Development of a novel osmotic membrane bioreactor for water reclamation

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**DEVELOPMENT OF A NOVEL
OSMOTIC MEMBRANE BIOREACTOR
FOR WATER RECLAMATION**

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

2012

Development of a novel
osmotic membrane bioreactor for water reclamation

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School of Civil and Environmental Engineering

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For my family

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About three years ago, I began a fresh chapter of my life as the first and only student at the Singapore Membrane Technology Centre (SMTC). Since that time, SMTC has grown considerably and today, there are more than 70 researchers and students at the centre. While I am naturally elated to see my works of passion coming to fruition, the completion of my PhD journey comes with mixed feelings. After all, this marks a milestone in my life, as I move forward to the next phase of experience.

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Table of contents

Acknowledgements.....	i
Table of contents.....	iii
Summary	vii
List of publication.....	ix
List of tables.....	xii
List of figures.....	xiii
List of symbols.....	xv
Chapter 1. Introduction.....	1
1.1 Background	1
1.2 Scope and objectives.....	3
1.3 Significance of the research.....	5
Chapter 2. Literature review and preliminary analysis.....	6
2.1 MBR technology for water reclamation	6
2.2 Forward Osmosis membrane process	9
2.2.1 Background.....	9
2.2.2 Physical concepts	10
2.2.3 Concentration polarisation phenomena.....	13
2.2.4 Flux behaviour of FO vis-a-vis RO	16
2.3 Membrane fouling in MBR system.....	21
2.3.1 Influencing factors	22
2.3.2 Fouling mechanisms	26
2.4 Issues of relevance to OMBR	29
2.4.1 Concentration factor and salt accumulation.....	30
2.4.2 Issues associated with flux, micro-pollutant removal and fouling ...	32
2.4.3 Fouling mitigation for OMBR	35
2.4.4 Concluding remarks.....	37

Chapter 3. General materials and methodologies	38
3.1 Introduction	38
3.2 The lab-scale OMBR system	38
3.3 Membranes.....	41
3.3.1 Thin-film composite (TFC) FO membrane.....	41
3.3.2 Cellulose-triacetate (CTA) FO membrane.....	42
3.4 General experimental methods	46
3.5 General analytical methods.....	49
Chapter 4. Stable-state study of an OMBR	51
4.1 Introduction.....	51
4.2 Experimental and modelling methods	52
4.2.1 Experimental protocol.....	52
4.2.2 Modelling method.....	53
4.3 Results and discussion	54
4.3.1 Water production and elevated mixed liquor concentration	54
4.3.2 Membrane properties derived from RO experiments	57
4.3.3 Visual and electron microscopic examination of used membranes ..	60
4.3.4 Scaling propensity check	61
4.3.5 Deviation of observed and expected concentration factor	63
4.4 Concluding remarks	66
Chapter 5. Effects associated with pharmaceutical removal	67
5.1 Introduction.....	67
5.2 Experimental and analytical methods	68
5.2.1 Experimental protocol.....	68
5.2.2 Pharmaceutical compounds and their analysis	70
5.2.3 Analytical methods for process parameters	72
5.2.4 Organic carbon characterisation	73
5.2.5 Methods for microbiological analysis.....	74
5.3 Results and discussion	75
5.3.1 Removal of pharmaceutical compounds	75

5.3.2	Assessment of process parameters: dissolved organic carbon, mixed liquor suspended solids and extracellular polymeric substances	78
5.3.3	Liquid chromatography – organic carbon detection analysis	83
5.3.4	Microbiological analysis	87
5.4	Concluding remarks	91
Chapter 6.	Factors affecting salt accumulation in OMBR.....	92
6.1	Introduction	92
6.2	Theory	94
6.2.1	Salt accumulation equations	94
6.2.2	Significance of B/A ratio	97
6.2.3	Relevance of dimensionless water production parameter.....	98
6.2.4	In-series model relating overall B/A ratio to individual layers.....	100
6.3	Experimental and modelling methods	103
6.3.1	Experimental protocol.....	103
6.3.2	Modelling method.....	104
6.3.3	Chi-square statistics for goodness of fit test	104
6.4	Results and discussion	105
6.4.1	Effects of SaRT/HRT and B/A ratios on steady state concentration factor	105
6.4.2	Concentration factor in relation to varying B/A ratio.....	107
6.4.3	Significance of secondary layer on overall B/A ratio.....	108
6.4.4	Practical application: evolution of B/A ratio	111
6.5	Concluding remarks	118
Chapter 7.	OMBR flux performance and potential assessment.....	119
7.1	Introduction.....	119
7.2	Theoretical background	120
7.2.1	Flux equations for forward osmosis.....	120
7.2.2	Conventional approaches for assessing flux performance.....	123
7.2.3	Novel flux-recovery analysis for assessment of flux efficiency	126
7.3	Experimental and modelling methods	131
7.3.1	Experimental protocol.....	131

7.3.2	Modelling analyses	133
7.4	Results and discussion	135
7.4.1	Modelling results	135
7.4.2	Observed flux performance from experiments	142
7.4.3	Discussion of factors affecting OMBR flux performance	152
7.5	Concluding remarks on assessment of OMBR flux performance	162
7.6	Potential of OMBR for water reclamation.....	164
7.6.1	OMBR for high recovery application	165
7.6.2	Hybrid OMBR-MBR system	167
7.6.3	Concluding remarks on potential of OMBR.....	169
Chapter 8.	Conclusions and recommendations.....	170
8.1	Conclusions.....	170
8.2	Recommendations.....	174
Appendices.....		176
Appendix A	Derivation of equations for ICP and CECF in FO.....	176
Appendix B	Role of ICP in FO and RO flux behaviour	180
Appendix C	Electrical impedance spectroscopy.....	196
Appendix D	Extraction and Analysis of Extracellular Polymeric Substances..	199
Appendix E	PCR-DGGE protocol.....	201
References.....		203

Summary

In this study, a novel osmotic membrane bioreactor (OMBR) was developed and systematically studied to assess performance-affecting factors. The study focused on membrane performance. On a foundation level, it was confirmed that internal concentration polarisation (ICP) is a unique phenomenon for the forward osmosis (FO)-based system and ICP could play a deterministic role in the flux behaviour. Elevated mixed liquor salinity is also an inherent issue of OMBR due to volumetric concentration of the influent and reverse salt transport due to transmission of draw solutes.

On a technology integration level, a long term investigation was conducted on a continuously operated OMBR system. It was found that stable water production and mixed liquor concentration could be achieved. Mild membrane fouling was observed, and could be explained by known factors. The experimentally observed salt concentration factor was significantly lower than expected, and points to the influence of the gel-like layer on the membrane surface with regard to the reverse transmission of draw solutes. Based on synthetic feed water, the OMBR could achieve excellent product water quality with product dissolved organic carbon generally $\leq 1 \text{ mgL}^{-1}$, which was in excess of 99 % organic removal. Furthermore, the high rejection of the studied pharmaceutical compounds allowed organic micro-pollutants to be concentrated in the bioreactor, which would enhance their rate of biodegradation. However, the biological process was found to play a key role in the overall performance of the OMBR, which was evident when it was temporarily inhibited by the pharmaceutical dosages, and resulted in the temporary impairment of product water quality.

On a systemic level, salt accumulation and flux performance are key issues for the OMBR. Salt accumulation in the OMBR is controlled by three factors: membrane, influent, and process. The role of the membrane is application-dependent and significant only when influent osmotic pressure is smaller or in the same order of magnitude as the salt to water permeability ratio.

Flux performance of the OMBR may be described by the transport parameters: water permeability (A), salt-to-water permeability ratio (B/A), and mass transfer coefficient (K_m). However, fouling has significant effects and could influence the transport parameters. Flux diminishment effects could be due to draw solute transmission, fouling resistance and cake-enhanced concentration polarisation. The flux efficiency factor: observed flux to reference flux ($J_{w,ob}/J_{w,re}$), is a new method developed to assess OMBR performance. It shows the inevitable trade-off between flux and recovery for a FO system. Application should aim for $J_{w,ob}/J_{w,re} \geq 0.8$ for the interested recovery. Level of flux, membrane orientation, membrane surface properties and structure are factors that influence OMBR performance. In general, a high flux and membrane orientation 'active layer facing draw solution' lead to more severe fouling than a lower flux and 'active layer facing feed water' orientation. Conversely, smooth and hydrophilic membrane surface and dense-like membrane structure could provide fouling relief. Fouling amelioration factors include aeration and osmotic backwash. It was shown that FO membrane design and selection need to be optimised with due consideration to application challenges. Other operational factors such as higher temperatures and mobile draw solutes are favourable to enhance FO performance due to increasing K_m .

The study substantiated the thesis that the OMBR is a potential technology for water reclamation. Experimentally, it has been shown that the OMBR can achieve stable water production and good product quality at high recovery (ϕ up to 95.8%), but there are important performance-affecting factors that need to be addressed. A novel FO membrane has shown potential, and achieved flux $\geq 20 \text{ Lm}^{-2}\text{h}^{-1}$ at low recovery with modest osmotic driving force ($0.5 \text{ mol}\cdot\text{kg}^{-1} \text{ NaCl}$) and under mild fouling conditions. However, membrane resistance to fouling would be a critical area for future research and development.

The study evaluates the potential of the OMBR for water reclamation, and points out significant future research areas to further develop the technology.

List of publication

Journal publication

1. Lay, W. C. L., Y. Liu and A. G. Fane (2010). "Impacts of salinity on the performance of high retention membrane bioreactors for water reclamation: A review." *Water Research* 44(1): 21-40.
2. Lay, W. C. L., T. H. Chong, C. Y. Tang, A. G. Fane, J. Zhang and Y. Liu (2010). "Fouling propensity of Forward Osmosis: investigation of the slower flux decline phenomenon." *Wat. Sci. Technol.* 61.4 (This paper was also accepted as oral presentation at the 6th IWA-LET conference, 2009).
3. Tang, C. Y., Q. She, W. C. L. Lay, R. Wang and A. G. Fane (2010). "Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration." *Journal of Membrane Science* 354(1-2): 123-133.
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List of tables

Table 2.1: Membrane properties as factors of influence on MBR fouling	23
Table 2.2: Biomass characteristics as factors of influence on MBR fouling.....	24
Table 2.3: Operating conditions as factors of influence on MBR fouling.....	25
Table 2.4: Postulated fouling mechanisms to explain sudden drop in performance for MBR systems	28
Table 2.5: Possible accumulation of retained constituents in an OMBR system	31
Table 3.1: Composition of the synthetic feed water	47
Table 3.2: Overview of experimental conditions.....	48
Table 4.1: Water quality check of selected ions on t = 73 d.....	62
Table 4.2: Assessment of scaling propensity of the mixed liquor	62
Table 5.1: Summary of main experimental parameters	69
Table 5.2: Information of dosed pharmaceuticals.....	71
Table 6.1: Brief description of the FO membranes used in this study.....	103
Table 7.1: Brief description of the FO membranes used in this study.....	132
Table 7.2: Overview of the experimental runs considered in this chapter.....	132
Table 7.3: Modelled scenarios for FO-RO flux ratio factor and apparent FO water permeability	134
Table 7.4: Modelled parameters for flux-recovery analysis	134
Table 7.5: Summary of experimental findings	149
Table 7.6: Overview of flux and performance assessment parameters	151
Table 7.7: Estimated saturation indices (SI) for mixed liquor of the OMBR experiments	159

List of figures

Figure 1.1: Schematic of OMBR application for water reclamation.....	2
Figure 1.2: Organisation of the thesis	5
Figure 2.1: Application of MBR technology for water reclamation (Qin et al. 2006) ..	6
Figure 2.2: Configurations of MBR: (a) side-stream; (b) submerged	8
Figure 2.3: Brief history of developments in FO/PRO	9
Figure 2.4: Physical concepts of (a) RO, and (b) FO.....	11
Figure 2.5: Relationship between RO, FO and PRO	11
Figure 2.6: Conceptual illustration of various concentration polarisation phenomena for an OMBR	15
Figure 2.7: Comparison of flux behaviour between FO and RO.....	19
Figure 2.8 Effect of equal loss of driving force on flux in FO and RO	20
Figure 2.9: Fouling road map in MBR systems.....	26
Figure 3.1: The submerged integrated OMBR system	40
Figure 3.2: Scanning electron microscope (SEM) images of the TFC membrane	41
Figure 3.3: Scanning electron microscope (SEM) images of the CTA membrane	43
Figure 3.4: Contact angle images of the CTA membrane	44
Figure 3.5: Atomic force microscopy (AFM) images of the CTA membrane	44
Figure 4.1: Water flux and mixed liquor concentration of the OMBR.....	54
Figure 4.2: Membrane properties as determined by RO experiments comparing the virgin membrane and the used membrane from the OMBR.....	58
Figure 4.3: Visual and microscopic examination of the used membrane from the OMBR.....	59
Figure 4.4: Comparison of observed and expected concentration factors for the OMBR experiment.....	63
Figure 5.1: Analyses of pharmaceuticals	77
Figure 5.2: Analyses of process parameters	81
Figure 5.3: EPS analyses.....	82
Figure 5.4: LC-OCD analyses.....	86
Figure 5.5: DGGE profiles from mixed liquor and membrane.....	87
Figure 5.6: Dendrogram analysis showing relative similarity between samples.....	88
Figure 5.7: Shannon-Weaver Index (H) of the analysed samples	89

Figure 6.1: Conceptual diagram of an OMBR system for salt accumulation analysis	94
Figure 6.2: In-series model for development of a secondary layer on a FO membrane	100
Figure 6.3: Steady state concentration factor as function of SaRT/HRT and $(B/A)/\pi_{in}$	106
Figure 6.4: Temporal variation of concentration factor for different $(B/A)/\pi_{in}$ ratios	108
Figure 6.5: Overall B/A ratio in dependence on A_{me}/A_{la} and B_{me}/B_{la}	109
Figure 6.6: Evolution of the B/A ratio for the TFC-membranes	112
Figure 6.7: Evolution of the B/A ratio for the CTA-membranes	112
Figure 6.8: Comparison of observed and modelled concentration factors	113
Figure 7.1: Conceptual illustration for FO-RO flux ratio factor and apparent FO water permeability	125
Figure 7.2: Conceptual illustration of flux – recovery analysis for an OMBR	129
Figure 7.3: Modelled water flux as function of osmotic driving force	135
Figure 7.4: (a) Modelled FO-RO flux ratio factor, and (b) apparent FO water permeability	137
Figure 7.5: Modelled flux-recovery analysis for (a) mild and (b) more severe condition.	141
Figure 7.6: Water flux and mixed liquor concentration for TFC experimental runs.	146
Figure 7.7: Water flux and mixed liquor concentration for CTA experimental runs	148
Figure 7.8: Flux-recovery analysis for (a) TFC, and (b) CTA experimental runs	150
Figure 7.9: Photographs of membranes upon removal from the OMBR:	158
Figure 7.10: Observed flux before and after osmotic backwash for (a) TFC-II, and (b) CTA-V	159
Figure 7.11: EDX analysis on TFC-II	160
Figure 7.12: EDX analysis on CTA-IV	160
Figure 7.13: EDX analysis on CTA-VI with membrane orientation AL-DS	161
Figure 7.14: The CLSM images of (a) TFC-II and (b) CTA-V	161
Figure 7.15: Flux-recovery analysis for a potential OMBR for water reclamation	165
Figure 7.16: Options for water reclamation	166
Figure 7.17: Hybrid OMBR-MBR system for water reclamation	168

List of symbols

A	Overall water permeability
A_{la}	Water permeability of secondary layer
A_{me}	Water permeability of membrane
A_m	Membrane area
AL-DS	Membrane orientation of active layer against draw solution
AL-FW	Membrane orientation of active layer against feed water
B	Overall salt permeability
B/A	Overall salt to water permeability ratio
B_{la}	Salt permeability of secondary layer
B_{me}	Salt permeability of membrane
c_{in}	Influent salt concentration
c_{ml}	Mixed liquor salt concentration
CECP	Cake enhanced concentration polarisation
CRCP	Cake reduced concentration polarisation
CF	Concentration factor
CLSM	Confocal laser scanning microscopy
CP	Concentration polarisation
CTA	Cellulose triacetate
D	Diffusion coefficient
DOC	Dissolved organic carbon
DGGE	Denaturing gradient gel electrophoresis
ds	Draw solution
EDX	Energy-dispersive X-ray spectroscopy
eff	Effective
EIS	Electrical impedance spectroscopy
EPS	Extracellular polymeric substances
FO	Forward osmosis
F/M	Food to microorganism ratio
GC-MS	Gas chromatography mass spectrometry
H	Shannon-Weaver index
HRMBR	High retention membrane bioreactor

HRT	Hydraulic retention time
k_{biol}	Biodegradation constant
K_d	Sorption constant
LC-OCD	Liquid chromatography – organic carbon detection
LMW	Low molecular weight
ICP	Internal concentration polarisation
J_s	Draw solute flux
J_w	Water Flux of a FO process
$J_{w,\text{ob}}$	Observed water flux of an operating FO process
$J_{w,\text{re}}$	Water Flux of a FO process derived from a reference condition
$J_{w,(\text{RO})}$	Water Flux of a RO process defined by $A_{\text{me}}(\pi_{\text{ds}} - \pi_{\text{ml}})$
$J_w/J_{w,(\text{RO})}$	FO-RO flux ratio factor
$J_w/(\pi_{\text{ds}} - \pi_{\text{ml}})$	Apparent FO water permeability
$J_{w,\text{ob}}/J_{w,\text{re}}$	Flux efficiency factor
k_{biol}	Biodegradation constant
k_{CECP}	Mass transfer coefficient due to CECP
K_d	Sorption constant
K_m	Mass transfer coefficient due to ICP inherent of a FO process
$K_{m+\text{foul}}$	Mass transfer coefficient encompassing ICP and fouling effects
K_{sp}	Solubility product constant
l_a	Secondary (fouling) layer
LC-OCD	Liquid chromatography – organic carbon detection
LMW	Low molecular weight
MBR	Membrane bioreactor
MD	Membrane distillation
MF	Microfiltration
me	Membrane
ml	Mixed liquor
MLSS	Mixed liquor suspended solids
M_w	Molecular weight
MWCO	Molecular weight cut-off
NFMBR	Nanofiltration membrane bioreactor
OLR	Organic loading rate

OMBR	Osmotic membrane bioreactor
ORT	Organic retention time
p	pressure
p_i	Proportion of the i th phylotype band
PCR	Polymerase chain reaction
PRO	Pressure retarded osmosis
Q	Product flow
Q_{in}	Influent flow
Q_w	Waste sludge flow
RO	Reverse Osmosis
R	Rejection
R_g	Ideal gas constant
R_h	Hydraulic resistance
S_{me}	Structural parameter of membrane
SAD_m	Specific aeration demand with respect to membrane area
SEM	Scanning electron microscopy
SI	Supersaturation index
SMP	Soluble microbial products
SRT	Solids retention time
SaRT	Salt retention time
T	Temperature
TDS	Total dissolved solids
TFC	Thin film composite
TOC	Total organic carbon
UF	Ultrafiltration
UPLC	Ultra performance liquid chromatography
V	Reactor volume

Greek symbols

Δ	Difference
δ	Thickness
ε	Porosity
η	Viscosity
φ	Recovery
μ	Chemical potential
ν	Van't Hoff factor
π	Osmotic pressure
π_{ds}	Osmotic pressure of the bulk draw solution
π_{in}	Osmotic pressure of the influent
π_{ml}	Osmotic pressure of the bulk mixed liquor
ρ	Density
τ	Tortousity
χ^2	Chi-square statistics

Chapter 1. Introduction

1.1 Background

The importance of water as a basic necessity to all living things cannot be overstated. Where water from natural sources is limited, water reclamation provides a strategic avenue to augment supply. In Singapore, water reclamation plays a crucial role in the four national taps strategy. The high-grade water that is reclaimed is known as NEWater (Tan 2009). The NEWater production adopts a dual-membrane approach, whereby secondary effluent is treated by a porous membrane process – Microfiltration (MF) or Ultrafiltration (UF), followed by a semi-permeable membrane process – Reverse Osmosis (RO) (PUB 2002). The dual-membrane approach is the established method for water reclamation and desalination applications (AWWA 2004).

With the rapid advancement of membrane bioreactor (MBR) technology, a new direction for used water treatment emerges. The MBR technology works on the premise of combining MF/UF and biological process in a one-step configuration. The technology therefore offers significant advantages in the form of compact footprint and consistent product quality, and is currently regarded as the state of the art for treatment of used water (Melin et al. 2006; Yang et al. 2006). The conventional MBR technology, however, has limitation in retaining smaller size organic micro-pollutants in accordance to the molecular weight cut-off (MWCO) of the MF/UF membranes. For these organic species, the organic retention time (ORT) is the same as the hydraulic retention time (HRT). The effect of this is that recalcitrant organics may not be well degraded, and the reuse potential of the product may be limited. This recognition provides the underlying motivation to develop beyond the state-of-the-art MBRs based on high retention membranes with the view for water reclamation applications. The quest is for high retention membrane bioreactor (HRMBR) systems that are capable of producing product water quality superior to conventional technologies, and favourable for water reclamation (Fane et al. 2009).

The osmotic membrane bioreactor (OMBR) belongs to the class of HRMBR systems. It is the novel integration of forward osmosis (FO) and biological process. The FO is a membrane separation process that technically exploits the natural phenomenon of osmosis, such that pure water from a feed water source spontaneously flows through a semi-permeable membrane under an osmotic driving force provided by a draw solution. A suitable post-treatment step, for instance RO or a thermal process such as membrane distillation can be subsequently applied to extract the purified water and regenerate the draw solution. A schematic diagram of an OMBR system is illustrated in the following figure.

Figure 1.1: Schematic of OMBR application for water reclamation

The increasing interest in FO-associated systems is unmistakable (McGinnis and Elimelech 2008; Lange 2010). This interest arises due to the multitude of potential advantages that the FO membrane process may offer. These may include (McCutcheon et al. 2005; Cath et al. 2006):

- good product water quality comparable to advanced desalination technology such as RO;
- no need for high hydraulic pressure as is the case for the pressure-driven RO;

- low electrical energy demand possible with suitable post-treatment step using low grade heat;
- high osmotic driving force attainable with suitable draw solution and hence high recovery achievable; and
- potentially low fouling tendency (assumption is that foulant compaction is related to hydraulic pressure).

The above perceived attributes may find a niche for the OMBR technology to be employed for larger scale water reclamation applications with aggressive water environment that has high fouling potential. The aspiration is for the technology to attain sustainable water production with high product quality at high recovery.

In spite of the interest in OMBRs, limited studies are available to provide a holistic assessment on the feasibility of this technology. A few studies have conducted short term experiments with FO in a side stream configuration to a bioreactor that provided insights into the process (Cornelissen et al. 2008; Qin et al. 2009), but overlooked longer term issues pertinent for real application. A more comprehensive study was conducted by (Achilli et al. 2009b) using a submerged OMBR. That study shows that the OMBR may achieve higher removal efficiencies compared to conventional MBRs and low fouling tendency under regular application of osmotic backwashing. However, fundamental issues such as flux behaviour of FO and effects associated with the concentrative mixed liquor environment of the OMBR need investigation. Further research questions remain, and factors that may affect OMBR performance as a technology for application are largely unknown. Therefore, there is a need for a systematic study to adequately assess the OMBR technology, and this need provides motivation for the thesis.

1.2 Scope and objectives

The thesis statement is that the OMBR is a potential technology for water reclamation, because it is able to achieve stable water production and good product quality at high recovery, but there are important performance-affecting factors that need to be addressed for technology optimisation. Such factors are invariably

complex, due to the multitude of coupled interactions amongst membrane, biology and the elevated saline environment. The research here seeks to provide a systematic study of these factors. The underpinning goal of this dissertation is to develop a novel OMBR that would be feasible for water reclamation.

The scope of the thesis focuses on the FO performance in an operational OMBR in view of the critical role that the membrane plays. The study therefore does not explicitly consider other system elements such as the biological process and the post-treatment process, but inferences to these elements in association with membrane performance are made where appropriate.

The organisation of this thesis is presented in Figure 1.2. It is formulated as a three tier approach that categorises chapters in groups, where each group provides basis for the next level of study. Each chapter aims to clarify a study objective that is linked to another.

The first three chapters form the foundation work for the thesis. Following Chapter 1 that provides a framework for the thesis, Chapter 2 is to review available literature and apply preliminary analysis to elucidate key issues pertaining to OMBR performance. Chapter 3 develops general methods and methodologies for the research used in the thesis.

The main research findings of the thesis are found in the Chapters 4 to 8. Chapter 4 is to derive stable-state observations from a long-term OMBR experiment under elevated salt condition. Chapter 5 is to research on effects associated with pharmaceutical removal with regard to water quality and biological process. Chapter 6 is to analyse factors affecting salt accumulation in OMBR. Chapter 7 is to provide a set of flux evaluation methods for OMBR and investigate potential of the technology for water reclamation. The common thread that runs through the chapters is to study factors affecting performance of an OMBR system.

Finally, Chapter 8 provides conclusions and recommendations that arise from this thesis.

Figure 1.2: Organisation of the thesis

1.3 Significance of the research

This research is envisaged to provide the following outcomes that would be of significance:

- 1) a fundamental understanding is provided on FO flux behaviour and issues of relevance to OMBR operation;
- 2) a new methodology is developed to assess factors affecting FO performance in the OMBR; and
- 3) the study offers an important case study for development of the novel OMBR technology for water reclamation.

Chapter 2. Literature review and preliminary analysis

This chapter provides a comprehensive review of the relevant literature and also includes preliminary modelling and analysis.

2.1 MBR technology for water reclamation

A typical water reclamation process is multiple-staged that can be broadly categorised into two main parts:

- (i) Activated sludge process comprising primary sedimentation, aeration and final sedimentation to produce secondary effluent; and
- (ii) Processes for production of high grade reclaimed water comprising a dual membrane process of micro-/ultra-filtration (MF/UF) and reverse osmosis (RO), followed by ultraviolet disinfection.

A membrane bioreactor based (MBR-based) water reclamation process combines the activated sludge process and a porous membrane separation (MF/UF) process. Compared to a typical water reclamation process, an MBR-based water reclamation process is able to substantially reduce the treatment facility footprint because the three steps: aeration, final sedimentation and MF/UF, are now replaced by one single MBR step. The concept of applying MBR technology for water reclamation is illustrated in the following figure.

Figure 2.1: Application of MBR technology for water reclamation (Adapted from Qin et al. 2006)

The MBR is currently regarded as the state-of-the-art technology for water reclamation and used water treatment. Advantages of applying MBR for water reclamation include (Melin et al. 2006; Qin et al. 2006; Yang et al. 2006; Henze et al. 2008):

- Small facility footprint (an MBR replaces the three processes: aeration, final and MF-UF);
- Compact bioreactor volume (an MBR is able to be operated at higher mixed liquor suspended solids (MLSS) concentration compared to a typical activated sludge process);
- Reduced sludge production (an MBR is able to be operated at longer solids retention time (SRT) compared to a typical activated sludge process without effect on the effluent quality);
- Opportunity to select for slow-growing bacterial populations with enhanced operation with longer SRT (e.g. Nitrification, Biodegradation of organic micro-pollutant)
- The final RO product water quality of an MBR-based water reclamation process is generally better and more consistent compared to a typical water reclamation process (synergistic effect of integration of membrane and biological process).

Conventionally, the membranes used in an MBR system are porous membranes that are either MF or UF. However, a limitation of the conventional MBR system is that organic micro-pollutants smaller than the molecular weight cut-off (MWCO) of the MF/UF membranes may not be effectively retained as discussed in section 1.1. The organic retention time (ORT) for these small size organic species is the same as the hydraulic retention time (HRT). The effect of this is that recalcitrant organics may not be well degraded, and the reuse potential of the product may be limited. This recognition provides the underlying motivation for this study to integrate high retention membrane processes such as Forward Osmosis (FO) and a biological process for water reclamation application. Review of the FO membrane process is provided in section 2.2.

There are two main MBR configurations that are applied: side-stream and submerged (Judd 2006), which are illustrated in the following figure.

Figure 2.2: Configurations of MBR: (a) side-stream; (b) submerged (Adapted from Judd 2006)

In the side-stream configuration, the membrane is located outside the bioreactor tank. Feed water is conveyed to an externally located membrane module where water permeation takes place. Fluid management in a side-stream membrane module is generally good, as feed water flows tangentially with the membrane surface (crossflow) and hence provide a scouring effect that mitigates fouling. However, the exertion in the form of feed water conveyance points out that the side-stream configuration can be relatively energy intensive (Henze et al. 2008).

In the submerged configuration, also known as the immersed configuration, the membrane is submerged under water, typically in the bioreactor tank. Membrane modules applied in submerged MBR systems are either hollow fibres or flat sheets. A limitation of the submerged configuration is poorer fluid management as compared to the side-stream configuration. To mitigate fouling, bubbling by means of aeration is needed to provide scouring for the membrane. An advantage of submerged membranes is that pressure vessels are not required, which reduces costs. Furthermore, as feed water conveyance is not required, the submerged configuration is generally less intensive than the side-stream configuration, and is more often used

in municipal applications (Melin et al. 2006). The submerged configuration is therefore the focus of this study (Section 3.2).

2.2 Forward Osmosis membrane process

2.2.1 Background

As early as the 1960s, FO has been viewed with interest as a promising technology for both water treatment and energy generation, the latter which is known as pressure-retarded osmosis (PRO). However, significant developments in FO/PRO have mostly taken place in the last decade, alongside the general advancement of membrane technology. Recent developments and new concepts for FO in the applications of seawater desalination and used water treatment and water reclamation have rekindled interest in the technology (Figure 2.1):

Figure 2.3: Brief history of developments in FO/PRO

2.2.2 Physical concepts

A basic concept to understanding FO and RO is osmosis. It is a natural phenomenon of solvent transport from a solution of lower concentration to another solution of higher concentration separated by a semi-permeable membrane. For most application, this solvent is water, and the pressure that must be applied to stop the water transport is known as the osmotic pressure. The osmotic pressure (π) is a thermodynamic property, and can be derived from chemical potential analysis. For dilute and ideal solutions, π can be estimated from the van't Hoff equation (Belfort et al. 1994; Melin and Rautenbach 2007):

$$\pi = v \cdot R_g \cdot T \cdot c \quad (2.1)$$

where v is the factor for mole increase due to the dissociation of solutes, R_g is the ideal gas constant, c is solute concentration, and T is temperature.

The working principle of RO is to apply a hydraulic pressure difference (Δp), greater than the osmotic pressure difference ($\Delta \pi$), to overcome osmosis and thus reverse the direction of water transport (Figure 2.4 (a)). On the other hand, FO is a process that operates at ambient pressure and gainfully exploits the natural osmosis phenomenon by using a selected draw solution of greater osmotic pressure to extract water from a feed water source (Figure 2.4 (b)). For FO, a post-treatment step will be required to produce purified water and regenerate draw solution.

Water transport in dense membrane processes may be described by the solution-diffusion model (Lonsdale et al. 1965; Baker 2004), which gives the relationship of the water flux (J_w) to the driving force ($\Delta p - \Delta \pi$):

$$J_w = A \cdot (\Delta p - \Delta \pi) \quad (2.2)$$

where A is the water permeability (units may be expressed as $[Lm^{-2}h^{-1}bar^{-1}]$). Based on this relationship, the following diagram illustrates the operating regimes for RO

and FO. For completeness, the PRO regime is also included. The relations give, for RO: $(\Delta p - \Delta \pi) > 0$, for FO: $\Delta p = 0$, and for PRO: $(\Delta p - \Delta \pi) < 0$.

Figure 2.4: Physical concepts of (a) RO, and (b) FO

Figure 2.5: Relationship between RO, FO and PRO (Adapted from Lee et al. 1981)

From the solution-diffusion model, the solute or salt flux through the membrane may be expressed as (Lonsdale et al. 1965; Baker 2004):

$$J_s = B \cdot (\Delta c_{me}) \quad (2.3)$$

where B is the salt permeability (units may be expressed as $[Lm^{-2}h^{-1}]$), and Δc_{me} is the wall concentration difference across the membrane.

With the definition of rejection (R):

$$R = 1 - \frac{c_{pe}}{c_{fe}}. \quad (2.4)$$

(c_{pe} : solute concentration in permeate and c_{fe} : solute concentration in feed)

the A and B values for a RO process may be related as follows:

$$B = \frac{(1-R)}{R} \cdot A \cdot (\Delta p - \Delta \pi) \quad (2.5)$$

For a FO process, however, because both J_w and J_s are dependent on the same net osmotic driving force, another form of B - A relation applies (Tang et al. 2010):

$$\frac{J_s}{J_w} = \frac{B}{A \cdot v \cdot R_g \cdot T} \quad (2.6)$$

The above expressions make plain a difference between FO and RO. For RO – equation (2.5) – J_w is related to a hydraulic pressure term while J_s is concentration dependent, so J_s and J_w for RO are not directly coupled. In general, when Δp varies, R would vary accordingly, such that B is justifiably not pressure dependent (Baker 2004). For FO, however – equation (2.6) – because $v \cdot R_g \cdot T$ is constant for a given operating condition, the extent of draw solute transmission J_s/J_w are coupled, and is directly related to the B/A ratio. The B/A ratio has units of pressure, and hence may also be viewed as the effective osmotic pressure due to reverse transmission of the draw solutes (Xiao et al. 2011). More discussion on the above is found in Chapter 6.

2.2.3 Concentration polarisation phenomena

As in all membrane separation processes, where parts of the constituents selectively permeate, and the rest are retained, concentration polarisation (CP) arises. For RO, it is the CP on the feed side that is of concern, and generally, it can be mitigated by favourable fluid management as it occurs external of the membrane (Fane 2005). For FO, another form of CP occurs within the support layer of the membrane, known as internal concentration polarisation (ICP) (Mehta and Loeb 1978a; McCutcheon and Elimelech 2007).

The ICP is an inherent phenomenon of FO that is due to the hindered diffusion of solutes in the membrane support layer. It acts to reduce osmotic driving force and because it occurs within the membrane support layer, it is generally not possible to be mitigated by fluid management. Two types of ICP can be distinguished depending on the membrane orientation. When the membrane active layer faces the draw solution (AL-DS), ICP occurs on the feed side, which is known as concentrative ICP, as the feed side salt concentration becomes elevated on the membrane wall. When the membrane active layer faces the feed water (AL-FW), ICP occurs on the draw side, which is known as dilutive ICP, as the draw side salt concentration becomes diluted on the membrane wall due to the permeating water flux. In general, the AL-DS orientation may derive higher flux than the AL-FW. However, the AL-DS orientation may be also more fouling prone, because foulants' entry into the membrane support layer on the feed side would have a severe plugging effect and could be more difficult to mitigate (Tang et al. 2010).

Complications arise when CP phenomena are coupled with fouling. For instance, a porous fouling layer may develop on the membrane surface, such that solutes diffusion within this fouling layer becomes severely hindered and cannot be mitigated by fluid management. The result is that an elevated solute concentration may occur on the membrane surface, and greatly diminish membrane performance (Hoek and Elimelech 2003). This phenomenon is known as cake enhanced concentration polarisation (CECP) or cake enhanced osmotic pressure. It has been demonstrated that CECP can have dominant performance diminishing effect on a FO process, especially

when this occurs in conjunction with reverse diffusion of draw solutes, culminating in an accelerated CECP mechanism (Lee et al. 2010).

It should be noted that a phenomenon of so called cake reduced concentration polarisation (CRCP) has also been reported (Kim et al. 2009). This may occur for a denser fouling cake such that the convection mechanism would be more hindered than diffusion mechanism. In this instance, the concentration on the membrane surface would be lower than what would be expected for a “normal” concentration polarisation, where convection $\sim$ diffusion. Between CECP and CRCP, CECP would have greater and adverse effect on flux performance, and is generally modelled as a limiting condition in this study. However, contrary to RO systems, where CECP and CRCP may alter salt transmission (Kim et al. 2009); this may not apply to FO systems with regard to draw solute transmission. This is because both draw solute flux and water flux are dependent on the same net osmotic driving force as noted in section 2.2.2.

For this study, a general conceptual illustration of the various concentration polarisation phenomena for an OMBR for both membrane orientations can be found in Figure 2.6.

Figure 2.6: Conceptual illustration of various concentration polarisation phenomena for an OMBR

(a) membrane orientation of 'active layer facing feed water' (AL-FW), and (b) 'active layer facing draw solution' (AL-DS).

(Adapted from Kim et al. 2009)

2.2.4 Flux behaviour of FO vis-a-vis RO

A theoretical equation to model water flux for an osmosis driven process was originally developed by Lee et al (1981) for a pressure-retarded osmosis (PRO) process (section 2.2.2). The equation is valid for a RO process when the hydraulic pressure term is greater than the osmotic pressure term ($\Delta p > \Delta \pi$), and for a FO process, the hydraulic pressure term is set to zero ($\Delta p = 0$). Later studies built upon this concept and derived modelling equations for both FO and PRO processes (McCutcheon and Elimelech 2007; Achilli et al. 2009a). However, most studies applied the analysis to well-defined feed and draw solutions, such that the effects of fouling under real operating conditions were not explicitly accounted for. For this purpose, fouling-incorporated water flux equations are developed by the author as follows.

The basis for deriving modelling equations is the resistance-in-series model (Schaefer et al. 2005):

$$J_w = \frac{\Delta \mu_{eff}}{\eta \cdot R_h} \quad (2.7)$$

where $\Delta \mu_{eff}$ is the effective chemical potential driving force, η is the dynamic viscosity of the permeate, R_h is the overall hydraulic resistance across the membrane. For RO: $\Delta \mu_{eff} = \Delta p - \text{CECP} \cdot \Delta \pi$, and for FO: $\Delta \mu_{eff} = \Delta \pi_{eff}$. The expression $1/\eta \cdot R_h$ may also be expressed as the overall water permeability (A).

Based on the osmotic pressure expressions with regard to ICP and CECP (see appendices), the following equations can be derived for both RO and FO with the membrane orientation (AL-FW) for a general case with bulk feed water osmotic pressure (π_{fe}), and bulk draw solution osmotic pressure (π_{ds}):

RO

(Derivation for the following equation can be found in Appendix A, and is developed based on the works of Lee et al (1981)):

$$J_w = A \cdot \left[\Delta p - (\pi_{fe}) \cdot e^{\left(\frac{J_w}{k_{CECP}}\right)} \right] \quad (2.8)$$

FO (AL-FW)

(Derivation for the following equation can be found in Appendix A, and is developed based on the works of Lee et al (1981)):

$$J_w = A \cdot \left[\left(\pi_{ds} + \frac{B}{A} \right) \cdot e^{-\left(\frac{J_w}{K_m}\right)} - \left(\pi_{fe} + \frac{B}{A} \right) \cdot e^{\left(\frac{J_w}{k_{CECP}}\right)} \right] \quad (2.9)$$

In addition to the common symbols, the symbols k_{CECP} and K_m refer to the mass transfer coefficients that describe CECP and ICP phenomenon, respectively. These relationships are analysed further in Chapter 7.

The term k_{CECP} may be further expressed as follows (Chong et al. 2008):

$$k_{CECP} = \frac{D_{ml} \cdot \varepsilon_{la}}{\delta_{la} \cdot \tau_{la}} \quad (2.10)$$

where D_{ml} is diffusion coefficient of the (mixed liquor) solutes within the fouling layer, and ε_{la} , δ_{la} , and τ_{la} are the porosity, thickness and tortuosity of the fouling layer,

respectively. It should be noted that the above equation may also apply to non-fouling situations by setting $\epsilon_{la} = \tau_{la} = 1$. In this instance, δ_{la} is the thickness of the boundary layer in accordance to the film model (Baker 2004).

In an analogous way, K_m is the mass transfer coefficient describing the ICP phenomenon within the membrane support layer, which may be described as (Tang et al. 2010):

$$K_m = \frac{D_{ds}}{S_{me}} = \frac{D_{ds} \cdot \epsilon_{me}}{t_{me} \cdot \tau_{me}} \quad (2.11)$$

where D_{ds} is the diffusion coefficient of the draw solute and S_{me} is a structural parameter related to the structural properties of the membrane support layer, namely: thickness (t_{me}), porosity (ϵ_{me}) and tortuosity (τ_{me}). The expression indicates that K_m may be positively enhanced by a greater diffusion coefficient (e.g. increasing temperature or using more mobile draw solute) or a smaller structural parameter (e.g. thinner and more porous support layer) (Cath et al. 2006; Gerstandt et al. 2008). Note that the term K_m is sometimes regarded as the inverse of the resistance to solute diffusion within the membrane support layer (Cath et al. 2006; McCutcheon and Elimelech 2007). However, in line with conventional mass transport literature (Cussler 1997) and membrane concentration polarisation concept (Baker 2004), the term K_m will be used consistently throughout this study.

Figure 2.7: Comparison of flux behaviour between FO and RO (Predicted by equations (2.8) and (2.9).)

General flux behaviour of FO vis-a-vis RO can be derived from equations (2.8) and (2.9), and is illustrated in Figure 2.7. Contrary to the linear RO flux curve, the FO flux curves have non-linear flux-driving force relationship inherent of a FO process. This is due to the effect of ICP expressed by the term $\exp(-J_w/K_m)$. With increasing driving (π_{ds}), the resultant increment in flux for a FO process is correspondingly offset due to the exponential effect of ICP. It can be observed that reducing the effect of ICP requires increasing K_m . From equation (2.11), K_m is inversely related to S_{me} , and hence may be enhanced with reducing thickness (t_{me}), or increasing porosity (ϵ_{me}), assuming that tortuosity (τ_{me}) remains constant.

The unique flux behaviour of FO also points out that the process may respond differently from that of the pressure-driven even under the same level of fouling. A more detailed study that discusses the role of ICP in FO and RO is provided in Appendix B. The following gives a brief discussion.

Figure 2.8 Effect of equal loss of driving force on flux in FO and RO
(Details can be found in Appendix B.)

The above diagram illustrates typical flux-driving force relations for FO and RO. Due to the curvature of the graphs, it can be observed that at the same initial flux ($J_{w,0}$) and under equal loss of driving force, the flux decline in FO is consistently smaller than that in RO, regardless of the nature of the fouling cake that is occurring. For FO, the effect of fouling and flux decline is to reduce ICP due to reduced flux. This provides an increase in the effective driving force that partially compensates for the fouling resistance. This does not apply for RO. The slower flux decline commonly observed in FO experiments therefore did *not* necessarily prove lesser fouling cake compaction as compared to the pressure driven RO (Lay et al. 2010a). However, FO is vulnerable to the transmission of the draw solutes, which elevates feed-side osmotic pressure and may exacerbate the loss in driving force via the CECP effect (Lee et al. 2010). It is evident that the transmission of draw solutes (reverse salt transport) can have significant effect on FO performance, and has to be minimised (Chapter 6).

The unique flux behaviour of FO systems points to the need for more sophisticated techniques for characterisation of fouling and concentration polarisation phenomena. One such technique that should be explored further is electrochemical impedance spectroscopy (EIS). Preliminary work has demonstrated that the EIS could provide high resolution and non-invasive means of in-situ analysis. Further discussion is provided in Appendix C.

2.3 Membrane fouling in MBR system

Fouling refers to the general phenomenon of loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores (Koros et al. 1996). Fouling encompasses inorganic scaling, organic fouling, colloidal fouling as well as biofouling. Fouling has always been a central issue in all membrane processes used for water and used water applications due to its significance to the operation and economics of the process. The extent of fouling determines the sustainable flux that is achievable under real operation (Belfort 1984).

Fouling is all the more significant for a MBR system, because of the direct interactions between the membrane and the biological components. Fouling in MBR systems is complex, because it is concomitantly bio-polymeric, as well as colloidal and particulate in nature (Judd 2006; Le-Clech et al. 2006; Meng et al. 2009; Tang et al. 2011). In an OMBR system, fouling could be more complex, due to the added impact of elevated salinity. This section briefly introduces general fouling concepts that would be applicable to MBR systems. A later section discusses issues that would be more specific to OMBR systems.

2.3.1 Influencing factors

Multiple inter-relationships among various influencing factors on fouling exist in a MBR system, and point to the complexity of the issue. However, current literature identifies three main groups of influencing factors (Judd 2006; Le-Clech et al. 2006; Meng et al. 2009; Tang et al. 2011):

- Membrane properties
- Biomass characteristics
- Operating conditions

The influencing factors are mutually engaged in dynamic interaction. Of direct impact on MBR fouling are the factors concerning biomass characteristics and fluid management. Other factors play indirect roles, though not necessarily of lesser importance. In general, membrane properties have more significant effects on fouling for shorter duration experiments rather than longer term studies. The reason is that due to the high fouling tendency of bioreactor mixed liquor, membrane surfaces typically get conditioned for fouling within the first few hours of operation. Once this occurs, foulant-foulant interactions may be more dominant compared to membrane-foulant interactions. The operating conditions can influence fouling physically by impacting on fluid management and/or biochemically by impacting on biomass characteristics. Current literature views soluble microbial products (SMP) and bound extracellular polymeric substances (EPS) as the more significant fouling parameters. The following tables give overview of the various influencing factors on fouling that are generally relevant for MBR systems, and are formulated based on existing literature (Judd 2006; Le-Clech et al. 2006; Meng et al. 2009; Tang et al. 2011). Applicability to OMBR is discussed where appropriate.

Table 2.1: Membrane properties as factors of influence on MBR fouling
(Judd 2006; Le-Clech et al. 2006; Meng et al. 2009; Tang et al. 2011).

Factor	Increase in factor	Effects
Hydrophilicity	decreases fouling	Hydrophilic surface reduces hydrophobic interactions between foulants and membrane.
Surface roughness	increases fouling	Filling-in-points are more susceptible to foulant deposition.
Pore size	increases fouling	Smaller pore size may result in surface cake fouling that is more reversible than internal pore plugging.
Narrow pore size distribution	decreases fouling	Membranes with higher isoporosity are less prone to pore fouling.
Membrane configuration	depends on fluid management	Hollow fibre modules typically have large surface area per unit volume and hence more compact design. Hollow fibre modules may also require lesser aeration and be back-flushed, but may entail higher cost for module manufacture than flat sheet. In some applications, however, hollow fibre modules are known to be vulnerable to various operational and integrity challenges. Hollow fibre bundles may also be prone to inter-fibre blocking.

Table 2.2: Biomass characteristics as factors of influence on MBR fouling
(Judd 2006; Le-Clech et al. 2006; Meng et al. 2009; Tang et al. 2011).

Factor	Increase in factor	Effects
Feed characteristics	depends on constituents	Type of carbon source plays a role, e.g.: glucose may foul more than sodium acetate; synthetic used water may foul more than real used water. Soluble and colloidal fractions are more fouling significant than particulates.
Floc characteristics	depends on characteristics	MBR floc sizes may be bimodal (5-20 μm and 240 μm). Not expected to block pores, but play a role in fouling cake. Hydrophobic/ surface charge of flocs link fouling to EPS and filamentous growth.
Filamentous bacteria	increases fouling	Filamentous growth results in foaming/ bulking sludge, and causes higher EPS level, higher viscosity, lower zeta potential, more irregular flocs and higher hydrophobicity.
Mixed Liquor Suspended Solids (MLSS)	depends on other biomass characteristics	No clear correlation between MLSS and other fouling characteristics. No significant effect between 8 and 12 g L^{-1} . MLSS reduce oxygen transfer and increase viscosity.
Viscosity	(generally) increases fouling	Increased viscosity dampens fibers movement, reduces oxygen transfer and back diffusion. But if shear rate can be maintained, greater shear stress generated may have mitigating effect on fouling.
Bound Extracellular Polymeric Substances (Bound EPS)	(generally) increases fouling	Bound EPS greatly affects other biomass characteristics and gives the 3-D matrix of biofouling cake, of which its structure (porosity) has great effect on fouling.
Soluble Microbial Products (SMP)	(more generally) increases fouling	SMP may be equated to soluble EPS, and is reportedly the most important fouling parameter for conventional MBRs. SMP may adsorb on to membrane surface, block pores, form gel and interact with other foulants. Polysaccharide, protein and colloidal fractions of SMP have all been correlated to MBR fouling.

Table 2.3: Operating conditions as factors of influence on MBR fouling (Judd 2006; Le-Clech et al. 2006; Meng et al. 2009; Tang et al. 2011).

Factor	Increase in factor	Effects
Temperature	decreases fouling	Decreasing temperature increases viscosity, decreases particle back-transport, intensifies de-flocculation, releases more EPS, and slows biodegradation. Higher temperature is favourable for mass transport.
Aeration	optimum exists	Aeration generally relieves fouling with surface shear induced by two-phase gas/liquid flow. However, excessive aeration may damage floc structure, reduce floc size and release EPS. Energy requirement also needs to be considered. Entrapment of air bubbles within membrane structures may also cause performance loss.
Solids retention time (SRT)	optimum exists	SRT is typically the master design and operating variable for bioprocesses. Benefits of long SRT include lower sludge production, allow for slow-growing nitrification, and removal of slow-to-degrade organics. Too long SRT result in high MLSS and increased EPS production due to higher level of endogenous metabolism and cell lysis. Practical SRT may be 10-30 d.
Hydraulic retention time (HRT)	optimum exists	Decreasing HRT may cause unsteady state conditions and increasing organic loading which aggravate fouling. Long HRT is not economically favourable. Typical HRT < 1d.
Food-to-microorganism ratio (F/M)	increases fouling	Increasing F/M may cause increase in EPS concentration, MLSS concentration, sludge viscosity and excessive growth of filamentous bacteria.
Operating flux (J_w)	increases fouling	Flux has exponential relation with concentration polarisation, and hence has significant effects on fouling and performance diminishment (especially with regard to CECP). Critical/ sustainable flux is system specific, and depends on membrane properties, hydrodynamics and biomass characteristics.

2.3.2 Fouling mechanisms

A presentation of the intricate fouling road map in MBR systems is given in Figure 2.9. Aspects that may be relevant to OMBR are highlighted. These aspects include coupled effects with concentration polarisation phenomena, influence on draw solute transmission and pore-blocking or -plugging mechanisms that may be significant for AL-DS membrane orientation. More discussion will be given in subsequent chapters.

Figure 2.9: Fouling road map in MBR systems (Le-Clech et al. 2006; Zhang et al. 2006b)

The fouling road map presented in the above figure may be used to explain the three main stages of fouling observed in MBR systems.

The first stage, which may also be referred as initial or conditioning fouling, occurs within the first few hours of operation. A conditioning film may form onto the membrane with regard to initial pore blocking or plugging, and passive adsorption of colloids and solutes before any deposition mechanism sets in. The second stage, or steady fouling, may be viewed as the steady operating zone where fouling (cake formation, biofilm growth and pore blocking) gradually occurs. When a critical condition is reached, such that local flux may exceed critical flux, severe fouling may take place with significant drop in membrane performance. For conventional pressure-driven MBRs, this third stage of fouling gives rise to a “jump” in the transmembrane pressure difference (TMP), and is hence also known as the TMP jump. A few mechanisms have been postulated to explain such a phenomenon, and an overview can be found in Table 2.4. Applicability to OMBR is discussed where appropriate.

Table 2.4: Postulated fouling mechanisms to explain sudden drop in performance for MBR systems

(Judd 2006; Le-Clech et al. 2006; Meng et al. 2009; Tang et al. 2011).

Mechanism	Description	Reference
Inhomogeneous fouling (area loss) model	Degree of fouling varies spatially along the membrane and causes flux redistribution with high fluxes shifted to the less fouled areas. Rapid fouling occurs as critical flux of foulants is exceeded.	Cho and Fane (2002)
Inhomogeneous fouling (pore loss/ narrowing) model	Progressive decrease of open pore number causes increase of local flux exceeding critical flux, and hence abrupt increase in TMP. This model focuses on microscopic scale, and is analogous to the above "area loss" model, which focuses on macroscopic scale. For OMBR, pore plugging may have significant diminishing effect on performance for AL-DS membrane orientation.	Ognier et al. (2004)
Critical suction pressure model	As critical suction pressure is reached, model latex foulants coalesce or collapse, which causes transition in the filtration resistance. Biofilms and foulants in MBRs are likely to possess similar tendency.	Chang et al. (2006)
Percolation theory	This model predicts that foulants deposition and compression cause loss of porosity in the fouling cake. At a critical condition, the fouling cake loses connectivity, and results in TMP jump. The model has physical basis, but does not reflect the gradual kinetics of typical TMP transient for conventional pressure-driven MBRs.	Hermanowicz (2004)
Inhomogeneous fiber bundle model	This model relates the standard deviation of fluxes of individual fibers to TMP increase, which may arise from flow maldistribution within the bundle leading to local blockages between fibers, and aggravated fouling.	Yeo et al. (2006)
Cake enhanced osmotic pressure model	This newly postulated mechanism demonstrates that the osmotic pressure of retained macrosolutes in conventional MBRs can be greatly increased due to its exponential relation to fouling cake formation, and gives a good fit to the TMP jump phenomenon. This fouling mechanism is expected to give significant effect in OMBR systems due to salt retention and reverse salt transport from draw solution.	Fane (2009)

2.4 Issues of relevance to OMBR

Due to salt retention and reverse salt transport from draw solution, the salt concentration in an OMBR system can be appreciably greater than its influent concentration. The resulting elevated salt condition can impact on physicochemical, microbiological and membrane performance of the system, which in turn are mutually engaged in a complex and dynamic interaction. In order to adequately investigate issues of relevance to OMBR require long term studies, which are currently in short supply in the literature. Several OMBR studies have conducted short term experiments with FO in side stream configuration, and have provided information on the technology (Cornelissen et al. 2008; Qin et al. 2009). However, results derived from short term studies may not be adequate for a holistic evaluation. A longer term study was conducted by (Achilli et al. 2009b) using a submerged OMBR over an experimental duration of about a month. However, fundamental issues such as flux behaviour and effects associated with the concentrative mixed liquor environment need investigation. Further research questions remain, and factors that may affect OMBR performance for application are largely unknown. Furthermore, as the OMBR is a concentration-driven process, draw solute transmission would be continuously occurring as long as there is a concentration difference between the feed liquid and the draw solution. While modelling indicates that stable-state operation may be attainable (Xiao et al. 2011), long term experimental study is required for confirmation. The feasibility of stable-state operation is significant for application.

The above underscores that long term research studies are necessary in order to address research gaps and further develop the technology.

NOTE: A more detailed review of the potential effects of raised salinity on the performance of high retention MBRs (including OMBR) can be found in:

Lay, W. C. L., Y. Liu and A. G. Fane (2010). Impacts of salinity on the performance of high retention membrane bioreactors for water reclamation: A review. *Water Research* 44(1): 21-40.

2.4.1 Concentration factor and salt accumulation

The concentration factor (CF) describes salt accumulation in an OMBR. The phenomenon is complex and involves the volumetric concentration of the influent and reverse transmission of the draw solutes. For a preliminary analysis, an ideal condition for the OMBR with complete retention and no reverse draw solute transmission across the membrane ($J_s = 0$) is discussed. In this instance, CF simplifies to the ratio SRT/HRT at stable-state operation as follows (Lay et al. 2010b):

$$CF = \frac{\pi_{ml}}{\pi_{in}} = \frac{c_{ml}}{c_{in}} = \frac{Q_{in}}{Q_w} = \frac{1}{(1 - \phi)} = \frac{SRT}{HRT} \quad (2.12)$$

For illustration, Table 2.5 shows the possible accumulation of some selected chemical constituents typical in domestic used water under various values of recovery (ϕ) and CF of the mixed liquor in an OMBR for the condition $J_s = 0$. The table is computed based on reference concentrations adapted from the literature for untreated medium-strength domestic used water (Tchobanoglous et al. 2004). It is to be pointed out that while this table provides useful reference for discussion, the presented concentrations could vary considerably from one source to the other. Furthermore, for OMBR systems with $SRT \geq 10$ d and $HRT \leq 1$ d, CF can be significantly large, and can result in a corresponding significant salt elevation in the mixed liquor. For real application with $J_s > 0$, the salt concentration can be further elevated. High levels of salt and the corresponding osmotic pressure could present an operational limit to the OMBR, which relies on osmotic pressure driving force. The optimum salt level and concentration factor will be a trade-off in terms of driving force and applied SRT and HRT.

Table 2.5: Possible accumulation of retained constituents in an OMBR system
(Assumption: $J_s = 0$)

Recovery CF = SRT/HRT	H	^a Influent concentration	0.5 2	0.75 4	0.8 5	0.9 10	0.95 20	0.967 30	0.975 40	0.99 100
Total dissolved solids										
^b TDS	[mgL ⁻¹]	500	1,000	2,000	2,500	5,000	10,000	15,000	20,000	50,000
Anions										
^c HCO ₃	[mgL ⁻¹]	100	200	400	500	1,000	2,000	3,000	4,000	10,000
^c CO ₃	[mgL ⁻¹]	10	20	40	50	100	200	300	400	1,000
Cl	[mgL ⁻¹]	50	100	200	250	500	1,000	1,500	2,000	5,000
SO ₄	[mgL ⁻¹]	30	60	120	150	300	600	900	1,200	3,000
Cations										
Ca	[mgL ⁻¹]	16	32	64	80	160	320	480	640	1,600
Mg	[mgL ⁻¹]	10	20	40	50	100	200	300	400	1,000
K	[mgL ⁻¹]	15	30	60	75	150	300	450	600	1,500
Na	[mgL ⁻¹]	70	140	280	350	700	1,400	2,100	2,800	7,000
Other constituents										
SiO ₂	[mgL ⁻¹]	10	20	40	50	100	200	300	400	1,000
^d COD	[mgL ⁻¹]	430	86	172	215	430	860	1,290	1,720	4,300

^a Medium strength untreated domestic used water (Tchobanoglous et al. (2004)).

^b TDS comprise fixed and volatile dissolved solids.

^c The actual concentration of HCO₃ and CO₃ ions would depend on the carbonate equilibrium.

^d assuming up to 10% of influent biodegradable COD is converted to non-readily degradable SMP and accumulates in the system.

A point to note is that contrary to conventional MBRs whereby SRT and HRT are uncoupled, SRT and HRT are integrally related via CF for the OMBR. And HRT is dependent on flux, which varies in accordance to the osmotic driving force between the draw solution and the mixed liquor. The implication here is that at a given CF, the SRT has to be controlled in dependence to the HRT, and vice versa. When the CF is low and at a given HRT, the resultant shorter SRT may not be sufficient to allow for adequate biological activities. Conversely, when the SRT is set to be longer, a commensurate longer HRT is necessary at the same CF, implying larger system volume and hence greater capital costs. The alternative would be to increase CF to allow for longer SRT and shorter HRT. However, there may be an upper limit to CF, because increasing the CF increases the salt concentration in the mixed liquor due to the retention effect of the high rejection FO membrane and the reverse salt transport from the draw solution. The point here is that SRT and HRT are related to the recovery (ϕ), which is a parameter of significant practical importance to membrane systems (Belfort 1984). On one hand, high recovery is desired for application. On the

other hand, high recovery inevitably results in large CF, and could have detrimental effects on the performance of an OMBR.

From the foregoing discussion, it is evident that salt accumulation is a systemic issue of significant practical relevance to the development of the OMBR technology.

2.4.2 Issues associated with flux, micro-pollutant removal and fouling

The first issue is that increasing salt concentration impacts on the flux performance of an OMBR system regardless of the state of membrane fouling. This is because a higher salt concentration of the mixed liquor will increase the feed side osmotic pressure as predicted by the Van't Hoff equation (2.1). Consequently, a larger driving force ($\Delta\pi_{\text{eff}} \uparrow$) is necessary in order to operate the FO process under an elevated salt environment. Furthermore, fouling may be aggravated by the elevated salinity (see below). In this instance, the fouling cake layer may further intensify performance reducing effect due to a CECF mechanism (section 2.2.3). This means that the membrane flux may reduce or a higher draw osmotic pressure may be necessary to maintain productivity. Therefore, a saline environment may imply that lower sustainable fluxes are attainable compared to non-saline environment. Theoretically, water production may be maintained or increased by increasing the driving force with a more concentrated draw solution for increasing salinity of the mixed liquor. However, sensitive and precise control to maintain flux of an OMBR by using a variable draw solution concentration may be difficult to implement. Furthermore, high draw solution concentration may run the risk of “osmotic deswelling” of membranes (Mehta and Loeb 1978b). In addition, the unique effect of internal concentration polarisation (ICP) on the flux performance of an OMBR complicates matters. A more concentrated draw solution would intensify ICP that results in two opposing effects. On one hand, ICP leads to smaller driving force utilisation. On the other hand, ICP provides a self-compensating effect that stabilises flux (section 2.2.4). Flux is a very significant aspect to the viability of the technology, because it relates to productivity (Cardew and Le 1999). Similar to the issue of salt accumulation, there is a deficiency of, and hence a need for, long term OMBR flux data. Assessment of long term OMBR flux performance is therefore another systemic issue that needs to be addressed.

The second issue is with regard to removal of organic micro-pollutants and the associated effects on water quality and the biological process. One underlying concept for OMBR is that the tight FO membrane will be able to more effectively retain persistent and low molecular weight organic micro-pollutants, and thereby facilitate their biodegradation and produce good product water quality. (Cartinella et al. 2006) has shown that FO could achieve high hormone removal using short-term batch experiments. However, longer-term study within an OMBR setup and under an elevated salt environment will be relevant. Further investigation with other types of organic micro-pollutant (e.g. pharmaceuticals) also need to be considered. In addition, possible effects on the biological process due to the elevated salinity also require research. It should be noted that the majority of microorganisms involved in conventional used water treatment, such as the activated sludge system, are non-halophilic. These microorganisms do not possess the mechanisms to cope with the osmotic stress exerted by an elevated salt environment (Woolard and Irvine 1995; Lefebvre and Moletta 2006). Consequently, increasing salinity will affect the microbial community and its biokinetics in a MBR system. Acclimation and introduction of halotolerant or halophilic microorganisms may therefore be necessary for the biological process of an OMBR due to the elevated mixed liquor salinity. In general, carbon removal may not be an issue for an acclimated biological process for higher salt range even beyond 50 gL^{-1} , but nutrients removal may be significantly impaired. Furthermore, it has been reported that higher salt levels may cause both soluble microbial products (SMP) and extracellular polymeric substances (EPS) in a MBR system to increase, and thereby may also have aggravating effects on fouling (Reid et al. 2006).

Finally, the third issue is the possible relation between salinity and membrane fouling. It has been reported that increased salinity may aggravate fouling and require more cleaning for a membrane process (Tam et al. 2006). In general, increasing salt concentration yields unfavourable physicochemical parameters for oxygen transfer, density, turbidity, viscosity, salt precipitation, solute interaction and colloid chemistry. Due to retention by FO membrane, concentration of potential scalants present in the feed water will necessarily be raised. Under the influence of concentration polarisation, this effect will be further aggravated, as the salt

concentration at the membrane surface will be considerably higher than in the bulk feed water. Consequently, supersaturation condition may arise and lead to scaling. Concomitantly, an elevated salt environment can also aggravate colloidal fouling by increasing the ionic strength of the water. This can be understood from the Deryagin-Landau-Verwey-Overbeek (DLVO) theory, which assumes the interaction between particles is balanced by the van der Waals' attractive force and the electrostatic repulsive force, and can be characterised by the Debye length (Gregory 2006). With increasing salt concentration, the Debye length will therefore be reduced. This effect is known as double layer compression, and the particles become destabilised as they come closer towards one another resulting in agglomeration. In this way, increasing salt concentration can aggravate fouling on membrane with the formation of a more densely packed cake layer (Faibish et al. 1998). This effect has been referred to as the salinity-promoted fouling in the literature (Reid et al. 2006), and has also been observed in practical studies treating saline sewage (Tam et al. 2006). Furthermore, higher salt concentration may aggravate fouling and reduce water permeability due to complex foulants' interactions based on colloidal and scaling chemistry (Sheikholeslami 2003; Tang et al. 2011). However, for an OMBR, fouling relations are complicated, because the elevated salt level is determined by the CF, and this in turn is linked to the other process parameters as discussed above (SRT and HRT), in addition to the reverse transmission of draw solutes. The effects associated with membrane fouling under an elevated salt environment are a complex area that needs research.

2.4.3 Fouling mitigation for OMBR

The significance of fouling to the OMBR has already been discussed above. The following gives a discussion on fouling mitigation for the OMBR.

In the first instance, it has been hypothesised that the OMBR may be a process with inherently low membrane fouling tendency, as FO does not entail the use of hydraulic pressure (Cath et al. 2006). However, the role of pressure, per se, rather than flux is a moot point at this stage (Lay et al. 2010a).

Fouling may be mitigated either by removing the foulants on the membrane or by optimising system parameters. While elaborate pretreatment methods are practised for dense membrane processes (Tanninen et al. 2005), these would not be applicable to MBR application. More over elementary sedimentation and / or chemical dosage of coagulants, flocculants or adsorbents to be discussed later, the choice of pretreatment for MBR systems is plainly limited. This means that no more than conventional fouling mitigation methods that are used in conventional MBR systems could be applied to OMBR systems.

Physical and chemical cleanings may be used to remove foulants from the membrane. Current physical techniques include air scouring, back washing, relaxation, but these would need to be optimised for the salt accumulating OMBR systems. Furthermore, specific cleaning chemicals and protocols would need to be developed. In this regard, osmotic backwash may be effective for OMBR systems (Achilli et al. 2009b). Osmotic backwash involves temporarily replacing the draw solution with low salinity water (e.g. Milli-Q water) so that flow of water through the membrane is reversed.

It is also possible to optimise system parameters by improving anti-fouling properties of membrane and optimising operating parameters. The former would involve membrane modification by increasing its hydrophilicity or by precoating it with substances that would limit the contact between foulants and membrane. The latter would include optimising aeration, hydrodynamics, SRT and operating at sustainable flux to avoid excessive fouling. It should be further noted that the choice of flux is

important, due to its exponential influence on concentration polarisation. The effect on fouling of operating at a flux closer to $10 \text{ Lm}^{-2}\text{h}^{-1}$ rather than 20 to $30 \text{ Lm}^{-2}\text{h}^{-1}$ (more typical of conventional MBR systems) would be very significant. For example, $\text{CP} = 2$ at $10 \text{ Lm}^{-2}\text{h}^{-1}$ becomes $\text{CP} = 8$ at $30 \text{ Lm}^{-2}\text{h}^{-1}$. To date, the reported fluxes of OMBRs have been around or below $10 \text{ Lm}^{-2}\text{h}^{-1}$ (Cornelissen et al. 2008; Achilli et al. 2009b), potentially providing fouling relief. The fact that these OMBRs tend to operate at lower fluxes is compensated for by the improved permeate quality.

The third option is to use strategic chemical methods that exploit the greater tendency of precipitation and coagulation in an elevated salt environment for process enhancement. The strategy is to chemically modify the characteristics of the mixed liquor to alleviate fouling. There has been a number of studies devoted to this area, and methods that have been successfully demonstrated include the addition of coagulants or flocculants such as ferric chloride (FeCl_3) or aluminium sulphate (alum), and/or adsorbent agents such as powdered activated carbon (PAC) (Itonaga et al. 2004; Wickramasinghe et al. 2004; Ng et al. 2006). The benefits may include better biodegradation of toxic compounds in the biological system in addition to ameliorating membrane fouling (Lesage et al. 2005), and concomitant removal of phosphorus, which is both a nutrient and a potential foulant (Song et al. 2008). However, chemical methods generally increase operating costs and result in chemical waste sludge that needs disposal, and therefore need careful consideration prior to implementation.

2.4.4 Concluding remarks

The foregoing literature review and preliminary analysis reveal research gaps and shed light on issues of relevance to OMBR development. Long term studies are necessary in order to address the research gaps and further develop the technology. The following presents research issues of priority for the OMBR, which this thesis seeks to address (parentheses indicate chapter of discussion):

- Long-term investigation on feasibility of stable-state operation for an OMBR. Investigation is needed to provide observations on long term water production and mixed liquor concentration, as well as fouling issues associated with the concentrative environment (Chapter 4).
- Research on micro-pollutant (e.g. pharmaceutical) removal and this in relation to effects on water quality and the biological process (Chapter 5).
- Systemic analysis on factors affecting salt accumulation in the OMBR (Chapter 6).
- Holistic evaluation of OMBR flux performance in relation to factors of relevance such as internal concentration polarisation and fouling, and assessment on potential of the OMBR technology for water reclamation (Chapter 7).

Chapter 3. General materials and methodologies

3.1 Introduction

The followings give a description of the general materials and methods that are applied throughout the thesis. Foundation work such as membrane characterisation is elaborated. Additional descriptions are given in subsequent chapters to address specific experimental and modelling issues, where necessary.

3.2 The lab-scale OMBR system

The OMBR system was supplied by AR Engineering (Singapore) and had a dual-track design that allowed experimentation under two similar or different operating conditions in submerged configuration (Figure 3.1). Each track comprised an aerated bioreactor with a set of monitoring and control systems, and a draw solution circulation loop. On the feed side, constant bioreactor volume was maintained by means of level control linked to a big feed tank stored in a fridge cooled at 4 °C. The feed tank was topped-up regularly to ensure that the feed line did not run dry. Air was supplied by compressed air through air diffusers located below the membrane modules. The aeration intensity was controlled, such that the aerobic environment was generally maintained in the bioreactors with $DO > 1 \text{ mgL}^{-1}$, and the corresponding specific aeration demand with respect to membrane area (SAD_m) was generally $> 1 \text{ m}^3_{\text{air}}\text{m}^{-2}\text{h}^{-1}$. The relatively high specific aeration demand may be considered typical for submerged flat-sheet systems, which may have SAD_m values that range between 0.6 and $1.5 \text{ m}^3_{\text{air}}\text{m}^{-2}\text{h}^{-1}$ (Judd 2006). The salt accumulation effect was monitored by a conductivity probe.

On the draw side, constant draw solution could be set and maintained by conductivity control linked to a concentrated draw reservoir. The product water was collected as overflow from the draw tank into the product tank and was measured with an ultrasound level sensor. The actual water flux through the membrane was then derived based on mass balance to account for the amount of concentrated draw solution dosed into the system. Independently, water flux was verified by physically checking against actual volume in the feed tank. Parameters such as conductivity and pH were also independently checked to ensure reliability of the reported results.

A system control software (Omron CX-Supervisor, Japan) was installed for system automation and data acquisition. Daily averaging was applied to minimise data noise.

(a) Photograph of the OMBR system

(b) Schematic diagram of the OMBR system

Figure 3.1: The submerged integrated OMBR system

3.3 Membranes

3.3.1 Thin-film composite (TFC) FO membrane

The first type was a novel thin-film composite (TFC) hollow fibre membrane with polyethersulfone UF-like substrate and polyamide-based RO-like skin that has shown promise for FO application (Wang et al. 2010a).

Figure 3.2: Scanning electron microscope (SEM) images of the TFC membrane (Wang et al. 2010a)

The morphology of the TFC membrane can be observed in Figure 3.2. Unlike conventional TFC membranes used for RO which would have a thick and dense support layer to withstand mechanical stress from application of hydraulic pressure, the novel TFC membranes used in this study are relatively thin and have macro-voids within the membrane support layer. The TFC membrane would be therefore favourable for FO application, as the mass transfer coefficient (K_m) of the membrane support layer would be positively enhanced by its slim and porous structure as noted in section 0. The transport parameters of the TFC membrane at ambient temperature are generally such that A_{me} : $1 - 3 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, $B_{me}/A_{me} < 0.1 \text{ bar}$, and K_m : $5 - 10 \text{ Lm}^{-2}\text{h}^{-1}$.

The active layer of the TFC membrane is found on the lumen of the membrane. For the OMBR experiments, draw solution was conveyed through the fibre lumen and the

mixed liquor was located on the shell side of the module. The membrane orientation adopted for the TFC membrane therefore was that of active layer facing draw solution (AL-DS). As such, the TFC membrane would have its support layer exposed to the range of foulants present in the mixed liquor. Compounded with factors due to the ridge and valley structure of the membrane, high flux, potential compaction of the support layer, air bubbles entrapment within the support layer, and integrity challenges inherent of hollow fibre module, the TFC membrane would be vulnerable to the effects of fouling.

3.3.2 Cellulose-triacetate (CTA) FO membrane

The second type of FO membrane used in this study was a flat sheet membrane, known as the cartridge type, supplied by Hydration Technology Innovations (HTI). The membrane was woven and made of cellulose triacetate material embedded about polyester mesh (CTA). Similar CTA membranes have already been used in a number of studies, and are currently regarded as the best available membrane for FO application (Cath et al. 2006; Achilli et al. 2009b).

The morphology of the CTA membrane can be observed in Figure 3.3. Compared to conventional RO membranes, this type of FO membrane is unique, due to its relatively thinness and lack of fabric support layer.

Figure 3.3 (a): The active layer shows a dense membrane with no pores observable.

Figure 3.3 (b): The support layer appears to be dense, but has occasional openings.

Figure 3.3 (c): The thickness of the membrane can be gauged around 50 μm based on the scale bar of the image. The mesh support can also be observed to be embedded within the membrane from the cross-sectional view of the membrane.

Figure 3.3 (d): Orderly display of openings along the edges of the underneath mesh can be made visible on the membrane support layer after immersion in ethanol. It should be noted that the active layer, however, did not provide such an observation after treatment with ethanol (results not shown). The unique morphology of the CTA membrane could have played a role in the similar and relatively favourable fouling behaviour observed between the two orientations for this membrane (Chapter 7).

The SEM analyses were conducted at the Environment laboratory of NTU.
Sample preparation protocol prior to SEM examination: Overnight immersion in MilliQ-water (except for (d), which was treated with ethanol), followed by freeze-drying and gold-coating.

Figure 3.3: Scanning electron microscope (SEM) images of the CTA membrane

(a) Active layer; (b) Support layer;

(c) Cross-section; (d) Support layer after treatment with ethanol.

The contact angle measurements were conducted with a goniometer (OCA model, Dataphysics, Germany) based on the sessile-drop method.

Figure 3.4: Contact angle images of the CTA membrane

(a): Active Layer; (b) Support Layer

The AFM analysis was performed at the Central Environmental Science and Engineering Laboratory (CESEL) of NTU

Figure 3.5: Atomic force microscopy (AFM) images of the CTA membrane

(a): Active Layer; (b) Support Layer

The membrane is hydrophilic ($< 90^\circ$) with measured contact angles around 70° for both membrane orientations (Figure 3.4). However, the CTA membrane may be considered less hydrophilic compared to a number of conventional polyamide RO membranes (Tang et al. 2009). Analyses from atomic force microscopy (AFM) indicate surface smoothness of the CTA membrane. Figure 3.5 (a): The root-mean-squared roughness (R_q) of the membrane active layer would be in the order of 20 – 30 nm, which would be considered smooth compared to most RO membranes (Tang et al. 2009). The peak-to-valley roughness value (R_{pv}) of the CTA membrane would be relatively large (≥ 100 nm), which may be indication of the undulating membrane structure due to presence of the mesh.

Figure 3.5 (b): Possibly due to openings on the support layer coupled with the undulating effect of the mesh, this side of the membrane gave greater roughness values. However, it is worthwhile noting that R_q of the CTA membrane for this orientation (≤ 60 nm) would still be considered smooth compared to typical fully aromatic uncoated polyamide RO membranes (~ 100 nm) (Tang et al. 2009). The relatively hydrophilic and smooth properties of the CTA membrane would have beneficial effects with regard to fouling (section 2.3).

The transport parameters of the CTA membrane at ambient temperature are generally A_{me} : $0.5 - 0.7 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, B_{me}/A_{me} : $0.8 - 2.5 \text{ bar}$, and K_m : $3 - 4 \text{ Lm}^{-2}\text{h}^{-1}$ (see also Chapter 4). The CTA membrane was applied in the bioreactor designated as R2. Prior to use, freshly cut CTA membrane coupons were stored in Milli-Q water at 4°C overnight. Both orientations: AL-FW and AL-DS were studied for this membrane, and are annotated accordingly (Table 3.2). It should be noted that the CTA membranes are vulnerable to degradation mechanisms both chemically and biologically due to limitations of the cellulose triacetate material (Baker 2004). Further discussion on membrane degradation can be found in Chapter 4.

3.4 General experimental methods

The OMBR experiments were conducted at ambient temperature of the laboratory, which generally was between 20°C and 22°C. The pH of the mixed liquor for both bioreactors varied within the range 6 – 8. Aerobic environment was maintained in the bioreactors, such that typically $DO > 1 \text{ mgL}^{-1}$. However, greater variation in operating conditions due to accidental circumstances was occasionally encountered, and is noted accordingly. Seed sludge for the OMBR was obtained from a local water reclamation plant. For each experiment run, a measured amount of mixed liquor (Q_w) was wasted from the respective bioreactor during weekdays but not on weekends. Consequently, some kind of “zig-zag” variation in both mixed liquor concentration and flux could be observed for all experimental runs (Xiao et al. 2011). Sludge wasting was performed consistently within each run, but varied between the different experiment runs. From derived flux and known membrane area (A_m), the product flow (Q) could be derived. The sum of Q and Q_w gave the influent flow (Q_{in}). The mixed liquor concentration for each experimental run was different and varied according to the volumetric concentration ratio and draw solute transmission for a given run (Chapter 6). Based on known Q_{in} and Q , recovery (ϕ) for each run could be derived as follows.

$$\phi = \frac{Q}{Q_{in}} \quad (3.1)$$

Two types of synthetic feed water were used in the studies (Table 3.1). The feed water was to simulate domestic sewage, and had a derived COD: N: P ratio of 100: 6: 1. While the chemical composition of both feed waters was proportionally the same, a lower concentration with regard to total organic carbon (TOC) was used in the experiment runs TFC-I and CTA-I (TOC = 200 ppm). All subsequent runs were conducted with a higher concentration feed water with TOC = 400 ppm.

Table 3.1: Composition of the synthetic feed water

	(a)	(b)
	[mg · kg ⁻¹ _{Tap Water}]	[mg · kg ⁻¹ _{Tap Water}]
Glucose	200	400
Sodium Acetate	200	400
Meat Extract	50	100
Peptone	50	100
KH ₂ PO ₄	25	50
MgSO ₄ · 7H ₂ O	70	140
FeCl ₃	20	40
NH ₄ Cl	70	140
Total organic carbon (TOC)	200	400

(a): Experiment runs: TFC-I and CTA-I

(b): Experiment runs: TFC-II to TFC-III, and CTA-II to CTA-VI

The draw solution used throughout the studies was sodium chloride (NaCl) solution. The choice of NaCl was that it is readily available, safe to use, and satisfies the required criteria: high solubility and osmotic pressure efficiency, chemically compatible, easy to regenerate and no risk of scaling (Cath et al. 2006; Achilli et al. 2009b).

An overview of the experimental conditions for all experiment runs can be found in Table 3.2. A fresh set of FO membranes was used for each experiment run.

Table 3.2: Overview of experimental conditions

Experiment run (membrane)	Influent TOC	Draw solution, bulk NaCl concentration	Membrane orientation	Membrane Area	Solids retention time	Bioreactor volume	Results and discussion in chapter(s)
	[ppm]	c_{ds} [mol·kg ⁻¹]	[-]	A_m [cm ²]	SRT [d]	V [L]	[-]
TFC-I	200	0.5	AL-DS	380	20	4	6
TFC-II	400	0.5	AL-DS	260	10	4	6 and 7
TFC-III	400	0.25	AL-DS	305	10	4	7
CTA-I	200	0.5	AL-FW	372	20	4	4, 5 and 6
CTA-II	400	0.5	AL-FW	372	10	4	6
CTA-III	400	0.5	AL-FW	744	10	5	7
CTA-IV	400	1.0	AL-FW	744	10	5	7
CTA-V	400	1.0	AL-FW	744	20	5	7
CTA-VI	400	1.0	AL-DS	744	20	5	7

3.5 General analytical methods

Reverse osmosis (RO) experiments were performed to obtain water permeability (A) and salt permeability (B) values of both virgin and used membranes. The A value of a FO membrane was determined from the stabilised pure-water flux. The B value was determined by relating it to the rejection (R) of NaCl solution based on the solution-diffusion theory (section 0), which is reproduced below for convenience:

$$B = \frac{(1-R)}{R} \cdot A \cdot (\Delta p - \Delta \pi) \quad (2.5)$$

Due to risk of degradation, the fouled CTA membranes were analysed immediately after removal from the system. The operating pressure of the RO experiment on the fouled CTA membranes was 15 bar and not varied. The choice of the operating pressure was based on experience and consideration of the experimental conditions, such as membrane area, experiment duration, and amount of permeate collected. In general, other pressures would have been possible, as B is justifiably not pressure dependent and R would vary accordingly as noted in section 2.2. However, care has to be exercised not to operate at too high a flux (pressure) for the RO experiment such that the effect of concentration polarisation could become overly severe, which would then require correction (Phillip et al. 2010). The orientation of the CTA membrane adopted for the RO experiments was that of ‘active layer facing feed’. Further details with regard to deriving intrinsic separation properties from RO experiments for the TFC and CTA membranes can be found in (Wang et al. 2010a) and (Lay et al. 2010a), respectively.

Electron microscopy examination of membranes was conducted using a Zeiss Evo scanning electron microscope (SEM). Prior to examination, the membrane samples were freeze-dried (Chris Alpha 1-4 LD), and then gold coated using a sputter coater (Emitech SC7620).

Scaling propensity was checked for the two common scalants CaSO_4 and CaCO_3 (Le Gouellec and Elimelech 2002; Lee and Kim 2009). Although the feed composition did not contain any calcium specific chemical, calcium was present in the tap water, with which the feed water was produced, and became concentrated in the mixed liquor. The risk of calcium scaling therefore could not be excluded. Analysis of cations was performed using a PerkinElmer Optima 2000 inductively coupled plasma-optical emission spectrometer (ICP-OES). Anions were analysed using a Dionex ICS-1000 ion chromatography system (ICS). Ion activity coefficient was estimated using the Davies relationship for ionic strength up to 0.5 M (Sawyer et al. 2003), which was then used to determine the ion activity product (IAP). The solubility product constants (K_{sp}) were obtained from reference literature (Lide 2008). Assessment of scaling propensity was derived based on the saturation index (SI) for each scalant as given below. Scaling may occur for $\text{SI} > 1$.

$$SI = \frac{IAP}{K_{sp}} \quad (3.2)$$

Osmotic pressure relationships were determined for the synthetic feed water and mixed liquor using a cryoscopic osmometer (Gonotec Osmonat 030). The OLI Studio Analyzer 3.1 software (OLI Systems Inc., Morris Plains, NJ) was used to determine the osmotic pressure of the draw solution. In view of carbonate equilibrium relations, and since there had been no external carbonate species in the system, the OLI software was also used to estimate the concentration of aqueous CO_3^{2-} ion at the known pH to assess scaling propensity.

Chapter 4. Stable-state study of an OMBR

4.1 Introduction

This chapter describes an experiment run that aims to comprehensively study an operating OMBR over a relatively long experimental duration of 73 days. The objective of this study is to probe stable-state OMBR performance under the elevated salt environment. Pertinent research questions that this study seeks to address are:

- As the OMBR is an osmosis-driven process, draw solute transmission would be continuously occurring as long as there is a concentration difference between the feed liquid and the draw solution. How could a stable-state mixed liquor concentration be attained in an OMBR?
- What would be the flux behaviour of a long-term operated OMBR under elevated salinity?
- Could there be material stability for the cellulose-triacetate (CTA) material based FO membrane in the aggressive biological environment?
- What could be the factors of relevance for membrane fouling?
- How would the experimentally observed salt concentration factor correspond to expected draw solute transmission?

4.2 Experimental and modelling methods

4.2.1 Experimental protocol

The general materials and methods adopted can be found in Chapter 3. Concerning this experiment run (CTA-I), the following applied. The CTA membrane had the orientation ‘active layer facing the feed water’ (AL-FW). Except for the first few days of the experiment, the amount of mixed liquor removed per weekday was 0.28 L inclusive of the samples taken for analysis. No sludge wasting was carried out on weekends. The average waste sludge flow on a weekly basis was 0.2 Ld^{-1} (5% of reactor volume), and therefore the average SRT was around 20 d. The HRT of the system was not constant, as this depended on the water flux, which reduced with increasing salinity of the mixed liquor. The initial HRT of R2 was approximately 33 h.

This experiment ran for 73 days, and certain pharmaceuticals were dosed into the feed tank on the 47th and 56th day. The dosages of the pharmaceuticals were to assess their removal and effects on the process, which will be discussed in Chapter 5. The measured TOC content, conductivity and pH of the synthetic feed water were: $195.7 \pm 9.3 \text{ ppm}$, $0.8 \pm 0.1 \text{ mScm}^{-1}$ and 6.5 ± 0.1 , respectively.

4.2.2 Modelling method

Salt concentration effects occur in all salt retentive systems when the in flowing salt load is not balanced by the out flowing salt load. For the OMBR, there is an additional salt flux term due to the “reverse salt transport” from the draw solution into the mixed liquor. This is discussed in detail in Chapter 6.

As the water flux is not a constant for a typical FO process, and reduces with increasing mixed liquor salt concentration, it is difficult to analyse salt accumulation in OMBR systems without knowledge of the FO flux behaviour. In this study, a simple numerical method was used to model the concentration effects of the studied OMBR as follows.

Salt mass balance for an OMBR:

$$\frac{d(\frac{\pi_{ml}}{\pi_{in}})}{dt} = \frac{Q}{V}(1 + \frac{B/A}{\pi_{in}}) - \frac{Q_w}{V}(\frac{\pi_{ml}}{\pi_{in}} - 1) \quad (4.1)$$

Approximation of the above:

$$\frac{\Delta(\frac{\pi_{ml}^{(t)}}{\pi_{in}})}{\Delta t} \approx \frac{Q^{(t)}}{V}(1 + \frac{B/A}{\pi_{in}}) - \frac{Q_w}{V}(\frac{\pi_{ml}^{(t-1)}}{\pi_{in}} - 1) \quad (4.2)$$

where:

$$\frac{\pi_{ml}^{(t)}}{\pi_{in}} = \Delta(\frac{\pi_{ml}^{(t)}}{\pi_{in}}) + \frac{\pi_{ml}^{(t-1)}}{\pi_{in}} \quad (4.3)$$

4.3 Results and discussion

4.3.1 Water production and elevated mixed liquor concentration

Results for the water production and mixed liquor salt accumulation of the experiment are presented in Figure 4.1. The water flux started from an initial value around $3.2 \text{ L m}^{-2} \text{ h}^{-1}$ under constant draw solution concentration at $0.5 \text{ mol} \cdot \text{kg}^{-1} \text{ NaCl}$ ($\sim 22.8 \text{ bar}$), and is about one fourth of what could be achieved with RO using an equivalent hydraulic pressure on the same type of membrane. The reason for the lower water flux is the presence of internal concentration polarisation (ICP) in the membrane support layer, which is an inherent feature of FO systems and diminishes the effective driving force across the membrane.

Figure 4.1: Water flux and mixed liquor concentration of the OMBR

As the experiment progressed, the water flux reduced with increasing mixed liquor salt concentration and hence osmotic pressure, and stabilised at around $2.7 \text{ L m}^{-2} \text{ h}^{-1}$ with no apparent flux decline thereafter. The corresponding concentration factor (CF) in terms of conductivity was 17.1 – 19.2, and the mixed liquor concentration range

(c_{ml}) was $13.7 - 15.4 \text{ mScm}^{-1}$, which would correspond to a NaCl concentration of about $7.2 - 8.1 \text{ gL}^{-1}$. This stable state of operation could be achieved, as the combined salt load from both influent and salt transmission from the draw solution entering the system balanced the outgoing salt load in the waste sludge. However, it is to be noted that different from conventional MBRs, the SRT and HRT are not strictly uncoupled in an OMBR, as these may be linked via the CF (section 2.4). For instance, a longer SRT would increase the mixed liquor salt concentration, which in turn reduces water flux and prolongs HRT. Analogously, any attempt to reduce the HRT by either increasing water flux or membrane area will result in a greater CF and mixed liquor salt concentration. Inevitably, the water flux will then readjust itself until a stabilised CF is reached. On another note, the dosage of pharmaceuticals on 47th and 56th day had no apparent effect on the water production and salt accumulation, though it had significant effects on the biological process and the product water quality (Chapter 5). The somewhat zigzag pattern for both stabilised J_w and c_{ml} as observed in Figure 4.1 may be attributed to the sludge wasting regime of this study as predicted by a separate modelling study (Xiao et al. 2011).

No membrane cleaning/washing was applied throughout this experiment, so the observation of stable water production suggested mild fouling. This observation, however, did not necessarily mean that the FO is an inherently low fouling membrane process. There could be other contributing factors to the lack of significant fouling. Firstly, there was the compensating effect of ICP acting under this membrane orientation (section 2.2.4). Secondly, the low operating flux of this experiment could also imply that the threshold/critical flux for fouling was not exceeded (Wang et al. 2010b). Thirdly, as the bioreactor was continuously aerated, the gas-liquid two-phase flow would have an alleviating effect on fouling due to the greater induced shear force on the membrane surface. Such enhancement effect due to continuous or intermittent aeration is well-known for membrane systems (Cui et al. 2003), and has also been demonstrated in a number of recent FO studies (Mi and Elimelech 2008; Lee et al. 2010). Finally, the relatively hydrophilic and smooth CTA-woven FO membrane used in this study could also have contributed to the low fouling effects (section 3.3.2). It is worth noting that the cellulose acetate type membrane has been known to exhibit

lower fouling tendencies even for the pressure-driven RO process (Elimelech et al. 1997).

Interestingly, the stable membrane performance throughout the experiment also indicates material stability in the aggressive mixed liquor environment. This observation is surprising, because membranes of cellulosic material are known to be chemically and microbiologically vulnerable, and was experienced in a previous experimental trial. During that trial, used CTA-woven FO membranes which had been in contact with biomass were degraded and gave very poor NaCl rejection after being stored in Milli-Q water for a few days (results not shown). The underlying mechanism for this is not clear, but the following hypotheses may offer explanation. Under the nutrient deficient Milli-Q water environment, cell detachment from the membrane surface took place as a natural survival response of bacteria in search for other habitats richer in nutrients (O'Toole et al. 2000; Davies 2002). In the process, degradative enzymes would have been released to digest the EPS matrix and facilitate cell detachment (Boyd and Chakrabarty 1994; Lee et al. 1996). These enzymes could also have resulted in degradation of the CTA membrane. Another possible explanation is that in the absence of other more readily biodegradable carbon sources, microorganisms had to utilise the CTA material as the carbon source for survival when the membranes were immersed in Milli-Q water. This would be in agreement with a study, where simulated used membranes experienced a faster rate of degradation (Murphy et al. 2001). However, in the presence of other carbon sources such as those present in the synthetic feed water, the CTA material may only gradually degrade over a significantly longer period of time, and impairment of membrane performance may not be noticeable within the 73 days experimental duration of this study. This hypothesis is in agreement with another study that used cellulosic membranes in a NFMBR. In that study, a gradual decrease in salt rejection due to membrane degradation was noticeable only after 80 days of operation (Choi et al. 2007a). Clearly, the above phenomenon requires further research as it relates to membrane stability for long term application in biologically active environment.

4.3.2 Membrane properties derived from RO experiments

The A and B properties of both virgin and used membranes are presented in Figure 4.2. While the properties of the virgin CTA-woven membranes tested in this study differ somewhat from other studies (Gray et al. 2006; Tang et al. 2010), the values are in general agreement with a similar order of magnitude. As pointed out by (Achilli et al. 2009b), there could be proprietary differences in permeability and selectivity with this kind of membrane.

From the RO experiments, neither the A nor the B value of the used membrane differed noticeably from the virgin membranes. This result supports the mild fouling observation as suggested in section 4.3.1, and is in agreement with other studies with regards to a reversible or an easier to remove fouling layer (Cornelissen et al. 2008). Considering the adopted membrane orientation, this observation is not totally unexpected. The ‘active layer facing feed’ orientation allows for cake layer formation, rather than pore plugging mechanism, and hence the effects of fouling would be subdued (Mi and Elimelech 2008; Tang et al. 2010). Furthermore, typical fouling resistance for MBRs is $10^{11} - 10^{12} \text{ m}^{-1}$, which would correspond to a permeability about $10^2 - 10^3 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ (Le-Clech et al. 2006). Compared to the permeability of the CTA-woven membranes, any effect due to the fouling resistance therefore would not be apparent, as it would be at least 2 orders of magnitude smaller than the effect due to the membrane. The un-cleaned fouled membrane was tested with the RO experiment upon removal from the OMBR experiment, therefore some NaCl solutes could remain within the gel layer. However, it was found that the possible effect on the RO experiment due to the presence of such entrapped NaCl within the gel-layer was not of significance, because otherwise both measured A and B of the fouled membrane would have lower and greater value respectively as compared to those of the virgin membrane, which was not the case here. However, it is to be pointed out that the RO-derived A and B values did not correspond to the observed concentration factor during the OMBR experiment, and this is discussed further later (section 4.3.5).

STABLE-STATE STUDY OF AN OMBR

Figure 4.2: Membrane properties as determined by RO experiments comparing the virgin membrane and the used membrane from the OMBR

a) Water permeability (A) for virgin membrane is $0.6 \pm 0.1 \text{ L m}^{-2}\text{h}^{-1}\text{bar}^{-1}$ ($n = 8$), and the error bar shown is the standard deviation obtained from the measurements;

b) Salt permeability (B) for virgin membrane is $1.0 \pm 0.2 \text{ L m}^{-2}\text{h}^{-1}$ ($n = 6$) and the error bar shown is the standard deviation obtained from the measurements;

c) B/A ratio for virgin membrane has an average value of 1.6 bar, and the error bar shown gives the maximum and minimum value as derived from a) and b).

STABLE-STATE STUDY OF AN OMBR

Figure 4.3: Visual and microscopic examination of the used membrane from the OMBR

- a) Photograph of the membrane module freshly taken out from the bioreactor immediately after the experiment
- b) SEM image of the surface of the used membrane showing deposition of gel-like layer
- c) SEM image of the cross section of the used membrane together with the thin gel-like layer

4.3.3 Visual and electron microscopic examination of used membranes

Visual examination of the used membranes upon immediate removal from the experimental system verified the mild fouling observation (Figure 4.3). While slight biomass deposition could be observed at the edge of the membrane – which occurred due to hydrodynamic dead zone induced by the module and the O-ring, no substantial deposition could be found on the larger part of the remaining membrane surface (a). The SEM images, however, were able to detect a thin layer of gel-like layer on the surface of the used membrane, which is similar in appearance (b) to fouling layer found in conventional MBRs. Its thickness, however, as deduced from the scale bar of the SEM image (c), is smaller than the typical thickness of 20 – 50 μm fouling layer found in MBRs (Meng et al. 2005; Lee et al. 2008).

Further investigation found extracellular polymeric substances (EPS) on the used membrane surface, but confocal laser scanning microscopy (CLSM) detected relatively small numbers of scattered bacterial cells (results not shown). This observation implied that there had been no mature biofilm formation, which agrees with the observation regarding the mild fouling condition discussed above. While this finding may appear surprising given the biologically active mixed liquor environment, there have been studies reporting that cellulose acetate type membranes, possibly due to the smooth membrane surface morphology, could have lesser bacterial adhesion and biofilm development (Ho et al. 1983; Campbell et al. 1999; Pang et al. 2005). The implication here is that membrane material and surface property have important effects in relation to fouling for FO processes.

4.3.4 Scaling propensity check

In view of the elevated salt concentration in the mixed liquor, membrane scaling in the form of salt precipitation could occur and result in serious flux decline (Gilron and Hasson 1987).

Table 4.1 gives a snap-shot analysis conducted towards the end of the experiment. In general, the concentration of ions present in the synthetic feed water was within the expected range. Analysis of ions in the mixed liquor shows that sodium and chloride were the dominant ionic species, which is expected due to reverse diffusion from the draw solution. No straight forward analysis could be made on the smaller sized ions such as K^+ , F^- and NO_3^- , as these mobile ions could permeate through the membrane and would be affected by electrostatic effects such as Donnan equilibrium (Donnan 1995; Hancock and Cath 2009). Furthermore, some ions could also be affected by biological processes, for example, NO_3^- would increase with nitrification and decrease with denitrification.

The scaling propensity assessment was conducted on $CaSO_4$ and $CaCO_3$, as these are the two commonly encountered scalants in membrane systems (Le Gouellec and Elimelech 2002; Lee and Kim 2009). From Table 4.2: it can be seen that while scaling of $CaSO_4$ might not have occurred ($SI < 1$), a higher scaling tendency existed for $CaCO_3$ with $SI > 1$ based on the K_{sp} for calcite – the least soluble anhydrous form of $CaCO_3$. However, only mild fouling was observed (section 4.3.2). Energy-dispersive X-ray (EDX) spectroscopy analysis on used membranes of another run did not detect the presence of multivalent ions (Chapter 7). The implication here is that scaling did not occur at the current level of elevated salinity. This may be explained as follows. Firstly, it is known that there is a metastable region for $CaCO_3$ precipitation, such that the lower limit for spontaneous crystallite formation is the solubility product of monohydrate calcium carbonate ($CaCO_3 \cdot H_2O$), and not that of calcite (Elfil and Roques 2001). This result is consistent with the derived $SI = 0.1$ for $CaCO_3 \cdot H_2O$ (Table 4.2). Secondly, the presence of organics in the mixed liquor could inhibit scaling, and this effect is already known for substances such as polysaccharides and humic acid (Kontrec et al. 2008). Thirdly, in view of the relatively low water flux

applied in this study, any concentration polarisation effect would be minor. Had the water flux been greater, the scaling tendency could have increased significantly due to the exponential form of concentration polarisation.

Table 4.1: Water quality check of selected ions on $t = 73$ d

	Concentration in mixed liquor [ppm]
<i>Cations</i>	
Ca^{2+}	238.8
Na^{+}	2769.6
K^{+}	160.4
Mg^{2+}	122.2
<i>Anions</i>	
F^{-}	9.3
Cl^{-}	4437.2
NO_3^{-}	22.5
SO_4^{2-}	658.1

Table 4.2: Assessment of scaling propensity of the mixed liquor

Scalant	IAP [mol L ⁻¹] ²	K _{sp} [mol L ⁻¹] ²	SI [-]
CaSO_4	$3.93 \cdot 10^{-6}$	$4.93 \cdot 10^{-5}$ (a)	0.1
CaCO_3	$8.69 \cdot 10^{-9}$	$3.36 \cdot 10^{-9}$ (a)	2.6
$\text{CaCO}_3 \cdot \text{H}_2\text{O}$	$8.69 \cdot 10^{-9}$	$7.09 \cdot 10^{-8}$ (b)	0.1

(a) derived from (Lide 2008)

(b) derived from (Kralj and Brecevic 1995)

4.3.5 Deviation of observed and expected concentration factor

Figure 4.4 shows the experimentally observed concentration factor ($CF = \pi_{ml} / \pi_{in}$) and the expected values based on the approximate model (equations (4.2) and (4.3)) with B/A values determined from the RO experiments. Three scenarios were modelled: (a) $B/A = 0.8$ bar which corresponds to the minimum value as derived from the tested virgin membranes, (b) $B/A = 1.7$ bar which corresponds to the value as derived from the used membrane of this study, and (c) $B/A = 2.5$ bar which corresponds to the maximum value as derived from the tested virgin membranes.

Figure 4.4: Comparison of observed and expected concentration factors for the OMBR experiment

In the first few days, the experimentally observed CF was in reasonable agreement with the modelled curves, and would have a B/A value in between (a) the minimum 0.8 bar and (b) the 1.7 bar of the used membrane derived from RO experiment. This was as expected. However, from around the 6th day onwards, deviation began to show up. At the stabilised state, the experimentally observed CF was around 17.1 – 19.2, which was significantly lower than the CF ~ 30 modelled for the minimum B/A value (a). This was a surprising finding, because the models were derived with known parameters (Q , Q_w and V) from the experiment, such that any volumetric effect was already accounted for. Possible effect due to cake-enhanced concentration polarisation for the reduced salt transmission was also considered, but found not likely to be a main underlying reason. This is apparent from equation (2.6) – section 0, as any reduction in J_s due to an enhanced salt concentration on the membrane surface would cause a corresponding decrease in J_w , which was not the case here. This is because both J_s and J_w rely on the same net salinity driving force. The only explanation for this discrepancy is that the overall B/A value had evolved during the OMBR experiment based on mass balance considerations.

The above observed phenomenon is not well understood, though it is possible that the increasing salinity in the mixed liquor changed the total electrochemical potential difference across the membrane, and hence the overall B/A value. Such a phenomenon has also been encountered in other processes that involve ions transport such as nanofiltration and ion exchange membrane processes (Higa et al. 1990; Murata and Tanioka 1997; Bowen and Welfoot 2005).

Furthermore, the gel-like layer found on the membrane surface was found to contain extracellular polymeric substances (EPS), and could have also played a role in influencing salt transmission and changing the overall B/A value across the membrane during the experiment. This mild fouling layer could act to effectively plug defects in the active layer of the membrane and thereby reduce salt passage (Tang et al. 2007). Furthermore, considering the high sorption properties of EPS, and their affinity for cations (Spath et al. 1998; Liu et al. 2004), this adsorbed layer on the membrane surface would also have altered the interfacial electrochemical potential, and in this instance, exerted a moderating effect on the transmission of ionic species across the membrane. The outcome of the above interactions would be reduced overall B/A value as observed on the OMBR. Subsequent RO experiments did not detect any significant change in the original B/A value, because the electrochemical potential of the solution in the OMBR was not the same as that in the RO experiment, and the labile gel-like layer could become detached from the membrane surface under the action of cross flow in the RO cell. It is worth noting that lower salt transmission induced by fouling was also observed in another OMBR study (Achilli et al. 2009b). Clearly, further research is needed to elucidate the nature of the gel-like layer that was adsorbed on the membrane surface, and its possible role in affecting salt transmission and hence overall system performance.

4.4 Concluding remarks

The studied OMBR system showed operational stability over the experimental duration of 73 days, which attested to the general feasibility of integrating FO and biological process. Key findings that address the research questions of this study are:

- 1) The mixed liquor salinity of the OMBR increased due to salt accumulation. However, a stable state could be attained, as the combined salt load from both influent and salt transmission from the draw solution entering the system balanced the outgoing salt load in the waste sludge.
- 2) In spite of the elevated mixed liquor salinity, the OMBR was able to achieve stable water flux near to $3 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ under constant draw solution concentration of $0.5 \text{ mol}\cdot\text{kg}^{-1}$ NaCl. The stable-state operation may be attributed to the mild fouling condition and the membrane orientation ‘active layer facing feed’, such that internal concentration polarisation occurred on the draw side of the membrane, which exerted a self-compensating effect on flux.
- 3) No deterioration in membrane performance was detected throughout the experiment run, although the CTA membrane was vulnerable to degradation in Milli-Q water environment after in contact with the biologically active mixed liquor of the OMBR.
- 4) Mild membrane fouling was observed, although no cleaning measure was applied throughout this experiment run. The mild fouling observation may be attributed to low operating flux, as well as material and surface properties of the CTA membrane.
- 5) The observed salt concentration factor from the experiment was significantly lower than expected. It shows that the gel-like layer on the membrane surface could have moderated salt transmission from the draw solution into the mixed liquor. Further research is needed to understand the nature of the gel-like layer and its possible effects on process performance for OMBR systems.

Chapter 5. Effects associated with pharmaceutical removal

5.1 Introduction

In Chapter 1, it is pointed out that an underlying concept for the OMBR is that the tight FO membrane will be able to more effectively retain persistent and low molecular weight (LMW) organic micro-pollutants, and thereby facilitate their biodegradation. This attribute is significant, because the small sized organic micro-pollutants may not be adequately biodegraded within the finite hydraulic retention time (HRT) of conventional MBRs with micro-porous MF/UF membranes, and pass into the product water. However, until recently, there has been little information available on the use of OMBRs relevant to this issue. A study by (Cartinella et al. 2006) using short-term batch experiments found that FO could achieve high hormone removal depending on feed solution chemistry. Further issues of concern would include other types of micro-pollutants, length of experimental duration, effects of the salt concentrative mixed liquor environment, and these in relation to the biological process performance. Consequently, the goal of this study is two-fold. Firstly, water quality issues concerning OMBR are examined. In this regard, the efficacy of removal of organic micro-pollutants by an OMBR is investigated. For this objective, selected pharmaceutical compounds were employed as the micro-pollutants of interest due to the increasing concern about the occurrence of such compounds in the environment (Ternes et al. 2004; Verliefde et al. 2007). Secondly, the study assesses process performance of the OMBR under real operating conditions with a concentrated mixed liquor environment, and in relation to the effects of the pharmaceutical compounds on the biological process.

5.2 Experimental and analytical methods

5.2.1 Experimental protocol

The materials and methods adopted are generally as detailed in Chapter 3. The experiment run referred to here is CTA-I, which is also discussed in Chapter 4. The experiment was conducted for a period of 73 days. A cocktail mix of pharmaceutical compounds containing carbamazepine, diclofenac, ibuprofen and naproxen were spike-dosed into the feed tank on the 47th and 56th day at concentrations of 20 – 25 ppb. In spite of the pharmaceutical dosages, stable operation in terms of flux and salinity could be achieved.

In the literature, there is a differentiation between apparent rejection and intrinsic rejection of a membrane towards a particular compound. The apparent rejection refers to the difference in the normalised concentration of a particular compound in the bulk solution between the feed and the permeate stream. On the other hand, the intrinsic rejection refers to the difference in the normalised concentration of a particular compound directly across the rejection layer of the membrane, which is difficult to measure. In this study, the apparent removal efficiency is the removal efficiency that is derived by measurement of the respective concentrations in the mixed liquor and draw solution. It provides indication of the product water quality in relation to the feed, but does not describe the removal mechanism of the membrane, for which concentration polarisation needs to be accounted for. Similar expression has been used in the literature (Jin et al. 2011).

On the 73rd day, the membranes were removed from the bioreactor and analysed. For convenience, the main experimental parameters of this study are summarised in Table 5.1

Table 5.1: Summary of main experimental parameters

Parameters	Units	Values
Initial water flux	$[\text{Lm}^{-2}\text{h}^{-1}]$	3.2
Stabilised water flux	$[\text{Lm}^{-2}\text{h}^{-1}]$	2.7
Stabilised mixed liquor concentration	$[\text{g}_{\text{NaCl equivalent}} \text{L}^{-1}]$	7.2 – 8.1
Draw solution concentration	$[\text{mol}_{\text{NaCl}} \text{kg}^{-1}]$	0.5
Average SRT	[d]	20
Initial HRT	[h]	33
TOC of feed water	$[\text{mgL}^{-1}]$	200
COD: N: P of feed water	[-]	100: 6: 1
Initial organic loading rate	$[\text{kg}_{\text{COD}}\text{m}^{-3}\text{d}^{-1}]$	0.4
Mixed liquor dissolved oxygen	$[\text{mgL}^{-1}]$	>1
Specific aeration demand (membrane)	$[\text{m}^3_{\text{air}}\text{m}^{-2}\text{h}^{-1}]$	>1
Mixed liquor pH	[-]	6.6 – 7.9
Mixed liquor temperature	$[\text{°C}]$	20 – 22

5.2.2 Pharmaceutical compounds and their analysis

Information on the selected pharmaceutical compounds can be found in Table 5.2. These are commonly studied pharmaceuticals due to their perceived health risk, and are on the list of priority organic micro-pollutants in many parts of the world (Khan and Ongerth 2004; Bellona and Drewes 2007; Verliefde et al. 2007). The compounds were also selected based on their physicochemical and biotransformation (biodegradation) properties. Adapted from the classification of (Joss et al. 2005) with regard to biological process removal efficiency, the pharmaceutical compounds used in this study could be broadly referred as: (a) no removal ($\sim 0\%$): carbamazepine, (b) partial removal ($< 40\%$): diclofenac, (c) moderate removal ($40\% - 90\%$): naproxen, and (d) high removal beyond quantification ($> 90\%$): ibuprofen. Neither the Henry coefficient ($< 10^{-5}$) nor the sorption constant ($K_d < 300 \text{ L kg}_{\text{SS}}^{-1}$) of the dosed pharmaceutical compounds were high enough to make volatilisation and sorption relevant removal mechanisms here (Joss et al. 2005; Sipma et al. 2010). Therefore, taking into consideration their concentrations in the product and waste streams, the removal of these compounds would be mainly via biotransformation mechanisms.

The analysis of pharmaceutical compounds was performed by the Water Research and Analytical Laboratory (WRAL) of PUB (Singapore). Two types of analysis were performed. The first was a gas chromatography – mass spectrometry (GC-MS, Agilent 6890-5973) scan with 250 mL of water sample after liquid-liquid extraction using methylene chloride and N_2 blow down. The limit of semi-quantification was estimated to be 1 ppb. The second analysis was performed using Ultra Performance Liquid Chromatography – Triple Quadrupole Tandem Mass Spectrometer (UPLC-MS-MS, Waters UPLC-Quattro Premier XE MS), and measurement was performed with an isotope dilution method using 10 mL of water sample for each analysis, and with the limit of detection at 1 ppb.

Table 5.2: Information of dosed pharmaceuticals

Pharmaceutical compound ^(a)	Carbamazepine	Diclofenac (-sodium)	Ibuprofen	Naproxen
Chemical structure
Molecular Weight [g mol ⁻¹]	236.27	318.13	206.28	230.26
CAS number	298-46-4	15307-79-6	15687-27-1	22204-53-1
Use ^(b)	anti-epileptic	analgesic	analgesic	analgesic
Possible microbial inhibition effect	Yes ^(c)	Yes ^(d)	Not known	Yes ^(c)
Charge at near neutral pH ^(e)	Neutral	Negative	Negative	Negative
Henry coefficient (air/water) [-] ^(f)	$4.4 \cdot 10^{-9}$	$1.9 \cdot 10^{-10}$	$6.1 \cdot 10^{-6}$	$1.4 \cdot 10^{-8}$
Sorption constant, K_d [L kg _{SS} ⁻¹] ^(g)	0.1	16	7	13
Biodegradation constant, k_{biol} [L g _{SS} ⁻¹ d ⁻¹] ^(f)	< 0.01	< 0.1	9 – 35	0.4 – 1.9

(a): All pharmaceutical compounds were obtained from Sigma-Aldrich

(b): (Bellona and Drewes 2007; Wang et al. 2008)

(c): (Wang et al. 2008)

(d): (Dutta et al. 2007)

(e): (Khan and Ongerth 2004; Verliefde et al. 2009)

(f): (Suarez et al. 2008)

(g): (Sipma et al. 2010)

5.2.3 Analytical methods for process parameters

The dissolved organic carbon (DOC) was derived from the total organic carbon (TOC) by subjecting the samples to centrifugation followed by filtration through a 0.45 μm membrane prior to measurement by a TOC Analyser (Shimadzu TOC-VCSH). No other treatment or dilution was applied to the samples. The negligible influence of salt in samples was verified up to 60 g L^{-1} of NaCl, although measurement of samples of high salt content is generally discouraged by the supplier, as it can greatly shorten the life of the instrument's consumables. The chemical oxygen demand (COD) was derived with the conversion factor 1 g TOC = 2.67 g COD. The mixed liquor suspended solids (MLSS) were determined in accordance to Standard Methods (APHA et al. 2005). The analysis of extracellular polymeric substances (EPS) was performed as previously described (Zhang et al. 2006b). A more detailed description of the method can be found in the appendices. Briefly, this method involved centrifugation of mixed liquor samples to separate the supernatant EPS from the biomass-associated (pellet) EPS. The supernatant was collected without any further treatment, and contained both soluble and loosely bound polymers (Nielsen et al. 1997; Liu et al. 2004). The remaining pellet was then re-suspended in Milli-Q water and subjected to an adapted 'formaldehyde plus NaOH' treatment for extraction (Zhang et al. 1999; Liu and Fang 2002). Measurement of the protein content was performed using the 'Bradford' method (Bradford 1976), and calibrated with bovine serum albumin (BSA) standard solution (Thermo Scientific 23209). Measurement of the polysaccharide content was done using the 'Dubois' method (Dubois et al. 1956), and calibrated with a glucose standard solution (Sigma-Aldrich G6918). The total EPS for a particular fraction (supernatant vs. pellet) was represented by the sum of the protein and polysaccharide components. It was further verified that the EPS method was suitable for samples with a NaCl content up to 30 g L^{-1} . For consistency, EPS concentrations were normalised with respect to MLSS in the unit $[\text{mg g}_{\text{SS}}^{-1}]$. All TOC and EPS measurements were made using duplicate samples each time point, and presented as averaged values.

5.2.4 Organic carbon characterisation

Organic carbon characterisation was determined by liquid chromatography – organic carbon detection (LC-OCD) by DOC-LABOR DR. HUBER (Germany). Briefly, the technique makes use of size exclusion chromatography with online organic carbon detection (OCD), coupled with a UV detector and organic nitrogen detector (OND). This technique is able to characterise organics of specific fractions (hydrophilic vs. hydrophobic; biopolymers vs. humic substances vs. building blocks vs. low molecular weight neutrals and acids), in accordance to their molecular weights. The technique has been successfully applied in a number of membrane and MBR studies to provide analyses (Huber 1998; Rosenberger et al. 2005; Zhang et al. 2006b). In this study, two LC-OCD analyses were performed. Each time, samples collected from both mixed liquor and draw solution were immediately filtered (0.45µm) and frozen at -20°C. The frozen samples were delivered in a specialised chilled box the next day for analysis. This deep freezing method for sample transport had been found to give more consistent results when compared to pasteurization or chemical preservation methods.

5.2.5 Methods for microbiological analysis

Mixed liquor samples were collected from the OMBR on days 0, 3, 7, 13, 28, 42, 56, 63, 73, and the membrane sampled on day 73 upon completion of the experiment. A detailed elaboration of the method used for Polymerase Chain Reaction – Denaturing Gradient Gel Electrophoresis (PCR-DGGE) can be found in the appendices. Briefly, a modified Cetyltrimethyl Ammonium Bromide (CTAB) protocol was used to extract DNA from the biomass. The PCR amplification was conducted in C1000TM Thermal Cycler with a reaction volume of 50 µL using primers F357 and R518. DGGE analysis was conducted using DcodeTM Universal Mutation Detection System (BIO-RAD). The gels contained a linear denaturant gradient ranging from 20% to 70%. Electrophoresis was performed at a constant voltage of 30 V for 30 min and subsequently at 100 V for 13 hours. DGGE gels were stained with ethidium bromide, destained in distilled water and imaged with a Gel DOCTM XR+ Imaging system (BIO-RAD). The DGGE profiles were analyzed with Quantity one V4.31 (BIO-RAD) and representative bands selected for further analysis. The Shannon Weaver Diversity Index (H) (Shannon and Weaver 1980; Schäfer and Muyzer 2001; Stamper et al. 2003) was applied to provide analysis of bacterial diversity as follows:

$$H = -\sum p_i \cdot \log p_i \quad (5.1)$$

Here, p_i is the proportion of the i th phylotype band in a lane, which corresponds to the intensity of that band in proportion to the intensity of all bands in the lane.

5.3 Results and discussion

5.3.1 Removal of pharmaceutical compounds

The FO membrane used in this study exhibited high retention properties as presented in Figure 5.1. The apparent removal efficiency is greater than 96% regardless of the pharmaceutical compounds used – neutral or charged, and is comparable to a tight RO/NF membrane (Bellona and Drewes 2007; Kimura et al. 2009). This result is also consistent with the study by (Cartinella et al. 2006), where it was demonstrated that an FO membrane could reject hormones of similar molecular weight ranges as the pharmaceutical compounds used in this study, depending on water recovery and feed solution chemistry. Interestingly, studies have found that organics present in surface water or treated effluent enhanced retention of micro-pollutants (hormones, pharmaceuticals as well as pesticides), as the larger macromolecules bind the smaller micro-pollutants, making rejection of these easier due to sieving effects or electrostatic repulsion between complexes and the membrane surface (Cartinella et al. 2006; Kimura et al. 2009). While the effect of the mixed liquor water matrix was not studied here, the above points to a further potential advantage of OMBR with regard to removing micro-pollutants.

A few unidentified peaks were observed in the GC-MS scan (Figure 5.1 a), whose concentration in the mixed liquor (r2) and the draw solution (d2) were significantly different. Due to poor match quality with the instrument library, these peaks were not further investigated. Therefore, UPLC-MS-MS analysis was applied to investigate the targeted compounds (Figure 5.1 b). Here, a few points can be discussed. Firstly, although the dosed pharmaceutical concentration was 20 – 25 ppb in the feed tank, the measured concentrations of the pharmaceutical compounds (with the exception of ibuprofen) in the mixed liquor were generally higher. This was due to the concentration effects brought about by the influent load and the high membrane retention less the amount in the wasted sludge.

Secondly, the concentrations of the pharmaceutical compounds in mixed liquor were in agreement with their known biodegradation characteristics (Table 5.2), which gives that the rate of biodegradation is such that ibuprofen > naproxen > diclofenac. The implication is that ibuprofen should be the first to be biodegraded in the bioreactor, followed by naproxen and then diclofenac. Not surprisingly, ibuprofen with the largest biodegradation constant among all studied compounds was not detected in the bioreactor on $t = 66$ d, even though the influent at that time could still contain small amounts of residual pharmaceutical load. Diclofenac was more persistent than naproxen, which was evident from the increased concentration on $t = 66$ d.

Thirdly, regardless of the concentrations in mixed liquor, the concentrations of all three compounds in the draw solution were consistently below 1 ppb, which was the limit of quantification. When compared to the measured concentration of the compounds in the mixed liquor, the observation verifies that these compounds are not detected in the product stream. This confirms that the highly retentive FO membrane is able to provide a primarily physical separation mechanism for removal of micro-pollutants.

Fourthly, as it is known that organic micro-pollutants follow primarily a pseudo first-order biodegradation reaction (Ternes et al. 2004; Joss et al. 2006), the high retention property of the FO membrane as demonstrated in this study may be favourable for enhancing the rate of biodegradation of these compounds in the bioreactor. This, in fact, is an underlying rationale for the development of the OMBR as noted in the introductory chapter. However, it is not clear if the elevated salinity, and/or accumulated SMP and other retained constituents in an OMBR could have effects on the biotransformation reactions of organic micro-pollutants, so clearly further research is required here.

EFFECTS ASSOCIATED WITH PHARMACEUTICAL REMOVAL

(a) GC-MS analysis of $t = 52$ d

	Concentration in mixed liquor [ppb]	Concentration in draw solution [ppb]	Apparent removal efficiency [%]
$t = 52$ d			
Naproxen	48.7	< 1	> 97.9
Diclofenac	55.2	< 1	> 98.2
Ibuprofen	30.2	< 1	> 96.7
$t = 54$ d			
Naproxen	64.5	< 1	> 98.4
Diclofenac	62.3	< 1	> 98.4
Ibuprofen	25.2	< 1	> 96.0
$t = 66$ d			
Naproxen	64.9	< 1	> 98.5
Diclofenac	71.3	< 1	> 98.6
Ibuprofen	< 1	< 1	N.A.

(b) UPLC-MS-MS analyses of $t = 52$ d, $t = 54$ d and $t = 66$ d

Figure 5.1: Analyses of pharmaceuticals

5.3.2 Assessment of process parameters: dissolved organic carbon, mixed liquor suspended solids and extracellular polymeric substances

From Figure 5.2 a, it can be observed that the OMBR generally achieved excellent product water quality with the draw solution (draw) DOC below 1 mgL^{-1} and the apparent total DOC removal efficiency based on influent to the OMBR greater than 99 %. This is as expected for an HRMBR, and agrees with what is reported in the literature for the tight FO membrane (Achilli et al. 2009b). The exceptions occurred when the biological process was temporarily impaired due to the dosage of pharmaceutical compounds (see below). It should be noted that the measured draw DOC did not equate exactly to the quality of the permeated water, because it contained about 10% input from a concentrated draw reservoir that maintained constant conductivity in the draw tank. However, this effect would be small, and for practical reason and consistency, the draw samples should be considered to reflect the product water quality throughout this study. The DOC of the OMBR mixed liquor supernatant also showed an interesting trend: it gradually increased from a relatively low value ($< 10 \text{ mgL}^{-1}$) at the beginning of the experiment to a stable $20 - 25 \text{ mgL}^{-1}$, which is higher than typical supernatant DOC of approximately $10 - 15 \text{ mgL}^{-1}$ for conventional MBRs (Tao et al. 2005; Zhang et al. 2006a). This could be explained by the high retention property of the FO membrane, which retained and accumulated both high and low molecular weight (MW) soluble microbial products (SMP) and other non-biodegradable organics in the mixed liquor. A similar observation was made in another HRMBR study using NF membranes, whereby the supernatant DOC of the NFMBR was about two to three times greater than the MFMBR (Choi et al. 2006).

The MLSS showed a decreasing trend over the duration of the experiment (Figure 5.2 b). This is expected, because the MLSS is related to the organic loading rate (OLR) at a given SRT (Tchobanoglous et al. 2004). In view of the relatively long HRT ($\geq 33\text{h}$), the resulting OLR in this study was relatively low ($\leq 0.4 \text{ kgCODm}^{-3}\text{d}^{-1}$). Accordingly, the MLSS decreased and stabilised at a food to microorganism (F/M) ratio of around $0.1 - 0.2 \text{ gCODgSS}^{-1}\text{d}^{-1}$, which was within expected range for a MBR process (Judd

2006). Observations of similar MLSS development were also found in other HRMBR studies with low OLR (Choi et al. 2006; Choi et al. 2007b).

EPS measurements revealed fluctuations in amount over time (Figure 5.3). This has been observed in other studies (Zhang et al. 2006b; Al-Halbouni et al. 2008) and is likely due to the fact that the production and composition of EPS depends on a number of factors including the physiological state of the microorganisms and various environmental factors (Liu et al. 2004). While the concentrations of EPS measured in this study were in general agreement with other MBR studies (Le-Clech et al. 2006), it is possible that the protein concentration might be underestimated in view of the adopted 'Bradford' method, which only detects proteins of macromolecular structure with at least 8-9 peptide bonds (Raunkjaer et al. 1994; Frolund et al. 1996). Nonetheless, this would not affect the conclusions of this study since the same method of analysis was consistently applied.

The possible inhibitory effects of the selected pharmaceutical compounds on biological processes are known (Dutta et al. 2007; Kruszewska et al. 2008; Wang et al. 2008), and apparent in both Figure 5.2 and Figure 5.3. Possibly compounded with the low OLR (Wang et al. 2008) and the lack of prior adaptation (Carballa et al. 2006), the adverse effect of the first dosage of the pharmaceutical compounds on biological process was severe (Figure 5.2 a): Both supernatant and draw DOC increased dramatically to approximately 30 mgL^{-1} and 5 mgL^{-1} respectively on $t = 52$ d, and the DOC removal efficiency decreased to approximately 97.5 %. The biological process, however, recovered relatively quickly. Within a few days, all DOC values returned to the pre-shock ranges. In terms of DOC removal, the second dosage of the pharmaceutical compounds had significantly milder effects, implying adaptation of the microorganisms to the pharmaceutical stress. Although a slight increase in the DOC values could be observed, the removal efficiency remained high at above 99 %.

Consistent with the above, the MLSS showed decreasing variation after the subsequent dosage of the pharmaceutical compounds (Figure 5.2 b). The lowest MLSS value was obtained on the 56th day (second dosage of the pharmaceutical

compounds), when it was approximately 1.2 gL^{-1} , and the corresponding F/M increased to around $0.3 \text{ g}_{\text{CODgSS}}^{-1}\text{d}^{-1}$. Compared to the DOC values, the recovery of MLSS was slower, as more time was required for the regeneration of biological biomass. Approximately 10 days later, the MLSS returned to a stable value above 2 gL^{-1} .

Variations of significant magnitude were also observed for the EPS concentrations after the dosage of the pharmaceutical compounds (Figure 5.3 a). Analyses of EPS composition before and after pharmaceutical dosage provided further insight (Figure 5.3 b and c). Both supernatant and pellet EPS concentrations in $\text{mg}\cdot\text{gSS}^{-1}$ increased after the dosage of the pharmaceutical compounds, which is the result of both increase in measured concentration and reduction of MLSS. This observation is expected, in view of the known toxicity mitigation effect provided by increased EPS production as a microbial response under the pharmaceutical stress (Aquino and Stuckey 2004; Liu et al. 2004). Concomitantly, increase in the protein : polysaccharide ratio was observed for both supernatant and pellet EPS. The increase in protein content could be a natural microbial response (Sheng et al. 2005), or could also indicate occurrence of cell lysis and release of intracellular polymers under the pharmaceutical stress (Nielsen et al. 1997; Lee et al. 2003).

It is worth noting that a biokinetics study carried out prior to the dosage of the pharmaceuticals revealed no microbial inhibition due to the existing elevated salt environment (Lay et al. 2010c). The above observations were therefore clearly attributed to the effects of the pharmaceutical compounds.

EFFECTS ASSOCIATED WITH PHARMACEUTICAL REMOVAL

(a) DOC concentrations and removal from the OMBR

(b) MLSS and F/M ratio from the OMBR

Figure 5.2: Analyses of process parameters

- i) Ratio as derived from the measurements (n = 28): protein = $1.1 \pm 1.1 \text{ mg gSS}^{-1}$, and polysaccharide = $3.3 \pm 1.8 \text{ mg gSS}^{-1}$.
 ii) Ratio as derived from the measurements (n = 8): protein = $2.6 \pm 2.1 \text{ mg gSS}^{-1}$, and polysaccharide = $5.1 \pm 0.5 \text{ mg gSS}^{-1}$.
 iii) Ratio as derived from the measurements (n = 28): protein = $15.6 \pm 6.1 \text{ mg gSS}^{-1}$, and polysaccharide = $21.0 \pm 7.4 \text{ mg gSS}^{-1}$.
 iv) Ratio as derived from the measurements (n = 8): protein = $25.8 \pm 9.4 \text{ mg gSS}^{-1}$, and polysaccharide = $26.2 \pm 5.9 \text{ mg gSS}^{-1}$.

Figure 5.3: EPS analyses.

(a) EPS concentrations over the study duration, (b) Protein-to-polysaccharide ratio of supernatant EPS before and after pharmaceutical dosage, and (c) Protein-to-polysaccharide ratio of pellet EPS before and after pharmaceutical dosage

5.3.3 Liquid chromatography – organic carbon detection analysis

In order to investigate further the nature of the DOC that permeated the FO membrane during the pharmaceutical episode, two LC-OCD analyses were performed (Figure 5.4). The analysis in Figure 5.4 (a) is from a sample collected inbetween the two pharmaceutical dosages ($t = 54$ d), whereas the analysis in Figure 5.4 (b) is from a sample collected 10 days after the second pharmaceutical dosage when the biological process was assumed to have reasonably recovered in terms of DOC removal ($t = 66$ d).

Consistent with the results of the foregoing section, the total DOC of the samples measured by the LC-OCD agreed well with the measurements of the TOC analyser, verifying the reliability of both instruments. By comparing mixed liquor concentrations between the two samples, it is apparent that the pharmaceutical effect caused an increase of DOC across all fractions in absolute values, and the effect seemed particularly pronounced for the low molecular weight (LMW) neutrals. Correspondingly, almost all (2922 ppb) of the total DOC of D2 (3010 ppb) that permeated the FO membrane on $t = 54$ d appeared to be composed of such compounds (X1) that were also chromatographically glucose-like (Figure 5.4 a). The origin of these organic compounds was not immediately evident, but they were undoubtedly associated with the impaired biological process caused by the pharmaceutical stress, and could be residual substrate, intermediates, or materials released from cell lysis. This result points to the importance of a functional biological process for optimised OMBR system performance. While the biological process was demonstrated to be robust and recovered quickly from the pharmaceutical episode, the implication here is that contingency measures need to be in place for real applications, in case such incidents occur.

As the bioprocess recovered sufficiently ($t = 66$ d), the LC-OCD profiles resembled that of other studies (Huber 1998; Rosenberger et al. 2005; Zheng et al. 2009; Meng et al. 2010). The draw solution samples revealed a profile that was characteristic of permeate from a tight membrane where organic compounds with a molecular weight greater than 500 g mol^{-1} were effectively retained by the FO membrane. While some LMW organic species could pass through the tight FO membrane, the removal efficiency of such compounds was high and above 90%: for building blocks = $(1 - 365/5244) \times 100\% = 93\%$, and LMW neutrals = $(1 - 93/4673) \times 100\% = 98\%$. The traces of biopolymers (21 ppb) found in D2 could be attributed to a small amount of secondary production in the draw tank since it was not possible to maintain this tank in a totally sterile environment.

EFFECTS ASSOCIATED WITH PHARMACEUTICAL REMOVAL

(a) LC-OCD analysis on t = 54 d – chromatogram

>> signal for D2 is 10x enlarged

(b) LC-OCD analysis on t = 66 d – chromatogram

EFFECTS ASSOCIATED WITH PHARMACEUTICAL REMOVAL

Sample	Approximate Molecular Weight in gmol^{-1}					
		>20000	~1000	300-500	<350	<350
	CDOC					
	Hydrophilic	Biopolymers	Humic substances	Building Blocks	LMW Neutrals	LWM Acids
	[ppb-C] / [%DOC]	[ppb-C] / [%DOC]	[ppb-C] / [%DOC]	[ppb-C] / [%DOC]	[ppb-C] / [%DOC]	[ppb-C] / [%DOC]
Mixed liquor (R2)	24068	2639	9382	5671	6376	n.q.
	100.0%	11.0%	39.0%	23.5%	26.5%	-
Draw solution (D2)	3010		*		2922 (X1)	*
	100.0%				97.1%	

* The remaining dissolved organic carbon (DOC) fractions were not reported and amounted to 88 ppb-C, which corresponded to about 2.9% of the total DOC concentration in D2.

(a) LC-OCD analysis on t = 54 d – result table

Sample	Approximate Molecular Weight in gmol^{-1}					
		>20000	~1000	300-500	<350	<350
	CDOC					
	Hydrophilic	Biopolymers	Humic substances	Building Blocks	LMW Neutrals	LWM Acids
	[ppb-C] / [%DOC]	[ppb-C] / [%DOC]	[ppb-C] / [%DOC]	[ppb-C] / [%DOC]	[ppb-C] / [%DOC]	[ppb-C] / [%DOC]
Mixed liquor (R2)	20591	2391	8283	5244	4673	n.q.
	100.0%	11.6%	40.2%	25.5%	22.7%	-
Draw solution (D2)	482	21	n.q.	365	93	2
	100.0%	4.4%	-	75.8%	19.3%	0.5%

n.q. not quantifiable

(b) LC-OCD analysis on t = 66 d – result table

Figure 5.4: LC-OCD analyses

5.3.4 Microbiological analysis

DGGE is a well-established fingerprinting technique used to study microbial ecology (Muyzer 1999). While possible biases and limitations of this technique exist (sampling, DNA extraction, PCR amplification and DGGE separation), the technique yields meaningful information on changes in microbial community composition (Ovreas et al. 1997; Nubel et al. 1999; Schäfer and Muyzer 2001).

Figure 5.5: DGGE profiles from mixed liquor and membrane

DGGE analysis of the OMBR sludge community (Figure 5.5) revealed that the community changed over time. At the beginning of the experiment the microbial community was relatively diverse and evenly spread (D0). As the experiment progressed up until the first dosage of the pharmaceutical compounds on the 47th day, changes in the banding pattern could be observed, whereby some bands became less pronounced or disappeared altogether from the mixed liquor: b1, b2, b4, b7, b13 and b14; whereas other bands seemed to be stable in the mixed liquor but not of high intensity: b3, b11 and b15. Some bands became more pronounced over time: b8, b9,

b10, b12, b16 and b17, indicating that these may represent the more salt tolerant species as the salinity of the mixed liquor was increasing over time. In fact, one band in particular (b10) became dominant in the community during this time. The introduction of the pharmaceutical compounds (D56 and D63) resulted in dramatic changes in the community as observed by DGGE with some bands being completely eliminated (b8 and b16) and others decreased in intensity (b9, b10 and b15), while some bands became the most dominant indicating tolerant or resistant species (b12, b17, b18 and b19). Some species (b9, b10 and b15) were seen to recover by the end of the experiment (D73). Interestingly, the banding profile of the community isolated from the surface of the membrane (M73) clearly indicated that certain species preferentially attached and remained on the membrane surface (b5 and b7) while being only a small component of the mixed liquor. This result agreed well with other MBR studies that found distinctly different microbial communities associated with the biofilm formation on membrane surfaces (Miura et al. 2007; Huang et al. 2008).

Figure 5.6: Dendrogram analysis showing relative similarity between samples

Figure 5.7: Shannon-Weaver Index (H) of the analysed samples

Both dendrogram analysis (Figure 5.6) and Shannon-Weaver index (Figure 5.7) give consistent observations. The main groupings in the dendrogram analysis reflect that the intra-group similarity is generally high: D0 and D3 (start-up period), D28 and D42 (stable period with regards to salinity), and D56 and D63 (pharmaceutical stress); while the inter-group similarity is lower, especially with regard to M73 and the mixed liquor samples. The Shannon-Weaver index (H) is an appropriate diversity index, as it measures both species numbers (evenness) and species abundance (richness). Communities with more species and even distribution of individuals therefore have a higher H than communities with either fewer species or disproportionate populations of each species (Nubel et al. 1999; Stamper et al. 2003). The index started from a relatively high number (~ 1) and was rather stable for the first week (D0 – D7), but decreased dramatically to approximately 0.63 in the following week (D13), indicating that the microbial community was in the process of adapting to the increasing salinity of the mixed liquor. After this transition, microbial diversity gradually increased again to a high of 0.93 on D42, indicating adaptation to the saline environment occurs after an initial decrease in species diversity, which is in agreement with other studies on microbial diversity in saline waters (Oren 2002; Lefebvre et al. 2006). Further, if microbial diversity can be linked to adaptation of the community and biodegradation

efficiency (Bond et al. 1995; Snaidr et al. 1997), then the implication here is that the biological performance of an OMBR – given adequate acclimation – should be equally favourable when compared to conventional MBRs with non-saline environments. In fact, the above was confirmed in a separate biokinetics study where no microbial inhibition was observed under the existing elevated salt environment (Lay et al. 2010c).

The pharmaceutical episode reduced microbial diversity, which was in line with the previous observation on process impairment. The index did not increase to pretreatment values although if the experiment were run for longer, the diversity may have continued to increase. The H index for the membrane sample (M73) was the lowest among all the analysed samples, indicating that a selected few species inhabited the membrane. Given that the membrane in this study was mildly fouled (Chapter 4), the role of the membrane associated microbial community in relation to membrane performance clearly needs further investigation.

5.4 Concluding remarks

This chapter investigated the integration of forward osmosis membrane and biological process with regards to pharmaceutical removal, process parameters, water quality issues and microbiological analysis over a duration of 73 days for the experiment run CTA-I. Key findings from this study include:

- 1) With the high retention property of the FO membrane, the OMBR was generally able to achieve excellent product water quality. The product dissolved organic carbon (DOC) had been generally $\leq 1 \text{ mgL}^{-1}$, and the apparent DOC removal efficiency was generally $\geq 99\%$.
- 2) The high rejection of the studied pharmaceutical compounds (apparent removal efficiency $\geq 96\%$) allowed these compounds to be concentrated in the bioreactor, which would enhance their rate of biodegradation. This attribute attests to the potential advantage of OMBR for water reclamation application.
- 3) The biological process was found to play a key role in the overall performance of the OMBR. During the impairment of the biological process caused by the pharmaceutical dosage, product water quality and other process parameters were correspondingly affected.
- 4) Microbiological analysis reveals that a selected few species inhabited the membrane. The role of the membrane associated microbial community in relation to membrane performance needs further investigation.
- 5) This study paves the way for further research on the microbiology of OMBR and its relation to system performance, as well as possible effects of both elevated salinity and other accumulated constituents and SMP.

Chapter 6. Factors affecting salt accumulation in OMBR

6.1 Introduction

The foregoing chapters have demonstrated the successful integration of FO within a MBR setup. In general, the integrated OMBR system has been able to achieve both stable water production and good product quality. However, salt accumulation has shown to be a systemic and complex issue for OMBR that needs to be addressed, and is the objective of this study.

Salt accumulation is a real and significant issue of concern for OMBR, because elevated feed salinity can have consequences in the form of diminished driving force, membrane scaling if the precipitation limit of the relevant salts is exceeded, and further impacts in physicochemical and biological ways as noted in Chapter 2. Here, salt accumulation is the result of two phenomena: retention of the influent and reverse transmission of solutes from the draw solution into the feed liquid. The first phenomenon is common to all desalting processes, as salts and solutes that cannot pass through the membrane get retained and accumulate in the feed liquid. The second phenomenon regarding draw solute transmission is unique to FO, and occurs due to the large concentration difference between the draw solution and feed liquid. This phenomenon is important, because it not only results in exacerbation of the above mentioned salt accumulation effects due to retention, but it could also mean additional economic costs for replenishment of the lost draw solutes, and further consideration is needed if the draw solute is of environmental concern.

With regard to salt accumulation, earlier literature indicated the importance of having high water permeability (A) and low salt permeability (B) for an ideal FO membrane (Lee et al. 1981; Cath et al. 2006). Recent studies have provided further discussion on the issue by deriving optimal membrane properties in terms of the B/A ratio for FO applications based on modelling and short-term experiments using well defined feed liquid and draw solutions (Phillip et al. 2010; Xiao et al. 2011). On the other hand, longer term fouling studies by different research groups that used mixed feed water matrix in OMBR setups have reported different draw solute or salt flux at similar

water flux during experiments (Cornelissen et al. 2008; Achilli et al. 2009b). Such observation is interesting because the implication is that the B/A ratio can evolve. (Cornelissen et al. 2008) supposed that the observation could be attributed to the method of salt flux determination, while (Achilli et al. 2009b) pointed out that this could be a beneficial effect of membrane fouling.

Results from the experiment run CTA-I (Chapter 4) suggest that the adsorbed secondary layer on the membrane surface could have altered the interfacial electrochemical potential or plugged defects in the rejection layer, and hence reduced the B/A ratio. Experimental results from the other runs (this chapter), however, showed that evolution of the B/A ratio of an operating FO system is a complex issue, such that the observed B/A ratio could be either increasing or reducing, and the trend could be associated with the effects of fouling.

The objective of this chapter is to derive a coherent framework for understanding and providing discussion on the phenomenon of the evolving B/A ratio and its effects on salt accumulation and draw solute transmission in OMBR. The basis of the framework is the solution-diffusion model (Lonsdale et al. 1965), which has been successfully used for describing FO and tight membrane processes (Loeb et al. 1997; Baker 2004; Cath et al. 2006; Melin and Rautenbach 2007). Although the study focuses on OMBR, results may be applied to other FO systems too.

6.2 Theory

6.2.1 Salt accumulation equations

Salt accumulation in an OMBR can be expressed via system mass balance (refer to Figure 6.1) with the following equation:

$$V \frac{dc_{ml}}{dt} = Q_{in}c_{in} - Q_w c_{ml} + J_s A_m \quad (6.1)$$

Rearranging the equation with the relationships: $Q_{in} = Q + Q_w$ and $Q = J_w \cdot A_m$, the following differential equation is derived:

$$\frac{dc_{ml}}{dt} + \frac{Q_w}{V} c_{ml} = \frac{Q_{in}}{V} c_{in} + \frac{Q}{V} \cdot \frac{J_s}{J_w} \quad (6.2)$$

Figure 6.1: Conceptual diagram of an OMBR system for salt accumulation analysis

Here, the submerged configuration is illustrated, though the concept is equally applicable to side-stream configuration. Further, it is assumed that suitable post treatment and draw solution replenishment for the OMBR are available to adequately extract product water, and regenerate and supply draw solution at constant concentration.

Analytical solution of equation (6.2) requires assumption that Q is constant. This is reasonable if performance and fouling are stabilised. It is also known that internal concentration polarisation (ICP) in FO provides a ‘self-compensating’ effect on driving force that helps to stabilise flux (section 2.2.4). With this assumption, equation (6.2) may be considered as a first order linear ordinary differential equation, and can be solved analytically (Jank and Jongen 1996) as follows:

$$\frac{c_{ml}(t)}{c_{in}} = e^{-\frac{t}{(V/Q_w)}} \left[\frac{c_{ml}^{t=0}}{c_{in}} - \left(\frac{Q_{in}}{Q_w} + \left(\frac{Q_{in}}{Q_w} - 1 \right) \left(\frac{J_s / J_w}{c_{in}} \right) \right) \right] + \left(\frac{Q_{in}}{Q_w} + \left(\frac{Q_{in}}{Q_w} - 1 \right) \left(\frac{J_s / J_w}{c_{in}} \right) \right) \quad (6.3)$$

The term (V/Q_w) describes the average time that salt components would be retained in an OMBR in dependence on the reactor volume (V) and the waste stream flow (Q_w). A new parameter is defined in this study as the salt retention time (SaRT):

$$SaRT = \frac{V}{Q_w} \quad (6.4)$$

Although the SaRT may have identical expression as the solids retention time (SRT), which is an important factor for biological process (Chapter 2), the two parameters describe very different phenomena. The SaRT relates to salt components accumulated in an OMBR, whereas the SRT relates to the bio-solids in that OMBR. For the purpose of discussion on salt accumulation and to avoid ambiguity, the term (V/Q_w) is referred to in this chapter as the SaRT.

For the assumption that Q and Q_w are constant, the hydraulic retention time (HRT) can be derived: $HRT = V/Q_{in}$, with $Q_{in} = Q + Q_w$. In this instance, equation (6.3) can be expressed as:

$$\frac{c_{ml}(t)}{c_{in}} = e^{-\frac{t}{SaRT} \left[\frac{c_{ml}^{t=0}}{c_{in}} - \left(\frac{SaRT}{HRT} + \left(\frac{SaRT}{HRT} - 1 \right) \left(\frac{J_s / J_w}{c_{in}} \right) \right) \right]} + \underbrace{\left(\frac{SaRT}{HRT} + \left(\frac{SaRT}{HRT} - 1 \right) \left(\frac{J_s / J_w}{c_{in}} \right) \right)}_{\text{steady state term}} \quad (6.5)$$

The solution, expressed as the concentration factor ($CF = c_{ml}(t)/c_{in}$) contains two terms. The first term gives the transient solution that tends to zero as t approaches infinity. It provides mathematical evidence for the observation made by (Xiao et al. 2011) that the expression $SaRT$ has controlling influence over the rate of increase of the mixed liquor salt concentration and can be viewed as a time constant for the system. The second term gives the steady-state solution, which can also be derived by setting $dc_{ml}/dt = 0$ in equation (6.2). Furthermore, it is worth noting that $c_{ml}^{t=0}$ is the mixed liquor concentration at $t = 0$, and in general, it is not necessary that $c_{ml}^{t=0} = c_{in}$.

6.2.2 Significance of B/A ratio

The water permeability (A) and salt permeability (B) are linked to water flux (J_w) and salt flux (J_s) respectively via the solution-diffusion model (Lonsdale et al. 1965). Both A and B are sum parameters to describe the transport properties of diffusing components in homogenous membranes on a fundamental level, and a discourse in this subject is beyond the scope of this study. Unless otherwise specified, the draw solute considered in this study is sodium chloride (NaCl) – typical for FO application (Cath et al. 2006). Although other types of draw solute are available, and could give rise to different B values (Achilli et al. 2010), the general validity of this study is not affected.

Assuming validity of the van't Hoff relation that linearly links π to c (refer also to section 0) , it can be shown that (Tang et al. 2010):

$$\frac{J_s}{J_w} = \frac{B}{A \cdot v \cdot R_g \cdot T} \quad (6.6)$$

where v is the van't Hoff coefficient, R_g is the ideal gas constant, and T is the absolute temperature in K.

The above expression makes plain the significance of the B and A values for a FO process. This is different from RO, where J_w is related to a hydraulic pressure term while J_s is concentration dependent, so J_s and J_w for RO are not directly coupled. For FO, however, because $v \cdot R_g \cdot T$ is constant for a given operating condition, the extent of draw solute transmission J_s/J_w , also known as the specific reverse salt flux (Hancock and Cath 2009), is directly related to the B/A ratio. The B/A ratio has units of pressure, and hence may also be viewed as the effective osmotic pressure due to reverse transmission of the draw solutes. The expression also makes clear that draw solute transmission in FO systems is not dependent on the structural parameter of the membrane, which is a parameter that is known to significantly determine internal concentration polarisation (ICP) and hence the attainable water flux (Gerstandt et al. 2008; Phillip et al. 2010). This explains the rationale for designing FO membranes

with a highly selective active layer (high A and low B) (Phillip et al. 2010; Wang et al. 2010a), though it is also demonstrated in this study that membrane properties alone do not determine the overall draw solute transmission for practical applications.

Strictly speaking, the van't Hoff relation is valid only for dilute solution under near ideal conditions (Melin and Rautenbach 2007). However, (Tang et al. 2010) has shown by modelling with established osmotic pressure software that deviation in water flux due to the linear van't Hoff relation is relatively small (<5%) even for relatively high draw solution concentrations (> 3M NaCl), and has substantiated soundness of the above analysis. The application of the van't Hoff relation also points to the equivalence of the concentration factor expressions:

$$CF = \frac{c_{ml}}{c_{in}} = \frac{\pi_{ml}}{\pi_{in}} \quad (6.7)$$

6.2.3 Relevance of dimensionless water production parameter

For practical applications, it is often the actual water production that is pertinent rather than the operating time. A membrane process that is operated for a longer duration at low flux may produce the same amount of water as one with a shorter duration at higher flux. This point is more relevant here, because J_w and hence Q for a typical FO process are not necessarily constant. In this instance, a dimensionless water production parameter $\int Q/V dt$ is introduced. If Q is constant, then this parameter has the following relation:

$$\int \frac{Q}{V} dt = \frac{Q}{V} \cdot t = \frac{(Q_{in} - Q_w)}{V} \cdot t = \left(\frac{Q_{in}}{Q_w} - 1 \right) \cdot \frac{t}{(V/Q_w)} = \left(\frac{SaRT}{HRT} - 1 \right) \cdot \frac{t}{SaRT} \quad (6.8)$$

When $SaRT/HRT \gg 1$, equation (6.8) can be approximated to:

$$\int \frac{Q}{V} dt \approx \frac{t}{HRT} \quad (6.9)$$

It can thus be seen that the parameter can be related to a form of production time normalised over the HRT. On a more fundamental level, there is an additional interpretation for the parameter. The fundamental differential equation (6.2) can be rearranged and integrated as given in equation (6.10):

$$\int \frac{dc_{ml}}{c_{in}} = \int \frac{Q}{V} \cdot \left(1 + \frac{J_s / J_w}{c_{in}}\right) dt - \int \frac{Q_w}{V} \cdot \left(\frac{c_{ml}}{c_{in}} - 1\right) dt \quad (6.10)$$

For initial start up of the process (t is small), when the salt concentration effect is relatively minor such that the order of $c_{ml}/c_{in} \approx 1$, and further if $Q > Q_w$ (typical for MBR application), then examination of equation (6.10) shows that the second integral term on the right hand side of the equation is comparatively negligible. In this instance, and applying van't Hoff relation, equation (6.10) can be simplified into equation (6.11).

$$\frac{\Delta \pi_{ml}}{\pi_{in}} = \frac{\Delta c_{ml}}{c_{in}} \approx \int \frac{Q}{V} \cdot \left(1 + \frac{J_s / J_w}{c_{in}}\right) dt = \int \frac{Q}{V} dt \cdot \left(1 + \frac{B / A}{\pi_{in}}\right) \quad (6.11)$$

The significance of this expression is that when a graph is plotted with concentration factor (π_{ml}/π_{in}) as the y-axis against $\int Q/V dt$ as the x-axis, the initial gradient of the curve is directly related to $(1 + (B/A)/\pi_{in})$ and allows for quick and visualised approximation of the extent of draw solute transmission.

6.2.4 In-series model relating overall B/A ratio to individual layers

When fouling occurs as a secondary layer on the membrane, the relation of the overall B/A to the individual layers of a membrane-plus-secondary layer configuration can be readily derived with an in-series model as depicted in Figure 6.2.

Figure 6.2: In-series model for development of a secondary layer on a FO membrane

For simplicity, the support layer of the membrane by itself alone is assumed to have negligible effect on the A and B values in the overall scheme of things. Alternatively, a third layer can be considered. For consistency, the membrane orientation 'active layer facing mixed liquor (feed water)' is illustrated. The model is equally applicable for the reverse membrane orientation, such that the secondary layer can form within or on the membrane support layer.

For an in-series model, the following relations based on the solution-diffusion theory are valid:

$$\begin{aligned} J_w &= A \cdot (\pi_{me-ds} - \pi_{ml-la}) \\ &= A_{me} \cdot (\pi_{me-ds} - \pi_{la-me}) = A_{la} \cdot (\pi_{la-me} - \pi_{ml-la}) \end{aligned} \quad (6.12)$$

$$\begin{aligned} J_s &= B \cdot (c_{me-ds} - c_{ml-la}) \\ &= B_{me} \cdot (c_{me-ds} - c_{la-me}) = B_{la} \cdot (c_{la-me} - c_{ml-la}) \end{aligned} \quad (6.13)$$

Manipulation of the above equations gives the followings:

$$\frac{J_w}{A} = \frac{J_w}{A_{me}} + \frac{J_w}{A_{la}} \quad (6.14)$$

$$\frac{J_s}{B} = \frac{J_s}{B_{me}} + \frac{J_s}{B_{la}} \quad (6.15)$$

The relations for the overall A and B respectively therefore are:

$$\frac{1}{A} = \frac{1}{A_{me}} + \frac{1}{A_{la}} \quad (6.16)$$

$$\frac{1}{B} = \frac{1}{B_{me}} + \frac{1}{B_{la}} \quad (6.17)$$

The above relations show that the overall A or B value is always smaller than the least of the respective values of the individual layers. This means that the presence of a secondary layer tends to reduce both A and B. In terms of water production, the reduced A generally has a negative effect, because J_w reduces correspondingly (refer also to Chapter 7).

Manipulation of equations (6.16) and (6.17) gives the following expression for the overall B/A ratio:

$$\frac{B}{A} = \frac{(1/A_{me} + 1/A_{la})}{(1/B_{me} + 1/B_{la})} = \frac{\frac{A_{me} + A_{la}}{A_{me} \cdot A_{la}}}{\frac{B_{me} + B_{la}}{B_{me} \cdot B_{la}}} = \frac{B_{me}}{A_{me}} \cdot \left(\frac{\frac{A_{me} + A_{la}}{A_{la}}}{\frac{B_{me} + B_{la}}{B_{la}}} \right) \quad (6.18)$$

And finally:

$$\frac{(B/A)}{(B_{me}/A_{me})} = \frac{(A_{me}/A_{la} + 1)}{(B_{me}/B_{la} + 1)} \quad (6.19)$$

This equation will be applied to study the effects of a secondary layer on the overall draw solute transmission and salt accumulation in the OMBR.

6.3 Experimental and modelling methods

6.3.1 Experimental protocol

The materials and methods adopted are generally as described in Chapter 3. The experiment runs referred to here are TFC-I, TFC-II, CTA-I, and CTA-II. The TFC membrane was located in the bioreactor R1, whereas the CTA membrane was located in the bioreactor R2. The synthetic feed water was consistent within each run, but of different concentration between the two runs. The average SaRT for the first run (Run I) was 20 d, and 10 d for the second run (Run II). For each run, an experimental duration of at least 3 x SaRT was observed. The HRT for each bioreactor varied according to the flux and hence mixed liquor concentration, but stabilised within the experimental time frame. For convenience, a brief description of the membranes used in this study is presented in Table 6.1.

Table 6.1: Brief description of the FO membranes used in this study

	Membrane in R1	Membrane in R2
Membrane type	Thin film composite (TFC)	Cellulose triacetate-woven (CTA)
Module type	Hollow fibre	Flat sheet
Orientation	AL-DS	AL-FW
A_{me} [$Lm^{-2}h^{-1}bar^{-1}$]	1 – 3	0.5 – 0.7
$(B/A)_{me}$ [bar]	< 0.1	0.8 – 2.5

6.3.2 Modelling method

The modelling of observed concentration factor for each experiment was conducted with a simple numerical method using suitable time steps as given in the below equations, similar to the method applied in Chapter 4. The equation (6.20) was derived from the salt accumulation differential equation (6.2), so as to consider volumetric effects brought about by a changing J_w and hence $Q^{(t)}$. An appropriate linear function was assumed for $(B/A/\pi_{in})$ for each experiment.

$$\frac{d(\frac{\pi_{ml}}{\pi_{in}})}{dt} \approx \frac{\Delta(\frac{\pi_{ml}}{\pi_{in}})}{\Delta t} = \frac{Q^{(t)}}{V} (1 + \frac{B}{A} \frac{1}{\pi_{in}}) - \frac{Q_w}{V} (\frac{\pi_{ml}^{(t-1)}}{\pi_{in}} - 1) \quad (6.20)$$

$$\frac{\pi_{ml}^{(t)}}{\pi_{in}} = \Delta(\frac{\pi_{ml}}{\pi_{in}}) + \frac{\pi_{ml}^{(t-1)}}{\pi_{in}} \quad (6.21)$$

6.3.3 Chi-square statistics for goodness of fit test

The chi-square statistics (χ^2) was applied as a quality control measure to determine the goodness of fit between the modelled concentration factors (E_i) and the experimental observed ones (O_i), and analysed as follows (Montgomery and Runger 2003):

$$\chi^2 = \sum_{i=1}^k \frac{(O_i - E_i)^2}{E_i} \quad (6.22)$$

6.4 Results and discussion

A number of B/A scenarios have been modelled and are presented below (sections 6.4.1 – 6.4.3), and are then compared to experimental data (section 6.4.4).

6.4.1 Effects of SaRT/HRT and B/A ratios on steady state concentration factor

The steady state concentration factor (π_{ml}/π_{in}) as given in equation (6.23) can be readily derived from equation (6.5) by setting t equal to infinity, and then applying van't Hoff relation for J_s/J_w .

$$CF = \frac{\pi_{ml}}{\pi_{in}} = \frac{c_{ml}}{c_{in}} = \left(\frac{B/A}{\pi_{in}} + 1 \right) \cdot \frac{SaRT}{HRT} - \frac{B/A}{\pi_{in}} \quad (6.23)$$

This relation allows a straight line graph to be plotted with π_{ml}/π_{in} as the y-axis against SaRT/HRT as the x-axis (Figure 6.3). The gradient of the line ($B/A/\pi_{in} + 1$) can then be considered as the sum of two effects: salt accumulation due to draw solute transmission and salt accumulation due to volumetric concentration of the influent. It is somewhat trivial to note the limiting condition for the relation is SaRT/HRT = 1, that is: the entire influent flow goes to the waste stream ($Q_{in} = Q_w$).

Figure 6.3 shows four cases as derived from analysis of equation (6.23). Although a range of B/A value has been reported for FO membranes, typically it is around 0.1 – 1 bar. In this instance, the four analysed cases can be considered to reflect different application scenarios. Case (a) gives the reference scenario with either zero draw solute transmission ($B = 0$) or π_{in} is infinitely large compared to B/A. This may mean an ideal FO membrane with 100% separation of the draw solutes. This case may also be understood to represent other desalting processes such as RO or distillation processes, whereby there is no draw solute transmission. Case (b) would give the scenario for saline waters like industrial water, brackish water or seawater, such that π_{in} is a magnitude of order larger than B/A. Case (c) represents the scenario for lower salinity water or for water reclamation involving domestic sewage, such that π_{in} is the same order of magnitude as B/A. This is also the typical application scenario for the

OMBR. Case (d) may represent specific application that involves ultra pure water or idealised FO experiments that use distilled or deionised water as feed water, such that π_{in} is a magnitude of order smaller than B/A .

Figure 6.3: Steady state concentration factor as function of $SaRT/HRT$ and $(B/A)/\pi_{in}$

- (a) $(B/A)/\pi_{in} = 0$;
- (b) $(B/A)/\pi_{in} = 0.1$;
- (c) $(B/A)/\pi_{in} = 1$;
- (d) $(B/A)/\pi_{in} = 10$.

Case (a) represents the reference scenario with zero draw solute transmission, such that π_m/π_{in} is wholly dependent on $SaRT/HRT$. Deviation from this reference case reflects the effect of draw solute transmission, as illustrated by the example for case (c) with $SaRT/HRT = 20$. For this example, draw solute transmission $(B/A/\pi_{in})$ contributes to nearly half of the salt accumulation (π_m/π_{in}) for the FO system.

Equation (6.23) reveals that salt accumulation in a FO system is controlled in three ways: membrane (B/A), influent (π_{in}), and process ($SaRT/HRT$ which is linked via ϕ). Furthermore, the role of B/A is application-dependent, and needs to be considered within the context of π_{in} . So, for example: water reclamation application where $B/A/\pi_{in} \sim 1$ (case (c)), selection of FO membrane with lower B/A would be an effective way to reduce salt accumulation, but the same measure if applied without

due consideration to seawater desalination – $B/A/\pi_{in} < 0.1$ (case (b)) – would only achieve a marginal result. In this instance, the more effective way to reduce salt accumulation in a FO system for this application is to operate at a lower SaRT/HRT or ϕ . The above underscores the point made by (Xiao et al. 2011) that a useful selection criterion for FO membrane depending on application is $B/A/\pi_{in} = 0.1$: above which select for a membrane with a lower B/A even at the expense of a moderately lower A , and below which select for a membrane with a larger A even at the expense of a moderately higher B/A . The foregoing discussion makes clear that sound knowledge of factors affecting salt accumulation is indispensable for optimisation of FO systems.

6.4.2 Concentration factor in relation to varying B/A ratio

Figure 6.4 shows modelling of concentration factor over the operation of an OMBR both from the perspective of time (t/SaRT) and production ($\int Q/V dt$) for a constant Q and Q_w scenario under different B/A ratios. Cases (a) and (b) are modelled for constant $B/A/\pi_{in}$ at 0.1 and 1, respectively. The other cases are modelled for changing $B/A/\pi_{in}$ either with a distinct step function: (c) and (e), or with a simple linear function: (d) and (f). For all cases, steady state in the form of a stabilised concentration factor is achieved by the third SaRT, a condition that may correspond well to the necessary acclimation time for a biological process (Wang et al. 2009). The implication here is that for adequate study of salt accumulation in an OMBR or a FO system, an experimental duration of at least $3 \times \text{SaRT}$ would be necessary. Furthermore, the figure shows the effects of changing B/A ratio. When π_{in} is constant, typical for most applications, increasing B/A results in greater steady state concentration factor (π_{ml}/π_{in}). The converse applies for decreasing B/A . The relation between the initial gradient of a presented case and the extent of its draw solute transmission ($\Delta\pi_{ml}/\pi_{in} \sim (1 + B/A/\pi_{in}) \cdot \int Q/V dt$) as discussed in section 6.2.3 is also readily apparent from the figure.

Figure 6.4: Temporal variation of concentration factor for different $(B/A)/\pi_{in}$ ratios

Constant Q and Q_w are assumed. The six modelled cases are:

- (a) $(B/A)/\pi_{in} = 0.1$;
- (b) $(B/A)/\pi_{in} = 1$;
- (c) $(B/A)/\pi_{in} = 1$ for $0 \leq t/SaRT < 1$, followed by a step decrease with $(B/A)/\pi_{in} = 0.1$ for $t/SaRT \geq 1$;
- (d) $(B/A)/\pi_{in}$ has a linear decreasing function $= 1 - 0.1 \cdot (t)$ for $0 \leq t/SaRT < 1$, followed by $(B/A)/\pi_{in} = 0.1$ for $t/SaRT \geq 1$;
- (e) $(B/A)/\pi_{in} = 0.1$ for $0 \leq t/SaRT < 1$, followed by a step increase with $(B/A)/\pi_{in} = 1$ for $t/SaRT \geq 1$;
- (f) $(B/A)/\pi_{in}$ has a linear increasing function $= 0.1 + 0.1 \cdot (t)$ for $0 \leq t/SaRT < 1$, followed by $(B/A)/\pi_{in} = 1$ for $t/SaRT \geq 1$.

6.4.3 Significance of secondary layer on overall B/A ratio

As evident from equation (6.19), the overall B/A ratio of a dual-layer FO system with respect to draw solute transmission is dependent on the respective A_{me}/A_{la} and B_{me}/B_{la} ratios, and can be graphically presented in Figure 6.5. The starting point for a clean FO membrane in the absence of any secondary layer with both A_{la} and B_{la} equal infinity, such that both A_{me}/A_{la} and B_{me}/B_{la} equal zero. Due to the scale of the Figure, this point is located outside the graph. For illustration purpose, it is indicated as (0) in the figure. Furthermore, the figure can be broadly divided into 4 quadrants based on the reference point $A_{me}/A_{la} = B_{me}/B_{la} = 1$. The desired goal is to have lower draw solute transmission: $(B/A)/(B_{me}/A_{me}) \leq 1$, while maintaining reasonably satisfactory

water permeability: $(A_{me}/A_{la}) \leq 1$, so it is apparent that the region of interest is the lower left quadrant. On the other hand, the upper right quadrant is to be avoided, because it gives both greater draw solute transmission and lower water permeability.

Figure 6.5: Overall B/A ratio in dependence on A_{me}/A_{la} and B_{me}/B_{la}

The overall B/A ratio is normalised over membrane property (denoted by subscript 'me') in relation to the respective relative effects of the secondary layer (denoted by subscript 'la') as derived from equation (6.19):

- (a) $B_{me}/B_{la} = 0$;
- (b) $B_{me}/B_{la} = 0.5$;
- (c) $B_{me}/B_{la} = 1$;
- (d) $B_{me}/B_{la} = 2$;
- (e) $B_{me}/B_{la} = 10$.

The presented graphs appear curved due to the logarithmic scale. Points labelled as (I) and (II) illustrate the possible evolution of the overall B/A ratio for two hypothetical membranes. Experimental observations however, give a point (I*) that would be beyond the limiting case (a) for the TFC membrane, though point (I) may correspond to the CTA membrane to a certain extent.

For discussion, consider two different types of FO membrane: (I) has high water permeability and high rejection for draw solute (i.e. high $A_{me(I)}$ and low $B_{me(I)}$) but is prone to severe fouling; whereas (II) has modest values for both water permeation

and draw solute rejection such that $A_{me(I)} \geq A_{me(I\ I)}$ and $B_{me(I)}/B_{me(I\ I)} \leq 10$, but is more fouling resistant. The B/A ratio of clean membrane between (I) and (I I) would be therefore $(B_{me}/A_{me})_{(I)} \geq 10 \cdot (B_{me}/A_{me})_{(I\ I)}$. To a certain extent, these two hypothetical membranes may represent the actual membranes used in the experimental studies.

Consider further that the same fouling layer would develop on both membranes and would have water (A_{la}) and salt permeability (B_{la}) properties such that $A_{me(I)} > A_{la} > A_{me(I\ I)}$ and $B_{me(I)} < B_{la} < B_{me(I\ I)}$. The effects of such a secondary layer on the two membranes are therefore for (I): $A_{me(I)}/A_{la} > 1$ and $B_{me(I)}/B_{la} < 1$ resulting in a greater overall B/A ratio with $(B/A)_{(I)}/(B_{me}/A_{me})_{(I)} > 1$, and for (I I): $A_{me(I\ I)}/A_{la} < 1$ and $B_{me(I\ I)}/B_{la} > 1$ resulting in a lower overall B/A ratio with $(B/A)_{(I\ I)}/(B_{me}/A_{me})_{(I\ I)} < 1$. The above results can also be succinctly read off from the figure.

The foregoing discussion shows that even at the same level of fouling, membrane (I) lands in the unfavourable upper right quadrant of the figure with overall B/A ratio that is worse off than the original membrane property; whereas membrane (I I) finds itself in the favourable lower left quadrant of the figure with a significantly improved overall B/A ratio. This finding demonstrates that contrary to popular belief (Phillip et al. 2010; Wang et al. 2010a), membrane with the highest A and lowest B does not necessarily give the best overall result in terms of draw solute transmission for a practical FO application, but rather, it may be more important to have an optimised membrane that is able to maintain or improve its overall B/A ratio under real operating conditions. More on the effects of fouling and other flux reducing mechanisms on the overall B/A ratio with experimental data are discussed in the subsequent section.

6.4.4 Practical application: evolution of B/A ratio

All four experimental runs were conducted on a longer term basis with duration longer than $3 \times \text{SaRT}$, such that the effects of salt accumulation and draw solute transmission could be closely monitored. The observed overall B/A ratios over each experimental run for the TFC membrane in R1 and for the CTA membrane in R2 are presented in Figure 6.6 and Figure 6.7, respectively.

The observed B/A ratios were derived from an averaging method, and hence inevitably presented fluctuations due to limitation in the instrument's sensitivity and also time-dependent flux and fouling behaviours, which were difficult to quantify in exact detail. However, clear trends with two distinct stages could be observed for each reactor, where the same type of membrane was used even though different operating conditions were applied between the two experimental runs.

For the TFC membrane (Figure 6.6), the first stage took place from the experimental beginning to about $\int Q/V dt = 18$. During this stage, the TFC membrane in both runs started off with a low overall B/A value (≤ 0.05 bar) that gradually increased with fluctuations to around 0.2 bar. The second stage occurred from around $\int Q/V dt = 18$ until the end of the experiment, where the overall B/A ratio showed a step increase with a significantly greater final average value that is about 10 times or larger than the respective initial value. For TFC-I, the final average overall B/A value was 0.7 bar, and for TFC-II, the final average overall B/A value was 0.5 bar.

For the CTA membrane (Figure 6.7), however, a different trend was observed. The first stage for R2 seemed to take place between experimental beginning and about $\int Q/V dt = 4$, during which the overall B/A ratio reduced. The second stage occurred after around $\int Q/V dt = 4$ until the end of the experiment, such that the CTA membrane in both runs gave the same average overall B/A value at around 0.3 bar that was distinctly smaller than its initial value.

Figure 6.6: Evolution of the B/A ratio for the TFC-membranes

For both experimental runs: a two stage evolution could be observed: a more gradual increase initially for $0 \leq \int(Q/V)dt < 18$, followed by a step increase around $\int(Q/V)dt = 18$. The arrow and the perforated line indicate approximate point of transition between the two stages.

Figure 6.7: Evolution of the B/A ratio for the CTA-membranes

For both experimental runs: a two stage evolution could be observed: a steep decrease initially for $0 \leq \int(Q/V)dt < 4$, and then levelled off at around 0.3 bar for $\int(Q/V)dt > 4$. The arrow and the perforated line indicate approximate point of transition between the two stages.

With the above derived overall B/A ratios, salt accumulation in the form of concentration factor ($CF = \pi_{ml} / \pi_{in}$) could be modelled for each experimental run as described in section 6.3.2 and presented in Figure 6.8.

Figure 6.8: Comparison of observed and modelled concentration factors

Goodness of fit test was conducted with Chi-square statistics (χ^2) as given in section 6.3.3.

Simple linear function was modelled for the respective observed evolving overall B/A ratio:

(a) TFC-I: $(B/A)/\pi_{in} = 1.5 \cdot 10^{-1} + 2.4 \cdot 10^{-2} \int(Q/V)dt$ for $0 \leq \int(Q/V)dt < 18$, and $(B/A)/\pi_{in} = 2.0$ for $\int(Q/V)dt \geq 18$, $\chi^2_{TFC-I} = 0.35 < \chi^2_{\alpha=0.05, v=73} = 93.94$;

(b) TFC-II: $(B/A)/\pi_{in} = 8 \cdot 10^{-2} + 1.7 \cdot 10^{-2} \int(Q/V)dt$ for $0 \leq \int(Q/V)dt < 18$, and $(B/A)/\pi_{in} = 1.0$ for $\int(Q/V)dt \geq 18$, $\chi^2_{TFC-II} = 0.60 < \chi^2_{\alpha=0.05, v=31} = 44.97$;

(c) CTA-I: $(B/A)/\pi_{in} = 3.5 - 6.6 \cdot 10^{-1} \int(Q/V)dt$ for $0 \leq \int(Q/V)dt < 4$, and $(B/A)/\pi_{in} = 0.9$ for $\int(Q/V)dt \geq 4$, $\chi^2_{CTA-I} = 0.51 < \chi^2_{\alpha=0.05, v=73} = 93.94$;

(d) CTA-II: $(B/A)/\pi_{in} = 1.6 - 2.4 \cdot 10^{-1} \int(Q/V)dt$ for $0 \leq \int(Q/V)dt < 4$, and $(B/A)/\pi_{in} = 0.6$ for $\int(Q/V)dt \geq 4$, $\chi^2_{CTA-II} = 0.39 < \chi^2_{\alpha=0.05, v=31} = 44.97$.

All models show good fit to the observed data, though it should be noted that the goodness of fit was in part due to the known volumetric parameters ($Q^{(i)}$, Q_w and V) from the experiments, which were applied in the models. Nonetheless, the fact that each model attained such good statistical results substantiates that the evolution of the overall B/A ratio was well approximated. Had this not been the case, entirely different

modelled values would have been resulted for different B/A ratios even when the same volumetric parameters were applied as shown in Chapter 4.

Referring to the effects of secondary layer as discussed in Figure 6.5, a somewhat superficial perception may be that the TFC membrane in R1 could be compared to point (I), while the CTA membrane in R2 could be compared to point (I I). This may be reasonable, since the $(B/A)_{me}$ ratio of the virgin TFC membrane is about 10 times smaller than that of the CTA membrane, such that even under the same fouling effects, the evolution of the B/A ratio for the two membranes could have been different: increasing trend for the TFC membrane in R1, and reducing trend for the CTA membrane in R2.

However, further analysis reveals more information. First, different fouling behavior was found for the two membranes. Post-experiment autopsies (results not shown) on the fouled membranes based on Energy-dispersive X-ray (EDX) spectroscopy analysis and reverse osmosis (RO) experiments under pure water condition found that the TFC membrane was severely fouled such that the overall A value for the fouled TFC membrane was reduced by about half compared to its virgin value ($A_{me}/A_{la} \sim 1$), whereas the CTA-woven membrane was mildly fouled such that there was no noticeable reduction in the overall A value ($A_{me}/A_{la} \sim 0$).

Second, the different initial A value of the membranes resulted in significantly higher initial flux in the TFC membrane as compared to the CTA-woven membrane. This could aggravate fouling in the TFC membrane both in terms of foulant deposition based on the critical and sustainable flux concepts (Bacchin et al. 2006; Wang et al. 2010b), and cake-enhanced concentration polarisation (Hoek and Elimelech 2003; Lee et al. 2010), although the latter should not affect salt transmission effects if the B/A ratio had remained unchanged as discussed in Chapter 4.

Third, the orientation of the two membranes needs consideration. The TFC membrane in R1 had the membrane orientation ‘active layer facing draw solution’, meaning that its support layer is fully exposed to foulants of the mixed liquor, and was thus very vulnerable to a multi-component fouling mechanism (Tang et al. 2011). Foulants that

entered into the membrane support layer would become entrapped within this layer and could not be mitigated by the aerated environment and hydrodynamics of the bulk liquid flowing outside the membrane. The consequence is an internal clogging mechanism that caused severe fouling in the TFC membrane, which could give rise to low foulant layer water permeability ($A_{me}/A_{la} \geq 1$), and greatly diminish the overall water permeability (Mi and Elimelech 2008; Tang et al. 2010). Such a fouling effect would have a comparatively milder effect on salt permeability, which has a diffusion-based mechanism, and hence would give $B_{me}/B_{la} \leq 1$. Therefore, the final result is such that the overall B/A ratio will increase correspondingly. It should be noted that further development of the TFC membrane aims for usage with ‘active layer facing feed’ orientation.

Fourth, closer examination of Figure 6.5 reveals that the fouled TFC membrane would correspond to the point (I*) and not (I), as the final evolved (B/A) value is about 10 times or larger than the initial value at $A_{me}/A_{la} \sim 1$. This is interesting, and seems to defy the physical relations presented, as the point (I*) lies beyond the limiting case of $B_{me}/B_{la} = 0$. Furthermore, the two stage evolution with a step increase in the overall B/A ratio at around $\int Q/V dt = 18$ is highly noteworthy. The observations are significant, because these imply that a simple fouling concept based on the formation of a secondary layer on the membrane is not able to adequately explain the observed phenomenon, such that there *must* be further flux diminishing mechanisms at work for the TFC membrane. While ongoing efforts aim at identifying and minimising such effects, the following may provide explanations for the above observations on the TFC membrane. Coupled with foulant deposition, the TFC membrane could be vulnerable to a number of effects:

- 1) It is known that UF-type membranes or substrates could suffer reduction in water permeability due to a compaction mechanism even at low pressures (Persson et al. 1995; Bohonak and Zydney 2005). As shown by (Bohonak and Zydney 2005), such loss in permeability could be particularly pronounced for a skin-side down orientation, which corresponded to the orientation of the TFC membrane in this study. Under the action of both water permeation and foulant deposition, it is possible that some voids in the support layer of the TFC membrane may collapse or be filled,

giving greater hydraulic resistance and hence lower overall A value but with marginal effect on salt transmission, which is diffusion-based. The consequence would be increase in the overall B/A ratio, which could be moderate and gradual initially until a critical number of voids have collapsed or been filled up. This phenomenon would have similar effects as the internal clogging mechanism discussed above, and experimentally it would be difficult to differentiate between the two mechanisms. However, the foregoing discussion points to another flux diminishing mechanism that may need consideration.

2) Submerged hollow fibre membranes in aerated systems have shown to exhibit unstable filtration behaviour due to presence of air bubbles entrapped within the membrane, attached onto the membrane surface or in the lumen of the fiber, causing mal-distribution of local fluxes and flow resistances (Chang et al. 2007; Chang et al. 2008). Similar to 1), the consequence would be diminishing overall A value and increasing overall B/A ratio. Such a phenomenon will be aggravated by fouling (Chang et al. 2007), in view of changed surface roughness, points of hydrophobicity and geometric characteristics that may apply to the TFC membrane. It may also partly explain the fluctuations of the observed B/A ratios in Figure 6.6.

3) Hollow fibre membranes typically face integrity challenges due to inevitable mechanical stresses from time-dependent structure-fluid interactions during operations (Huisman 2004; Childress et al. 2005). Mechanical forces either in the form of local shear forces or vibrations could be induced by the aerated environment and would exert stresses on the membrane and module. It is possible that as a certain stress point was exceeded, nano-defects in the membrane or module for the TFC membrane could have been produced, giving rise to a jump in the overall B/A ratio. It is known too that such a phenomenon can be aggravated by fouling (Huisman 2004).

The flat sheet CTA membrane in R2, on the contrary, had the membrane orientation ‘active layer facing mixed liquor’, and would have less of the above mentioned challenges (refer also to Chapter 4). The favourable orientation with the dense and relatively smooth surface of the CTA-woven membrane allowed for fouling mitigation by the two phase liquid flow in the aerated mixed liquor. Furthermore, the

moderate A value of the CTA-woven membrane resulted in relatively low initial flux that would be advantageous in terms of fouling. The resulting fouling on the CTA-woven membrane was mild, such that the secondary layer formed on the membrane could have plugged defects in the membrane active layer and moderated salt transmission as discussed in Chapter 4. The behaviour of the CTA-woven membrane may be characterised by point (I I) in Figure 6.5.

Finally, while the foregoing analysis sheds light on the effects of fouling on draw solute transmission and salt accumulation in the experimental OMBR runs, result interpretation needs to be made in the proper perspective. The effects of fouling on FO performance remain a complex area that needs more research. Further studies are planned for the TFC hollow fibre membranes to adopt the orientation of ‘active layer facing mixed liquor’. Furthermore, it should be noted that despite the unfavourable fouling condition, the TFC-II continued to produce greater water flux compared to the CTA runs (Chapter 7). In addition, the average final overall B/A ratio of the fouled TFC membranes remained < 1 bar, and well within reasonable working range for FO systems. In the light of the findings of this study, research efforts should aim at developing FO membranes with the desired properties of high A value, low B/A ratio and also high resistance to fouling. The study makes clear that sound knowledge of factors affecting salt accumulation is essential for optimisation of FO systems.

6.5 Concluding remarks

A simple framework has been developed for analysis of salt accumulation in OMBR, and may be applicable for other FO systems too. The analysis is able to qualitatively explain the phenomena observed, and provides following discussion:

- 1) Salt accumulation in OMBR is controlled by three factors: membrane, influent, and process. In this regard, the role of the membrane is application-dependent and significant only when influent osmotic pressure is smaller or in the same order of magnitude as the salt to water permeability ratio (B/A).
- 2) Experimental duration of 3 x salt retention time (SaRT) is necessary for adequate study of salt accumulation in OMBR, where the SaRT is a newly introduced parameter defined as system volume divided by the waste stream flow. Although SaRT may have the same expression as SRT, the two parameters describe different phenomena. The SaRT relates to salt components accumulated in an OMBR, whereas the SRT relates to the bio-solids in that OMBR.
- 3) Fouling can cause the evolution of the overall B/A ratio in OMBRs. The relationship is dependent on the relative A_{me}/A_{la} and B_{me}/B_{la} ratios. Generally, a reducing overall B/A ratio can be associated with mild fouling, and an increasing overall B/A ratio can be associated with severe fouling and further flux reducing mechanisms.
- 4) With regards to reducing draw solute transmission and hence salt accumulation in an OMBR, the desired membrane properties are high A value, low B/A ratio and high resistance to fouling.
- 5) Analysis of the evolving overall B/A ratio in OMBR provides a method to obtain fundamental information on the system behavior for optimisation of OMBR performance.

Chapter 7. OMBR flux performance and potential assessment

7.1 Introduction

On a systemic level, there are two main issues concerning the performance of OMBR. The first issue relates to salt accumulation, and has been discussed in Chapter 6. The second issue relates to flux performance of OMBR. This is because flux determines productivity, and ultimately, viability of the technology. In this study, a novel approach is developed to assess factors affecting flux performance of OMBR. A brief discussion on potential of the OMBR technology is presented at the end of this chapter.

Flux of a membrane process is largely influenced by both membrane intrinsic properties and fouling, which is complex (Belfort 1984). For a FO system, it is an even more complex affair, due to the added intricacy of internal concentration polarisation (ICP) as noted in the literature review. The ICP is a phenomenon inherent to the osmosis driven membrane process, and is due to hindered diffusion of solutes within the membrane support layer. In general, ICP acts to diminish the overall driving force across a membrane (Loeb et al. 1997; Cath et al. 2006), but under the membrane orientation ‘active layer facing feed water’, it provides a self-compensating mechanism that could maintain relatively stable flux under fouling conditions (Chapter 4). Consequently, an analysis of flux and this in relation to the underlying intricate factors of influence is of significant application relevance.

The goal of this study is to provide a platform for discussion of factors affecting the performance of an OMBR, although it would also be applicable to the other FO systems. Consequently, the term ‘FO’ may be used interchangeably with ‘OMBR’ in the text, depending on which term may be more relevant to the context. The study provides a simple theoretical framework deriving different methods to assess flux performance of an OMBR. The methods were then systematically applied to modelled scenarios and experimental observations from six OMBR runs with the objective of obtaining information on the process.

7.2 Theoretical background

7.2.1 Flux equations for forward osmosis

The flux equations for FO are discussed in Chapter 2. In general, external concentration polarisation effects are not considered, as these could be mitigated by fluid management and are typically minor compared to the greater effects of internal concentration polarisation (ICP) or cake enhanced concentration polarisation (CECP) (Lee et al. 1981; Gray et al. 2006). For convenience, an overview is presented below.

For a FO process with the membrane orientation of active layer facing feed water (AL-FW):

$$J_w = A \cdot \left[\left(\pi_{ds} + \frac{B}{A} \right) \cdot e^{-\left(\frac{J_w}{K_m} \right)} - \left(\pi_{ml} + \frac{B}{A} \right) \cdot e^{\left(\frac{J_w}{k_{CECP}} \right)} \right] \quad (7.1)$$

Here, the subscripts ‘ml’ and ‘ds’ denote mixed liquor and draw solution, respectively.

For general applicability, A and B are the overall water and salt permeability coefficients and may be related to the respective coefficients of a membrane (subscript ‘me’) and fouling layer (subscript ‘la’) based on the resistance-in-series approach as follows (section 6.2.4):

$$\frac{1}{A} = \frac{1}{A_{me}} + \frac{1}{A_{la}} \quad (7.2)$$

$$\frac{1}{B} = \frac{1}{B_{me}} + \frac{1}{B_{la}} \quad (7.3)$$

Furthermore, K_m is the mass transfer coefficient describing the ICP phenomenon within the membrane support layer, which may be described as:

$$K_m = \frac{D_{ds}}{S_{me}} = \frac{D_{ds} \cdot \varepsilon_{me}}{t_{me} \cdot \tau_{me}} \quad (7.4)$$

where D_{ds} is the diffusion coefficient of the draw solute and S_{me} is a structural parameter related to the structural properties of the membrane support layer, namely: thickness (t_{me}), porosity (ε_{me}) and tortuosity (τ_{me}).

The effects of CECP may be expressed via a mass transfer coefficient as follows:

$$k_{CECP} = \frac{D_{ml} \cdot \varepsilon_{la}}{\delta_{la} \cdot \tau_{la}} \quad (7.5)$$

where D_{ml} is diffusion coefficient of the solutes within the fouling layer, and ε_{la} , δ_{la} , and τ_{la} are the porosity, thickness and tortuosity of the fouling layer, respectively.

It should be noted that another form of concentration polarisation known as the cake reduced concentration polarisation (CRCP) has also been reported (Chapter 2). While CECP may enhance the solute wall concentration on the membrane, CRCP may reduce the solute wall concentration on the membrane. Between CECP and CRCP, CECP would have greater and adverse effect on flux performance, and is modelled as a limiting condition in this study. However, contrary to RO systems, where CECP and CRCP may alter salt transmission (Kim et al. 2009); this may not apply to FO systems with regard to draw solute transmission. This is because both draw solute flux and water flux are dependent on the same net osmotic driving force – equation (2.6).

Analogous to the foregoing, a FO process with membrane orientation of active layer facing draw solution (AL-DS) under assumption of negligible external CP effects may be modelled as:

$$J_w = A \cdot \left[\left(\pi_{ds} + \frac{B}{A} \right) - \left(\pi_{ml} + \frac{B}{A} \right) \cdot e^{\left(\frac{J_w}{K_{m+foul}} \right)} \right] \quad (7.6)$$

Symbols given in equation (7.6) are defined as above, except for the parameter K_{m+foul} , which should be understood to be a complex overall mass transfer coefficient that couples both ICP and fouling mechanisms. In the absence of fouling or other performance diminishing effects, $K_{m+foul} = K_m$.

It may also be noted from equations (7.1) and (7.6) that the flux behaviour for the different membrane orientations (AL-FW versus AL-DS) could be different, but would converge at higher recovery (Chou et al. 2010). Unless otherwise stated, the membrane orientation assumed for the modelled scenarios of this study is that of AL-FW. For the experimental investigations, however, both membrane orientations were tested and are commented on accordingly.

7.2.2 Conventional approaches for assessing flux performance

Conventional approaches for describing flux performance of a FO process are the FO-RO flux ratio (Xu et al. 2010), and the apparent water permeability (Mehta and Loeb 1978b; Mehta 1982), or variants of these such as the performance ratio (McCutcheon et al. 2006), RO-FO flux ratio (Cornelissen et al. 2008), or specific water flux (Martinetti et al. 2009; Cath et al. 2010). In most instances, the underlying rationale is to assess the performance of a FO process relative to its pressure-driven counterpart under the same amount of driving force. On a more fundamental level, these methods may also provide further mechanistic information on the processes. For instance, the FO-RO flux ratio (referred as performance ratio in (McCutcheon and Elimelech 2007)) may indicate flux inefficiency due to ICP, and offers important implications for improved membrane design. The apparent FO water permeability, referred to as specific water flux in (Cath et al. 2010), could be used to indicate flux decline due to fouling, and not due to changes in operating conditions and driving force.

In this study, the FO-RO flux ratio and apparent FO water permeability are defined in equation (7.7) and (7.8), respectively.

$$\text{FO-RO flux ratio} = \frac{J_w}{J_{w(RO)}} \text{ with} \quad (7.7)$$

$$J_{w(RO)} = A \cdot (\Delta p - \Delta \pi) = A \cdot (\pi_{ds} - \pi_{ml})$$

The FO-RO flux ratio may be applied to assess the relative performance of a FO process based on the deviation from a modelled RO process for the same apparent driving force across the membrane ($\pi_{ds} - \pi_{ml}$). In accordance with equation (7.7), the RO flux takes into account membrane water permeability and osmotic pressure of the mixed liquor but excludes effects of fouling and CECP.

$$\text{Apparent FO water permeability} = \frac{J_w}{(\pi_{ds} - \pi_{ml})} \quad (7.8)$$

The above parameter is referred to here as the apparent FO water permeability, because it gives a FO flux that is normalised to the apparent driving force across the membrane, and has the units $[\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}]$. Similar to the FO-RO flux ratio, the apparent FO water permeability is able to assess the relative performance of a FO process based on deviation from a modelled condition. However, the difference between the two parameters pertains to the omission of the water permeability coefficient. As such, the use of the apparent FO water permeability may be advantageous to compare performance of membranes with different water permeability coefficient, and in addition, provides an assessment of the utilisation of the available osmotic driving force. In general, high driving force utilisation is desired, such that the targeted water production may be achieved with a lower draw solution concentration (Garcia-Castello et al. 2009). Furthermore, high draw solution concentration may run the risk of “osmotic deswelling” of membranes (Mehta and Loeb 1978b).

From equation (7.7), the FO-RO flux ratio ($J_w/J_{w(RO)}$) simplifies to (assumptions: $B/A \approx 0$, $B/A < \pi_{ml} \ll \pi_{ds} \cdot e^{-(J_w/K_m)}$, and negligible effects of fouling and CECP: $J_w \ll k_{CECP}$):

$$\frac{J_w}{J_{w(RO)}} \approx e^{-\left(\frac{J_w}{K_m}\right)} \quad (7.9)$$

Similarly, from equation (7.8), the apparent FO water permeability ($J_w/(\pi_{ds} - \pi_{ml})$) may be simplified to:

$$\frac{J_w}{(\pi_{ds} - \pi_{ml})} \approx A \cdot e^{-\left(\frac{J_w}{K_m}\right)} \quad (7.10)$$

Figure 7.1: Conceptual illustration for FO-RO flux ratio factor and apparent FO water permeability

The RO flux curve can be derived from the relation $J_w = A(\Delta p - \Delta \pi_{ml})$, and the FO-flux curve can be derived from equation (8.1) for the AL-FW membrane orientation. Assumptions: $\pi_{ml} = 0$, $B/A = 0$ and negligible effects of fouling and concentration polarisation. The points (a) and (b) serve to illustrate that while point (a) results in more favourable values for $J_w/J_{w(RO)}$ and $J_w/(\pi_{ds} - \pi_{ml})$, it produces a lower water flux and has a smaller flux compensating capacity as compared to point (b) due to a smaller osmotic driving force.

Figure 7.1 illustrates the two above parameters derived for a given membrane with $\pi_{ml} = 0$, $B/A = 0$ and negligible effects of fouling and CECP. From the figure, it can be observed that the FO-RO flux ratio graphically describes the “gap” between the FO flux curve and the RO flux curve, and reflects the extent of ICP (i.e. the factor K_m). This “gap” gets wider with increasing $(\pi_{ds} - \pi_{ml})$, due to the exponential effect of ICP on flux. The apparent FO water permeability gives the slope of a straight line from the origin in a graph that is plotted J_w as the y-axis against $(\pi_{ds} - \pi_{ml})$ as the x-axis. Such a straight line has decreasing slope with increasing $(\pi_{ds} - \pi_{ml})$. The apparent FO water permeability therefore is a measure of driving force utilisation, which includes the effects of both A and K_m . More discussion of the above can be found in section 7.4.1.

7.2.3 Novel flux-recovery analysis for assessment of flux efficiency

The foregoing shows that the conventional approaches with FO-RO flux ratio and apparent FO water permeability may provide information on a FO system. Following the example in Figure 7.1, consider the points (a) and (b). The two parameters would give smaller values with increasing driving force due to the non-linear flux-driving force curve, and could be readily understood as the manifestation of ICP, since absence of fouling had been assumed. Consequently and superficially, this may seem to suggest that operating at point (a) would be more favourable than point (b).

However, practical considerations may provide an alternative view point. Firstly, the matter of fact is that higher flux could be attained in point (b) as compared to (a). A higher productivity would bring about economic benefits. Secondly, the larger extent of ICP at (b) could provide a correspondingly greater flux compensating capacity (section 2.2.4), such that if there had been a loss in driving force due to fouling and/or CECF which would be inevitable for real operations, point (b) would be able to maintain a more stable water production than (a). Finally, the discussion thus far does not provide a direct link to a practical process parameter. This provides motivation to derive a new method for assessing flux performance of a FO system that would be of practical relevance.

Recovery is a process parameter of significant practical importance (Belfort 1984). Higher recovery means greater output for the same input, and the implications include (AWWA 2004): reduction in the quantity of source water required, reduction in pretreatment facility capacity and pumping, and volume minimisation of concentrate that needs disposal. All of the above are important for a practical application. In particular, the last attribute points to the goal of zero-liquid discharge, which is of great environmental relevance and significance. Therefore, high recovery is generally desired for a membrane process, so long as the process is able to operate within limits of scale formation and/or excessive osmotic pressure of the retentate, while maintaining adequate product water quality and sustainable energy consumption.

Furthermore, recovery (ϕ) has additional significance for a membrane bioreactor (MBR) system, because it relates to the solids retention time (SRT) and hydraulic retention time (HRT) as presented in equation (7.11). The SRT and HRT could have various effects on the overall performance of an MBR system (Chapter 2).

$$\frac{SRT}{HRT} = \frac{1}{(1 - \phi)} \quad (7.11)$$

A graphical presentation of experimentally observed flux and recovery could provide important information on an operating FO process as shown by (Martinetti et al. 2009). Expanding from this concept, the following develops a new and quantitative approach that may be applied to assess the flux performance of a FO system. This novel approach is named *flux-recovery analysis* in this study.

When steady-state operation or reasonably stable flux may be assumed, the mixed liquor osmotic pressure of an OMBR can be related via a salt mass balance as follows (Chapter 6):

$$CF = \frac{\pi_{ml}}{\pi_{in}} = \frac{c_{ml}}{c_{in}} = \left(\frac{B/A}{\pi_{in}} + 1 \right) \cdot \frac{SaRT}{HRT} - \frac{B/A}{\pi_{in}} \quad (6.23)$$

The equivalent expression of SaRT and SRT allows for substitution of equation (7.11) into equation (6.23) as follows:

$$\frac{\pi_{ml}}{\pi_{in}} = \left(\frac{B/A}{\pi_{in}} + 1 \right) \cdot \frac{1}{(1 - \phi)} - \frac{B/A}{\pi_{in}} \quad (7.12)$$

In equation (7.12), the term $1/(1-\phi)$ represents the volumetric concentration factor (Chapter 6), whilst the term (B/A) signifies the effect of draw solute transmission contributing to the overall salt accumulation in an OMBR. By application of this expression, a general equation that links flux to recovery can be derived for a FO process with membrane orientation ‘AL-FW’ – see equation (7.1):

$$J_w = A \cdot \left[\left(\pi_{ds} + \frac{B}{A} \right) \cdot e^{-\left(\frac{J_w}{K_m} \right)} - \left(\pi_{in} + \frac{B}{A} \right) \cdot \left(\frac{1}{1-\phi} \right) \cdot e^{\left(\frac{J_w}{k_{CECP}} \right)} \right] \quad (7.13)$$

Furthermore, a reference condition can be defined as one with negligible effects of draw solute transmission ($B/A = 0$), fouling ($A = A_{me}$) and concentration polarisation ($k_{CECP} = \infty$), and $B/A < \pi_{ml} \ll \pi_{ds} \cdot e^{-(J_w/K_m)}$, but with otherwise constant membrane and process parameters as the actual application scenario. In this instance, a so-called reference flux ($J_{w, re}$) curve can be derived as per equation (7.14).

$$J_{w, re} = A_{me} \cdot \left[\pi_{ds} \cdot e^{-\left(\frac{J_w}{K_m} \right)} - \pi_{in} \cdot \left(\frac{1}{1-\phi} \right) \right] \quad (7.14)$$

The reference condition therefore gives the highest attainable flux for a given recovery, and hence accounts for the volumetric concentration effect. Note that the $J_{w, re}$ curve is application dependent, and is defined only for given membrane properties, draw solution osmotic pressure (π_{ds}) and influent osmotic pressure (π_{in}).

Figure 7.2: Conceptual illustration of flux – recovery analysis for an OMBR.

The SRT/HRT graph is incorporated in the graphic to show its direct relation to ϕ . The reference flux ($J_{w, \text{re}}$) is derived for an OMBR application with $\pi_{\text{ds}} = 46.9$ bar, $\pi_{\text{in}} = 0.5$ bar, $A = 2 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, and $K_m = 10 \text{ Lm}^{-2}\text{h}^{-1}$. As an arbitrary example, the OMBR would be operated at $\phi = 90\%$ (SRT/HRT = 10, and corresponding $J_{w, \text{re}} = 13.8 \text{ Lm}^{-2}\text{h}^{-1}$) and $J_{w, \text{ob}} = 10 \text{ Lm}^{-2}\text{h}^{-1}$. The flux efficiency factor here would be therefore: $J_{w, \text{ob}} / J_{w, \text{re}} = 10/13.8 = 0.72$.

As illustrated in Figure 7.2, the $J_{w, \text{re}}$ curve makes plain the trade-off between flux and recovery. While relatively stable $J_{w, \text{re}}$ could be maintained at low recovery, it may reduce drastically at high recovery due to volumetric concentration effects even without fouling and other performance diminishing effects. Theoretically, a feasible operating range may be located between the two extremes to achieve reasonably high recovery while maintaining adequate flux. However, the actual operating range is application dependent, and may need to be derived under economic considerations.

$$\text{Flux efficiency factor} = \left(\frac{J_{w,ob}}{J_{w,re}} \right)_{\varphi_{ob} = \varphi_{re}} \quad (7.15)$$

Accordingly, the ratio of the actual experimentally observed flux and the reference flux at the same recovery ($J_{w,ob} / J_{w,re}$), defined here as the *flux efficiency factor*, provides a quantitative assessment on the flux performance of an operating FO process relative to its reference condition. Following the above definition, $J_{w,ob}/J_{w,re}$ is always ≤ 1 , dimensionless and has an ‘efficiency’ connotation. The interpretation here is that the smaller this ratio, the less efficient is the analysed FO system with respect to the reference condition. Visually, this gives the distance between the operating point to the $J_{w,re}$ curve at the corresponding recovery. Consequently, $J_{w,ob}/J_{w,re}$ provides useful information on flux performance diminishing factors in the form of draw solute transmission (B/A), fouling resistance in the form of its effect on water permeability (A_{me}/A_{la}) and cake-enhanced concentration polarisation (k_{CECP}), which are often difficult to measure in a practical application.

7.3 Experimental and modelling methods

7.3.1 Experimental protocol

The materials and methods adopted are generally as described in Chapter 3. For convenience, description of the membranes and the experiment runs considered in this study are presented in Table 7.1 and Table 7.2.

The observed flux derived in this study was the stable flux derived towards the end of an experiment run. Where no stable condition could be observed, the observed flux was the average of the final three day flux points. The mixed liquor concentration for each experimental run was different and varied according to the volumetric concentration ratio and draw solute transmission for a given run.

Altogether, six OMBR runs were studied. These were TFC-II and TFC-III, and CTA-III to CTA-VI. While the experiment runs TFC-II, CTA-III and CTA-IV were started with fresh mixed liquor at low concentration, the other experiment runs were started at higher concentrations. All experimental findings were expressed with the dimensionless water production parameter ($\int Q/V dt$) as discussed in Chapter 6.

Osmotic backwash was conducted for TFC-II at $\int Q/V dt \sim 16$, and for CTA-V at $\int Q/V dt \sim 57$. The osmotic backwash was performed by stopping draw solution circulation and passing MilliQ water through this loop for an hour. However, unique of this study is that, instead of employing an external saline solution (Achilli et al. 2009b), the elevated salinity of the mixed liquor was gainfully used here to provide the natural reverse osmotic driving force. No significant effect on the bioreactors was found during osmotic backwash. This technique could be readily used in practice.

In general, scaling propensity assessment was performed in accordance to the method described in Chapter 3. The concentrations of Ca^{2+} and SO_4^{2-} ions in the influent feed water were measured to be 17.1 ± 2.8 ppm and 68.1 ± 9.8 ppm, respectively. The concentration of aqueous CO_3^{2-} ion was derived using the OLI software in view of carbonate equilibrium relations, and because there had been no external carbonate

species added in the system. Based on known concentration factor for each experimental run, the mixed liquor concentration of these ions could be estimated, and the corresponding saturation indices (SI) could be derived. Scaling may occur for SI > 1.

As part of membrane autopsy, energy-dispersive X-ray (EDX) spectroscopy analysis was performed on used membrane samples at the Facility for Analysis, Characterisation, Testing and Simulation (FACTS) of NTU. The Confocal laser scanning microscopy (CLSM) examination was performed at the Advanced Environmental Biotechnology Centre (AEBC) of NTU.

Table 7.1: Brief description of the FO membranes used in this study

	Membrane in R1	Membrane in R2
Membrane type	Thin film composite (TFC)	Cellulose triacetate-woven (CTA)
Module type	Hollow fibre	Flat sheet
Orientation	AL-DS	AL-FW
A_{me} [$Lm^{-2}h^{-1}bar^{-1}$]	1 – 3	0.5 – 0.7
$(B/A)_{me}$ [bar]	< 0.1	0.8 – 2.5

Table 7.2: Overview of the experimental runs considered in this chapter

Reference experiment (membrane)	Draw solution, bulk		Membrane orientation	Membrane Area	Bioreactor volume
	NaCl concentration	Osmotic pressure			
	c_{ds} [mol·kg ⁻¹ NaCl]	π_{ds} [bar]	[-]	A_m [cm ²]	V [L]
TFC-II	0.5	22.8	AL-DS	260	4
TFC-III	0.25	11.3	AL-DS	305	4
CTA-III	0.5	22.8	AL-FW	744	5
CTA-IV	1.0	46.9	AL-FW	744	5
CTA-V	1.0	46.9	AL-FW	744	5
CTA-VI	1.0	46.9	AL-DS	744	5

7.3.2 Modelling analyses

In this study, two modelling analyses were performed.

The first analysis (Table 7.3) sought to discuss effects of transport parameters (A , B/A and K_m) by comparing five different scenarios as given in the table. The scenarios were selected to give representative FO membranes with well-defined conditions. As such, membrane orientation was AL-FW, and low recovery with negligible feed water osmotic pressure and negligible effects of fouling and CECP were assumed.

The second analysis (table 7.4) sought to provide discussion based on the flux-recovery analysis as developed in section 7.2.3. For this work, realistic operating conditions were considered. The modelled feed water had an influent osmotic pressure (π_{in}) of 0.5 bar, which would correspond to the experiments, and also to practical applications with total dissolved solids (TDS) concentration in the range 500 – 1000 ppm (Belfort 1984; AWWA 2004). The modelled draw solution had osmotic pressure (π_{ds}) of 46.9 bar, which would correspond to a NaCl concentration of 1 mol·kg⁻¹, and may be typical of FO studies for similar application (Cath et al. 2006). By assuming a set of operating parameters (AL-FW membrane orientation, π_{ds} , π_{in} , A_{me} , and K_m), the analysis considers (a) a mild condition and (b) a more severe condition regarding performance diminishing effects on an operating FO process. These performance diminishing effects include: draw solute transmission (B/A), fouling resistance with regard to its effect on water permeability (A_{me}/A_{la}) and cake-enhanced concentration polarisation effects (k_{CECP}) as discussed in section 7.2.3. The foulant referred to in the model was silica particles of 20 nm based on the method of (Lay et al. 2010a). The mild condition would depict a relatively thin foulant layer about 5 – 10 μ m thick. The more severe condition would depict a thicker layer about 30 – 50 μ m thick.

Table 7.3: Modelled scenarios for FO-RO flux ratio factor and apparent FO water permeability

Scenario	Transport parameters		
	A [Lm ⁻² h ⁻¹ bar ⁻¹]	B/A [bar]	K _m [Lm ⁻² h ⁻¹]
i)	1	0.1	5
(i i)	2	0.1	5
(iii)	1	0.1	10
(iv)	2	0.1	10
(v)	1	1	5

Table 7.4: Modelled parameters for flux-recovery analysis

parameters	Reference	(a) Mild	(b) Severe
Membrane orientation	AL-FW	AL-FW	AL-FW
π_{ds} [bar]	46.9	46.9	46.9
π_{in} [bar]	0.5	0.5	0.5
A _{me} [Lm ⁻² h ⁻¹ bar ⁻¹]	2	2	2
K _m [Lm ⁻² h ⁻¹]	10	10	10
B/A [bar]	0	0.1	1
A _{me} /A _{la} [-]	n.a.	0.1	0.5
k _{CECP} [Lm ⁻² h ⁻¹]	n.a.	100	18.7

7.4 Results and discussion

This section commences with the results of modelling flux performance (7.4.1), and is followed by experimental observations and analysis (7.4.2).

7.4.1 Modelling results

7.4.1.1 FO-RO flux ratio factor and apparent FO water permeability

For a general impression, the five modelled scenarios (Table 7.3) are presented in a flux-driving force diagram (Figure 7.3). Scenario (i) may be viewed as a baseline condition. Scenario (i i) shows the effect of increasing water permeability (A) alone; scenario (iii) shows the effect of increasing mass transfer coefficient (K_m) alone; scenario (iv) shows the combined effect of increasing both A and K_m ; and finally, scenario (v) shows the unfavourable scenario of increasing draw solute transmission (B/A).

Figure 7.3: Modelled water flux as function of osmotic driving force

For ease of reference, the properties of the five modelled FO membranes are reproduced as follows:

- (i) $A = 1 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, $B/A = 0.1$ bar; and $K_m = 5 \text{ Lm}^{-2}\text{h}^{-1}$
- (i i) $A = 2 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, $B/A = 0.1$ bar; and $K_m = 5 \text{ Lm}^{-2}\text{h}^{-1}$
- (iii) $A = 1 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, $B/A = 0.1$ bar; and $K_m = 10 \text{ Lm}^{-2}\text{h}^{-1}$
- (iv) $A = 2 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, $B/A = 0.1$ bar; and $K_m = 10 \text{ Lm}^{-2}\text{h}^{-1}$
- (v) $A = 1 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, $B/A = 1$ bar; and $K_m = 5 \text{ Lm}^{-2}\text{h}^{-1}$

For illustration, the pure water permeability lines are included in the graphic.

Figure 7.3 makes plain the non-linear flux-driving force relationship inherent of a FO process. With increasing $(\pi_{ds} - \pi_{ml})$, any increment in flux becomes more and more offset by the exponential effect of ICP (refer also to Chapter 2).

The relative effects of the various transport parameters can also be observed from the example in the figure. Comparing scenarios (i), (i i) and (iii), both A and K_m have significant influence over the attainable FO flux. With smaller osmotic driving force (in the example: $(\pi_{ds} - \pi_{ml}) \leq 10$ bar), A has greater significance than K_m . With greater osmotic driving force ($(\pi_{ds} - \pi_{ml}) \geq 20$ bar), K_m is the dominant influence. There is a transition region ($10 \text{ bar} < (\pi_{ds} - \pi_{ml}) < 20 \text{ bar}$), where both A and K_m are of about equal importance. This observation can be readily understood by consideration of ICP. Flux is higher with greater osmotic driving force, such that the effect of ICP, and hence K_m , is dominant. In contrast, when osmotic driving force is small, flux and hence the effect of ICP is correspondingly small. In this instance, A has more influence on flux than K_m . The attainable flux may only be doubled (scenario iv), when both A and K_m are doubled with respect to the baseline condition. At the other end, scenario (v) seems to suggest that the term ' B/A ' by itself only has a small effect on the attainable flux. This apparent observation may apply, because both negligible recovery ($\phi \sim \pi_{ml} \sim 0$) and negligible CECP ($k_{CECP} \sim \infty$) had been assumed for a well-defined condition. For a real application where both π_{ml} and k_{CECP} may be considerable, B/A will have significant effect on the final observed flux (this is discussed in section 7.4.1.2). The foregoing discussion substantiates conventional wisdom that a high performing FO process should have high A , low B/A , and large K_m (Cath et al. 2006; McCutcheon and Elimelech 2007; Wang et al. 2010a). However, all three parameters may also be influenced by fouling or operational effects. A mild fouling condition could have negligible effects on A and K_m , but beneficial effect on B/A , whereas a more severe fouling condition may adversely affect all there parameters depending on membrane orientation (Chapter 6). From equation (7.4), it can also be noted that the factor K_m may be enhanced by membrane design with thinner and more porous support layer, or by operating at higher temperature or using more mobile solutes – both would have the effect of increasing diffusion coefficient (McCutcheon and Elimelech 2006; Cornelissen et al. 2008).

(a)

(b)

Figure 7.4: (a) Modelled FO-RO flux ratio factor, and (b) apparent FO water permeability

For ease of reference, the properties of the five modelled FO membranes are reproduced as follows:

- (i) $A = 1 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, $B/A = 0.1 \text{ bar}$; and $K_m = 5 \text{ Lm}^{-2}\text{h}^{-1}$
- (ii) $A = 2 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, $B/A = 0.1 \text{ bar}$; and $K_m = 5 \text{ Lm}^{-2}\text{h}^{-1}$
- (iii) $A = 1 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, $B/A = 0.1 \text{ bar}$; and $K_m = 10 \text{ Lm}^{-2}\text{h}^{-1}$
- (iv) $A = 2 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, $B/A = 0.1 \text{ bar}$; and $K_m = 10 \text{ Lm}^{-2}\text{h}^{-1}$
- (v) $A = 1 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, $B/A = 1 \text{ bar}$; and $K_m = 5 \text{ Lm}^{-2}\text{h}^{-1}$

Figure 7.4 (a) presents the FO-RO flux ratio factor ($J_w/J_{w(RO)}$) for the five modelled scenarios. As noted in section 7.2.2, $J_w/J_{w(RO)}$ may be visualised to describe the “gap” between the FO flux curve and the RO flux curve, and $J_w/J_{w(RO)}$ is always ≤ 1 . With small $(\pi_{ds} - \pi_{ml})$ and hence low flux, the effect of ICP may be marginal, such that $J_w/J_{w(RO)} \approx 1$. With increasing $(\pi_{ds} - \pi_{ml})$, the parameter has a declining trend of an exponential form due to ICP. In general, the “gap” may be widened by a steeper RO curve or a flatter FO curve. In this regard, a membrane with higher A generally gives less favourable $J_w/J_{w(RO)}$, because the effect of A is larger on RO than on FO, thus making the “gap” bigger. Similarly, a membrane with smaller K_m makes the “gap” bigger due to the ICP effect on the FO flux curve. From the figure, it can be observed that scenario (iii) gives the most favourable $J_w/J_{w(RO)}$ because it has the lowest A and biggest K_m , though it does not give the highest flux among all modelled scenarios. In an analogous way, scenario (i i) gives the least favourable $J_w/J_{w(RO)}$ because it has the highest A and smallest K_m , though it does not give the lowest flux among all modelled scenarios. The other three scenarios (i), (iv) and (v) are almost non-distinguishable for this parameter. The foregoing discussion shows the difficulty of interpreting $J_w/J_{w(RO)}$ as a standalone analysis due to different A and K_m values across the five scenarios. More conclusive analysis on $J_w/J_{w(RO)}$ may be made for a case where the A value would be constant or comparable – for example, scenario (i i) and (iv). In this instance, the role of K_m shows up.

Figure 7.4 (b) indicates that the apparent FO water permeability ($J_w/(\pi_{ds} - \pi_{ml})$) may reflect better the flux performance of the modelled scenarios. It does not have the difficulty issue as the parameter $J_w/J_{w(RO)}$ when comparing membranes of different A and K_m , as these are already implicitly considered in the parameter (section 7.2.2). As noted earlier, $(J_w/(\pi_{ds} - \pi_{ml}))$ has an added advantage of providing information concerning driving force utilisation. When the downstream post-treatment process (for example, RO) is sensitive to draw solution concentration (Cath et al. 2006; Achilli et al. 2009b), it may be necessary to select for a FO system that gives a more favourable $J_w/(\pi_{ds} - \pi_{ml})$. However, when a sustainable downstream post-treatment process (for example, membrane distillation or a thermal process, and given adequate supply of waste heat) is not exactly sensitive to draw solution concentration (Cath et

al. 2006; McCutcheon et al. 2006), this information may be of lesser importance from the application perspective. However, it should be pointed out that $J_w/(\pi_{ds} - \pi_{ml})$ reduces in magnitude and may be less precise with increasing $(\pi_{ds} - \pi_{ml})$. As can be observed from the figure, it becomes more difficult to discern $J_w/(\pi_{ds} - \pi_{ml})$ between the scenarios: (i i) and (iii), or (i) and (v). This, again, may be attributed to the effect of ICP resulting in the non-linear flux-driving force relationship.

7.4.1.2 Flux-recovery analysis

The foregoing discussion shows that both parameters ($J_w/J_{w(RO)}$) and ($J_w/(\pi_{ds} - \pi_{ml})$) are useful and provide information on the process under different circumstances. However, a common limitation to both parameters would be their practical relevance and for larger osmotic driving force $(\pi_{ds} - \pi_{ml})$. In this instance, the use of flux-recovery analysis as developed in section 7.2.3 may be advantageous.

The results of a flux-recovery analysis as applied to the two modelled conditions (Table 7.4) with (a) mild and (b) more severe performance diminishing effects are given in Figure 7.5. The analysis is further categorised into five curves (i)-(v) to show the individual and combined effects of B/A , A_{me}/A_{la} and k_{CECP} . Curve (i) gives the reference flux ($J_{w,re}$) which applies universally for both (a) and (b) of this particular example. The $J_{w,re}$ curve shows that the maximum recovery (i.e. ϕ_{max} for $J_{w,re} = 0$) attainable for this hypothetical FO system would be around 98.9%. At the other end, for recovery (ϕ) lower than 80%, $J_{w,re}$ would be greater than $15 \text{ Lm}^{-2}\text{h}^{-1}$ and relatively stable. A target operating range in this example may be ϕ : 80% – 95%, with $J_{w,re} = 10 - 15 \text{ Lm}^{-2}\text{h}^{-1}$ for a balance trade-off.

As illustrated in Figure 7.5 (a), the extent of all three performance diminishing effects for the modelled mild condition is subdued. For $\phi < 90\%$, the flux efficiency factor ($J_{w,ob}/J_{w,re}$) even for curve (v) is consistently > 0.9 , meaning that flux loss due to such effects are less than 10% for this range of recovery. For ϕ : 90% – 95%, $J_{w,ob}/J_{w,re}$ remains relatively high and is within the range 0.8 – 0.9. Further observations can be made on curves (i i)-(iv). For lower recovery, A_{me}/A_{la} (curve iv) is the dominant performance diminishing effect. There is a transition region for ϕ : 80% – 90%, such

that all three effects have comparable influence over flux. For $90\% < \phi < 98\%$, however, the order of influence is such that: $A_{me}/A_{la} < k_{CECP} < B/A$. This is because at high recovery, salt accumulation due to volumetric concentration (SRT/HRT) is severe, which gets aggravated with draw solute transmission (B/A) – equation (7.12). The elevated osmotic pressure of the mixed liquor has a direct reducing impact on the osmotic driving force difference across the membrane (curve i i), which outweighs the other two effects (A_{me}/A_{la} and k_{CECP}). The effect of k_{CECP} by itself is also greater at higher recovery (curve iii), because it exponentially increases the feed-side osmotic pressure on the membrane surface. It can accelerate the effect of salt accumulation and worsen the diminishing effect on flux (Lee et al. 2010). However, the effect of k_{CECP} lessens as flux reduces, which can be understood from the term $\exp(J_w/k_{CECP})$ in equation (7.1). The effect of A_{me}/A_{la} , however, stays static throughout.

Figure 7.5 (b) shows the effects of a more severe performance diminishing condition. The severity of this condition shows up in the flux efficiency factor ($J_{w,ob}/J_{w,re}$), such that for $\phi = 0\%$, $J_{w,ob}/J_{w,re}$ is already smaller than 0.8 for curve (v). As recovery increases, $J_{w,ob}/J_{w,re}$ reduces, such that for $\phi \geq 90\%$, $J_{w,ob}/J_{w,re} \leq 0.5$. And at ϕ around 96.8%, water production would cease for the hypothetical FO system under this condition (curve v). It is worth noting that the individual effects (curves (i i)-(iv)) here behave qualitatively similar to that of the mild condition. At low recovery, A_{me}/A_{la} (curve iv) is the dominant effect. At higher recovery, the order of influence remains $A_{me}/A_{la} < k_{CECP} < B/A$ due to the increasing mixed liquor concentration. The implication here for FO operations is that if B/A is a given for a particular application, cake-enhanced concentration polarisation (k_{CECP}) will be an important performance diminishing mechanism that needs to be addressed, especially when high recovery and high flux are demanded. This conclusion corroborates with findings from other FO studies (Lay et al. 2010a; Lee et al. 2010).

(a)

(b)

(i) Reference flux for clean membrane: $B/A = 0$ bar, $A_{me}/A_{la} = 0$, and $k_{CECP} = \infty$ $\text{Lm}^{-2}\text{h}^{-1}$. (ii) Effect of draw solute transmission only: $B/A = 0.1$ bar, $A_{me}/A_{la} = 0$, and $k_{CECP} = \infty$ $\text{Lm}^{-2}\text{h}^{-1}$. (iii) Effect of CECP only: $B/A = 0$ bar, $A_{me}/A_{la} = 0$, and $k_{CECP} = 100$ $\text{Lm}^{-2}\text{h}^{-1}$. (iv) Effect of fouling on water permeability only: $B/A = 0$ bar, $A_{me}/A_{la} = 0.1$, and $k_{CECP} = \infty$ $\text{Lm}^{-2}\text{h}^{-1}$. (v) All of the above effects: $B/A = 0.1$ bar, $A_{me}/A_{la} = 0.1$, and $k_{CECP} = 100$ $\text{Lm}^{-2}\text{h}^{-1}$.	(i) Reference flux for clean membrane: $B/A = 0$ bar, $A_{me}/A_{la} = 0$, and $k_{CECP} = \infty$ $\text{Lm}^{-2}\text{h}^{-1}$. (ii) Effect of draw solute transmission only: $B/A = 1$ bar, $A_{me}/A_{la} = 0$, and $k_{CECP} = \infty$ $\text{Lm}^{-2}\text{h}^{-1}$. (iii) Effect of CECP only: $B/A = 0$ bar, $A_{me}/A_{la} = 0$, and $k_{CECP} = 18.7$ $\text{Lm}^{-2}\text{h}^{-1}$. (iv) Effect of fouling on water permeability only: $B/A = 0$ bar, $A_{me}/A_{la} = 0.5$, and $k_{CECP} = \infty$ $\text{Lm}^{-2}\text{h}^{-1}$. (v) All of the above effects: $B/A = 1$ bar, $A_{me}/A_{la} = 0.5$, and $k_{CECP} = 18.7$ $\text{Lm}^{-2}\text{h}^{-1}$.

Figure 7.5: Modelled flux-recovery analysis for (a) mild and (b) more severe condition.

7.4.2 Observed flux performance from experiments

Figure 7.6 and Figure 7.7 show the observed water flux and mixed liquor concentration for the TFC and CTA experiment runs, respectively. Osmotic backwash was conducted for TFC-II and CTA-V, and these were indicated in the figures accordingly. Variation in the observed data occurred in part due to the sludge wasting regime as noted in Chapter 4. However, variation was also encountered due to accidental operations events, such as temporary fluctuation of laboratory temperature, disruption of air supply, and malfunction of draw solution control, which had effects on the experiments to be discussed later on in this section. For experimental runs that were started with fresh mixed liquor (TFC-II, CTA-III and CTA-IV), the course of salt accumulation in the mixed liquor with increasing concentration (c_{ml}) could be observed. In general, water flux (J_w) reduced with increasing c_{ml} , which determined the overall osmotic driving force across the membrane. The effect is more pronounced for the membrane orientation AL-DS than for AL-FW, due to the effect of ICP. In most cases, a relatively stable condition could be observed for an OMBR after sufficiently long run time. Such stable state of operation could be achieved, when the combined salt load from both influent and salt transmission from the draw solution entering the system balanced the outgoing salt load in the waste sludge. In a few instances, however, no consistent stable condition was observed (TFC-III and CTA-IV), and this may be attributed to effects of fouling to be discussed later.

As illustrated in Figure 7.6 (a), the relatively high A and K_m of the TFC membrane gave a relatively high initial flux ($>20 \text{ Lm}^{-2}\text{h}^{-1}$) at the beginning of the experiment. It should be noted that the draw solution used was of a relatively modest concentration at $0.5 \text{ mol}\cdot\text{kg}^{-1} \text{ NaCl}$, which was comparable to seawater salinity. However, flux decline, due to the coupled effects of fouling, was drastic as c_{ml} increased. At a point when c_{ml} was reasonably stable (around 11 mScm^{-1}), osmotic backwash was applied, and a fouling amelioration effect could be immediately observed (more on the effects of osmotic backwash is discussed in section 7.4.3.2). Thereafter, water flux decreased back to a value near to $4 \text{ Lm}^{-2}\text{h}^{-1}$, and remained fairly stable till the end of the experiment. It is worth noting that although this membrane exhibited fouling, its long

term stable flux was higher than for the less fouling prone CTA membrane (refer to Figure 7.7).

As illustrated in Figure 7.6 (b), The initial flux of this run was deliberately set lower by using a draw solution of lower concentration, and was around $6 \text{ Lm}^{-2}\text{h}^{-1}$. The objective of this experiment was to ascertain the effects of initial flux with respect to fouling. The figure shows that while the rate of flux decline could be retarded, the eventual flux decline was still observed. As the mixed liquor concentration was fairly stable for the earlier part of the experiment run, the observed flux drop could be attributed to the effects of fouling. The mixed liquor concentration reduced towards the later part of the experiment, due to the lower flux which resulted in longer HRT and a corresponding drop in the volumetric concentration factor. The final average flux of this run was around $2.5 \text{ Lm}^{-2}\text{h}^{-1}$.

Figure 7.7 shows the experimental results for the four CTA runs. The runs CTA-III to CTA-V were operated with the same membrane orientation (AL-FW) but different π_{ds} and SRT, so that different initial flux and recovery could be experimented. The run CTA-VI was continued from CTA-V with the same π_{ds} and SRT, but with reverse membrane orientation (AL-DS).

As illustrated in Figure 7.7 (a), the initial flux of the CTA membrane was modest as compared to the TFC membrane, even though both started with approximately the same osmotic driving force ($\pi_{\text{ds}} - \pi_{\text{ml}}$). This observation could be explained by the differences in the transport parameters between the membranes (refer also to Chapter 3). The draw solution had the same concentration as that of TFC-I at $0.5 \text{ mol}\cdot\text{kg}^{-1}$ NaCl, and the observed stable flux of CTA-III was around $2.6 \text{ Lm}^{-2}\text{h}^{-1}$.

The run CTA-IV was conducted with a higher draw solution concentration at $1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaCl}$, which was doubled that of CTA-III, but this did not result in doubling of the initial flux due to the effect of ICP (section 7.4.1.1). This experiment run also encountered a greater frequency of accidental events. The relatively higher flux points at the earlier part of the experiment could be explained in part by higher fluctuating laboratory temperature. Malfunction of the draw solution control also caused more fluctuating flux points during this experiment run. The air compressor broke down on several occasions, which might have been the reason that a particular air supply line to the CTA-bioreactor became choked during the experiment. This, in turn, explained the more severe fouling condition found after the experiment, where one of the two modules from CTA-IV was massively covered with biomass (section 7.4.3.2). It is worth noting that a continuous decline in flux was observed throughout this experiment run. The final observed flux of CTA-IV was around $3.0 \text{ Lm}^{-2}\text{h}^{-1}$.

The run CTA-V was continued from CTA-IV after replacement with a fresh set of membranes. The initial flux of this run immediately raised to above $4 \text{ Lm}^{-2}\text{h}^{-1}$, even though both π_{ds} and π_{ml} were matching to the previous run at that point of operation. This result verifies that the lower observed flux of CTA-IV could be attributed to fouling. However, as CTA-V was operated with a greater $\text{SRT} = 20 \text{ d}$, further salt accumulation with increasing c_{ml} occurred until a relatively stable condition was attained for $\int Q/V \text{ dt} > 30$. An osmotic backwash was conducted at $\int Q/V \text{ dt} \sim 57$, but the amelioration effect was modest compared to TFC-II (section 7.4.3.2). The observed stable flux of CTA-V was around $2.9 \text{ Lm}^{-2}\text{h}^{-1}$.

The run CTA-VI had the same operating conditions as CTA-V, except that the membrane orientation was reversed. Interestingly, the flux for this run was relatively stable, but the mixed liquor concentration reduced as the experiment progressed. The observed stable flux of CTA-VI was around $3.2 \text{ Lm}^{-2}\text{h}^{-1}$, which was slightly greater than that of CTA-V, though the mixed liquor concentration was also correspondingly lower. This observation is remarkable, because firstly, it implies that the reverse orientation (AL-DS) for this particular membrane did not result in extensive fouling as would be expected of this orientation, though some fouling did occur (more on this will be discussed in section 7.4.3.2). Secondly, the matching flux for both CTA-VI and CTA-V means that the volumetric concentration effect would have been comparable for both runs. The declining c_{ml} in CTA-VI therefore suggests that draw solute transmission could have been significantly alleviated for CTA-VI as compared to CTA-V. This observation may be attributed to the beneficial defects plugging effect provided by the mild fouling condition (Chapter 4), and may imply that the effect would be greater in the AL-DS orientation than the AL-FW orientation for this particular type of CTA membrane. It should be mentioned that the above observations were verified with a subsequent experiment trial that employed the AL-DS membrane orientation (results not shown). A summary of findings of all the six experimental runs and their respective derived recovery are presented in Table 7.5.

Figure 7.6: Water flux and mixed liquor concentration for TFC experimental runs

(a) TFC-II and (b) TFC-III. Note that different scales are used to suit the graphical presentation.

Figure 7.7: (a) CTA-III and (b) CTA-IV

Figure 7.7: Water flux and mixed liquor concentration for CTA experimental runs

(a) CTA-III, (b) CTA-IV, (c) CTA-V, and (d) CTA-VI. Note that different scales are used to suit the graphical presentation

Table 7.5: Summary of experimental findings

Reference experiment (membrane)	Observed flux $J_{w,ob}$ [Lm ⁻² h ⁻¹]	Average SRT [d]	Derived HRT [h]	SRT/HRT ratio [-]	Derived Recovery ϕ [%]
TFC-II	3.8 ± 0.3	10	34.6	6.9	85.6
TFC-III	2.5 ± 0.1	10	42.4	5.7	82.3
CTA-III	2.6 ± 0.1	10	23.1	10.4	90.4
CTA-IV	3.0 ± 0.2	10	20.3	11.8	91.5
CTA-V	2.9 ± 0.1	20	22.4	21.4	95.3
CTA-VI	3.2 ± 0.2	20	20.3	23.7	95.8

(a)

(b)

Figure 7.8: Flux-recovery analysis for (a) TFC, and (b) CTA experimental runs.

OMBR FLUX PERFORMANCE AND POTENTIAL ASSESSMENT

Table 7.6: Overview of flux and performance assessment parameters

OMBR experiment	Observed flux (average)	Reference flux ($\varphi_{re} = \varphi_{ob}$)	FO-RO Flux ratio factor	Apparent FO water permeability	FO Flux efficiency factor
	$J_{w,ob}$	$J_{w,re}$	$J_{w,ob} / J_{w(RO)}$	$J_{w,ob} / (\pi_{ds} - \pi_{ml})$	$J_{w,ob} / J_{w,re}$
	[Lm ⁻² h ⁻¹]	[Lm ⁻² h ⁻¹]	[-]	[Lm ⁻² h ⁻¹ bar ⁻¹]	[-]
TFC-II	3.8	9.4	0.06	0.20	0.40
TFC-III	2.5	7.8	0.13	0.30	0.32
CTA-III	2.6	2.8	0.24	0.15	0.93
CTA-IV	3.0	4.3	0.12	0.07	0.70
CTA-V	2.9	3.5	0.12	0.08	0.83
CTA-VI	3.2	4.0	0.14	0.09	0.80
Achilli et al. (2009b)	9.0	< 11.0 ^{a)}	–	–	> 0.82 ^{b)}

^{a)} This is derived from the reported clean water flux, which may be approximated to $J_{w,re(\varphi=0\%)}$.

^{b)} $(J_{w,ob}/J_{w,re})_{\varphi ob} = J_{w,ob(\varphi ob)}/J_{w,re(\varphi=0\%)} \cdot (J_{w,re(\varphi=0\%)}/J_{w,re(\varphi ob)}) > J_{w,ob(\varphi ob)}/J_{w,re(\varphi=0\%)} = 9/11 = 0.82$

7.4.3 Discussion of factors affecting OMBR flux performance

7.4.3.1 Flux performance analysis of experimental results

From the observed results, analysis of flux performance could be performed for all the experiment runs. Flux-recovery analysis is given in Figure 7.8, while Table 7.6 gives an overview of flux and the performance assessment parameters derived for this study.

As illustrated in Figure 7.8, the $J_{w, re}$ curves show different maximum attainable recovery (ϕ_{max}) for the experiment runs depending on the respective draw solution concentration, such that: $\phi_{max} \sim 95.5\%$ for TFC-III; $\phi_{max} \sim 97.8\%$ for TFC-II and CTA-III; and $\phi_{max} \sim 98.9\%$ for CTA-IV to CTA-VI. In addition, the TFC membranes give higher $J_{w, re}$ curves than the CTA membranes. This could be attributed to difference in the transport parameters (A , B/A , and K_m) between the two membranes as discussed in the previous section. Due to the different membrane orientation, the $J_{w, re}$ curve of CTA-VI lies higher than that of CTA-IV and CTA-V for lower recovery, but the curves converge at higher recovery as noted in section 7.2.1.

The performance of the OMBR runs could be read off from Table 7.6 and can also be inferred from their relative position in Figure 7.8. Different information may be obtained from the individual parameters. The first column of the table shows the actually observed flux for each experiment run. It shows that TFC-II gives the highest flux, TFC-III the lowest, and the remaining CTA runs lie in between the two. This observation, however, does not regard the different driving force and recovery across the experiment runs. The second column gives the $J_{w, re}$ at the observed recovery for the respective runs, and both TFC-II and TFC-III give more favourable results in view of the membrane transport parameters as noted above. The third column gives the respective FO-RO flux ratio factor ($J_{w, ob} / J_{w(RO)}$), where the TFC membranes generally give lower values with respect to the CTA membranes. Aside from the effects of fouling (section 7.4.3.2), another reason why the TFC membranes are unfavourable in this aspect is due to the relatively high A value of the membrane (section 7.4.1.1). It

can also be observed that within each type of membrane, lower driving force ($\pi_{ds} - \pi_{ml}$) gives larger $J_{w,ob} / J_{w(RO)}$ due to the effect of ICP. Interestingly, the fourth column shows that the TFC membranes had more favourable apparent FO water permeability ($J_{w,ob} / (\pi_{ds} - \pi_{ml})$) than the CTA membranes. This means that the TFC membranes could advantageously produce comparatively larger flux with smaller osmotic driving force. This attribute is of significance with regard to post-treatment options whereby the draw solution concentration needs to be limited – e.g. post-treatment is RO (section 7.4.1.1).

Results of practical relevance could be obtained from the flux efficiency factor ($J_{w,ob} / J_{w,re}$) as presented in the final column. It shows that while the TFC membranes may be viewed favourably for the previously mentioned criteria, these membranes did not perform to their potential and operated at lower efficiencies compared to their reference condition, thus indicating more severe performance diminishing effects (section 7.4.3.2). On the other hand, the CTA membranes could achieve relatively high $J_{w,ob} / J_{w,re} \geq 0.8$ with recovery up to 95.8% (CTA-VI), verifying the milder performance diminishing conditions. The greater fouling experienced in CTA-IV due to aeration disruption shows up with an observably lower $J_{w,ob} / J_{w,re}$ as compared to CTA-V. In this regard, it can also be observed that $J_{w,ob} / J_{w,re}$ may be a more effective parameter to discern and assess the performance efficiency of an operating FO process than $J_{w,ob} / J_{w(RO)}$ and $J_{w,ob} / (\pi_{ds} - \pi_{ml})$. The slightly lower $J_{w,ob} / J_{w,re}$ of CTA-VI (0.80) as compared to CTA-V (0.83) at comparable recovery suggests that slightly greater performance diminishing effects could be associated with the AL-DS orientation, but these would not be significant (difference is $0.83 - 0.80 = 0.03$). As a validity check, the analysis was also applied to another longer term OMBR study by (Achilli et al. 2009b). As that study was conducted with different osmotic driving force and mixed liquor concentration, comparison of flux in isolation with other studies is difficult. Herein is an advantage of applying the flux-recovery analysis, because the above mentioned effects are already implicitly considered in the analysis. The analysis gives $J_{w,ob} / J_{w,re} > 0.82$, which verifies the low fouling condition as reported in that study and attests the general applicability of the analytical method developed here.

7.4.3.2 Effects of fouling and fouling amelioration

Membrane autopsies after the experiment runs confirmed that, in general, the TFC membranes were more heavily fouled than the CTA membranes. This finding is in agreement with the foregoing analysis and discussion on performance diminishing effects.

As illustrated in Figure 7.9, visually, the TFC membranes could be observed to have greater biomass attachment than the CTA membranes – except for CTA-V, where the aeration to one of the CTA modules was disrupted. This observation demonstrates the significance of aeration as a fouling amelioration factor (Cui et al. 2003).

Osmotic backwash has been shown to be an effective fouling amelioration method for the FO processes (Holloway et al. 2007; Achilli et al. 2009b). The results of the osmotic backwash applied in TFC-II and CTA-V are presented in Figure 7.10. Not surprisingly, the effectiveness of this fouling amelioration method was found greater in the more severely fouled TFC-II membrane than the mildly fouled CTA-V membrane. With the TFC-II membrane, application of the osmotic backwash was able to immediately restore flux from $4.4 \text{ Lm}^{-2}\text{h}^{-1}$ to $6.3 \text{ Lm}^{-2}\text{h}^{-1}$, which was an improvement of about 43%. The corresponding flux efficiency factor ($J_{w,ob}/J_{w,re}$) at that point of operation increased from 0.56 to about 0.79, verifying the observed flux restoration and a mild fouling state that would be comparable to the CTA membranes. For the CTA-V membrane, however, the effect of osmotic backwash was modest as noted in section 7.4.2. Nonetheless, flux improvement could still be observed, and the flux was about $2.8 \text{ Lm}^{-2}\text{h}^{-1}$ and $3.0 \text{ Lm}^{-2}\text{h}^{-1}$ before and after the osmotic backwash, which corresponded to $J_{w,ob}/J_{w,re}$ of 0.82 and 0.87, respectively. The findings verify that when regularly applied, the osmotic backwash may be an effective fouling amelioration method, which agrees with previous studies (Holloway et al. 2007; Achilli et al. 2009b). The in-situ osmotic backwash used in this study may have practical advantages over the ex-situ approach used in other studies.

Table 7.7 shows the estimated saturation indices (SI) for CaSO_4 and CaCO_3 of the mixed liquor for each experiment run. The purpose of this check is to provide indicative information on scaling propensity. It is acknowledged that scaling as a crystallisation process with nucleation and kinetics effects is complex (Gloede and Melin 2008), and the multi-components fouling phenomenon occurring in the mixed liquor of an OMBR adds on to this complexity (Tang et al. 2011). The SI derived for CaCO_3 also needs to be interpreted with caution, because nucleation behaviour of CaCO_3 was reported to be associated with that of monohydrate calcium carbonate ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$), rather than that of calcite as used in this study (Elfil and Roques 2001). For such a case, the SI values derived for CaCO_3 may be significantly reduced by a factor of about 20 in view of the significantly greater K_{sp} value for $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ (Chapter 4). Nonetheless, Table 7.7 shows that risk of scaling for the OMBR runs is pertinent and that the tendency could be particularly significant for CTA-V and CTA-VI as compared to the other OMBR runs due to the higher mixed liquor concentration brought about by the higher recoveries.

The occurrence of mixed salt fouling in the TFC membrane was verified by energy-dispersive X-ray (EDX) spectroscopy analysis (Figure 7.11). Multivalent elements such as Ca, Mg, Fe, and Al were detected within the membrane support layer of TFC-II. It should be noted that although elements such as Ca and Al were not found in the feed water composition, these could enter the bioreactors via the local tap water, with which the synthetic feed water was made. Such compounds could be retained and concentrated in the mixed liquor of the OMBR. The mixed salt fouling observation could be explained by the coupled ICP and fouling effect – $\exp(J_w/K_{\text{m+foul}})$ – due to the AL-DS orientation of the TFC membrane (section 7.2.1). As such, foulants could become 3 – 5 times or more concentrated within the membrane support layer than the already concentrated mixed liquor. Under such circumstances, complex colloidal and scaling interactions could occur and result in a severe fouling condition (Tang et al. 2011). It is worth noting that the pH in the OMBR coincides largely with the minimum solubility of Al- and Fe-salts (Sawyer et al. 2003), and could have further aggravated the fouling effects.

On the other hand, the CTA membranes exhibited mild fouling tendency. Observation on CTA-IV even seems to suggest reversibility of foulants attachment, when entire pieces of biomass detached spontaneously from the membrane surface after being left standing in the feed water for a short while (Figure 7.9). Such a phenomenon was not observed for the TFC membranes. While EDX analysis found a range of multivalent elements in the detached biomass, the underlying membrane surface from CTA-IV (AL-FW orientation) did not reveal such elements. Subsequent EDX analyses on both CTA-V (AL-FW orientation, result not shown) and CTA-VI (AL-DS orientation, see Figure 7.13) also did not detect the presence of multivalent elements, which means that their presence would be insignificant and below the instrument's detection limit.

Furthermore, it is interesting to note the different biofilm attachment between the TFC membrane and the CTA membrane observed from the confocal laser scanning microscopy (CLSM) examination. Images in Figure 7.14 were selected from TFC-II and CTA-V, and images from other runs indicate similar observation. In general, the TFC membrane showed distinct presence of biofilm attached onto the membrane. On the other hand, the CTA membrane (except CTA-V) showed relatively small numbers of scattered bacterial cells. This observation implied that there had been no mature biofilm formation, which agrees with the observation that the CTA membrane generally exhibited mild fouling condition (refer also to Chapter 4).

Observations of the more severe flux reducing condition on the TFC membranes may be explained by known factors (refer to Chapter 6), such as: membrane orientation (the TFC membranes had AL-DS orientation, which would be more vulnerable to fouling that could not be mitigated by hydrodynamics), membrane surface and material properties (hydrophobic and roughness structure of the polyamide material), greater initial flux, and possibly, compaction of the support layer, air bubbles entrapment within the support layer, and integrity challenges known for hollow fibre membranes. Analogously, the generally more favourable observations on the CTA membranes with regard to fouling could be explained by the more favourable AL-FW membrane orientation (except CTA-VI, see below), hydrophilic and smoother

membrane material properties, lower initial flux, and lesser or no tendency of effects such as support layer compaction, air bubbles entrapment, or integrity challenges.

However, observation on TFC-II and CTA-VI seems confounding and needs further investigation. Both runs had the same membrane orientation (AL-DS) and comparable fluxes, but gave disparate results with regard to fouling as evident from their respective $J_{w,ob}/J_{w,re}$ values. It may be argued that the greater scaling propensity of the mixed liquor of CTA-VI (highest SI in Table 7.7) and the lower K_m of the CTA membrane should have resulted in an even more severe mixed salt fouling within the CTA membrane support layer for the AL-DS orientation – due to $\exp(J_w/K_{m+foul})$ as above, but this was not the case.

The above observation is not well understood, but may be attributed to the differences in the physical structure and material of the membranes (Chapter 3). It seems to suggest that even if the two membranes would have comparable K_m in magnitude and adopt the same AL-DS orientation: the TFC membranes would observe a more severe fouling condition with CECP-like mechanism within its porous support layer, whereas the CTA membranes would observe a more favourable CRCP-like coupled with defects plugging mechanism on its smooth and dense-like support layer that result in mild fouling effect on flux and reduced draw solute transmission. Clearly, more research is needed to elucidate the underlying phenomena. The observation here, however, shows that membrane properties play a significant role in fouling behaviour. Therefore, designing or selecting membranes with numerically favourable transport parameters but without due consideration to flux diminishing effects are not adequate to guarantee high performance efficiency for a FO process. It should be noted that further development of the TFC membranes aims for usage with the AL-FW orientation as well as optimisation with regard to fouling resistance. Fouling control strategies and membrane improvement are expected to further enhance the performance of the TFC membrane.

OMBR FLUX PERFORMANCE AND POTENTIAL ASSESSMENT

(a)

(b)

(c)

(d)

Figure 7.9: Photographs of membranes upon removal from the OMBR:

- (a) TFC-II: Biomass-attachment could be observed on the TFC membranes
- (b) CTA-IV: Unusual biomass attachment could be observed on one of the two CTA modules due to aeration disruption
- (c) CTA-V: Minimal biomass attachment typically observed for the CTA membranes
- (d) CTA-IV: Detachment of biomass from membrane after left standing in the synthetic feed water for a short period of time

Figure 7.10: Observed flux before and after osmotic backwash for (a) TFC-II, and (b) CTA-V

Table 7.7: Estimated saturation indices (SI) for mixed liquor of the OMBR experiments

Reference experiment	SI CaSO_4 [-]	SI CaCO_3 [-]
TFC-II	0.2	3.4
TFC-III	0.1	2.9
CTA-III	0.4	4.6
CTA-IV	0.4	5.1
CTA-V	1.0	7.5
CTA-VI	1.1	7.9

Figure 7.11: EDX analysis on TFC-II

(a) SEM picture of analysed spectrum (view as indicated), and
(b) analysis of elements

Figure 7.12: EDX analysis on CTA-IV

(a) Analysis of elements on foulant layer (frontal view), and
(b) analysis of elements on underlying membrane (frontal view).

Figure 7.13: EDX analysis on CTA-VI with membrane orientation AL-DS
 (a) Analysis of elements on the membrane surface that faced the mixed liquor (frontal view), and
 (b) analysis of elements within the membrane support layer (cross-sectional view).

Figure 7.14: The CLSM images of (a) TFC-II and (b) CTA-V.

7.5 Concluding remarks on assessment of OMBR flux performance

In this study, a novel approach has been developed for assessment of factors that affect flux performance of the FO-based OMBR. Based on modelling and experimental investigations, the main findings of this study include:

- 1) The performance of a FO system may be characterised by the assessment parameters: FO-RO flux ratio ($J_w/J_{w(RO)}$), apparent FO water permeability ($J_w/(\pi_{ds} - \pi_{ml})$), and the newly developed flux efficiency factor ($J_{w,ob}/J_{w,re}$). The parameters ($J_w/J_{w(RO)}$) and ($J_w/(\pi_{ds} - \pi_{ml})$) offer information on the extent of internal concentration polarisation inherent of a FO system, and driving force utilisation, respectively. The $J_{w,ob}/J_{w,re}$ factor has practical relevance and reveals the inevitable operational trade-off between flux and recovery (ϕ) for a FO system.
- 2) The derived $J_{w,ob}/J_{w,re}$ factors corresponded well to experimental observations and provided discerning indication for flux efficiency. Modelling indicates that mild performance diminishing condition may give $J_{w,ob}/J_{w,re} \geq 0.8$, but a more severe one may give $J_{w,ob}/J_{w,re} \leq 0.5$ for the same interested range of recovery.
- 3) High water permeability (high A), low salt-to-water permeability ratio (low B/A), and large mass transfer coefficient (large K_m) improve the performance of a FO system, but these may also be influenced by operational and fouling effects, such as draw solute transmission, fouling resistance and cake-enhanced concentration polarisation. It was shown that membrane properties also play a significant role in fouling behaviour. Fouling amelioration factors include aeration and osmotic backwash. The in-situ osmotic backwash employed in this study may be a simple and effective method to be applied in the practice.

- 4) The TFC membranes have shown potential for FO application, and possess comparatively high membrane intrinsic transport parameters. The TFC membranes achieved flux $\geq 20 \text{ Lm}^{-2}\text{h}^{-1}$ at low recovery by using modest osmotic driving force ($0.5 \text{ mol}\cdot\text{kg}^{-1}$ NaCl) that is comparable to seawater concentration (TFC-II). The TFC membranes achieved $J_w / (\pi_{ds} - \pi_{ml}) \geq 0.2 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, which reflects relatively high efficiency in terms of driving force utilisation. It therefore suggests that the TFC membranes may be advantageously applied for scenario whereby the draw solution concentration needs to be limited (e.g. post-treatment is RO). However, the TFC membranes were prone to relatively more severe fouling, and attained $J_{w,ob}/J_{w,re} < 0.5$ for the recovery range 80 – 90%. Nonetheless, in spite of the vulnerability to fouling, the TFC membranes were able to achieve the highest stable-state flux during the experiments (TFC-II: $3.8 \text{ Lm}^{-2}\text{h}^{-1}$). Furthermore, osmotic backwash was able to achieve considerable flux restoration with $J_{w,ob}/J_{w,re}$ increased to about 0.79 (TFC-II), which could be compared to a mild fouling state. Fouling control strategies and membrane improvement are expected to further enhance the performance of the TFC membrane.

- 5) The CTA membranes possessed comparatively lower membrane intrinsic transport parameters, and were less favourable in terms of driving force utilisation. However, the CTA-membranes possessed generally good fouling resistance. The experiment run CTA-IV demonstrates that the OMBR could achieve stable water production with both relatively high flux efficiency ($J_{w,ob}/J_{w,re} = 0.8$) and high recovery ($\phi = 95.8\%$). High flux efficiency and high recovery are important attributes for practical application, and demonstrate the potential of the OMBR technology.

- 6) The study clarifies that FO membrane design and selection need to be optimised with due consideration to application challenges. Membrane resistance to fouling would be a critical area for future research and development of FO membranes.

7.6 Potential of OMBR for water reclamation

The study has demonstrated to this point that the OMBR technology could achieve stable water production with good product water quality at relatively high flux efficiency (≥ 0.8) and high recovery ($\geq 95\%$) with modest driving force provided by NaCl draw solution up to a concentration of $1 \text{ mol}\cdot\text{kg}^{-1}$. This is due to the focus of this study with regard to membrane performance within the OMBR. The choice of draw solution and the corresponding post treatment step for regeneration of draw solution were not further explored. Other types of draw solution may provide greater osmotic driving force (Achilli et al. 2010). Alternatively, if a post-treatment step that is relatively insensitive to draw solution concentration such as membrane distillation could be favourably and sustainably employed – for example, with adequate supply of waste-heat – then higher NaCl concentration may be used (Cath et al. 2006; McGinnis and Elimelech 2008). Under such circumstances, the potential of OMBR may be further enhanced.

The objective of this discussion is two-fold. Firstly, it is to evaluate the greater potential of the OMBR for water reclamation under a non-constraint draw solution scenario that may apply in the longer term. The evaluation will compare the OMBR technology against other options for water reclamation. The benchmark for this evaluation is the NEWater process (PUB 2002). Secondly, it is to consider the potential of a hybrid process combination of OMBR and conventional MBR that may ameliorate limitations due to salt accumulation effects, and may apply for application in the nearer future.

7.6.1 OMBR for high recovery application

Figure 7.15 shows a flux-recovery analysis for an OMBR under a non-constraint draw solution scenario. The draw solution assumed is 5 mol·kg⁻¹ NaCl solution, which would provide osmotic pressure of about 309 bar. Implicitly assumed is the availability of a suitable post-treatment step for sustainable draw solution regeneration that may be developed in the longer term (e.g. membrane distillation with adequate supply of waste heat). Model assumptions can be applied to a realistic application with a mild fouling condition as discussed in the previous sections.

Figure 7.15: Flux-recovery analysis for a potential OMBR for water reclamation

Model assumptions:

AL-FW membrane orientation

$\pi_{\text{ds}} = 309$ bar, $\pi_{\text{in}} = 0.5$ bar, $A_{\text{me}} = 2 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, $K_{\text{m}} = 10 \text{ Lm}^{-2}\text{h}^{-1}$,

$B/A = 0.1$ bar, $A_{\text{me}}/A_{\text{la}} = 0.1$, and $k_{\text{CECP}} = 100 \text{ Lm}^{-2}\text{h}^{-1}$

Evident from the flux-recovery analysis, favourable results could be obtained under a non-constraint draw solution scenario. Relatively high flux ($\geq 20 \text{ Lm}^{-2}\text{h}^{-1}$) could be achieved for recovery up to near 98% ($\text{SRT}/\text{HRT} \sim 50$). With consideration of performance diminishing effects that include draw solute transmission (B/A), fouling resistance with regard to its effect on water permeability ($A_{\text{me}}/A_{\text{la}}$) and cake-enhanced

concentration polarisation effects (k_{CECP}), the flux efficiency remains high (≥ 0.8) for the operating recovery range of interest. The high flux efficiency may be attributed to the compensating effect provided by internal concentration polarisation (ICP) with the substantial amount of driving force, and point to the interesting role that ICP may play in the entire scheme of things for FO systems. On one hand, ICP is a form of driving force inefficiency. On the other hand, ICP may provide a beneficial effect for stable water production in a sustainable manner as noted in section 2.2.4.

Figure 7.16 compares various technology options for water reclamation. For simple comparison, a consistent influent of 100 “units” (the “units” here is to serve a scalar function, and may be $L \cdot h^{-1}$, $m^3 \cdot h^{-1}$ or $m^3 \cdot d^{-1}$ depending on application specification) is supplied to all three options. Consideration is made to reflect realistic recoveries attainable for an application scenario.

Figure 7.16: Options for water reclamation

Recoveries for the individual processes are assumed based on information from (PUB 2002; AWWA 2004; Judd 2006) and this study.

* Recovery should be 100% for the OMBR post-treatment step, if complete regeneration of draw solution is attained. This example considers a loss of 5% that may occur for a practical application.

It can be observed from the comparison in Figure 7.16 that the OMBR option may achieve the highest output (≥ 90 units), followed by the MBR+RO option (~ 76 units) and the conventional NEWater option may achieve the lowest output (< 70 units).

The foregoing discussion makes clear that the potential of the OMBR technology is that it not only could offer superior product water quality, it is also an option that could achieve very high recovery and aims towards the higher environmental goal of waste minimisation (zero-liquid discharge). When suitable post-treatment step is available, the OMBR may present a sustainable option favourable for water reclamation. However, conclusive evaluation of technology feasibility will need to include economic considerations.

7.6.2 Hybrid OMBR-MBR system

Salt accumulation is inevitable for a salt-retentive system such as an OMBR (Chapter 6). When the osmotic driving force provided by the draw solution could be limiting or there could be other system constraints, it may be necessary to control the concentration factor in the mixed liquor. In this instance, a hybrid OMBR-MBR system may be considered (Figure 7.17).

Figure 7.17: Hybrid OMBR-MBR system for water reclamation

The hybrid OMBR-MBR system would comprise a conventional MBR process and an OMBR process in a single aeration tank and may be applied for scenarios where the concentration factor in the mixed liquor needs to be controlled.

Figure 7.17 shows a plausible schematic for a hybrid OMBR-MBR system. For illustration, a 50-50 apportionment of the influent is considered between the OMBR and the conventional MBR. Further optimisation may be performed with regard to the apportionment factor. It is evident from this simple example that the hybrid OMBR-MBR system would still perform favourably with a total recovery that is $> 80\%$ at a significantly lower concentration factor. This is because the conventional MBR process, which employs porous membrane, would be able to substantially remove part of the salt load in the system. The simplicity of such a process arrangement suggests that the hybrid OMBR-MBR system may be an option to explore in the nearer future.

7.6.3 Concluding remarks on potential of OMBR

The analyses presented demonstrate the favourable prospect of the OMBR technology. Assessment shows that the OMBR option compared favourably to both conventional NEWater process and the MBR+RO option. The promise of OMBR for achieving high water recovery is based on the assumption that driving force for the separation could be provided by a draw solution with high osmotic pressure, and this could be coupled with a suitable post-treatment step to concomitantly produce high-grade product water and regenerate draw solution on a sustainable basis (e.g. post-treatment could be membrane distillation with adequate supply of waste heat). In contrast, it would not be feasible for a RO-based process to generate the same amount of driving force, as the ensuing consumption of electrical energy would be prohibitively large.

In the longer term, when a non-constraint draw solution situation could be attained with development of an optimised post-treatment, the OMBR may be a favourable and sustainable option for water reclamation to fulfil the twin goal of good product water quality and high recovery. For the nearer future, the hybrid OMBR-MBR system may be an option that can be further explored, and applied for water reclamation.

Chapter 8. Conclusions and recommendations

8.1 Conclusions

The osmotic membrane bioreactor (OMBR) is a novel integration of forward osmosis (FO) and biological process in a membrane bioreactor (MBR) set-up. The interest in OMBR is derived from the recognition that a system based on high retention membranes offers potential benefits for water reclamation.

In this thesis, a submerged OMBR system is systematically studied and developed. The focus of the study is on membrane performance. The thesis substantiates the proposition that the OMBR is a potential technology for water reclamation, because it is able to achieve stable water production and good product quality at high recovery, but there are important performance-affecting factors that need to be addressed for technology optimisation. Literature review shows that internal concentration polarisation (ICP) is a unique phenomenon for the forward osmosis (FO)-based system that is differentiated from pressure-driven membrane processes. The ICP plays a deterministic role in the flux behaviour of the FO-based system. It was also discussed that fouling is a complex and, concomitantly, very significant factor that affects the performance of a MBR system. Elevated mixed liquor salinity is another inherent issue of an OMBR due to volumetric concentration of the influent and reverse salt transport of draw solutes through the FO membrane.

The thesis found that factors affecting the performance of an OMBR system can be characterised by four inter-linked research themes:

Chapter 4 describes a long term investigation on the membrane performance of a continuously operated OMBR system. The investigation found that stable water production and mixed liquor concentration could be achieved, which attested the feasibility of the OMBR system. In spite of the known vulnerability of the CTA membrane with regard to biological or chemical degradation, no deterioration in membrane performance was detected throughout the experimental duration. Fouling

was also mild for the CTA membrane. In this regard, issues of relevance include membrane orientation, flux, aeration, ICP, as well as membrane properties in terms of hydrophilic material and surface smoothness. Interestingly, the observed salt concentration factor from the experiment was significantly lower than expected, and may be attributed to the gel-like layer that developed on the membrane surface.

Chapter 5 is a complementary investigation to Chapter 4, and focuses on water quality issues and effects of pharmaceuticals on process performance. It was found that the OMBR was generally able to achieve good product water quality based on synthetic feed water. The product dissolved organic carbon (DOC) of the OMBR had been generally $\leq 1 \text{ mgL}^{-1}$, and the corresponding organics removal was in excess of 99 %. Further study is needed to ascertain the effectiveness of OMBR for organics removal using real sewage as feed. The OMBR was also able to effectively retain the dosed pharmaceuticals with apparent removal efficiency $> 96\%$. The implication here is that organic micro-pollutants could be concentrated in an OMBR, and could be advantageous to enhance the rate of biodegradation of the organic micro-pollutants. It was also found that the biological process was found to play a key role in the overall performance of the OMBR. Impairment of product water quality was observed when the biological process was temporarily inhibited by the pharmaceutical dosages. Further research is needed to quantitatively study the fate of organic micro-pollutants on an OMBR system in relation to the process microbiology under the elevated salinity environment.

Building upon the preceding studies, Chapters 6 and 7 focus on systemic issues of an OMBR system in the form of salt accumulation and flux performance, respectively.

Chapter 6 develops an analytical framework to study salt accumulation in an OMBR. The framework was able to qualitatively explain the phenomena observed, and provided information on the system. It was shown that salt accumulation in the OMBR is controlled by three factors: membrane, influent, and process. In this regard, the role of the membrane is application-dependent and significant only when influent osmotic pressure is smaller or in the same order of magnitude as the salt to water permeability ratio (B/A). A new parameter referred to as the salt retention time

(SaRT) has been defined, and it was shown that experimental duration of 3 x SaRT would be necessary for adequate study of salt accumulation in OMBR. Fouling can cause the evolution of the overall B/A ratio in the OMBR. In general, reducing overall B/A ratio can be associated with mild fouling, and increasing overall B/A ratio can be associated with severe fouling and further flux reducing mechanisms. In this regard, the desired membrane properties are high A value, low B/A ratio and high resistance to fouling.

The consequence of salt accumulation as discussed in Chapter 6 has a significant effect on the flux performance of an OMBR system, because the effective driving force across the FO membrane is reduced. Chapter 7 therefore aims to provide an assessment of the factors affecting the flux performance of an OMBR in a more systematic manner.

In Chapter 7, it was derived that OMBR flux performance may be characterised by the assessment parameters: FO-RO flux ratio ($J_w/J_{w(RO)}$), apparent FO water permeability ($J_w/(\pi_{ds} - \pi_{ml})$), and the newly developed flux efficiency factor ($J_{w,ob}/J_{w,re}$). The parameters ($J_w/J_{w(RO)}$) and ($J_w/(\pi_{ds} - \pi_{ml})$) provide information on the extent of internal concentration polarisation inherent of a FO system, and driving force utilisation, respectively. The $J_{w,ob}/J_{w,re}$ factor has practical relevance and reveals the inevitable operational trade-off between flux and recovery (ϕ) for a FO system. The derived $J_{w,ob}/J_{w,re}$ factors corresponded well to experimental observations and provided discerning indication for flux efficiency. Mild performance diminishing conditions may give $J_{w,ob}/J_{w,re} \geq 0.8$, but a more severe one may give $J_{w,ob}/J_{w,re} \leq 0.5$ for the analysed range of recovery ($\phi = 80\% - 95\%$). It was shown that desirable membrane properties for achieving high flux are high water permeability (high A), low salt-to-water permeability ratio (low B/A), and large mass transfer coefficient (large K_m). However, these properties may also be influenced by operational and flux diminishing effects that include draw solute transmission, fouling resistance and cake-enhanced concentration polarisation. The membrane structure and orientation may play an important role in this. In general, the membrane orientation 'active layer facing draw solution' (AL-DS) and with a porous support layer structure facing the mixed liquor may be more severely fouled as in the case of the TFC membrane

compared to the membrane orientation 'active layer facing feed water' (AL-FW) and with smooth surface and more dense structure as in the case of the CTA membrane. However, in spite of the severity of fouling, the TFC membrane was able to achieve the highest stable-state flux during the experiments (TFC-II: $3.8 \text{ Lm}^{-2}\text{h}^{-1}$). At the beginning of the experiment and under mild fouling conditions, the TFC-II membrane achieved a flux $\geq 20 \text{ Lm}^{-2}\text{h}^{-1}$ using modest osmotic driving force ($0.5 \text{ mol}\cdot\text{kg}^{-1}$ NaCl) that is comparable to seawater concentration, and revealed potential for OMBR application. However, fouling plays a key role in the final attainable flux of the available TFC membranes, and membrane resistance to fouling would be a critical area for future research and development. Recent developments by colleagues (Qi et al. 2011; Wei et al. 2011) have produced flat sheet TFC FO membranes giving stable fluxes in the OMBR of around $6 \text{ Lm}^{-2}\text{h}^{-1}$ under similar experimental conditions as applied in this study. Even higher flux values could be obtained with more concentrated draw solution. Fouling amelioration factors include aeration and osmotic backwash. It was shown that FO membrane design and selection need to be optimised with due consideration to application challenges. It should also be noted that higher temperatures and mobile ions are generally favourable to enhance FO performance due to increasing K_m . The experimental findings confirm that the OMBR could achieve stable water production at high recovery, as demonstrated by the experiment run CTA-VI with $J_{w,ob}/J_{w,re} = 0.8$ and $\phi = 95.8\%$.

Concluding Chapter 7 is a brief discussion on the potential of the OMBR technology for water reclamation. It was demonstrated that the OMBR may be a favourable option for water reclamation, as it fulfils the goal of good product water quality and high recovery. However, there are performance-limiting factors as outlined in this thesis that need further research to develop the technology.

8.2 Recommendations

Further research and development are required to develop the OMBR technology. Building on the works presented in this thesis, the following three research areas are of immediate relevance and merit future study:

(i) *Fundamental phenomena and characterisation techniques*

The OMBR has unique physical characteristics that are different from conventional pressure-driven membrane processes. Further study of the FO-based system on a fundamental level is needed. This thesis has shown that fouling plays a key role in the performance of an OMBR. It was also discussed that a secondary foulant layer would have influence on the reverse permeation of the ionic draw solutes such as NaCl, and that the phenomenon could be explained macroscopically based on a resistance-in-series approach. However, further research is required to clarify issues such as: the bi-directional diffusion phenomenon of a FO-based system – components from draw solution permeating into feed water and vice-versa; the relative impact of flux per se versus that of hydraulic pressure on foulant compaction; as well as complex foulant-foulant and foulant-membrane interactions under the elevated salt environment. In this regard, potential characterisation techniques such as the electrical impedance spectroscopy (EIS) may be a useful tool to study an FO-based system at a more detailed level. Future study should aim at acquiring understanding of the fundamental phenomena to further develop the OMBR technology.

(ii) *Fate of organic micro-pollutants in an OMBR system*

The presented work has provided a qualitatively study on the retention of pharmaceuticals in an OMBR system, and their effects on the biological process. Future study should aim at quantitatively understanding the removal mechanism of these organic micro-pollutants that encompasses both sorption and biodegradation. In this regard, it is suggested to develop a dynamic model that is able to numerically analyse the fate of organic micro-pollutants in an OMBR system.

(iii) *Effects of salt accumulation on biological and physicochemical aspects*

The presented work has provided a discussion on salt accumulation in an OMBR system: the factors that contribute to it and its effect on membrane performance. Future study should aim at studying the effects of elevated salt environment on the biological and physicochemical aspects and under real sewage environment. In this regard, the effects of salt accumulation and/or retained mixed liquor constituents on the efficacy of the biological process need more research. This pertains not only to biological processes concerning carbon removal, but also to other biological processes concerning nutrients removal such as nitrification, denitrification and phosphorus accumulating organisms. In a similar vein, effects of salt accumulation on the physicochemical aspects such as oxygen transfer and colloid chemistry merit further investigation.

Appendices

Appendix A Derivation of equations for ICP and CECP in FO

Internal concentration polarisation

The internal concentration polarisation (ICP) for FO membrane is derived based on a solute mass-balance in the membrane support layer with the structural properties: thickness t_{me} , porosity ϵ_{me} and tortuosity τ_{me} . The effective diffusion of draw solutes in this porous structure is given by $D \cdot \epsilon_{me}$.

At steady state (A. Fig. 1 – dilutive ICP is presented, see section 2.2.3):

$$-D \cdot \epsilon_{me} \frac{dc}{dx} = J_s + J_w \cdot c \quad \text{A. (1)}$$

Rearranging A. (1) gives a first-order variables separable differential equation, which can be solved when the boundary conditions are known (Jank and Jongen 1996).

$$\frac{dc}{(C + \frac{J_s}{J_w})} = -\frac{J_w}{D \cdot \epsilon_{me}} dx \quad \text{A. (2)}$$

A. Fig. 1: Internal concentration polarisation within the membrane porous support layer (based on a similar approach in Loeb et al. (1997))

The boundary conditions are:

At $x = 0$: $C = C_{ds}$

At $x = \tau_{me} \cdot t_{me}$,

(Solute travel distance from the bulk solution to the membrane wall): $C = C_{ds-me}$

Further, the following relations may apply:

$$J_w = A \cdot (\pi_{ds-me} - \pi_{fe-me}) \approx A \cdot R \cdot T \cdot (c_{ds-me} - c_{fe-me})$$

$$J_s = B \cdot (c_{ds-me} - c_{fe-me})$$

$$S_{me} = t_{me} \cdot \tau_{me} / \epsilon_{me}$$

The solution to the differential equation A. (2) can be expressed in J_w (A. (3)):

$$-\frac{J_w}{D/S_{me}} = \ln \left(\frac{A \cdot \pi_{ds-me} + B}{A \cdot \pi_{ds} + B} \right) \quad \text{A. (3)}$$

Rearrangement with π_{ds-me} (draw side osmotic pressure on the membrane wall) as the subject gives:

$$\pi_{ds-me} = \frac{(A \cdot \pi_{ds} + B) \cdot \exp\left(-\frac{J_w}{D/S_{me}}\right) - B}{A} \quad \text{A. (4)}$$

It should be noted that the mass-transfer parameter (D/S_{me}) is also known as the mass transfer coefficient (K_m) describing the ICP phenomenon within the membrane support layer, or the inverse of the solute resistivity for diffusion (K) within membrane porous support layer (Cath et al. 2006; Tang et al. 2010). It has been pointed out that such an approach does not take into account the concentration dependency of the diffusion coefficient D , and a modified empirical model was suggested to correlate D to solution concentration c using virial-type expression (Tan and Ng 2008). As a matter of fact, liquid diffusion is a complex affair, and D is dependent on a number of factors (Stokes-Einstein equation) that may include temperature, particle size and viscosity, the latter which may be related to the obstruction effect of solute concentration (Robinson and Stokes 2002). In this regard, an empirical expression for D provides little insight or utility to the underlying

physical phenomenon, which is really defined by the structural parameter ($S_{me} = t_{me} \cdot \tau_{me} / \epsilon_{me}$) of membrane porous support layer. On this basis, the above ($K_m = D/S_{me}$) approach is adopted in this thesis, where S_{me} may play the role as a fitting parameter. This is also the established approach adopted in most FO/PRO studies (Cath et al. 2006; Tang et al. 2010).

Cake-enhanced concentration polarisation

The cake-enhanced concentration polarisation (CECP) (also known as cake-enhanced osmotic pressure) generated due to fouling layer on FO membrane can be derived in an analogous manner as per that for ICP (A. Fig. 2). The differences are that the convention for the diffusive flux is in the opposite direction due to the concentrative nature of the concentration gradient, and that the fouling cake layer gives the structural properties: thickness δ_{la} , porosity ϵ_{la} and tortuosity τ_{la} . More discussion on CECP can be found in (Hoek and Elimelech 2003).

At steady state (A. Fig. 2):

$$D \cdot \epsilon_{la} \frac{dc}{dx} = J_s + J_w \cdot c \quad \text{A. (5)}$$

Rearranging gives:

$$\frac{dc}{(C + \frac{J_s}{J_w})} = \frac{J_w}{D \cdot \epsilon_{la}} dx \quad \text{A. (6)}$$

A. Fig. 2: Cake-enhanced osmotic pressure within the fouling cake layer

The boundary conditions are:

At $x = 0$: $C = C_{fe}$

At $x = \tau_{la} \cdot \delta_{la}$,

(Solute travel distance from the bulk solution to the membrane wall): $C = C_{fe-me}$

Again, the following relations may apply:

$$J_w = A \cdot (\pi_{ds-me} - \pi_{fe-me}) \approx A \cdot R \cdot T \cdot (c_{ds-me} - c_{fe-me})$$

$$J_s = B \cdot (c_{ds-me} - c_{fe-me})$$

$$\delta^* = \delta_{la} \cdot \tau_{la} / \epsilon_{la}$$

Similarly, the solution to the differential equation can be expressed in J_w :

$$\frac{J_w}{D/\delta^*} = \ln \left(\frac{A \cdot \pi_{fe-me} + B}{A \cdot \pi_{fe} + B} \right) \quad \text{A. (7)}$$

Note: The parameter (D/δ^*) is also known as the hindered mass transfer coefficient (k^*) in fouling cake layer.

Rearrangement with π_{fe-me} (feed side osmotic pressure on the membrane wall) as the subject gives:

$$\pi_{fe-me} = \frac{(A \cdot \pi_{fe} + B) \cdot \exp\left(\frac{J_w}{D/\delta^*}\right) - B}{A} \quad \text{A. (8)}$$

Appendix B Role of ICP in FO and RO flux behaviour**Introduction**

A frequent hypothesis regarding FO fouling propensity is that FO would have lower fouling tendency because it does not entail the use of hydraulic pressure (Cath et al. 2006). The explanation offered was that fouling cake-layer compaction would be reduced in the absence of hydraulic pressure. Part of this hypothesis is construed on the observation of slower flux decline in FO experiments. The scientific implication of this view is that there is a difference in the relative impact on foulant compaction by flux and pressure. Such a view, however, could be contradictory to the well-established critical flux concept (Field et al. 1995), which gives pressure as the driving force, but it is the drag force of the moving fluid (flux) that acts as the agent for fouling. What this means is that regardless of the type of driving force, the effect of membrane fouling should be comparable under similar flux and operational conditions. The significance of membrane fouling has already been clarified in Chapter 2.

The objective of this study was to investigate and understand the flux behaviour of FO and RO under well controlled experimental conditions. The study comprised experimental and modelling work, and performed comparative analysis between FO and RO under similar fouling conditions.

identical and given by the channel dimensions of 24.8 cm by 3.1 cm. Both cells could be run with cross flow on both sides of the membrane. For the RO cell, the inlet valve on the permeate side was closed to give the standard RO configuration. For the FO cell, cross flow were run on both the feed and the draw side co-currently to minimise mechanical strain on the membrane. The driving force for the RO loop was supplied by a high-pressure pump (Speck Triplex NP10/10-140S) that generated feed-side pressures up to 20 bars. The driving force for the FO loop was supplied by recirculating sodium chloride (NaCl) draw solution, which was maintained at constant concentration by means of a conductivity control linked to a concentrated NaCl ($5 \text{ mol}\cdot\text{kg}^{-1}$) solution reservoir. The NaCl solution was used here as the draw solution, as it is typically the appropriate choice that satisfies the required criteria: high solubility and osmotic pressure efficiency, chemically compatible, easy to regenerate and no risk of scaling.

Fluid conveyance in the FO loop was provided by centrifugal pumps (Calpeda NMX 32/125AE), and the transmembrane hydraulic pressure difference was less than 0.1 bar, which was insignificant as compared to the osmotic pressure difference. Flows in the system were adjusted by valves located on the main and the bypass lines, which gave feed-side cross flow velocities in the order of 0.1 ms^{-1} . For the FO loop, the draw-side was set after adjusting the feed-side cross flow velocity and the pressures on both sides of the membrane, and was in the order of 0.5 ms^{-1} for the experiments. The feed water temperature for the experiments was maintained between 24°C and 26°C by the system chillers. For RO experiments, product water was collected and measured directly by a weighing balance (AND GX-30K). For FO experiments, product collection was performed by a level control in the product holding tank connected to the weighing balance through a solenoid valve. The product water flux in $\text{Lm}^{-2}\text{h}^{-1}$ was then derived by normalising the measured product rate over the membrane area, correcting with the amount of draw solution dosed into the system and accounting for the density of the draw solution. Osmotic pressure was measured by a cryoscopic osmometer (Gonotec OSMONAT 030) up to 3 Osmol/kg ($\sim 1.5 \text{ mol}\cdot\text{kg}^{-1}$) or derived from the literature for higher osmotic pressure values. Outputs of the parameters: pressures, flow rates, temperatures, conductivity and product collection were obtained via a data acquisition system (IDEC PLC with LabVIEW).

The same type of membrane (cartridge type) from Hydration Technology Innovations (Albany, OR) was used in all experiments. The membrane was made of cellulose triacetate (CTA) embedded about a polyester screen mesh (Chapter 3). The same membrane orientation was consistently adopted in this study with the active layer facing against the feed water (AL-FW). Prior to use, the membrane was cut to size and stored in Milli-Q water at 4°C overnight. A fresh piece of membrane was used in each fouling experiment.

Model foulant solution used in this study was 200 ppm of 10 – 20 nm silicon dioxide nanoparticles (Sigma-Aldrich). Milli-Q water was used to prepare all liquid solutions in this study. The experimental protocol was consistently applied as follows: prior to the addition of foulant, a common precompaction and equilibration step was applied to the membrane by subjecting it in the RO cell to feed pressure of 20 bar and background electrolyte concentration of 1 gL⁻¹ NaCl for 2 hours. For the FO experiments, the membrane was transferred to the FO cell right after the precompaction and equilibration step, and this was followed by an additional equilibration step for conditions on both the feed and the draw side to stabilise. Analysis of the experimental data was performed on the first 15 hours after the addition of foulant. To reduce data noise that was associated with the data acquisition system, three-point averaging method was applied.

Process modelling

An overview of the equations used in this study can be found in A. Table 1. The water flux equations are implicit functions that could be solved by numerical or graphical method. The basis of the modelling was the resistance-in-series model incorporated with the cake-enhanced concentration effect (CECP) effect. For FO modelling, it was necessary to consider internal concentration polarisation (ICP). Both CECP and ICP concepts are already discussed in Chapter 2.

At this juncture, the difference in the nature of the driving force between RO and FO can be noted. For RO, the intrinsic flux given by the driving force is $A_{me} \cdot \Delta p$, and is constant for a given driving force (Δp). For FO, however, the intrinsic flux depends on the product of $(A_{me} \cdot \pi_{ds} + B_{me})$ and ICP ($= \exp(-J_w/K_m)$). So, even when the overall driving force for a FO process (π_{ds}) is constant, the effective driving force changes according to the ICP. The above explains the logarithmic relationship between the water flux and the overall driving force for the FO process, and that any change in flux has a direct and inverse impact on the effective driving force across the membrane. Estimation for the hydraulic resistance of the foulant layer ($R_{h,la}$) and hence its effect on water permeability (A_{me}/A_{la}) is based on the method of (Chong et al. 2008).

Salt concentration occurs in all salt retentive membrane systems, as pure water permeates through the membrane, leaving behind the concentrate and elevating the osmotic pressure of the bulk feed water. For FO, this effect is intensified due to the reverse salt flux that is transmitted from the draw solution into the feed water (section 2.4.1). For RO, $J_s = 0$ is applied, as salt flux will be from the feed to the permeate, and does not contribute to salt accumulation. The approach here is to explicitly account for the elevated salt concentration in the bulk feed water as function of recovery (ϕ), salt-to-water flux ratio (J_s/J_w) and influent concentration (c_{in}). Another approach that relates J_s/J_w to the salt to water permeability ratio (B/A) is discussed in chapter Chapter 6. The reference salt used throughout this study for the total dissolved solids (TDS) contained in the feed water and for the draw solution is NaCl.

A. Table 1: Modelling equations

RO: <i>Intrinsic flux given by the driving force</i> <i>Flux loss due to CECP</i> $J_w = \frac{A_{me} \cdot (\Delta p - \exp(\frac{J_w \cdot \delta^*}{D}) \cdot \pi_{fe})}{(1 + \frac{A_{me}}{A_{la}})}$ <i>Water transport</i> <i>Normalised effect on water permeability</i>		
FO: <i>Intrinsic flux given by the driving force</i> <i>ICP</i> <i>Flux loss due to CECP</i> $J_w = \frac{(A_{me} \cdot \pi_{ds} + B_{me})(\exp(-\frac{J_w}{K_m})) - (A_{me} \cdot \pi_{fe} + B_{me})(\exp(\frac{J_w \cdot \delta^*}{D}))}{(1 + \frac{A_{me}}{A_{la}})}$ <i>Water transport</i> <i>Normalised effect on water permeability</i>		
where: $\frac{1}{A} = \frac{1}{A_{me}} + \frac{1}{A_{la}}$ $A = \frac{1}{\eta \cdot R_{h,la}}; A_{me} = \frac{1}{\eta \cdot R_{h,me}}; A_{la} = \frac{1}{\eta \cdot R_{h,la}}$		
A_{me}	$[\text{ms}^{-1}\text{bar}^{-1}]$	Membrane water permeability
B_{me}	$[\text{ms}^{-1}]$	Membrane salt permeability
Δp	$[\text{bar}]$	Transmembrane (hydraulic) pressure
π_{fe}	$[\text{bar}]$	Osmotic pressure of the bulk feed solution
π_{ds}	$[\text{bar}]$	Osmotic pressure of the bulk draw solution
K_m	$[\text{Lm}^{-2}\text{h}^{-1}]$	Mass transfer coefficient for ICP ($K_m = D/S_{me}$)
D	$[\text{m}^2\text{s}^{-1}]$	Diffusion coefficient of the reference solute (NaCl)
η	$[\text{Pa}\cdot\text{s}]$	Viscosity of permeating liquid (Konneke et al.)
δ^*	$[\text{m}]$	Enhanced fouling cake thickness ($\delta^* = \delta_{la} \cdot \tau_{la} / \epsilon_{la}$)
S_{me}	$[\text{m}]$	membrane structural parameter ($S_{me} = t_{me} \cdot \tau_{me} / \epsilon_{me}$)
$R_{h,la}$	$[\text{m}^{-1}]$	Hydraulic resistance fouling layer: $R_{h,la} = \rho_p \cdot (1 - \epsilon_{la}) \cdot \delta_{la} \cdot \alpha_{la}$
Salt accumulation		
$c_{fe} = \frac{\frac{\phi \cdot J_s}{J_w} + c_{in}}{(1 - \phi)}$		
c_{fe}	$[\text{gL}^{-1}]$	steady state feed concentration
c_{in}	$[\text{gL}^{-1}]$	influent feed concentration
ϕ	$[-]$	system recovery (= product flow/ feed flow)
J_s	$[\text{gm}^{-2}\text{h}^{-1}]$	salt flux
J_w	$[\text{Lm}^{-2}\text{h}^{-1}]$	water flux

Results and discussion

Result from FO – RO experiments

The following figure shows the normalised flux decline over time of the experiments. The baseline for the normalisation was set to an assumed steady-state flux ($J_{w,0} = J_w$ at $t = 2$ h), so as to take into account the initial flux drop in FO as explained below.

Experimental conditions:

$J_{w,0}(\text{RO}) = 12.8 \text{ Lm}^{-2}\text{h}^{-1}$, $J_{w,0}(\text{FO}) = 11.6 \text{ Lm}^{-2}\text{h}^{-1}$, Feed: 200ppm SiO_2 in 1 gL^{-1} NaCl

A. Fig. 4: Observed flux decline in FO and RO

The RO and FO experiments were conducted with the driving forces of 19.2 bar and $1.4 \text{ mol}\cdot\text{kg}^{-1}$ NaCl draw solution, respectively. The water permeability of the CTA-FO membrane used here (Chapter 3) was relatively low ($< 1 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) compared to conventional RO composite membranes (Tang et al. 2009). This could explain the relatively low fluxes observed (about $13 \text{ Lm}^{-2}\text{h}^{-1}$) in this current study, which were in the same flux range for this type of membrane as reported in the literature (Cornelissen et al. 2008; Achilli et al. 2009b).

It was observed that the flux decline in RO was gradual and steady, which was consistent with the critical flux concept and also observed in the constant pressure RO

studies (Tang et al. 2007). For FO, there was a sudden drop in flux initially, followed by a gentle decline. This behaviour was observed in repeated experiments, but the exact timing of this sudden drop in flux could vary within the first few hours of the experiments. This sudden flux drop behaviour in FO could be attributed to the reverse salt transport from the draw solution into the feed solution, which would elevate the feed-side osmotic pressure and aggravate fouling on the membrane surface (double layer compression at higher ionic strength), that in turn exacerbate the CECF effect. Such an effect was also observed by (Lee et al. 2010), who referred to the phenomenon as accelerated cake-enhanced osmotic pressure. Thereafter, however, the flux in FO was relatively stable. As shown in the following figure, visual examination of the membrane coupons after the experiments found white deposits on the membrane surface, which indicated that fouling had occurred in both RO and FO.

A. Fig. 5: White deposits found on membrane and indicated fouling

In this study, slow flux decline was observed in both FO and RO under the given conditions. A common explanation for this could be the low experimental fluxes, which might have been around the critical flux for the particular feed conditions (Chong et al. 2008). In addition, the membrane material was hydrophilic and relatively smooth (Chapter 3), which could alleviate fouling. These factors could also contribute to the slow flux decline observed in the experiments.

Modelling analyses

To understand the slow flux decline phenomenon observed in FO, three scenarios were modelled. Both A. Fig. 6 and A. Fig. 7 represented possible operating conditions for water reclamation application with the influent TDS of around 1 gL^{-1} . The figure A. Fig. 6 (scenario I) assumed that the salt transport in FO was negligible ($J_s = 0$) – an ideal assumption but unlikely to be valid especially for smaller size draw solutes such as NaCl. The figure A. Fig. 7 (scenario I I) aimed to model a more realistic scenario for water reclamation application. Here, J_s was assumed to be around $5 \text{ gm}^{-2}\text{h}^{-1}$, which would be a low to moderate value of the salt flux that may be encountered in application.

The figure A. Fig. 8 (scenario III) examined a high concentration application such as that of seawater desalination with the influent TDS in the range of 30 gL^{-1} . For consistency, $J_s = 5 \text{ gm}^{-2}\text{h}^{-1}$ was considered for all modelled scenarios where reverse salt transport from draw solution was of concern. Other assumed parameters include: model foulant is 20nm SiO_2 ($\rho_p=2.6\text{gcm}^{-3}$, $\epsilon_{la}=0.4$, $\tau_{la}=2.5$, $\alpha_{la}=1.6 \cdot 10^{15} \text{ mkg}^{-1}$), $A_{me} = 2.2 \cdot 10^{-7} \text{ ms}^{-1}\text{bar}^{-1}$, $D = 1.61 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$, $S_{me} = 0.4 \cdot 10^{-3} \text{ m}$, $\phi = 0.5$ and $J_w(t=0) \sim 20 \text{ Lm}^{-2}\text{h}^{-1}$.

The investigation was conducted assuming constant overall driving force operation, that is: a constant feed pressure for RO, and a constant overall osmotic pressure difference (bulk feed water to bulk draw solution) for FO. The performance is modelled as fouling progresses (i.e. the thickness of the fouling cake (δ_{cake}) increases). The results are organised into three presentations: (i) normalised flux in FO and RO, (i i) flux analysis in FO, and (iii) flux analysis in RO. For flux analysis, the intrinsic flux given by the driving force is apportioned into three components with the dimension $[\text{Lm}^{-2}\text{h}^{-1}]$: for water transport permeating through the membrane (J_w), for overcoming permeability effect of fouling (A_{me}/A_{la}), and for accounting for the increased osmotic pressure on the feed-side of the membrane wall due to the CECP effect (CECP).

A. Fig. 6: Effects of fouling on modelled scenario I: $c_{in} = 1 \text{ gL}^{-1}$ and $J_s = 0 \text{ gm}^{-2}\text{h}^{-1}$

Description: (i) Flux decline FO vs RO, (i i) flux analysis for FO, (iii) flux analysis for RO.

Further assumptions: $\Delta p = 26.6\text{bar}$, and $\pi_{ds} = 104.5\text{bar}$

(i)

(i i)

(iii)

A. Fig. 7: Effects of fouling on modelled scenario II: $c_{in} = 1 \text{ gL}^{-1}$ and $J_s = 5 \text{ gm}^{-2}\text{h}^{-1}$

Description: (i) Flux decline FO vs RO, (i i) flux analysis for FO, (iii) flux analysis for RO.

Further assumptions: $\Delta p = 26.6\text{bar}$, and $\pi_{ds} = 154.2\text{bar}$

A. Fig. 8: Effects of fouling on modelled scenario III: $c_{in} = 30 \text{ gL}^{-1}$ and $J_s = 5 \text{ gm}^{-2}\text{h}^{-1}$

Description: (i) Flux decline FO vs RO, (i i) flux analysis for FO, (iii) flux analysis for RO.

Further assumptions: $\Delta p = 70.4\text{bar}$, and $\pi_{ds} = 300\text{bar}$

The model also considered the salt concentration effect. Even when fouling had not yet occurred, the steady-state feed concentration (c_{fe} at $\delta_{la} = 0$) would be higher than its influent concentration (c_{in} at $t=0$) due to the concentration factor imposed by the recovery (ϕ).

For scenario I (A. Fig. 6), where $J_s = 0$, the salt concentration effect in FO equals that in RO. From (i), a slightly slower flux decline could be observed in FO as compared to RO. By comparing (i i) and (iii), as fouling progresses, the magnitudes of CECP and A_{me}/A_{la} increase comparably in both FO and RO. For illustration, at $t = 0$, the intrinsic flux given by the driving force for FO would be $20.7 \text{ Lm}^{-2}\text{h}^{-1}$. This would breakdown to cover the actual permeating flux ($20.1 \text{ Lm}^{-2}\text{h}^{-1}$), and flux loss due to the CECP effect ($0.6 \text{ Lm}^{-2}\text{h}^{-1}$). As the equilibrium of the feed concentration is attained but fouling has not yet set in (i.e. $\delta_{la} = 0 \text{ }\mu\text{m}$), the feed-side concentration doubles due to the salt concentration effect ($\phi = 0.5$). The intrinsic flux then would be $21.0 \text{ Lm}^{-2}\text{h}^{-1}$, which would cover the actual permeating flux ($19.8 \text{ Lm}^{-2}\text{h}^{-1}$), and flux loss due to the CECP effect ($1.2 \text{ Lm}^{-2}\text{h}^{-1}$). As fouling progresses, for example at $\delta_{la} = 5 \text{ }\mu\text{m}$, the intrinsic flux for FO would be $21.0 \text{ Lm}^{-2}\text{h}^{-1} = 19.1 (J_w) + 0.5 (A_{me}/A_{la}) + 1.4 (\text{CECP})$. What these examples illustrate is that at the same bulk feed concentration (c_{fe}) and similar level of fouling (A_{me}/A_{la} and CECP), FO is expected to give a slower flux decline than RO. This is because while the effective driving force for RO is constant (Δp), the effective driving force for FO *increases* with reducing flux as the effect of ICP lessens: $\text{ICP} \sim \exp(-J_w/K_m)$. The result of this is that the flux decline in RO increases non-linearly under the double action of A_{me}/A_{la} and CECP, whereas the flux decline in FO is mitigated by the ICP.

In scenario II (A. Fig. 7), where $J_s = 5 \text{ gm}^{-2}\text{h}^{-1}$ is assumed, the salt concentration effect in FO ($c_{fe} = 17.6 \text{ gL}^{-1}$ at $\phi = 0.5$) is significantly greater than that in RO ($c_{fe} = 2 \text{ gL}^{-1}$ at $\phi = 0.5$) due to the reverse salt transport from the draw solution. The increase in the bulk feed concentration (c_{fe}) accounts for the initial flux drop observed in FO between $t=0$ (influent) and $\delta_{la} = 0$ (steady-state) due to the increased osmotic pressure of the feed solution. As fouling progresses, the effective driving force in FO increases due to

the effect of the reduced ICP at lower membrane flux, but CECF also gets excessively exacerbated and magnifies the increased feed osmotic pressure. The overall result is that similar rate of flux decline may be expected in both FO and RO. This scenario may agree with the experimental observation in the previous section. Comparison between scenarios I and II makes plain the significance of the reverse salt transmission, which needs to be addressed for real application.

For scenario III (A. Fig. 8), at the same J_s but higher c_{in} , the salt concentration effect in FO ($c_{fe} = 75.6 \text{ gL}^{-1}$ at $\phi = 0.5$) lessens on a proportional basis, and would be marginally greater than that in RO ($c_{fe} = 60 \text{ gL}^{-1}$ at $\phi = 0.5$). In a way, this observation is analogous to that of scenario I in that the bulk feed concentration (c_{fe}) of RO vs. FO is fairly similar. The difference is that the CECF effect is now much more severe due to the higher feed osmotic pressure. This did not affect the analysis under the same level of fouling, and a slower flux decline could be observed in FO as compared to RO. The explanation for this is again due to the mitigating effect of the ICP for FO as flux reduces.

The foregoing discussion can be pictorially illustrated using a pure water flux – driving force diagram as presented in the following figure. Here, the graph for RO is linear. For FO, the graph is logarithmic due to the effect of $ICP \sim \exp(-J_w/K_m)$. Due to the curvature of the graphs, it can be observed that at the same initial flux ($J_{w,0}$) and under equal loss of driving force, the flux decline in FO is consistently smaller than that in RO, regardless of the nature of the fouling cake that is occurring. However, this benefit can be negated by the transmission of the draw solutes, which elevates feed-side osmotic pressure and then exacerbates the loss in driving force via the CECP effect. It is evident that the transmission of draw solutes (reverse salt transport) can have significant effect on FO performance, and has to be minimised. This effect is discussed in more detail in Chapter 6.

A. Fig. 9: Effect of equal loss of driving force on flux in FO and RO

Concluding remarks

This study investigated flux behaviour in FO and RO under similar fouling conditions based on a combined experimental-modelling approach. From the experimental study, it was found that at relatively low fluxes ($12\text{--}14 \text{ Lm}^{-2}\text{h}^{-1}$), both RO and FO exhibited slow flux decline. However, there was an initial drop in flux for FO, which could be attributed to the reverse salt transport from the draw solution into the feed water that could have increased the osmotic pressure on the membrane feed-wall, aggravated fouling and exacerbated the CECF effect. The observation verifies the significance of draw solute transmission in FO systems.

In this study, it was demonstrated that the slower flux decline commonly observed in FO experiments did not prove lesser fouling cake compaction as compared to the pressure driven membrane processes. There could be other contributing factors to this such as the use of hydrophilic and smooth membranes, and in particular, the counteracting effect of internal concentration polarisation (ICP). The ICP plays a unique and significant role in stabilising water flux in FO. This is because the effect of fouling and flux decline is to reduce ICP. This provides an increase in the effective driving force that partially compensates for the fouling resistance for FO. The ICP mechanism does not apply for RO.

The unique flux behaviour of FO systems also points to the need for more sophisticated techniques for characterisation of fouling and concentration polarisation phenomena. One such technique that should be explored further is electrochemical impedance spectroscopy (EIS), which is discussed in the subsequent appendix.

Appendix C Electrical impedance spectroscopy

The electrical impedance spectroscopy (EIS) has been recognised as a feasible non-invasive analytical technique for membrane processes (Chen et al. 2004). (Kavanagh et al. 2009) demonstrated the potential of this technique and obtained information on fouling of RO membranes in a four-terminal electrical cell using CaCO_3 as the model foulant. The aim of this study was to experimentally explore the phenomena of concentration polarisation and fouling in FO using high resolution EIS technique.

Materials and methods

The EIS experiments were conducted using the spectrometer system supplied by INPHAZE Pty Ltd (Sydney, Australia). The system allowed the membrane to be held in place in a four-terminal chamber and obtained impedance information as frequency varied. The membrane used for the EIS experiments was the cartridge type from Hydration Technology Innovations (Albany, OR). The membrane was made of cellulose triacetate (CTA) embedded about a polyester screen mesh (Chapter 3). The same membrane orientation was consistently adopted in this study with the active layer facing against the feed water (AL-FW). Prior to use, the membrane was cut to size and stored in Milli-Q water at 4°C overnight. A fresh piece of membrane was used in each experiment.

For the fouling experiments, the feed solution was 1 g L⁻¹ of BSA with 10 mM NaCl as background electrolyte. The draw solution was 1 M MgSO_4 that provided bulk osmotic driving force of about 24 bar. Each solution was supplied from a reservoir volume of around 2 L, and re-circulated via a peristaltic pump with separate connections into the EIS chamber. Water flux was measured by an electronic balance. For the fouling experiments, the initial flux was around 4 Lm⁻²h⁻¹. For concentration polarisation investigation, flux could be varied by using different concentration or another solute (sucrose). The experiment duration was generally 13 to 15 hours. Conductivity measurement of both solutions typically gave a difference less than or

around $0.2 \text{ mS}\cdot\text{cm}^{-1}$ by the end of each experiment, indicating that dilution and concentration effects were small, and transmission of the draw solute was negligible.

Results and discussion

The analysis of the EIS measurement was performed based on the Maxwell-Wagner model, which relates the total impedance (Z) to the elements of the system as follows:

$$Z = \sum_{k=1}^K Z_k = \sum_{k=1}^K \frac{1}{G_k + j\omega C_k} \quad \text{A. (9)}$$

Here, G_k and C_k represent the conductance and capacitance of a particular element k , respectively, and ω is the angular frequency of the alternating current (a.c.) electrical field.

A. Fig. 10: Exploration of EIS for fouling and concentration polarisation analysis

The EIS measurement picked up BSA fouling sensitively and provided a distinct response with more elements detected. Interestingly, the EIS also observed flux-dependent conductance response for different draw and feed solutions, which corroborated with the capacitance measurement that revealed a dip in the lower frequency range < 1 Hz (results not shown). The implication here is that interfacial phenomena were observed, and the shift in the conductance response was associated with the dilutive or concentrative nature of the concentration polarisation occurring.

Preliminary conclusion

The EIS technique is able to reveal the effects of fouling and concentration polarisation in FO. Future work should focus on quantitatively relating the impedance response to its physical interpretation. The preliminary work here demonstrated that the EIS could provide high resolution and non-invasive means of in-situ analysis on a FO system.

Appendix D Extraction and Analysis of Extracellular Polymeric Substances

Some EPS are attached onto the bio-flocs (pellet EPS), whereas some of which are released into the surrounding liquid medium in soluble or loosely bound form (supernatant EPS).

Chemicals used for the EPS analysis are as follows:

Chemical	Amount per sample
Bradford dye reagent	3 ML
5% Phenol	1 ml
Conc 95-97% Sulphuric Acid	5 ml
1N Sodium hydroxide	800 µl
37% Formaldehyde	12 µl

EPS Extraction

10ml of activated sludge samples are collected from the bioreactors and centrifuged at 4000 rpm for 10 minutes. The supernatant and pellet were separated. The supernatant is collected without any further treatment, and comprises both soluble and loosely bound polymers. The remaining pellet is then re-suspended with Milli-Q water and subjected to an adapted ‘formaldehyde plus NaOH’ treatment for extraction as follows. The pellet samples are topped up with Milli-Q water up to 10ml, and added with 0.012ml of formaldehyde (37%). Both Pellet and Supernatant samples are to be kept in the fridge at 4°C. After one hour, 0.8mL NaOH (1N) is added to the pellet samples (to detach EPS surrounding the cells) and the samples are kept inside the fridge for 3 more hours. After 3 hours, each pellet sample is extracted into 2 mL eppendorf tubes, which are centrifuged at 13200 rpm, 20min at 4°C for liquid-solid separation prior to analysis.

EPS Analysis

Polysaccharides and proteins are typically the dominant components in the extracted EPS. The sum of the amount of total EPS is represented by the total amount of polysaccharides and proteins.

Polysaccharides in the EPS can be determined according to the Phenol-sulphuric acid method with glucose as standard by using a spectrophotometer at 490nm. The protein concentration can be determined using Bradford reagent with bovine serum albumin (BSA) as standard, which causes absorption maximum of the dye in 595nm. Duplicate measurements were done for reproducibility check.

Protein Determination

Protein blank: 3mL of Bradford protein dye reagent and 0.1mL of Milli-Q water

Protein supernatant: 3mL of protein dye reagent and 0.1mL of supernatant

Protein pellet: 3mL of protein dye reagent and 0.1mL of pellet's supernatant

After that, mix well and allow the samples to stand for about 10-15 minutes at room temperature prior to analysis.

Polysaccharides Determination

Polysaccharide blank: 1mL Milli-Q water, 1mL phenol, 5mL sulphuric acid

Polysaccharide supernatant: 1mL supernatant, 1mL phenol, 5mL sulphuric acid

Polysaccharide pellet: 1mL pellet's supernatant, 1mL phenol, 5mL sulphuric acid

After that, mix well and allow the samples to stand for about 10-15 minutes at room temperature prior to analysis.

Appendix E PCR-DGGE protocol

DNA extraction

A modified Cetyltrimethyl Ammonium Bromide (CTAB) protocol was applied to extract DNA from the sludge samples (biomass). After washing with phosphate buffered saline solution (PBS), sludge samples were dissolved in 0.5 mL of 5% CTAB, and 0.5 mL of Phenol/Chloroform/Isoamyl alcohol (25:24:1), and then transferred to a crystal-tube with several glass beads. Cells were lysed for 30 s at the speed of 4.5 in Fast-Prep beadbeater (MP biomedical). Tubes were centrifuged at full speed in a chilled microcentrifuge for 5 min (Thermo scientific Micro 17 centrifuge). Subsequently, the top aqueous layer (supernatant) was extracted and mixed with an equal volume of chloroform/isoamyl alcohol (24:1) to form an emulsion. After centrifuging in a chilled micro-centrifuge, the top layer (supernatant) was again extracted and 2 volumes of PEG solution was added to precipitate nucleic acids by incubating overnight at 4 °C.

On the next day, the tubes were centrifuged in a chilled micro-centrifuge for 10 min. The supernatant was decanted and the remaining pellet washed with 70% ice-cold ethanol (200 µL). Finally the ethanol wash and any remaining liquid were removed, as the pellet was dried for 20 min. The pellet DNA was dissolved in RNase free water and stored at -20 °C prior to further analysis.

To examine DNA quality, 2µL of extract was run on 0.8% agarose gels and visualized using ethidium bromide staining. Concentration of DNA was adjusted by Nonodrop (Thermo Scientific spectrometer, Nanodrop 1000) to 50-100 ng µL⁻¹ as the appropriate concentration for PCR.

PCR amplification and DGGE

PCR was conducted in C1000TM Thermal Cycler with a reaction mixture of 50 μ L containing 0.4 μ M of each primer: 0.2 μ M of deoxynucleoside triphosphate, 5 μ L of 10 $\times$ Taq Buffer with KCl (Fermentas), 1.5 mM magnesium chloride, 5U of Taq polymerase, and 1 μ L template DNA. The primers used for PCR were the F357 with GC clamp (5'-CGC CCG CCG CGC GCG GCG GGC GGG GCG GGG GCA CGG GGG GCC TAC GGG AGG CAG CAG-3') and R518 (5'-ATT ACC GCG GCT GCT GG-3'), between which is the V3 region of 16S rDNA.

The temperature profile was designed as follows: Initial denaturation at 95 °C for 5 min, 35 cycles of denaturation at 95 °C for 30 s, annealing at 56 °C for 30 s and extension at 72 °C for 45 s. Finally, the reaction mixture was kept at 72 °C for 10 min, and then at 12 °C. The PCR amplicons were stored at 4 °C prior to loading onto the polyacrylamide gels.

The DGGE was conducted by DcodeTM Universal Mutation Detection System (BIO-RAD). Samples containing approximately equal amount of PCR products were loaded onto 10% polyacrylamide gels (40%Acrylamide/Bis-acrylamide(37.5:1)) in 1 $\times$ TAE buffer (50 $\times$ TAE consists of 242 g Tris base, 57.1 mL Acetic acid, 100 mL 0.5M EDTA per 1L solution, pH 8.0). The gels contained a linear denaturant gradient ranging from 20 % to 70 %. Electrophoresis was run at a constant voltage of 30 V for 30 min and subsequently at 100 V for 13 hours. DGGE gels were stained with ethidium bromide, followed by destaining in distilled water and photographed using a gel photo taking system (Gel DOCTM XR+ Imaging system, BIO-RAD) to acquire images for further analysis.

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