strong adsorption of alginate at the membrane surface with a reduction of 28-32% of initial DOC, thus confirming that alginate is a relatively strong foulant for this membrane.

4.2.3 Tests with humic acids

Table 4.7 and Figures 4.12 and 4.13 show the results from the humic acid fouling tests. Humic acid was tested in concentrations of about 40 mg/L (TOC equivalent) with the CTA-NW membrane in FO mode. The observed flux decline was 2-4% in a smaller range. The corresponding TOC adsorption was about 7%. The CTA-ES membrane was studied as well in FO mode. The flux decline was 3-4% which is comparable while the TOC adsorption was slightly higher (9-10%) than the CTA-NW membrane.

Table 4.5   Flux decline and TOC adsorption with HA (CTA NW and TFC membranes, FO mode, experiment run for 15 h, * initial conc. estimated)

Foulant	Foulant	TOC	DS, NaCL initial conc.	Baseline flux avg.	Flux with foulant avg.	Flux decline	TOC adsorbed	TOC adsorbed
	mg/L	mg/L		$L/m^2 \cdot h$	$L/m^2 \cdot h$	%	mg/L	%
CTA- NW								
HA	~ 62 *	40.5	1M	7.38	7.08	4.1	2.91	7.2
HA	~ 62 *	40.2	2M	9.76	9.55	2.1	2.75	6.8
HA	~ 62 *	41.3	4M	12.82	12.41	3.2	2.88	7.0
CTA ES								
HA	~ 62 *	40.3	2M	18.23	17.86	1.6	3.46	8.6
HA	~ 62 *	40.3	3M	22.95	21.94	4.8	2.8	9.9
HA	~ 62 *	39.5	4M	25.52	24.88	4.8	4.04	10.2
TFC-ES								
HA		30	2M	16.3	16.3	0	-	-
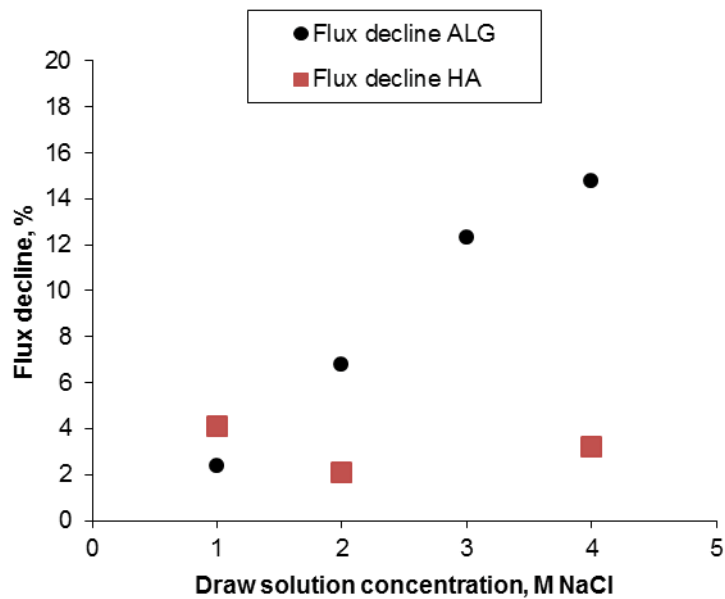
Fig. 4.11 Flux decline of model foulants (CTA NW membrane, FO mode, model foulant in DI water)
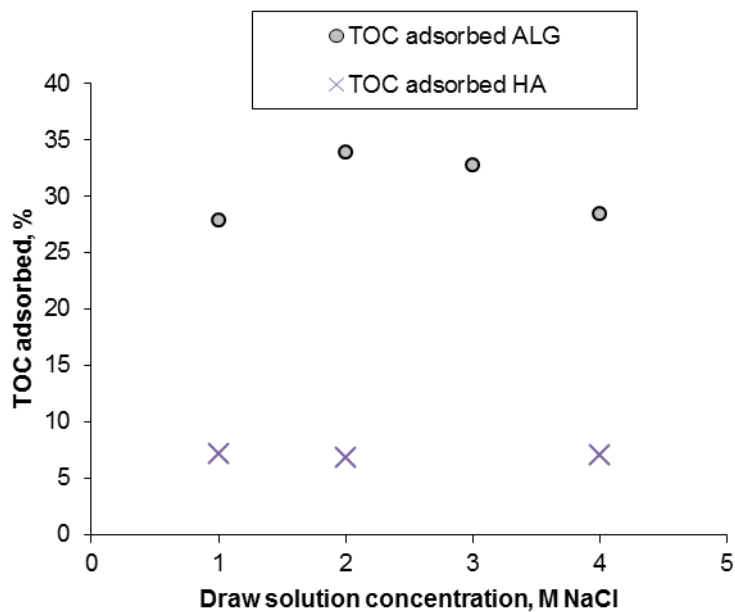
Fig. 4.12 TOC adsorption of model foulants (CTA NW membrane, FO mode, model foulant in DI water)

Figure 4.14 shows, however, that other than in alginate fouling, humic acid has a very low affinity to the membrane and was sorbed only to a minor extent at around 7%.
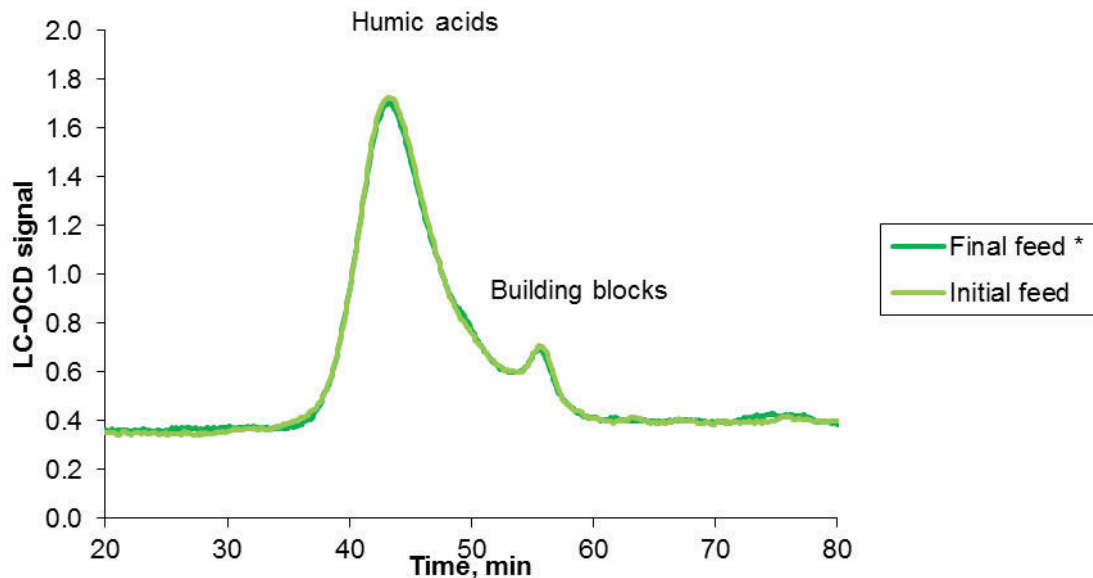
Fig. 4.3 **Humic acid test:** LC-OCD chromatogram of the FS at the begin and the end (*normalized concentration) of 15-h-lab test (CTA membrane, 25°C, FS: HA, DS: 4M NaCl, initial DOC = 41.3 mg/L, initial pH = 6.58)

Xie et al. (2013) investigated the impact of humic acid fouling on the micropollutant rejection of FO by selecting two pharmaceutically active compounds, i.e. carbamazepine and sulfamethoxazole. The humic acid attachment at the surface of the membrane increased due to complexation with calcium ions in the feed solution and this effect is further increased due to reverse flow of sodium ions at the membrane surface from NaCl draw solute. The humic acid attachment at the surface of membrane impacts to decrease in the membrane salt (NaCl) permeability coefficient but membrane pure water permeability coefficient remains relatively unchanged. The humic acid investigation by Xie et al. (2013) corresponds very much with our study (compare results as given in Table 4.7). Humic acid concentrations of about 40 mg/L (TOC equivalent) were used as FS for FO treatment. The TOC adsorption was in the range of 7-10%, however, the corresponding flux decrease ranged from 2-5%. Although the

humic acid adsorption was up to 10% the flux declined to a maximum of 5% only. This study is further confirmed by LC-OCD chromatogram (Fig. 4.14). There is not much adsorption of humic acid on the surface of the membrane when used as the model compound. Fig. 4.15 shows that RO concentrate contains calcium ions, due to the formation of complexation. Strong adsorption of humic acid was observed on the membrane's surface.

Mi and Elimelech (2008) found that FO fouling is controlled by the coupled influence of chemical and hydrodynamic interactions. They further indicated that calcium binding, permeation drag, and hydrodynamic shear force are the major controlling factors for the development of a fouling layer at the membrane's surface. However, these controlling fouling factors vary with the type of foulant. Cake formation is attained rapidly with stronger intermolecular adhesion forces and hydrodynamic conditions for favourable foulant deposition. The fouling rate is affected by both the intermolecular adhesion forces and hydrodynamic conditions. However, once the cake layer is formed, all three typically used model foulants (alginate, bovine serum albumin and humic acid) have very similar flux decline rates and any further changes in hydrodynamic conditions do not influence the membrane fouling behavior.

Lee et al. (2010) made the following observations regarding model foulants:

1. Significant permeate flux decline in FO for alginate and humic acid when compared to BSA.
2. The flux decline is generally attributed to the formation of an organic layer which causes total hydraulic resistance.
3. The thickness and compactness of the organic fouling layer control flux decline.
4. The structure of the organic layer is controlled by both physical (applied pressure and cross-flow velocity, etc.) and chemical properties (pH, ionic strength, and divalent cations).

In particular the divalent calcium cations form a compact, thick and dense fouling layer when cross-linked with organic macromolecules.

4.2.4   Summary of results and conclusions

Effect of alginate on the FO membrane:

- Alginate as a model compound with moderate concentration of 25 mg/L has no significant influence on flux decline, which indicates that alginate is less fouling at low concentrations

- With alginate in an increased concentration of about 75 mg/L, moderate flux decline flux was observed while its adsorption at the surface of the membrane was about 27-34%, which is more pronounced than at lower concentrations.

Effect of humic acid on the FO membrane:

- Humic acid as a model foulant does not cause a significant flux decline. The flux decreased 2-4% for CTA membranes and TOC adsorbed on the surface of membrane is about 7.0%. It demonstrates that humic acid is not a very strong foulant for this membrane.

4.3   Tests with real RO concentrate

Table 4.8 and Figure 4.17 show the results for the RO concentrate fouling tests. RO concentrate was tested in concentrations of 38 mg/L (TOC equivalent) with the CTA-NW membrane in FO mode. The observed flux decline was about 10-26% in a high range. The corresponding TOC adsorption was between 3-6%. Then the TFC-ES membrane was studied in FO mode. The flux decline is very prominent ranging from 35-55% while the TOC adsorption was about 2-9%. However, the flux decline was more pronounced depending on the DS concentration (1-4 M NaCl) in both cases.

4.3.1 Organic fouling

Forward osmosis fouling tests with RO concentrate showed it contributed less to organic fouling in the FO system. Humic acids were the leading foulants in all studied membranes (Fig. 4.15). Biopolymers such as polysaccharides (PS) were not significant with respect to fouling specifically because the RO concentrate displays only low PS concentration due to the membrane pre-treatment.
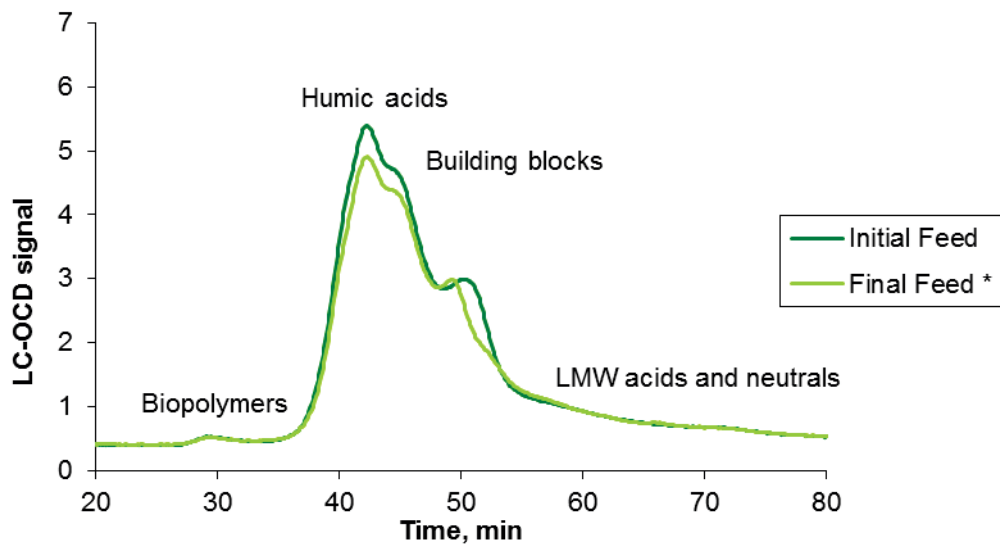
Fig. 4.14 LC-OCD chromatogram of the FO feed solution at the begin and the end (*normalized concentration) of 15-h-lab test with RO concentrate (TFC membrane polyamide, 25°C, FS: RO concentrate, DS: 2M NaCl, initial DOC = 38 mg/L, initial pH = 7.8)

After a membrane filtration time of 15 hours, between 2 to 9% of the initial TOC (38 mg/L) was adsorbed with a slightly higher adsorption tendency at higher fluxes (Table 4.8).

Table 4.6 Flux decline and TOC adsorption with RO concentrate (CTA NW and TFC membranes, FO mode, ROC, pH = 7.8, unadjusted)

Feed solution	DOC, initial	Draw solution	Baseline flux avg.	Flux with ROC avg.	Flux decline	TOC adsorbed
	mg/L		$L/m^2 \cdot h$	$L/m^2 \cdot h$	%	%
CTA-NW						
RO conc.	38	1M NaCl	6.8	6.1	10.3	2.8
RO conc.	38	2M NaCl	8.9	6.7	24.7	5.8
RO conc.	38	4M NaCl	11.8	8.7	26.3	4.2
TFC -ES						
RO conc.	38	1M NaCl	14.3	9.3	34.9	2.1
RO conc.	38	2M NaCl	18.9	10.0	47.1	8.7
RO conc.	38	4M NaCl	22.1	10.0	54.7	6.1

Model solutions thus well indicated the fouling propensity of tested membrane types.

Table 4.7   LC-OCD results for the ROC fouling tests: Initial and normalized final concentrations (DOC-Labor, ChromCalc version 2013**)**

Sample	DOC Dissolved ppb-C % DOC	HOC Hydrophobic ppb-C % DOC	CDOC Hydrophilic ppb-C % DOC	>>20.000 BIO- polymers ppb-C % DOC	Humic Subst. (HS) ppb-C % DOC	300-500 Building Blocks ppb-C % DOC	<350 LMW Neutrals ppb-C % DOC
C2M0	3566 100%	102 2.9%	3464 97.1%	42 1.2%	1916 53.7%	963 27.0%	544 15.2%
C2Me	3134 100%	n.q. --	3160 100.8%	35 1.1%	1723 55.0%	939 29.9%	463 14.8%
C4M0	3480 100%	77 2.2%	3403 97.8%	38 1.1%	1935 55.6%	917 26.3%	514 14.8%
C4Me	3188 100%	18 0.6%	3171 99.4%	36 1.1%	1703 53.4%	955 29.9%	477 15.0%
P1M0	3488 100%	48 1.4%	3440 98.6%	45 1.3%	1968 56.4%	905 26.0%	522 15.0%
P1Me	3303 100%	n.q. --	3321 100.5%	45 1.4%	1719 52.1%	1016 30.8%	525 15.9%
P2M0	3406 100%	28 0.8%	3379 99.2%	29 0.9%	1693 49.7%	1161 34.1%	494 14.5%
P2Me	3153 100%	119 3.8%	3034 96.2%	26 0.8%	1435 45.5%	1132 35.9%	440 14.0%

Sample code :

- C- CTA membrane
- P- Polyamide membrane
- 1,2,4 M: (1,2,& 4 Molar NaCl respectively as DS)
- 0 – Initial concentration of FS
- e – Final concentration of FS

Table 4.9 shows that mainly humic substances and to some degree building blocks are being adsorbed at the surface of the membrane, while bio-polymers present only at around 1% of the total DOC did not contribute to the adsorbed DOC.
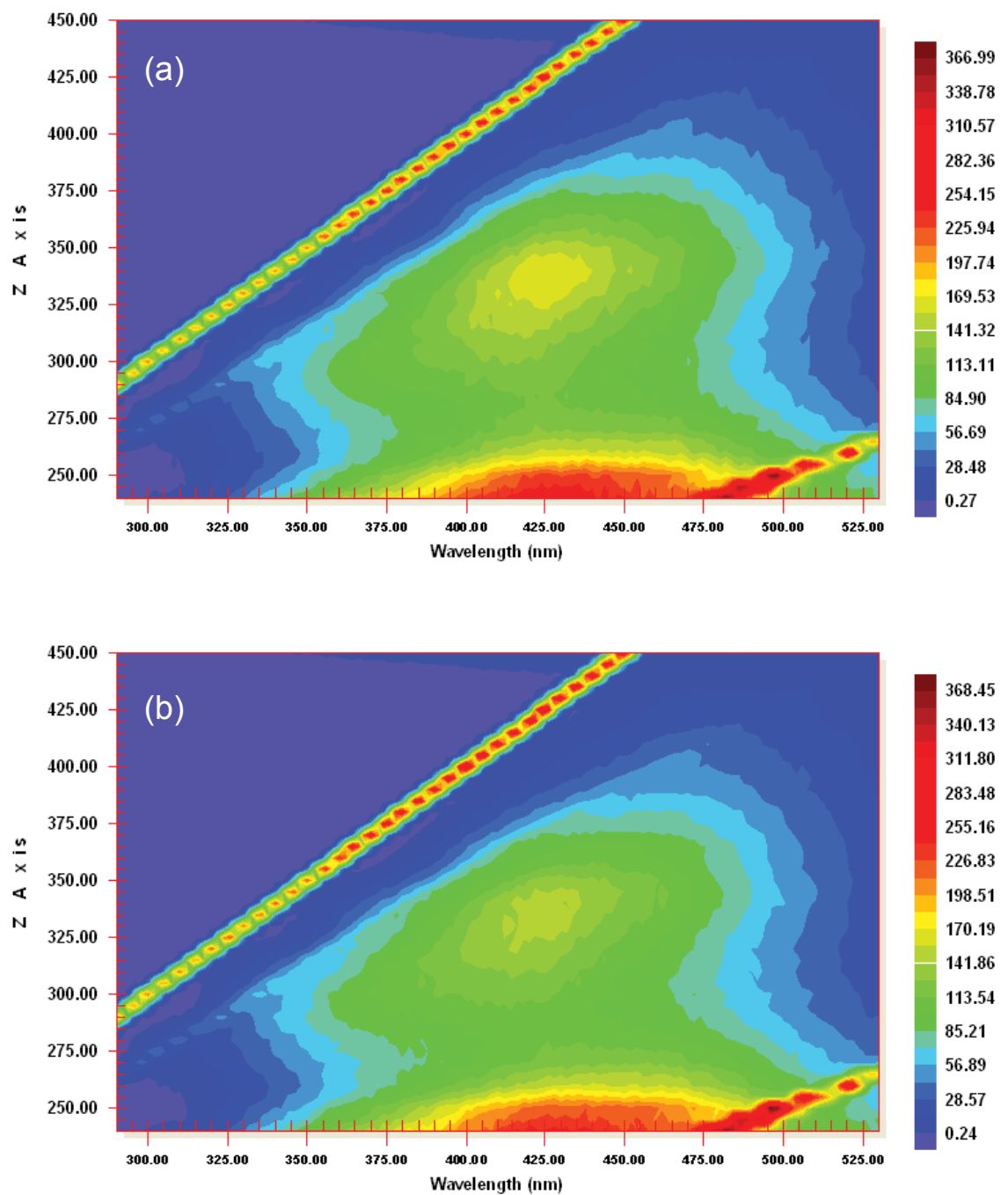
Fig. 4.15   FEEM of the FO feed solution at the beginning (a) and end (b) (*normalized concentration) of 15-h-lab test with RO concentrate (TFC membrane polyamide, 25°C, FS: RO concentrate, DS: 2M NaCl, initial DOC = 38 mg/L, initial pH = 7.8)

The fluorescence excitation emission measurement confirmed a low to moderate sorption of the humic-like substances (Fig. 4.16). Although organic fouling appears not to be primary concern in FO, several methods can be employed for pre-treatment of ROC, including granular activated carbon (Kazner et al., 2013) or ozonation followed by biological activated carbon (Lee et al., 2009). These further reduce the risk of organic fouling and also reduce the DOC concentration by up to 50 to 60%. Decreases in the micropollutant load prior to FO can occur. For long-term operation as studied by McGinnis et al. (2013), reducing bioavailable organics is particularly important to minimize organic fouling and biofouling.

4.3.2   Combined inorganic and organic fouling

Although organic fouling was rather insignificant, a rapid flux decline within the first 7 hours of operation was observed (Fig. 4.18). Elemental analysis (see Fig. 4.20) revealed a significant decrease in calcium and potassium on the cation side as well as phosphate, carbonate and sulphate on the anion side. Table 4.10 gives an overview of the solubilities of several scaling relevant salts. Modelling of the potential scaling with PHREEQC confirmed the high risk of formation of poorly soluble salts, particularly calcite, dolomite and hydroxyapatite. Compared to the baseline filtration tests, the scaling led to a flux reduction of 10 to 25% (CTA membrane) and 35 to 55% (PA membrane). Hydraulic flushing and chemical cleaning could only partly recover the performance of the membrane.
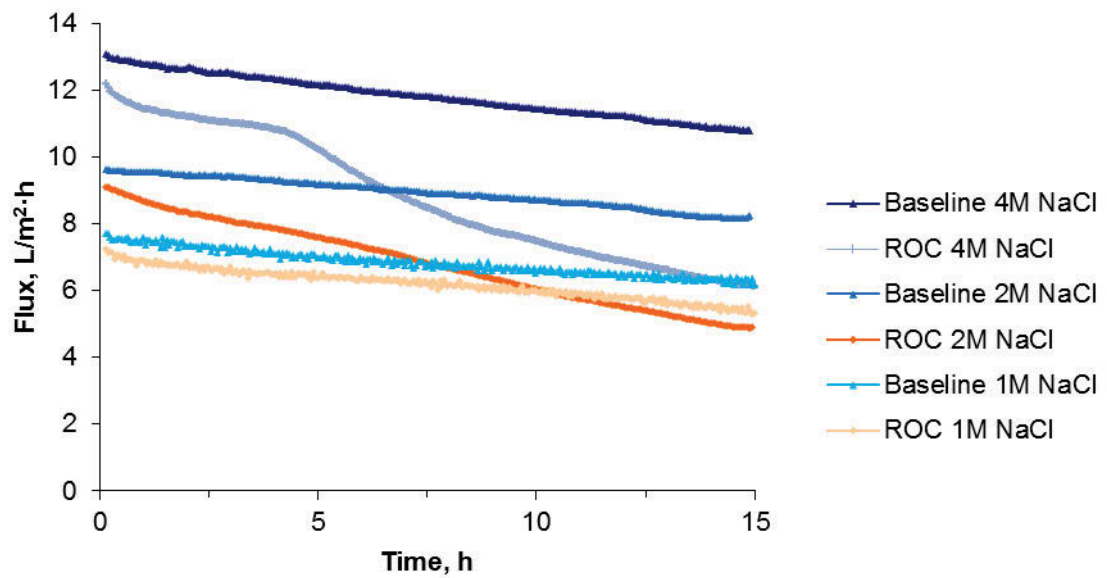
Fig. 4.16   Fouling of FO membrane by RO concentrate with unadjusted pH (CTA membrane, 25°C, initial pH = 7.8, final pH= 8.95)
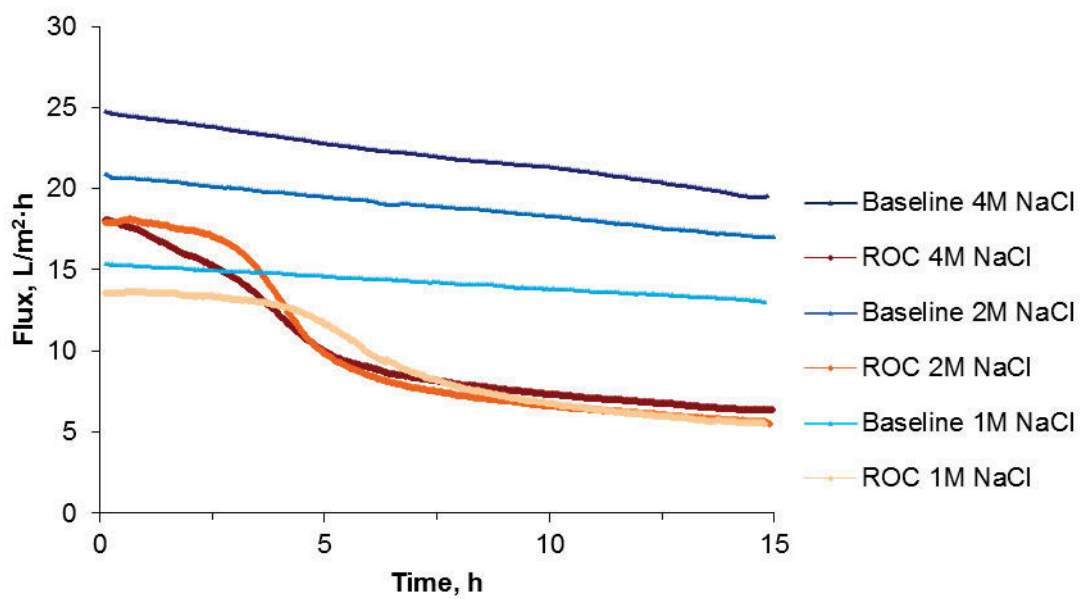
Fig. 4.7   Fouling of FO membrane by RO concentrate with unadjusted pH (TFC PA membrane, 25°C, initial pH = 7.8, final pH= 9.0)

Table 4.8   Solubility of selected sparingly soluble salts (25°C, High risk scalants)

	Solubility Product		Saturation concentration	
			g/L	mg/L
Carbonates				
$CaCO_3$ (Calcite)	$3.36 \cdot 10^{-9}$	mol^2/L^2	0.0058	**5.8**
$MgCO_3$	$3.0 \cdot 10^{-5}$	mol^2/L^2	0.5537	553.7
Sulphates				
$CaSO_4 \cdot 2H_2O$	$3.14 \cdot 10^{-5}$	mol^2/L^2	0.6057	605.7
$SrSO_4$	$8.0 \cdot 10^{-7}$	mol^2/L^2	0.0976	97.6
$BaSO_4$	$1.0 \cdot 10^{-9}$	mol^2/L^2	0.0074	**7.4**
Halides				
MgF_2	$6.0 \cdot 10^{-9}$	mol^3/L^3	0.1139	113.9
SrF_2	$7.9 \cdot 10^{-10}$	mol^3/L^3	0.1169	116.9
CaF_2	$2.0 \cdot 10^{-10}$	mol^3/L^3	0.0460	46.0
NaCl	$3.87 \cdot 10^{1}$	mol^2/L^2	363.34	363335
Phosphates				
$Ca_3(PO_4)_2$	$1.3 \cdot 10^{-32}$	mol^5/L^5	$1.30 \cdot 10^{-4}$	**0.13**
$Sr_3(PO_4)_2$	$1.0 \cdot 10^{-31}$	mol^5/L^5	$2.86 \cdot 10^{-4}$	**0.29**
$Ba_3(PO_4)_2$	$6.0 \cdot 10^{-39}$	mol^5/L^5	$1.37 \cdot 10^{-5}$	**0.01**

Speciation Modeling

Speciation modelling is useful in situations where the possibility of mineral dissolution or precipitation needs to be known, as in water treatment, aquifer storage and recovery, artificial recharge, and well injection. PHREEQC can execute a range of calculations including speciation and saturation-index as shown in Fig. 4.19.

PHREEQC Model results
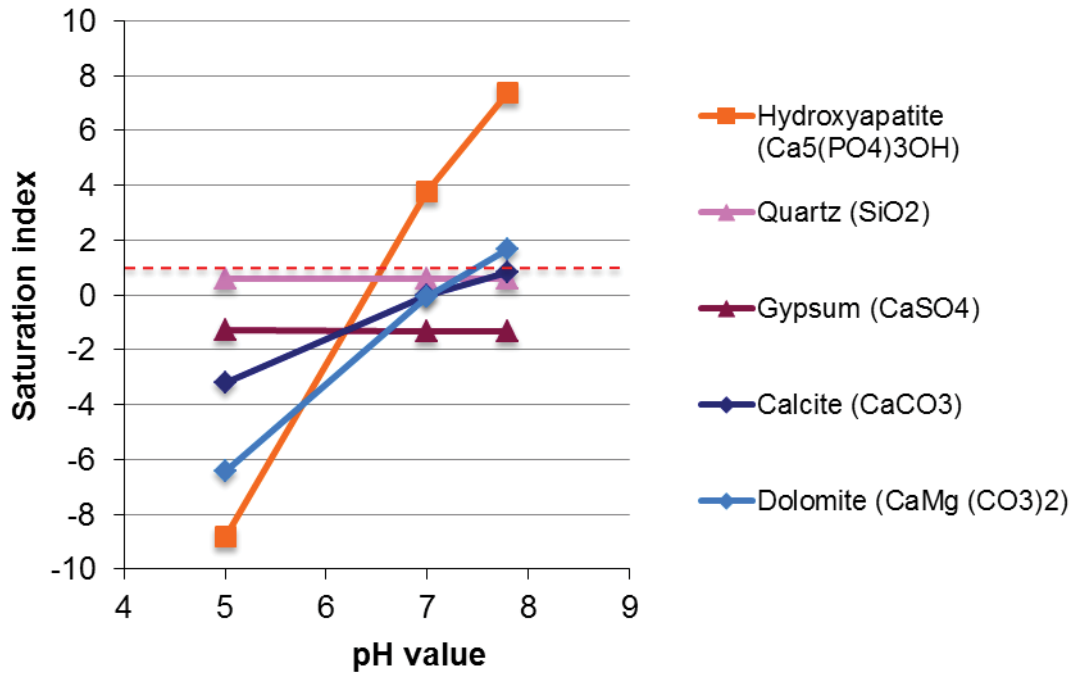
Fig. 4.8   PHREEQC modeling
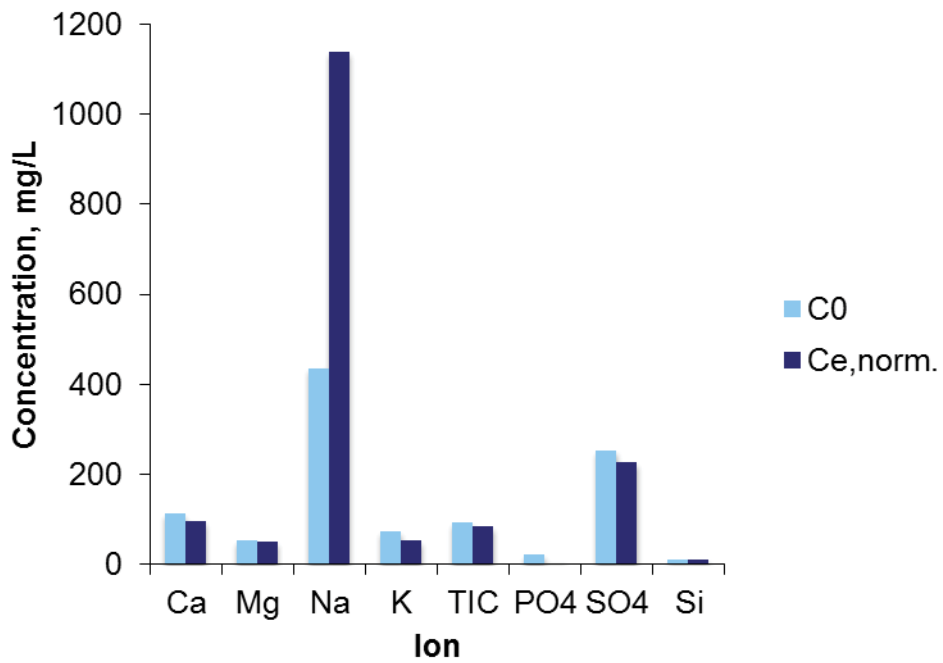
Fig. 4.19   Ion balance

Fig. 4.20 depicts the final normalized concentrations of Ca, Mg, K, total inorganic carbon (TIC), PO_4 and Si decreases in the feed solution, so these components attach at the surface of membrane causing scaling. Table 4.10 highlights that these are sparingly soluble salts having very low solubility. Only the Na concentration is increased due to the reverse flow of sodium ions from the draw solution to the feed side. In all tests a pH increase of about 1.2 pH values was observed, further increasing the scaling risk, particularly of carbonate and phosphate containing compounds.

4.3.3 Tests with RO concentrate and pH adjustment

A moderate reduction of the feed solution pH was subsequently tested. When decreasing the initial FS pH to about pH 5, only a minor flux decline was observed, comparable to the initial model foulant tests with HA (Fig. 4.13). The pH increased during the filtration test from initially pH 5.0 to pH 8.1 at the end of the test. Depending on the type of scalants, further scaling risk-reducing measures such as anti-scalants or softening might be necessary as suggested by Adham et al. (2007) and Martinetti et al. (2009).
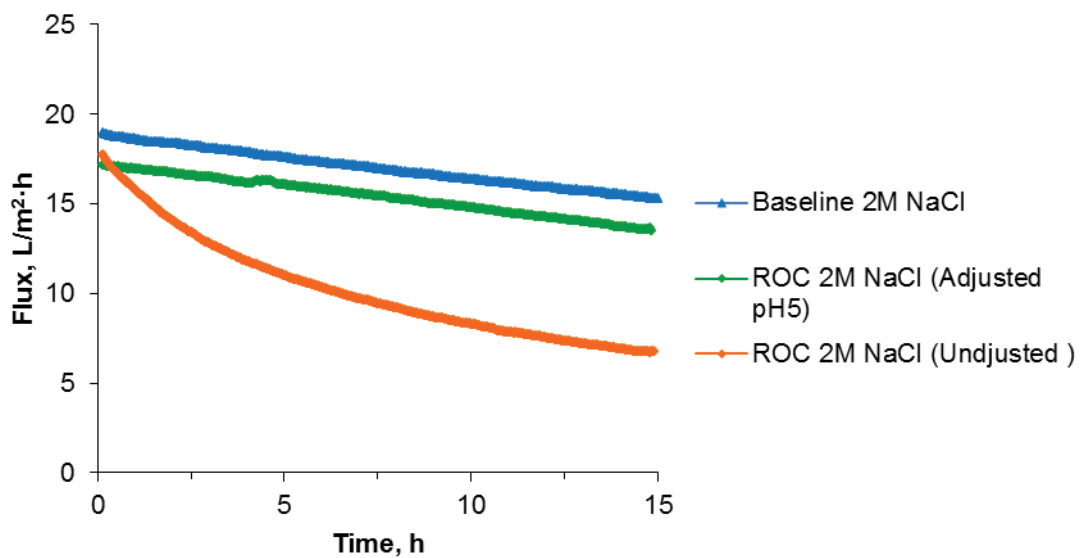
Fig. 4.20   Comparison of FO fouling by RO concentrate with adjusted and unadjusted pH (TFC PA membrane, 25°C)

4.3.4 Increase of feed salinity during FO treatment
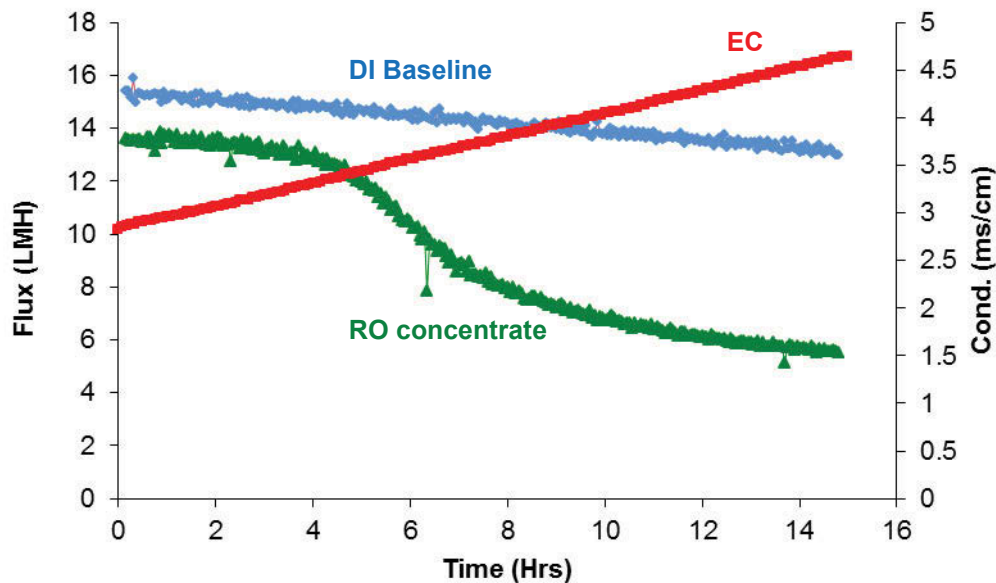
Fig. 4.21 Salinity increase during FO due to concentration of the FS and reverse flux (FS: ROC, DS: 2 M NaCl; TFC membrane in FO mode; T = 25°C)

Fig. 4.22 presents the increase in salinity during the ROC filtration test. It shows that salinity increases continuously irrespective of the measured scaling. This suggests that the salinity increase is dominated by the main feed ions sodium and chloride due to increase in concentration and reverse solute flow. Conductivity measurement thus cannot detect carbonate or phosphate scaling when NaCl dominates the process.

4.3.5 Conclusions

- Forward osmosis appears to be a very promising technology for RO concentrate treatment.
- Apart from selecting the proper draw solution and membrane, which must be regarded as the key questions, organics and inorganics play a major role in the sustainable operation of FO systems.
- Scaling was a major impediment to the FO process and should be controlled for instance by pH adjustment or softening.

- Low concentrations of main inorganic scalants such as phosphate, silica and carbonates are a prerequisite for high recovery and successful operation of FO for RO concentrate treatment.

- Tests suggest that bulk organics have an impact on FO performance only to a minor extent in the short term, but may be removed prior to the concentration and desalting units, e.g. FO + crystallizer for sustainable long-term operation of the desalting systems and control of the level of refractory organics in the complete treatment system.

- Combinations of oxidative and (biological) granular activated carbon processes have potential in the pre-treatment process and would further improve the quality of the FO permeate.

4.4 Removal of trace organic pollutants

4.4.1 Introduction

Organic micropollutants are a major concern in water recycling due to their potentially hazardous effects on human beings and the natural environment. They occur in elevated concentrations in ROC (Kazner et al., 2013) and have to be removed, if the FO permeate is to be blended with the main RO permeate.

The pharmaceutical compounds' rejection by two commercial membranes - cellulose triacetate (CTA) and thin film composite (TFC) - was first studied by Hancock et al. (2011), Jin et al. (2012) and Alturki et al. (2013). It was revealed that membrane interfacial properties, physicochemical properties of the micropollutant molecules and feed solution pH play an important role in their rejection.

The aim of our study is to recycle permeate collected from the FO system using RO concentrate as feed to the FO for reducing the volume of RO concentrate. The FO permeate must be free from all micropollutants and impurities in order to comply with the requirements of high quality recycled water. To study the retention behavior of micropollutants, two membranes, i.e. CTA and TFC were applied in the FO system and the resultant permeate was analyzed.

4.4.2 General removal characteristics

The initial concentrations and compound properties are given in Table 4.11.

Table 4.9 Properties of the detected micropollutants and their initial concentrations

	MW (g/mol)	LogD at pH 8	Charge at pH 8*	Reporting level ng/L	**C FS, avg (ng/L)	C FS, STDEV (ng/L)
Paracetamol	151	0.54*	neutral	5	443	40
Caffeine	194	0.11*	neutral	10	977	627
Ibuprofen	206	0.44*	negative	5	295	13
Primidone	218	0.91	neutral	5	254	13
Naproxen	230	- 0.25*	negative	5	1331	58
Carbamazepine	236	0.37	neutral	5	2522	166
Gemfibrozil	250	0.79*	negative	5	494	23
Sulfamethoxazole	253	- 1.23*	negative	5	680	39
Atenolol	266	- 1.87*	positive	5	588	29
Amtriptyline	277	3.93*	positive	5	278	34
TCEP	285	- 7.25*	negative	10	353	96
Trimethoprim	290	1.02	neutral	5	434	18
Diclofenac	296	1.06*	negative	5	591	21

* calculated by ACD/Labs I-Lab 2.0 software - ilab.acdlabs.com ** Concentration in feed solution

Figure 4.23 shows the rejection of the selected micropollutants by the CTA and TFC membranes. The rejection varies between 40 and 97% for the CTA membrane and between 73 and 99% for the TFC membrane. The rejection appears to be mainly governed by size exclusion while solute charge plays a minor role.

However, not all compounds behave as predicted. As shown in Fig. 4.23 the TFC membrane performs significantly better than the CTA membrane in terms of rejecting micropollutants. This confirms the findings of Jin et al. (2012) where the TFC polyamide membrane performed better than the CTA membrane, rejecting pharmaceutical compounds at >94%. However, Jin et al. (2012) spiked model pharmaceutical compounds in concentrations of 250μg/L while the present study used real RO concentrate from Sydney Olympic Park as feed solution.
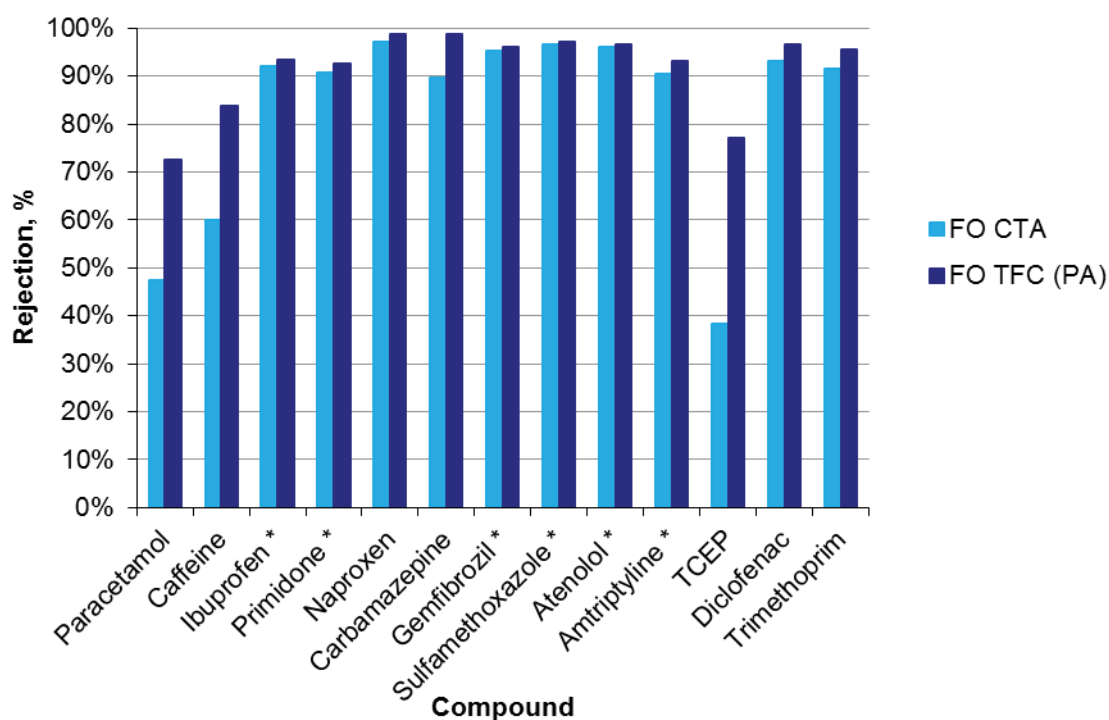
Fig. 4.2   Average retention of selected organic micropollutants from ROC by FO (CTA and TFC membrane, FS: ROC with DOC = 38 mg/L, DS: 1 – 4 M NaCl, 25°C, * Permeate concentration < LOQ)

Xie et al. (2013) investigated the impact of humic acid fouling on the micropollutant rejection of FO by selecting two pharmaceutically active compounds, i.e. carbamazepine and sulfamethoxazole. They observed that humic acid fouling increased the rejection of micropollutants. Carbamazepine rejection increased from 90% to 94%

with the addition of HA and further increased to 98% when adding up to 4 mM Calcium (CTA membrane). The present study detected a carbamazepine rejection of about 90%, although the ROC concentrate contained humic acid and calcium in comparably high concentrations (ca. $17 - 20$ mg/L HA and 2.4 mM Ca^{2+}).

4.4.3 Influence of draw solution concentration

Draw solution concentration was varied to study the influence of increasing transmembrane pressure with increasing osmolarity. From reverse osmosis it is known that increasing pressure compresses the membrane and thus increases the micropollutant rejection. However, FO membranes are operated at low hydraulic pressure and are much thinner than RO membranes. As shown in Figures 4.24 to 4.26 there is a tendency of increased rejection with rising pressure irrespective of the membrane being tested. The rejection increases more markedly for compounds which are – initially at low DS concentrations - poorly rejected such as paracetamol. Caffeine, however, behaved in an opposite way with reduced rejection at increased DS concentration. Finally some compounds such as TCEP do not behave as predicted.
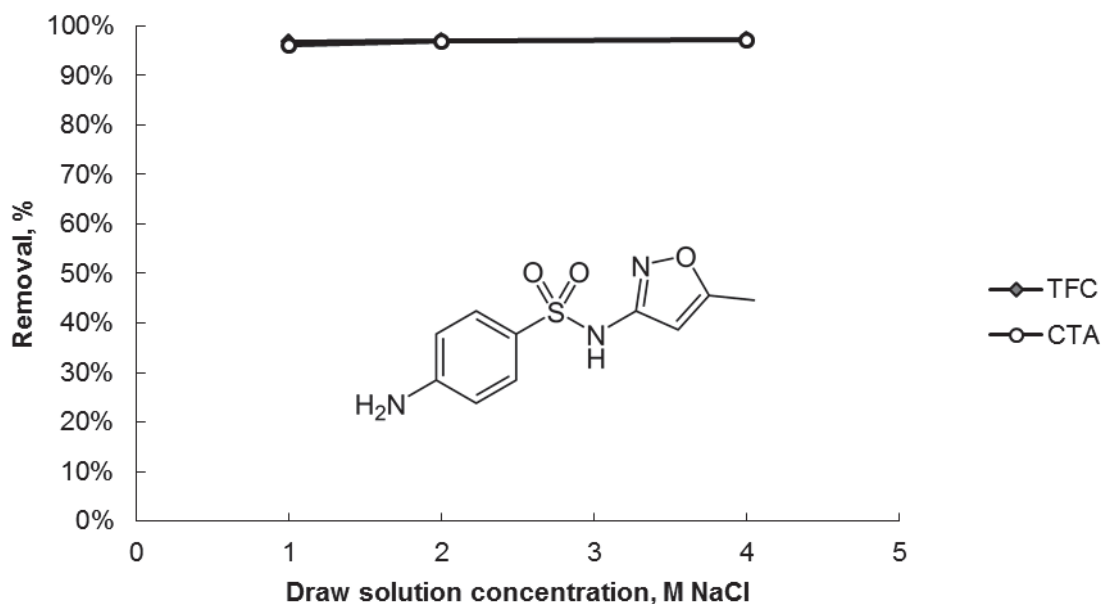
Fig. 4.23 Retention of sulfamethoxalzole from ROC in FO (MW = 253.28 g/mol, LogD at pH 7.5 = - 1.51, negatively charged at pH = 7.5)
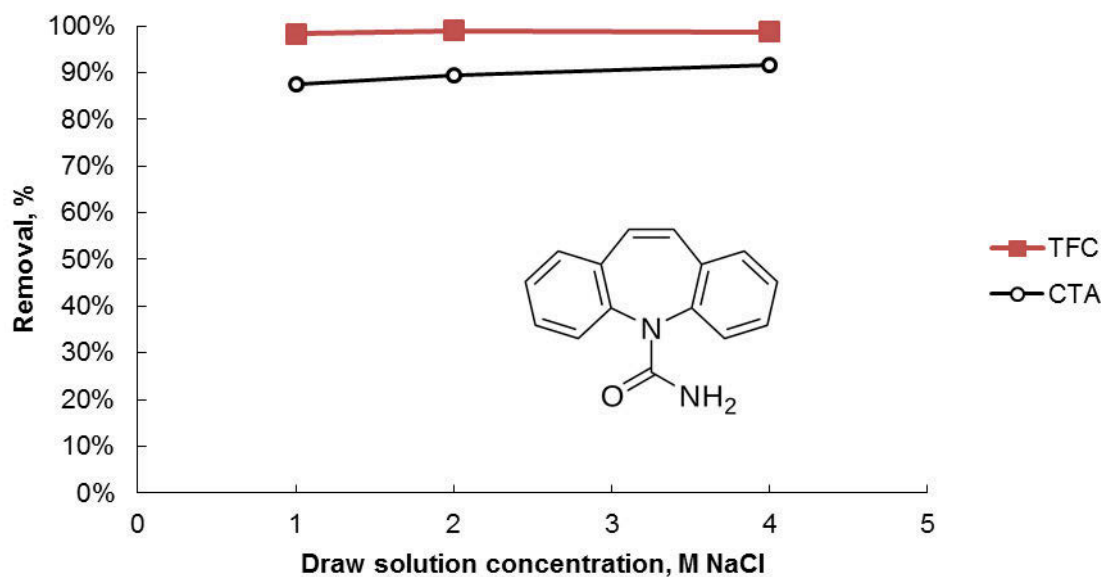
Fig. 4.24 Comparison of FO fouling by RO concentrate with adjusted and unadjusted pH (TFC PA membrane, 25°C)
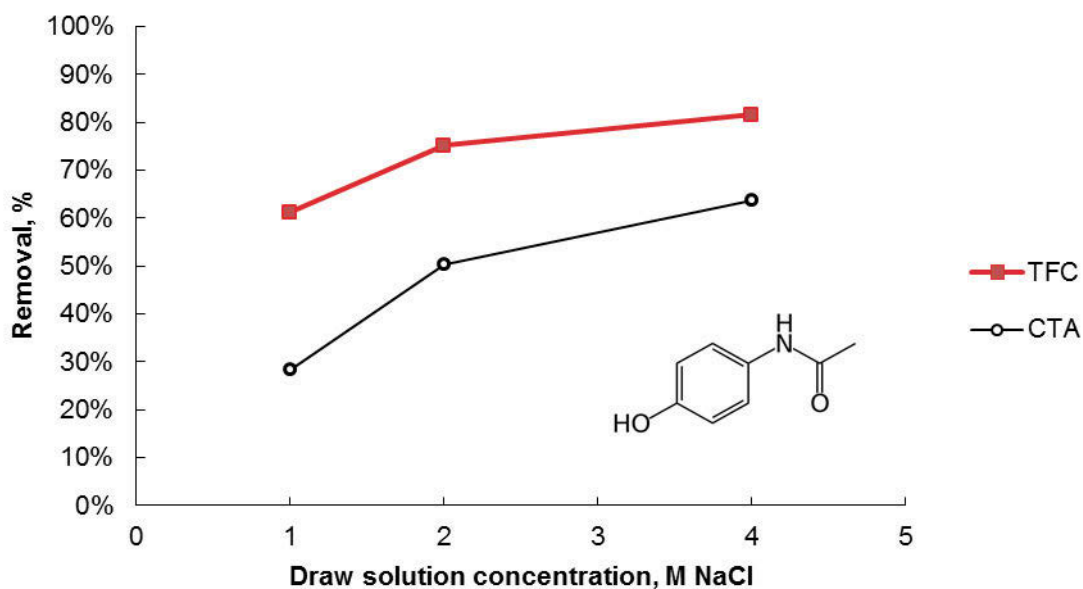
Fig. 4.25 Retention of paracetamol from ROC in FO (MW = 151 g/mol, Log D at pH 7.5 = 0.54, neutrally charged at pH = 7.5)
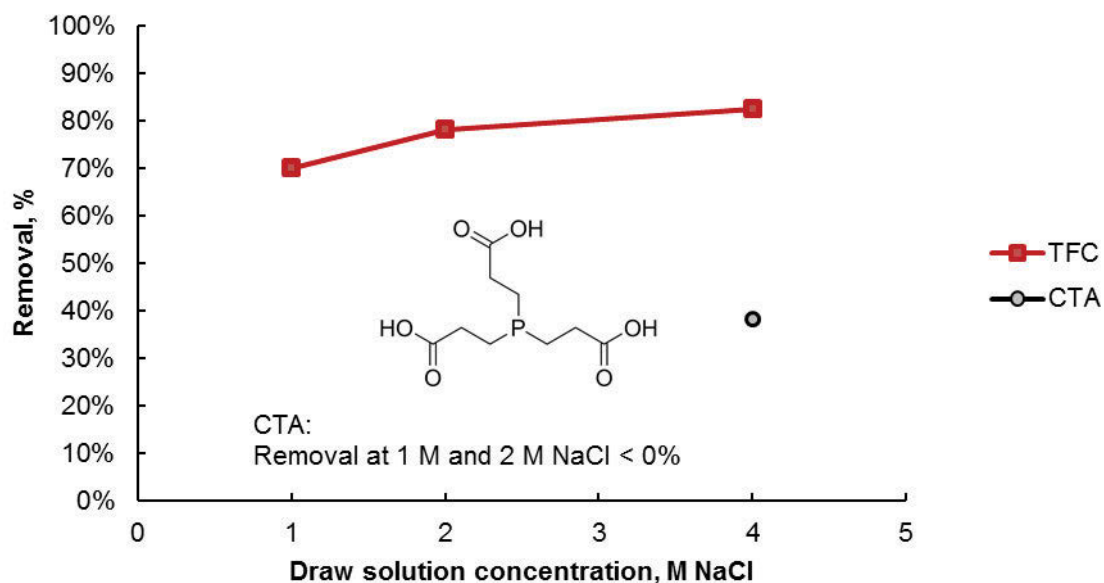
Fig. 4.26 Retention of TCEP from ROC in FO (MW = 285.49 g/mol, Log D at pH 7.5 = - 7.2, negatively charged at pH = 7.5)
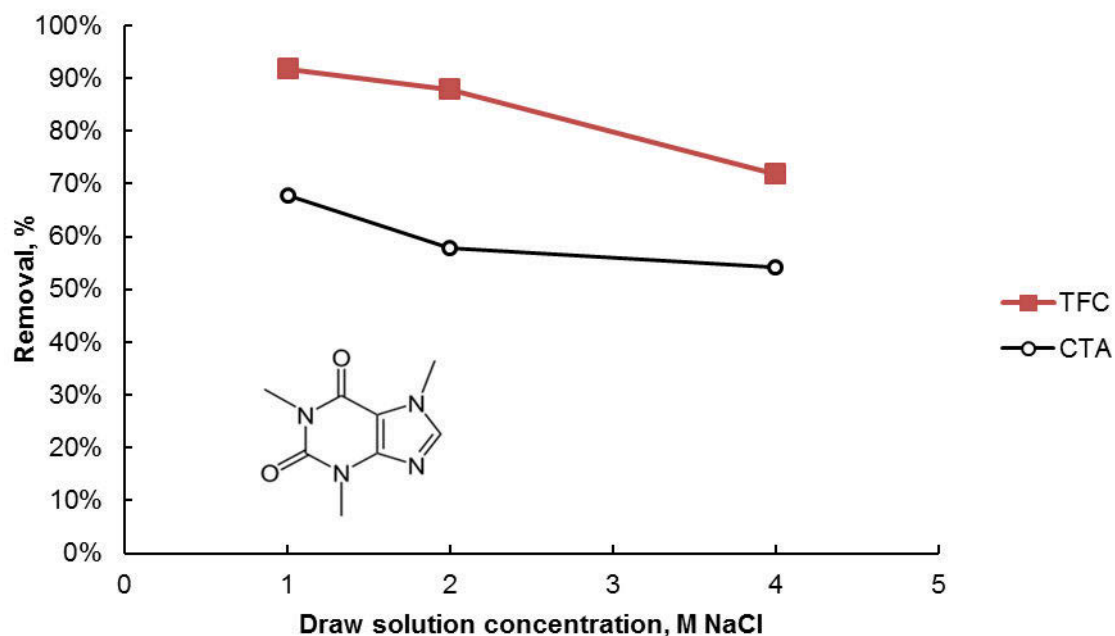
Fig. 4.27 Retention of caffeine from ROC in FO (MW = 194.19 g/mol, Log D at pH 7.5 = 0.11, neutrally charged at pH = 7.5)

4.4.4   Results and conclusions

- Trace organics are present in elevated concentrations (up to a few µg/L) in RO concentrate.

- Micropollutant rejection varies between different membrane types and feed water composition.

- The applied tests with real RO concentrate show slight deviations from the spiking tests with higher solute concentrations mainly used in other studies.

- Small size micropollutants with a molecular weight below 200 g/mol are rejected incompletely. The rejection pattern particularly of the CTA membrane resembles more NF than RO.

- An incomplete retention of micropollutants does not allow blending of the FO permeate with the mainstream RO permeate.

- Further treatment for removing micropollutants from the FO permeate is required. Granular activated carbon or other organic removal technologies such as ozonation are applicable for pre-treatment of the FO feed. Alternatively post-treatment of the FO permeate can reduce the micropollutant concentrations to acceptable levels.

5   Summary of results and conclusions

This present study investigated forward osmosis (FO) for RO concentrate treatment. FO appeared to be a promising technology leading to zero liquid discharge. Organic fouling and inorganic scaling were the main membrane foulants. Main flux decline was due to inorganic scaling, which was controlled by pH adjustment. Some micropollutants were only partly removed by FO. The major topics investigated in this study are outlined below.

5.1   Evaluation of membrane

Two main membranes TFC (PA) and CTA membrane were studied. The former membrane had a clean water flux of 12 to 16 LMH (1M NaCl, DS) in FO mode and 25 LMH in PRO mode while the later has a clean water flux 7-8 LMH with similar operating conditions.

- Thin film composite (TFC) PA membrane has higher flux than CTA membrane in FO mode and even higher in PRO mode under the same test conditions.

5.2   Effect of draw solution concentration

The draw solution concentration is directly proportional to flux. With 1, 2 and 4M NaCl the resultant flux was increased from 6-13 LMH for the CTA membrane.

- High impact of osmolality is evident in the draw solution.

5.3   Effect of cross-flow velocity (CFV)

To assess the impact of CRV in this bench scale set-up, three velocities were applied on FS and DS sides to observe the effect on flux, i.e. 8.8, 13.9, and 19.4 cm/s. The optimum velocity was 13.9 cm/s.

- Minimum CFV required to counteract ECP was 13.9 cm/s in this set-up.

5.4 Influence of DS/FS flow directions

Both co-current and counter-current flow patterns were tested with the bench scale FO apparatus, the later producing a slightly higher flux than the former.

- Minor influence of flow direction in the studied scale.

5.5 Reverse solute flow

CTA and TFC (PA) membranes were checked for reverse solute flow, using RO concentrate as FS and NaCl as DS. The two CTA membranes performed better in terms of reverse solute flow. However, the TFC (PA) membrane had a higher flux.

- CTA membrane is preferable in terms of reverse flow

5.6 Hydraulic flushing and chemical cleaning

Partial activity of TFC (PA) membrane was restored after hydraulic flushing. However, chemical cleaning was critical since the membrane's properties changed resulting in an increased reverse solute flow. Further research is needed to study this point in more depth.

- Partial recovery of flux with hydraulic flushing.

5.7 Alginate as model foulant

PA membrane was studied for alginate fouling in both FO and PRO modes and the tests indicate that alginate is a strong foulant for PA membrane in PRO mode. The resulting flux decreases sharply in this mode but on the other hand in FO mode moderate fouling occurred. However, the flux decline concerning the CTA membrane was 2-15%.

- Moderate fouling in FO mode and strong fouling in PRO mode when using alginate as model foulant.

5.8 Humic Acid (HA) as model foulant

Both CTA and TFC (PA) membranes in FO mode were checked for fouling. A reasonable amount of TOC was adsorbed on the surface of the membrane; however, corresponding flux was not affected much.

- Low fouling effect on membrane with HA as the model foulant.

5.9 Organic fouling and scaling from RO concentrate

Both CTA and TFC (PA) membranes were studied in FO mode for fouling. In a flux study with RO concentrate as FS, the results showed that both membranes are prone to fouling/scaling. This effect increased when the pressure of draw solution also increased.

- Scaling was a major impediment to the FO process and should be controlled for instance by pH adjustment or softening.

5.10 Study of micropollutants

The membrane plays an important role, for the retention of micropollutants. The rejection of trace organic compounds depends on the molecular weight of the respective compound. Paracetamol and caffeine (MW < 200 g/mol) are poorly rejected compared to other compounds due to their relatively low molecular weight. Finally all the compounds do not behave as predicted, for example TECP.

- TFC (PA) membrane is better at rejecting micropollutants than CTA and increasing permeate flux increases the retention of micropollutants.

5.11 Recommendations

The study showed that forward osmosis is a promising technology for RO concentrate treatment and opens new avenues for further research work:

- Recovery of nutrients and salts from RO concentrates in water reclamation
- Recovery of draw solution and its reuse, to make FO operation continuous
- Post-treatment of permeate to produce high quality recycled water

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7   Figures and tables

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Thesis-Related Publications and Presentations

- Submitted for publication in Water Science and Technology 2013

  Forward Osmosis for the Treatment of RO Concentrate from
  Water Reclamation: Process Performance and Fouling Control

Authors: Christian Kazner[1,2] Shahzad Jamil[1], , Sherub Phuntsho[1], Hokyong Shon[1], Thomas Wintgens[2] and Saravanamuth Vigneswaran[1]

- **Conference Presentation:** (7th IWA Specialized Membrane Technology Conference · Toronto, Canada · 25 – 29 August 2013)

Forward Osmosis for the Treatment of RO Concentrate from
Water Reclamation: Process Performance and Fouling Control

Authors: Shahzad Jamil[1], Christian Kazner[1,2], Sherub Phuntsho[1], Hokyong Shon[1], Thomas Wintgens[2] and Saravanamuth Vigneswaran[1]

[1] University of Technology Sydney, Centre for Technology in Water and Wastewater
[2] University of Applied Sciences and Arts Northwestern Switzerland, Institute of Ecopreneurship (Presented by Shahzad Jamil)