NOVEL MEMBRANE HYBRID SYSTEMS AS PRETREATMENT TO SEAWATER REVERSE OSMOSIS

by

SANGHYUN JEONG

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Doctoral of Philosophy

School of Civil and Environmental Engineering
Faculty of Engineering and Information Technology
University of Technology, Sydney (UTS)
New South Wales, Australia

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CERTIFICATE OF AUTHORSHIP/ORIGINALITY

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

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Signature of Candidate

Sanghyun Jeong

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2. ***Jeong, S.**, G. Naidu, S. Vigneswaran. (2013) Submerged membrane adsorption bioreactor as a pretreatment in seawater desalination for biofouling control. Bioresource Technology (DOI: http://dx.doi.org/10.1016/j.biortech.2013.01.021).
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1. ***Jeong, S.**, T.V. Nguyen, S. Vigneswaran. Submerged membrane coagulation hybrid system as pretreatment to organic matter removal from seawater. The 3rd International Seawater Desalination Workshop. 3-6 November 2010, Jeju, Republic of Korea.
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LIST OF ABBREVIATIONS

AFM	: Atomic force microscopy
AOC	: Assimilable organic carbon
ASW	: Artificial seawater
ATP	: Adenosine tri-phosphate
ATR-FTIR	: Attenuated total reflection–Fourier transform infrared spectroscopy
BB	: Building blocks
BCA	: Bicinchoninic acid
BDOC	: Biodegradable dissolved organic carbon
BFR	: Biofilm formation rate
BOM	: Biodegradable organic matter
BP	: Biopolymers
BPP	: Biomass production potential
CDOC	: Chromatographic dissolved organic carbon
CFF	: Contact flocculation-filtration
CFU	: Colony forming unit
CH	: Carbohydrates
CLSM	: Confocal Laser Scanning Microscopy
COD	: Chemical oxygen demand
DAPI	: 4'-6-diamidino-2-phenylindole
DBF	: Deep bed filter
DBPs	: Disinfection by-products
DI	: De-ionized
DO	: Dissolved oxygen
DOC	: Dissolved organic carbon
DON	: Dissolved organic nitrogen
EBCT	: Empty bed contact time
EDTA	: Ethylene-diamine-tetra-acetic acid
EDX	: Energy dispersive spectroscopy
EPS	: Extracellular polymeric substance
FEEM	: Fluorescence excitation–emission matrix
FE-SEM	: Field emission scanning electron microscope
FI	: Fluorescence index

GAC : Granular activated carbon
HOC : Hydrophobic organic carbon
HPC : Heterotrophic plate count
HPI (HF) : Hydrophilic
HP-SEC : High pressure size exclusion chromatography
HPO (HB) : Hydrophobic
HRT : Hydraulic retention time
HS : Humic substances
LC-OCD : Liquid chromatography-organic carbon detection
LMW : Low molecular weight
LN : Low molecular weight neutrals
MBR : Membrane bio-reactor
MF : Microfiltration
MLSS : Mixed liquor suspended solids
MTC : Normalized flux
MWCO : Molecular weight cut-off
MWD : Molecular weight distribution
NF : Nanofiltration
NMR : Nuclear magnetic resonance
NOM : Natural organic matter
NPD : Normalized pressure drop
OM : Organic matter
OUR : Oxygen uptake rate
PAC : Powder activated carbon
PBS : Phosphorus buffer solution
PCR : Polymerase chain reactions
PI : Propidium iodide
PN : Protein
PS : Polysaccharides
PSS : Polystyrene sulfonates
PVDF : Polyvinylidene fluoride
PWP : Pure water permeability
Py-GC/MS : Pyrolysis gas chromatography/mass spectrometry
RMSE : Root mean square error

RO	: Reverse osmosis
SADm	: Specific Aeration Demand
SDI	: Silt density index
SDS	: Sodium dodecyl sulfate
SEC	: Size exclusion chromatography
SMAHS	: Submerged membrane adsorption hybrid system
SMCAHS	: Submerged membrane coagulation-adsorption hybrid system
SMCHS	: Submerged membrane coagulation hybrid system
SMABR	: Submerged membrane adsorption bioreactor
SMHSs	: Submerged membrane hybrid systems
SMS	: Submerged membrane system
SPE	: Solid phase extraction
SS	: Suspended solids
SUVA	: Specific ultraviolet absorbance
SW	: Seawater
SWOM	: Seawater organic matter
SWRO	: Seawater reverse osmosis
TDC	: Total direct cell count
TDS	: Total dissolved solids
TEP	: Transparent exopolymer particles
TMP	: Trans-membrane pressure
TOC	: Total organic carbon
TPI	: Transphilic
TSS	: Total suspended solids
UF	: Ultrafiltration
UF-MFI	: Ultrafiltration-modified fouling index
UV	: Ultraviolet
VSS	: Volatile suspended solids
XRD	: X-ray diffraction

LIST OF SYMBOLS

A_b : Membrane area blocked by particles

A_m : Initial membrane area

α : Complete blockage model constant

β : Pore constriction model constant

b : Constant (L/mg)

C_b : Concentration of deposits in bulk phase

C_e : Equilibrium concentration of solute in the bulk of the solution (mg/L)

C_{PAC} : PAC concentration within the reactor (g/L)

γ : Cake formation model constant

d : Internal diameter of the tube (cm)

δ : Pore length

δ_{PAC} : Age of PAC (d)

$\Delta P(0)$: Initial trans-membrane pressure

$\Delta P(t)$: Trans-membrane pressure

G : Velocity gradient (/s)

g : Gravitational acceleration (cm/s^2)

H : Headloss through the flocculator (cm H_2O)

J/J_0 : Permeate flux decline

J_0 : Initial permeates flux (kPa)

J_c : Critical flux

$J(t)$: Operating permeate flux

J_w : Water flux (L/m^2h)

K_F : Freundlich constant indicative of the adsorption capacity

k_H : Ho rate constant for adsorption, function of temperature (g/mg. min)

m_d : Deposited mass of foulants

m_{PAC} : Mass of PAC in reactor (g)

n : An experimental constant indicative of the adsorption intensity

N : The number of pores on the membrane

N_0 : Initial cell concentration (Cells/L)

N_{max} : Maximum cell concentration (Cells/L)

q : The amount of adsorbate at equilibrium (mg/g)

q_e : The amount of solute adsorbed per gram of adsorbent (mg/g)

q_m : Saturation amount of organic adsorbed (mg/g)

q_t : The amount of adsorbate at any time t, (mg/g)

Q : Flow rate (cm^3/s)

Q_R : Replaced volume (L/d)

ρ_d : Density of the deposit

$R_c(t)$: Cake resistance

R_m : Sum of the intrinsic membrane resistance

r_p : Pore radius

$r_{p,0}$: Pore radius before fouling

$R_t(0)$: Initial filtration resistance

$R_t(t)$: Total filtration resistance

$S_1 - S_0$: Consumed substrate concentration (μg-C/L)

t : Operating time

μ : Solution viscosity

V : Volume (cm^3)

V_r : Reactor volume (L)

v : Linear flow rate (cm/s)

Y : Growth yield (cells/μgC-acetate)

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ABSTRACT

In this study, novel submerged low pressure membrane (microfiltration) systems coupled with physico-chemical treatment such as coagulation/flocculation or adsorption, termed in this study, as "submerged membrane hybrid systems (SMHS)" were investigated as pretreatment for seawater reverse osmosis (SWRO).

Coagulation as pretreatment: In recent years, coagulation and subsequent media-filtration as well as low pressure membrane-based system such as microfiltration (MF) and ultrafiltration (UF) have been used as pretreatment methods for seawater reverse osmosis desalination. Coagulation can remove colloidal matters and dissolved organic compounds which cause irreversible membrane fouling. In this study, a commonly used ferric chloride ($FeCl_3$) was used as coagulant for removing organic compounds from seawater. The coagulation by $FeCl_3$ at optimum dosage removed a majority (95%) of hydrophobic compounds. In addition, the ultrafilter modified fouling index (UF-MFI) decreased considerably from 15,848 s/L^2 with raw seawater to 3,025 s/L^2 with seawater after coagulation. It was observed that critical flux was increased from 20 L/m^2-h in the conventional submerged membrane system to 55 L/m^2-h in submerged membrane coagulation hybrid system (SMCHS). The SMCHS led to a high DOC removal efficiency (more than 70%) while keeping the development of trans-membrane pressure (TMP) significantly lower than that of conventional submerged membrane system (SMS).

Prediction of DOC removal by $FeCl_3$ coagulation using mathematical modeling: Coagulation removes colloidal matters and dissolved organic carbon (DOC) which can cause irreversible membrane fouling. However, how DOC is removed by coagulant is not well-known. Jar test was used to study the removal of hydrophobic and hydrophilic

DOC fractions at various doses (0.5-8.0 mg-Fe^{+3}/L) of $FeCl_3$ and pH (5-9). Natural organic matter (NOM) in seawater and treated seawater were fractionated by liquid chromatography-organic carbon detector (LC-OCD). Compared to surface water, the removal of DOC by coagulation was remarkably different. Majority of DOC could be easily removed with very low coagulant dose (<5.0 mg-Fe^{+3}/L) and the removal efficiency did not significantly deteriorate with pH, but remaining DOC composition has changed. Hydrophobic fraction (HB) is better removed at high pH while hydrophilic fraction (HF) is better removed at low pH. A model which assumes that the removal occurs by adsorption of un-dissociated compounds onto ferric hydroxide was formulated and successfully validated against the jar test data.

The effect of flocculation on the performance of MF in SMCHS was also investigated with modified poly ferric silicate (PFSi-δ). Both PFSi-δ and $FeCl_3$ were found to be suitable in removing organic compounds. The results show that PFSi-δ was better than $FeCl_3$ in terms of removing turbidity and DOC, particularly in removing hydrophilic compounds. It was observed that PFSi-δ (1.2 mg Fe^{3+}/L) and $FeCl_3$ (3.0 mg Fe^{3+}/L) led to an increase of critical flux from 20 L/m^2·h to 35 L/m^2·h and 55 L/m^2·h, respectively.

The removal of different fractions of organic matter in seawater was investigated using titanium tetrachloride ($TiCl_4$) as flocculant and compared with that of $FeCl_3$. The hydrophobic compounds removal was predominant by both flocculants. However, the removal of hydrophilic organic compounds, such as humics and low-molecular weight neutral compounds of seawater was superior with $TiCl_4$ compared to $FeCl_3$.

This study also investigated the effect of powder activated carbon (PAC) dosed in a submerged membrane adsorption hybrid system (SMAHS) in removing organic matter from seawater. The addition of PAC into submerged microfiltration reactor not only

improved critical flux from 20 L/m^2.h to 40 L/m^2.h but also helped reduce the TMP of the system. The analyses of organic matter fraction showed that PAC was able to remove most of hydrophobic compounds (more than 96%) and a significant amount of hydrophilic compounds (78%).

Submerged membrane adsorption hybrid system with flocculation as pretreatment: Biofouling on RO membranes is the most serious problem which affects RO process efficiency and increases its operation cost. The biofouling cannot be effectively removed by the conventional pre-treatment traditionally used in desalination plants. SMS coupled with adsorption and/or coagulation can be a sustainable pre-treatment in reducing membrane fouling and at the same time improving the feed water quality to the seawater reverse osmosis. The addition of PAC of 1.5 g/L into SMAHS could help to remove significant amount of both hydrophobic compounds (81.4%) and hydrophilic compounds (73.3%). When this SMAHS was combined with $FeCl_3$ coagulation of 0.5 mg of Fe^{3+}/L, dissolved organic carbon removal efficiency was excellent even with a lower dose of PAC (0.5 g/L). It should be noted that PAC addition was only at the start and no further PAC addition was made during experiment. The SMAHS and the submerged membrane coagulation–adsorption hybrid system (SMCAHS) can significantly remove the total bacteria which contain also live cells. As a result, microbial adenosine triphosphate (ATP) concentration in treated seawater and foulants was considerably decreased. These led to a significant reduction of assimilable organic carbon (AOC) during the initial stage of RO operation. In this study, AOC method was modified to measure the growth of bacteria in seawater by using the *Pseudomonas* P.60 strain.

Application of fouling model in SMAHS: The application of three different membrane fouling models namely pore blockage, pore constriction, and cake formation models

showed that cake formation was the predominant fouling mechanisms causing fouling in SMHSs.

Characterization of SMAHS effluent: Organic matter in seawater before and after pretreatment was characterized in terms of XAD fractionation, molecular weight distribution (MWD) and fluorescence. A detailed study on the seawater organic matter (SWOM) structure was made through ^{1}H-nuclear magnetic resonance (^{1}H-NMR),pyrolysis-gas chromatography mass spectrometry (Py-GC/MS) and liquid chromatography mass spectrometry-ion trap-time of fright (LC/MS-IT-TOF). The three dimensional-fluorescence emission-excitation matrix (3D-FEEM) showed a removal of humic-like materials by SMHSs. In addition, a humic-like relative to protein-like compounds was reduced significantly but aromaticity of humic-like materials was increased. After pretreatment by SMHSs, humics and biopolymers of over 900 Da. were found to be reduced and their structure associated with element composition was also changed.

RO membrane foulant characterization: The organic and biological foulants on RO membrane operated with seawater pretreated by SMHSs were characterized. Organic foulants on RO membrane were characterized in terms of MWD, fluorescence and extracellular polymeric substance (EPS) analyses. The organic foulants were mainly composed of high molecular weight matters representing biopolymers in the foulants. The 3D-FEEM analysis showed that protein-like materials were dominant with samples pretreated by SMHSs. Humic-like materials which have lower aromaticity were also present in the foulant. Biological foulants were investigated in terms of total direct cell (TDC) count, cell viability and biomass activity (in terms of ATP). Biological fouling was found to be reduced by organic removal with SMHSs. The fouled membranes were characterized using environmental SEM/EDX, attenuated total reflection-Fourier

transform infrared spectrometry, zeta-potential measurement, atomic force microscopy, and contact angle measurement.

Development of a rapid AOC test: One strategy to minimize biofouling is the pre-treatment of seawater prior to RO application. In this regard, there is a need for tools that can be used to assess the influent water which allows for the subsequent selection of the optimum pretreatment methods. One parameter that is directly linked to biofouling potential is the concentration of AOC in the feed-water, where high nutrient levels are associated with increased growth potential of the microbial fouling community. A rapid and accurate of AOC method was developed for marine (sea) waters. This method is based on quantifying the bioluminescence response of the marine bacterium *Vibrio fischeri* MJ-1. Compared to previous methods, this new *V. fischeri* method was rapid (within 1h), sensitive (detection limit=0.1 μg-C glucose equivalents/L) and highly suitable for seawater samples. *V. fischeri* method was evaluated using real seawater samples. The results showed positive reproductive AOC values. The new *V. fischeri* AOC method developed has a highly promising potential to be practically adopted as a rapid indicator of AOC concentration and hence biofouling potential of influent marine water.

Submerged membrane adsorption bioreactor (SMABR) as sustainable pretreatment was investigated. SMABR removed organic matter by adsorption and biological degradation. At a PAC residence time of 66 d (1.5% of daily PAC replacement), higher organic removal was achieved with a high removal of biopolymers, humics and hydrophobic organics. A continuous MBR operation with the optimal PAC residence time of 66 d was conducted and compared with MBR with no PAC replenishment in terms of the removal of organic and microbes. High removal of organics of up to 72% was maintained with only a marginal increment of trans-membrane pressure and stable

bioactivity (TDC and ATP) during the 50 d of operation. The SMABR was found to be a sustainable biological pretreatment to RO with only a small amount of PAC requirement (2.14 g of PAC/m^3 of seawater treated).

Contact flocculation filtration as pretreatment: Deep bed filtration has traditionally been used as a pretreatment in seawater desalination. The performance of contact flocculation–filtration (CFF) as pretreatment of SWRO was evaluated in terms of pressure drop through the filter and removal of organics and turbidity. The performances of CFF were experimentally evaluated with different flocculant doses (0.5–3.0mg Fe^{3+}/L) and rapid mixing times (1.7–14.4s). The headloss also significantly decreased when the flocculant dose was reduced from 3.0 to 0.5 mg Fe^{3+}/L. However, the organic matter removal was lower at a lower dose of ferric chloride.

In this study, it was also investigated the potential of CFF acting as a biofilter in addition to its major function of flocculation and particle/floc separation. Two different media (sand; S-CFF and anthracite; A-CFF) were tested. Bacterial activity in the filter bed was assessed in terms of cell number, ATP measurement and microbial community over the filter run of 90 d. With the growth of an active microbial population on the filter bed medium, significant removal of organic compounds, especially low molecular weight (LMW) organics, from the seawater was achieved. It was found that CFF functions both as flocculation and separation unit and also as biofilter with moderate efficiency in reducing biofouling potential. A-CFF needed longer time to achieve bio-stabilization but it showed more effective biofiltration potential than S-CFF.

CHAPTER 1

University of Technology Sydney

Faculty of Engineering& Information Technology

INTRODUCTION

1.1 BACKGROUND OF RESEARCH

1.1.1 Water scarcity

Water supply and sanitation will face enormous challenges over the coming decades. The water industry will need to meet rapidly growing global requirements and in the present day, water scarcity already affects every quarter of the globe (UN-Water, 2007) (**Figure 1.1**). Especially, around 1.2 billion people (almost one-fifth of the world's population) live in areas of physical scarcity are threatened by serious water shortage. The current rate of water usage in the 21st century is more than twice the rate of population increase compared to the last century (UN-Water, 2007).

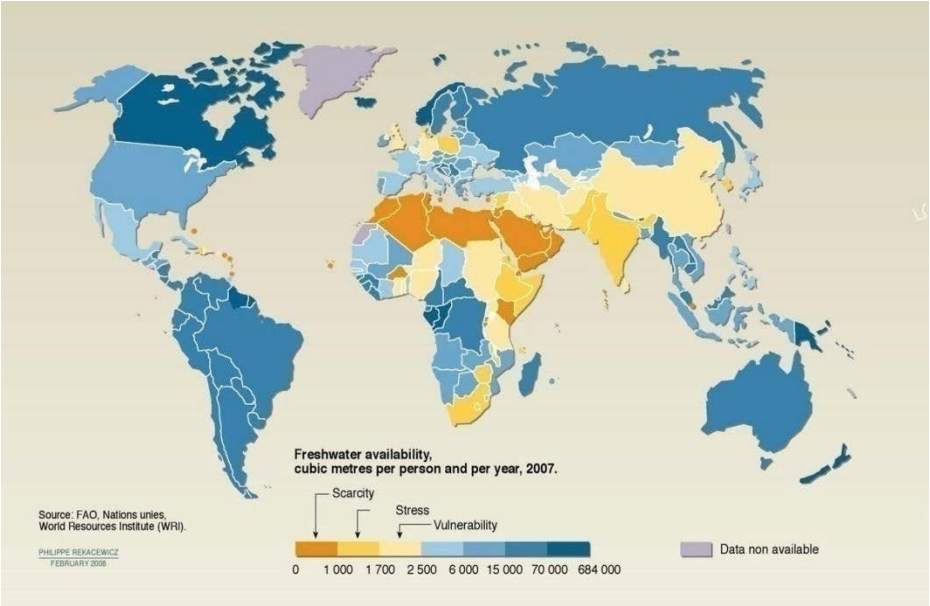


Figure 1.1 World water scarcities (Source: Vital Water Graphics, UNEP).

There is no new (creatable) water source on the planet. The available volume of water is recycled through a process of circulation between the earth and the atmosphere, known as 'the hydrologic cycle' (Shannon et al., 2008). This means that despite a rapidly growing population, the volume of available and accessible freshwater is always limited. Supplying this growing population therefore depends on the capacity (and the will) to

manage the resource differently so that it can serve more people. Therefore, development of an alternative water source is inevitable.

1.1.2 Seawater and Desalination

In this context, seawater desalination is identified as a potential technology for water resource to support the ever increasing water demands (Elimelech, 2006). In recent years, numerous large-scale seawater desalination plants have been built in water-stressed countries to augment available water resources, and construction of new desalination plants is expected to increase in the near future. Despite major advances in desalination technologies, seawater desalination is still more energy intensive compared to conventional technologies for the treatment of fresh water (Elimelech and Phillip, 2011).

Since the first major seawater desalination plant was commissioned in Perth, Australia in 2006, five more major urban plants have been completed or are under construction, representing more than AUD 10 billion in infrastructure investment. There has also been a major potable water recycling scheme constructed in Brisbane (the Western Corridor Scheme) capable of producing 230 ML/d of potable grade water. However, at the time of writing, the water is only used as cooling water for power stations because the scheme has not commenced pumping into public water supply reservoirs.

There are also two industrial seawater desalination plants being constructed at Karratha for an iron ore project and one is planned for Whyalla in South Australia for the BHP-Billiton's Olympic Dam copper-uranium expansion project. A location map of desalination plants is shown in **Figure 1.2**.

Figure 1.2 Locations of Major Australian Desalination Plants (Adopted from Palmer, 2012).

1.1.3 Seawater Reverse Osmosis (SWRO)

Seawater reverse osmosis (SWRO) desalination was chosen as the most appropriate technique since RO demonstrated its usefulness as a cost-effective solution for producing drinking water, compared to other desalination technologies such as thermal distillation (Fritzmann et al., 2007; Malaeb and Ayoub, 2011). However, one of the major challenges for the SWRO system is membrane fouling.

1.1.4 Membrane fouling

A major issue in RO desalination operations is a membrane fouling phenomenon that adversely affects filtration performance. It usually leads to a serious decline in the flux and quality of permeate, ultimately resulting in an increase in the operating pressure over time (Matin et al., 2011). It also requires frequent chemical cleaning and ultimately shortens membrane life, thus imposing a large economic burden on RO membrane plant operation. Due to the problems of fouling on the desalination system, from 2003 till the

present, many studies were done on this issue, looking at monitoring, prevention and control of fouling to treatment methods (**Figure 1.3**).

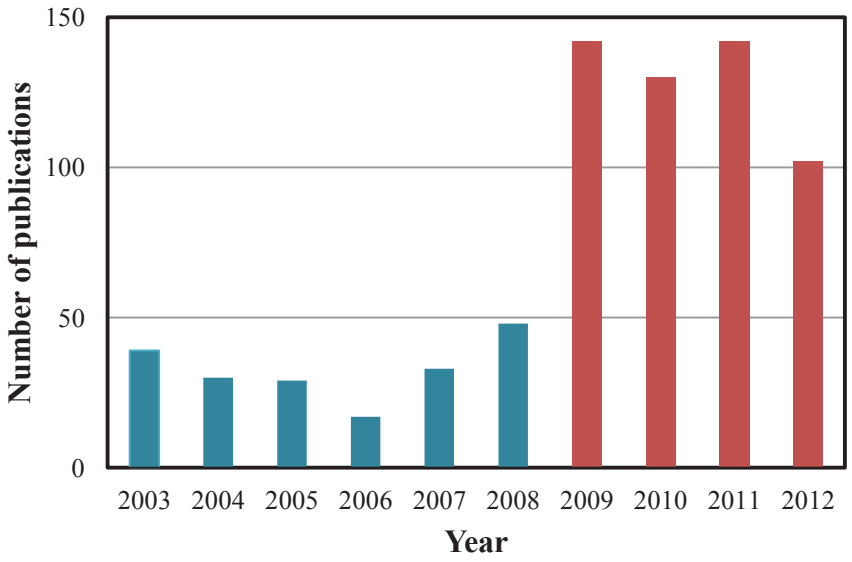


Figure 1.3 Annual peer reviewed publications on fouling in desalination in the period 2003-2012. The total number of papers is 712 (Scopus database: November 2012).

The main foulants of RO membranes include particulate/colloidal fouling, inorganic fouling (including scaling), organic fouling and biofouling. The particulate/colloidal fouling is mainly caused by suspended solids and metal-based hydroxides which can accumulate on the surface and form a cake layer on the membrane. Organic compounds do not only cause adsorptive fouling but can also act as an energy source of microorganisms. Microorganisms such as bacteria, fungus or algae can produce biopolymers that aggregate to the surfaces of membranes and develop a biofilm. This leads to serious operational problems since it accelerates the chemical decomposition of RO membranes. Unlike the first three types of fouling which to a large extent can be reduced by pretreatment, biofouling (biological fouling) can be difficult to control, since deposited microbial cells can grow, multiply and relocate.

1.1.5 Biofouling

Biofouling is defined as the accumulation of microorganisms accompanied with agglomeration of extracellular materials on the membrane surface. When a microorganism adheres to the membrane surface, it starts building up aggregates/ biofilm matrix (Al-Juboori and Yusaf, 2012). Even if 99.99 % of all bacteria are eliminated by pre-treatment (e.g. microfiltration or biocide application), a few surviving cells will enter the system, adhere to surfaces, and multiply at the expense of biodegradable organic substances dissolved in the bulk aqueous phase. Therefore, membrane biofouling occurs extensively on RO membranes even after significant periodic direct cleaning of membranes and continuous upstream application of biocides and disinfectants such as chlorine (Flemming, 1997; Flemming et al., 1997). Further, polymeric membranes are sensitive to oxidizing disinfectants and hence continuous biocide addition from using disinfectant and biocide can affect the growth of resistant strains of bacteria (Kang et al., 2007; Shannon et al., 2008).

1.1.6 Relationship with organic matter and biofouling

Organic fouling is governed by the interactions between the organic foulants themselves and results in the formation of biofilm through activities of micro-organisms on the membrane surface (Ridgway and Flemming, 1996; Brauns et al., 2002; Tran et al., 2007). Biofouling on the RO membrane starts from the adsorption of organic matter to membrane surface. This is followed by the adhesion of microorganisms and growth of the adhered cells. Subsequently, a biopolymer matrix continuously is formed. Thus organic and biofouling developments are mutually related. Even low concentrations of appropriate carbon sources can readily lead to substantial bacterial re-growth on the membrane. Thus the removal of biodegradable organics as well as microbial inactivation at the same time will effectively control the biofouling.

1.1.7 Pretreatment

Since seawater reverse osmosis (SWRO) performance strongly depends on the raw seawater quality, a pretreatment for raw seawater is generally required (Sutzkover-Gutman and Hasson, 2010). In other words, feed water with a consistent high quality is important for a successful RO desalination operation. A poor quality of feed water may shorten the RO membrane operation period and increase maintenance cost. It is therefore essential to remove or reduce undesirable materials in raw seawater to acceptable levels prior to feeding into the RO.

The main purpose of pretreatment is to remove undesirables from the water, which otherwise could adversely affect the RO operation. Conventional pretreatment technologies such as coagulation, deep bed filtration, dissolved air flotation and low pressure membrane-based pretreatment methods such as ultrafiltration and microfiltration can be chosen according to the raw seawater characteristics (suspended solids, turbidity, organic matters, etc.) (Bonnélye et al., 2004).

1.1.8 Low pressure membrane filtration

Low pressure membrane systems such as microfiltration (MF) and ultrafiltration (UF) are considered to be the most reliable, cost-effective and sustainable method in water treatment (Fane et al., 2005). MF can be used to separate suspended solids, colloids and bacteria and control bacterial nutrition in feed water. The UF, on the other hand can completely remove viruses and some of the organic macromolecules. A review comparing the past pretreatment practices (both conventional and membrane (MF and UF)-based pretreatment methods) indicates that membrane-based pretreatment provides consistent feed quality to the RO plant (Prihasto et al., 2009). Thus, MF can be used as a pretreatment for SWRO (Pearce, 2007; Bonnélye et al., 2008).

1.2 RATIONALE OF RESEARCH

1.2.1 New membrane hybrid system as a pretreatment to control organic fouling and biofouling

Traditionally, flocculation and deep bed filtration have been used as pretreatment in SWRO. In new desalination plants, low-pressure membranes are used as pre-treatment. The ability of filtration and low-pressure membrane to remove dissolved organic matter present in seawaters is limited. Furthermore, when MF membrane is used alone, the suspended solids carrying organic materials and different types and sizes of particles and undisposed organic matters can deposit and accumulate on the MF surface. These small particles then cause the pore blocking of MF membrane during filtration, resulting in the permeate flux decline over time and an increase in trans-membrane pressure (TMP).

However, if MF is integrated with other physico-chemical technologies such as coagulation/flocculation and adsorption, membrane fouling can be alleviated. By doing so, it can remove suspended solids, colloids, microorganisms as well as the organic matter. If the dissolved organic matter content and microorganisms in seawater can be reduced prior to their contact with the membranes, the membrane filtration period can be extended. This system also restricts the biofouling potential as it reduces the organic matter and provides a positive barrier to pathogens. It also ensures higher RO flux and less fouling.

1.2.2 Subsequent problem of biodegradable organic matter

Organic matter plays a crucial role in formation of RO foulant. Organic fouling is generally acknowledged as a serious problem for membrane processes and limits the widespread use of the membranes. A fraction of this organic matter is also easily

biodegradable, and when it is accumulated on the membrane surface, in the presence of microorganisms, it will result in the formation of biofilm. This means that organic matter is the precursor to biological growth which progresses to biofouling.

Microorganisms are ubiquitous in systems but can grow and make biofilms in the presence of nutrients and favourable conditions. To this end, all nutrients in water represent a potential energy source for biomass production—if microorganisms are disinfected during pretreatment, this inactive bacterial biomass remains and can be used as nutrients for the production of a new bacterial biomass. Therefore, it is pertinent to investigate the inactivation of the problematic bacteria in seawater pretreatment to minimize the risk of fouling.

1.2.3 Biofouling potential to detect early biofouling

Fouled membranes can be cleaned, but irreversible fouling can also occur. Permanently fouled or chemically degraded membranes must be replaced. Membranes are a significant capital investment. Early biofouling prediction (or warning) has the potential to reduce the operating and membrane cost by enabling early remediation steps to be implemented. An accurate and rapid detection of biofouling potential of feed water (or treated water) is essential. This information can be used to optimize and select the pretreatment by careful monitoring the effectiveness of the pretreatment process.

The assimilable organic carbon (AOC) assay is used as an indicator of the biological growth potential of the water (or biofouling potential) and could be a suitable parameter for predicting of fouling potential. AOC is readily assimilated and utilized by microorganisms resulting in an increase of biomass. Thus, AOC can influence biological fouling (biofouling) in water treatment systems and distribution processes. Indeed, a high level of AOC is directly linked with rapid biofilm formation and loss of

performance in membrane processes. Presently available AOC tests takes too long (few days) and the strains used are not representative of seawater.

1.2.4 New approaches to pretreatment for biofouling control

The biofouling potential consists of ubiquitous microorganisms and the availability of nutrients. The most important factors affecting biofouling potential are nutrient concentrations and shear forces rather than the microbial cell density in the water phase (Vrouwenvelder et al., 2011). The further adhesion of cells to the biofilm does not contribute significantly to biofilm accumulation after the initial stage of biofouling. Cells can also be reduced by an effective biocide treatment, while the nutrient concentration does not decrease. Rather, nutrients may actually increase when the biocide reacts with recalcitrant organic molecules, making it more bio-available (Flemming, 1997a; Flemming et al., 1997).

Thus, the removal of biodegradable organics as well as microbial inactivation at the same time would be necessary to effectively control biofouling. A promising option to control biofouling is membrane bio-reactor (MBR). The removal of organics and nutrients (such as ammonia, nitrate and phosphorus) by MBR can be achieved through the microbial decomposition of these matters.

Deep bed filter (DBF) used as pretreatment can also function as a biofilter. Here, biofilm is developed on the medium and it helps in decomposing biodegradable organic material. Following the adsorption of organic matter onto the filter media, the initial degradation is accomplished by extracellular enzymatic hydrolysis of macromolecules to smaller substrates, which can then be transported into the biofilm. Further degradation takes place by a diverse microbial biofilm community being developed.

Two pretreatment options mentioned above can reduce RO membrane biofouling by eliminating biodegradable organic matter (BOM). They are robust and environmentally friendly due to reduced usage of chemicals (coagulants and biocides). Further, they require little maintenance and energy.

1.3 OUTLINE (STRUCTURE) OF THIS THESIS

To control of organic fouling and biofouling, membrane hybrid systems coupled with coagulation and adsorption were employed. Alternative coagulants such as poly ferric silicate (PFSi) and titanium tetrachloride ($TiCl_4$) were applied with commonly used ferric chloride ($FeCl_3$). Powder activated carbon (PAC) was used in submerged membrane system (MF) to couple the adsorption process.

The performances of membrane hybrid systems were evaluated in terms of the reduction of organics and biofouling potential. Their membrane fouling was quantified using fouling models. Organic matters in effluent from the low pressure microfiltration membrane-based hybrid system were also identified in detail. Moreover, a foulant study was done to assess both organic and biofouling. This study included the fouled RO membrane characterisation to better understand the organic fouling and biofouling.

Rapid and accurate measurement of easily biodegradable substances (Assimilable organic carbon; AOC) present in the feedwater makes it possible to detect the biofouling potential. In this study, submerged membrane adsorption bioreactor (SMABR) and contact flocculation filtration as a biofilter were evaluated in terms of their effectiveness for biofouling control. Their performances were evaluated in terms of biological activity and biofouling potential reduction.

Figure 1.4 presents the outline of this thesis.

Chapter 2 (literature review) presents (i) a detailed review of the membrane fouling, especially biofouling, (ii) different pretreatment methods to control fouling, (iii) assessment tools for feed water quality, and (iv) monitoring of fouling factors. More detailed and specific literature review is also incorporated in **Chapters 4** to **7**.

The general experimental investigation used in this study is explained in **Chapter 3**. This includes basic materials, methods and experimental analyses. The description of specific experimental and analytical methods can be found in the respective chapters.

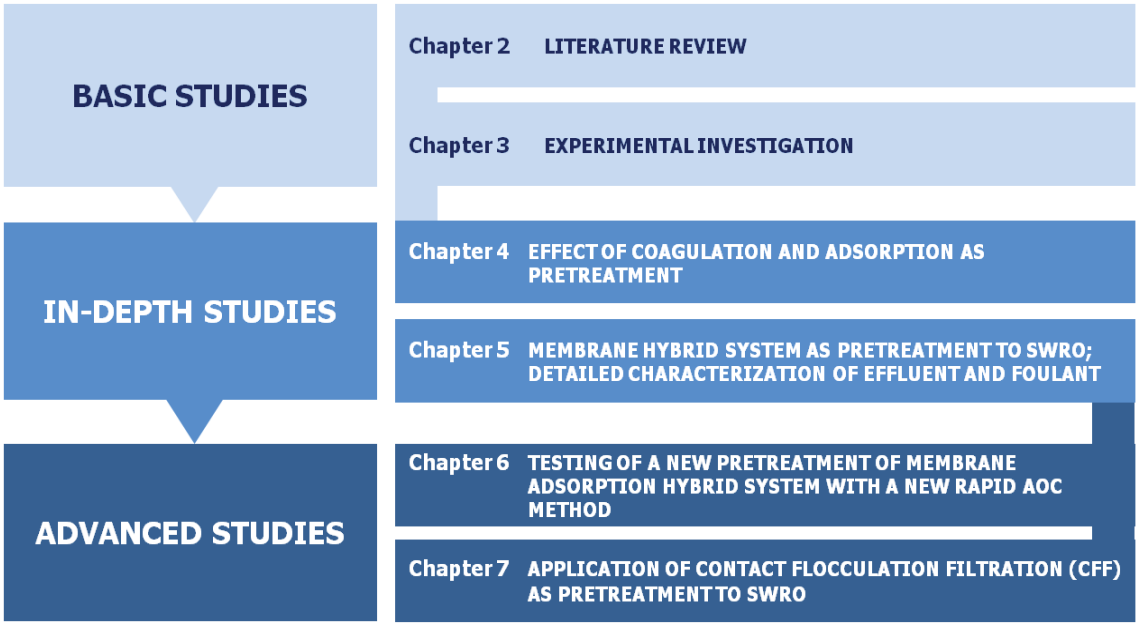


Figure 1.4 Outline (structure) of this thesis.

Chapter 4 evaluates the effect of coagulation and adsorption as seawater pretreatment. This chapter includes: (i) evaluation of the effect of $FeCl_3$ coagulation as pretreatment in combination with submerged membrane system; (ii) experimental and modelling study of $FeCl_3$ coagulation in seawater; (iii) the comparison of $FeCl_3$ with poly ferric silicate (PFSi) coagulation; and (iv) titanium tetrachloride ($TiCl_4$) coagulation in removing organic matter from seawater.

In order to understand the membrane hybrid systems and evaluate them as pretreatment to SWRO, detailed approaches and studies are essential. Thus, **Chapter 5** investigates (i) the submerged membrane hybrid systems (SMHSs) as pretreatment to reduce the organic and biofouling and (ii) applies a membrane fouling model for SMHSs. Detailed

study of (iii) organic matters in the SMHS effluents, and (iv) foulants on RO membrane with pretreated water by SMHSs are also discussed in this chapter.

Chapter 6 proposes (i) a newly developed assimilable organic carbon (AOC) bioluminescence-based test to measure the biofouling potential (or bacterial re-growth) in seawater. In order to remove organic pollutants in seawater through biological activity and adsorption process, (ii) a submerged membrane adsorption bio-reactor (SMABR) was designed and its performance was evaluated through a long-term experimental trial.

Contact flocculation-filtration (CFF), which is deep bed filtration (DBF) coupled with in-line flocculation, has been used as pretreatment for RO desalination mainly to reduce colloidal fouling. Its performance to reduce organic fouling is often overlooked. The removal of organic matter by CFF test was evaluated through a long-term operation (**Chapter 7**). The biological fouling reduction was also studied both through short-term and long-term experiments.

Chapter 8 presents conclusions and suggestions for further study. In addition to this, each chapter (chapter 4 to 7) gives the summary of specific findings at the end of each of these chapters.

CHAPTER 2

University of Technology Sydney

Faculty of Engineering& Information Technology

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter aims to elucidate the important issues associated with the use of pretreatment systems for biofouling control. The focus here is on the various factors influencing the formation of biofouling on reverse osmosis (RO) membranes (biofouling potential). This review also highlights the need for an indicator to assess microbial contamination in seawater. The specific review on the pretreatment, seawater characterization methods and biofouling indicator are given in **Chapters 4** to **7**.

2.1.1 Reverse osmosis (RO)

RO is a separation process in which external pressure greater than the osmotic pressure is applied (Williams, 2003). As a result, pure water flows from the high concentration side to the low concentration side through a semi-permeable barrier (RO membrane). It allows selective passage of a particular species (solvent, usually water) while partially or completely retaining other species (ions and microorganisms). In osmosis, the solvent (water) flows from the lower concentration part to the higher concentration part to equlize the concentration differences on both sides of the membrane. By contrast in the RO process, an external pressure much greater than the osmotic pressure is applied to the salt water side. This forces the water (free from the salt and other contaminants) to pass from the salt water side to the clean water side. During this process, the contaminants on the concentration solute are sieved by the RO membrane (Khan et al., 2010).

2.1.2 Biofouling problem

The use of reverse osmosis membrane technology for seawater desalination is limited by biofouling problems that adversely affect filtration performance (Vrouwenvelder, 2009a). The major types of fouling in RO membranes are scaling (inorganic), organic,

particulate (or colloidal) and microbiological. The first three types of fouling are reduced to a great extent through pretreatment while biofouling can be difficult to control, since deposited microbial cells can grow, multiply and relocate. Biofouling is mainly the accumulation of microorganisms accompanied with agglomeration of extracellular materials on the membrane surface. When a microorganism adheres to the membrane surface, it starts building up aggregates as a biofilm matrix (Wingender et al., 1999). Even if 99.99 % of all bacteria are eliminated by pretreatment (such as microfiltration or biocide application), a few surviving cells will enter the system, adhere to surfaces, and multiply at the expense of biodegradable substances dissolved in the bulk aqueous phase. Therefore, membrane biofouling has been found to occur extensively on RO membranes even after significant periodic cleaning of membranes and continuous upstream application of biocides and disinfectants such as chlorine (Flemming, 1997a). Moreover, polymeric membranes are sensitive to oxidizing disinfectants. Continuous biocide addition can (from the usage of disinfectant and biocide) also affect the growth of resistant strains of bacteria (Kang et al., 2007; Shannon et al., 2008). Biofouling causes a decline in permeate flux and salt rejection, frequent cleanings and a high energy demand in water treatment systems (Vrouwenvelder and van der Kooij, 2001). It can be controlled by removing the biodegradable components from the feed water (Flemming, 1997a; Vrouwenvelder et al., 2011).

Fouling requires frequent chemical cleaning. This ultimately shortens the membrane life and consequently imposes a large economic burden on the RO membrane plant operation (up to 50% of the total operation costs) (Ridgway, 2003). Chemicals such as anti-scalants and acids used for scaling control in RO membranes differ greatly in their

ability to promote the growth of microbes. Certain commercially available anti-scalants can cause biofouling (Vrouwenvelder et al., 2000).

2.1.3 Biofouling mechanisms

Biofouling is caused by unacceptable biofilm formation. The process of forming biofilm on a surface of the membrane involves three subsequent phases (**Figure 2.1**): (i) transport of microorganisms to the surface, (ii) attachment to the substratum, and (iii) growth at the surface (Al-Juboori and Yusaf, 2012).

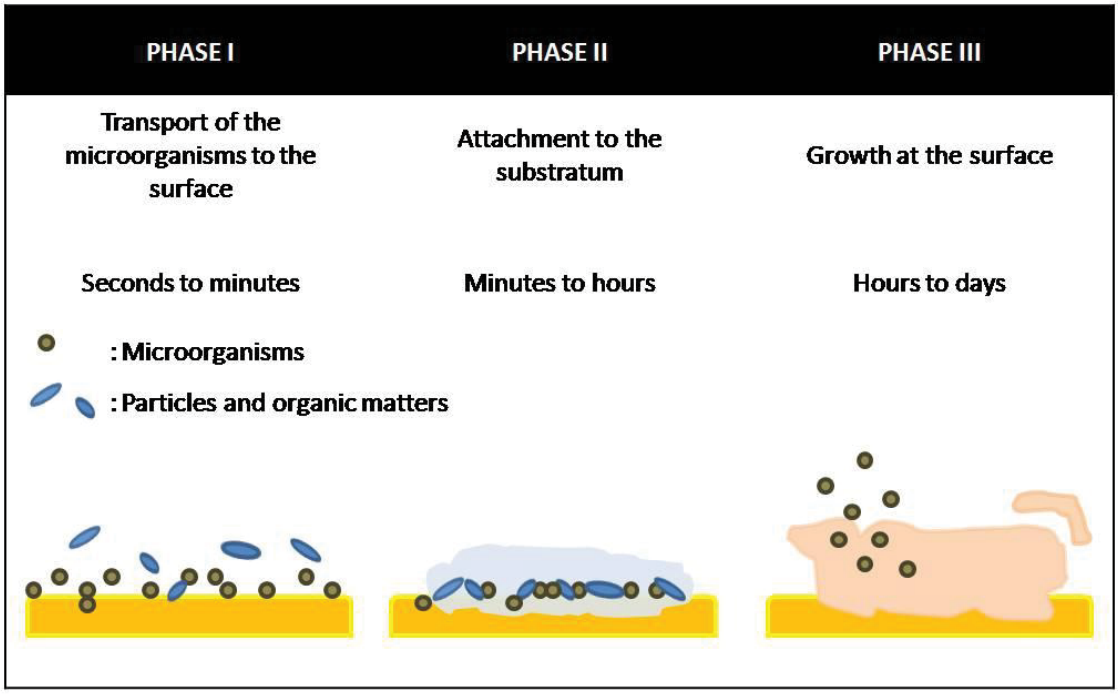


Figure 2.1 Schematic illustration of steps involved in biofilm formation.

The first stage of biofilm formation is the deposition of the dissolved and/or suspended particles, colloid and nutrients from bulk feed water when the feed water comes in contact with the membrane. As a result, during the initial few seconds or minutes of operation, various inorganic and organic compounds as well as bacterial cells are

retained at the water and membrane interface. The attachment of bacteria to the membrane surface is supposed to be mediated through initial micro-colonies. It is accelerated by extracellular polymeric substance (EPS) production and aggregation with organic matters. Subsequently, a biofilm develops by regulating the differentiation from microcolonies into much more sophisticated stacks of bacterial cells with excreted organic polymer matrix of microbial origin. Above all, initial irreversible attachments of bacterial cells and organic matter (macromolecules) occur after a few minutes of contact with the membrane and feed water. This is difficult to remove and requires additional forces to remove it (Flemming and Schaule, 1988). Therefore intensive treatment of feed water is needed before the feed water contacts the membrane.

Numerous factors influence the initial bacterial development on the membrane surfaces, including: (i) water chemistry of the feed water such as pH, temperature, ionic strength and presence of total dissolved solids; (ii) condition of feed water such as the type of micro-organism, the concentration of cells in the suspension, the amount and types of nutrients provided to the cells; and (iii) properties of the membrane such as surface charge, roughness and hydrophobicity (Schneider et al., 2005).

2.1.4 Biofouling control and prevention strategies

Most of the operating costs in RO plants are due to repair of damage caused by biofouling and its monitoring and prevention (Amjad, 1993; Flemming, 2002). This imposes a large economic burden on the plants and limits the widespread application of membrane separation technology (Flemming et al., 1997b).

Biofouling reduction strategies can be divided into control and prevention of membrane biofouling. Firstly, biofouling control involves membrane remediation by chemical cleaning which is carried out to restore the membrane flux. The current method in controlling the biofouling is to increase cleaning frequency, but this leads to a rising

usage of cleaning chemicals, more production of wastewater and decreased membrane life-time. Consequently, after a number of cleaning cycles the membrane modules become irreversibly fouled and need to be replaced to restore water production levels. This results in a loss of the water supply plant capacity (Matin et al., 2011).

In comparison with control, biofouling prevention is related to the reduction of biofouling potential by removal of nutrients and bacteria from the feed water of membrane systems. For example this can be achieved by using a pretreatment of microfiltration or ultrafiltration. Also inactivation of bacteria is possible by applying biocide dosage or UV irradiation. It involves less cost and smaller energy consumption, while minimizing the use of chemicals and impact on the environment. Thus, prevention is more viable for managing biofouling problems than attempting to control the issue of biofouling. Largely, two strategies are employed: i) feed water pre-treatment including eliminating of nutrients, organics as well as bacteria, and ii) membrane modification to prevent the adhesion or/and inactivation of bacteria that is absorbed. At present, the latter still needs to be investigated further for application. On the other hand, the former has been reported to be beneficial for trouble-free and cost-effective desalination that consistently gives a well-filtered and foulant-free feed to the RO system. For selection of suitable pretreatment, it is important to quantify raw water propensity for biofilm generation through the assessment of feed water. An accurate understanding of foulants through their characterization and monitoring is required.

Design and operation of seawater reverse osmosis desalination (SWRO) processes strongly depend on the raw seawater quality to be treated. The performance of seawater RO systems relies on the production of high quality pretreated water. Seawater pretreatment is a key component of every membrane desalination plant. The main purpose of the pretreatment system is to remove particulate, colloidal, organic, mineral

and microbiological contaminants present in the source seawater and to prevent their accumulation on the downstream SWRO membranes and protect the membranes from fouling. The nature and content of foulants in the source seawater affects the performances of the different pretreatment systems used.

In this chapter, various methods for better characterization of raw seawater samples as well as assessment of different pretreatment performance are presented.

2.2 SEAWATER REVERSE OSMOSIS (SWRO) IN DESALINATION

2.2.1 General

Seawater has a salt concentration of 3.2-4.0%, depending where it is situated. Because of high salinity, only membranes with salt rejections of 99.3% or more can produce potable water in a single pass. Application to seawater desalination of the first-generation cellulose acetate membranes, with rejections of 97-99%, is limited. Most (99%) RO membranes are thin film composite polyamide flat sheets (in spiral wound modules), and suitable seawater membranes are available and used in new desalination plants. The osmotic pressure of seawater is about 25 bar, and the osmotic pressure of the brine can be as much as 40 bar, so osmotic pressure affects the net operating pressure in a plant markedly (Barker, 2004; Lauer, 2006). RO is extensively used in the desalination process but one of its major problems is membrane fouling. Raw seawater requires considerable pretreatment before it can be desalinated (**Figure 2.2**) to protect the RO membrane from fouling.

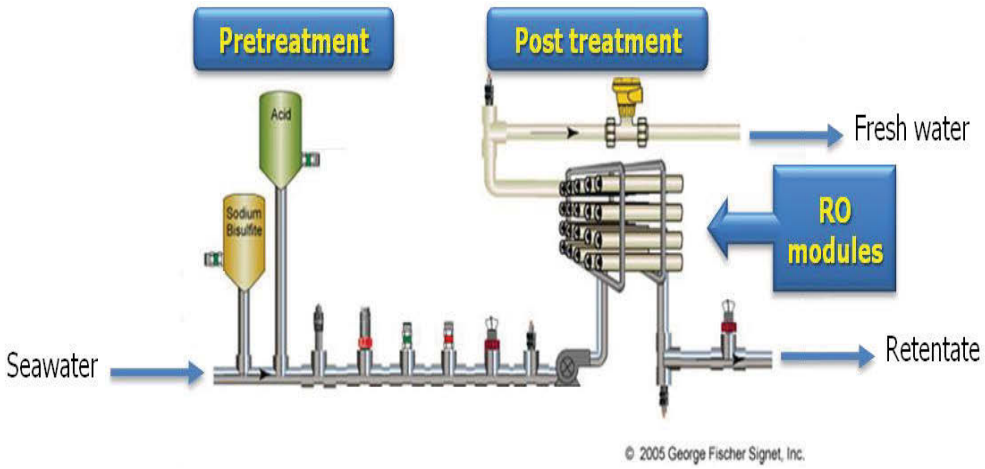


Figure 2.2 Flow scheme showing the three steps in a typical seawater reverse osmosis system.

In a RO process, the osmotic pressure is overcome by applying external pressure higher than the osmotic pressure on the seawater. Thus, water flows in the reverse direction to the natural flow across the membrane, leaving the dissolved salts behind with an increase in salt concentration. No heating or phase separation change is necessary. The major energy required for desalting is for pressurizing the seawater feed. A typical large seawater RO plant (Ayyash et al., 1994; Al-Badawi et al., 1995; Nada et al., 1995; Baig and Al-Kutbi, 1999) consists of four major components (**Figure 2.2**): feed water pre-treatment, high pressure pumps, membrane separation, and permeate post-treatment. Raw seawater flows into the intake structure through trash racks and screens to remove debris in the seawater. The seawater is cleaned further in a multimedia gravity filter which removes suspended solids. Typical filter media used are anthracite, silica and granite or only sand and anthracite. From the media it flows to the micron cartridge filter that removes particles larger than 10 microns. Filtered seawater provides a protection to the high pressure pumps and the RO section of the plant. The high pressure pump raises the pressure of the pretreated feed water to the pressure appropriate for the membrane. The semi-permeable membrane restricts the passage of dissolved salts while permitting water to pass through. The concentrated brine is discharged into the sea.

2.2.2 SWRO in Australia

Australia is the driest continent on Earth and despite this the installed desalination capacity is still around 1% of the total world's desalination capacity. The percentage of Australian desalination plants using different desalination technologies in 2000 are presented in **Figure 2.3**. Seawater reverse osmosis (SWRO) is the only type of desalination technology currently used or proposed for future large-scale desalination plants in Australia. Every capital city except Darwin has considered building at least

one desalination plant as a means of providing water security after several years of unprecedented drought that have significantly reduced dam storage levels. Perth was the first major city to use desalinated water for its drinking water supply and by early 2009 Sydney (**Figure 1.2**) was the second city. Thirteen other large-scale SWRO plants are being built or planned at several locations for the purpose of supplying drinking water (El Saliby et al., 2009). The processes used in Perth SWRO plant are presented in **Figure 2.4**.

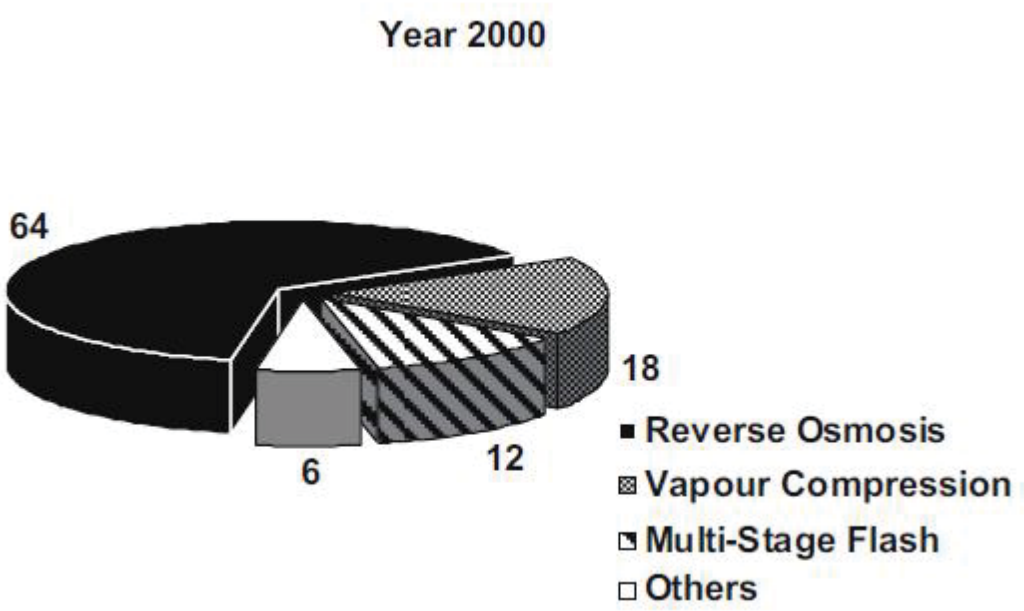


Figure 2.3 Percentage of Australia's desalination plants using different desalination technologies in 2000 (Source: El Saliby et al., 2009).

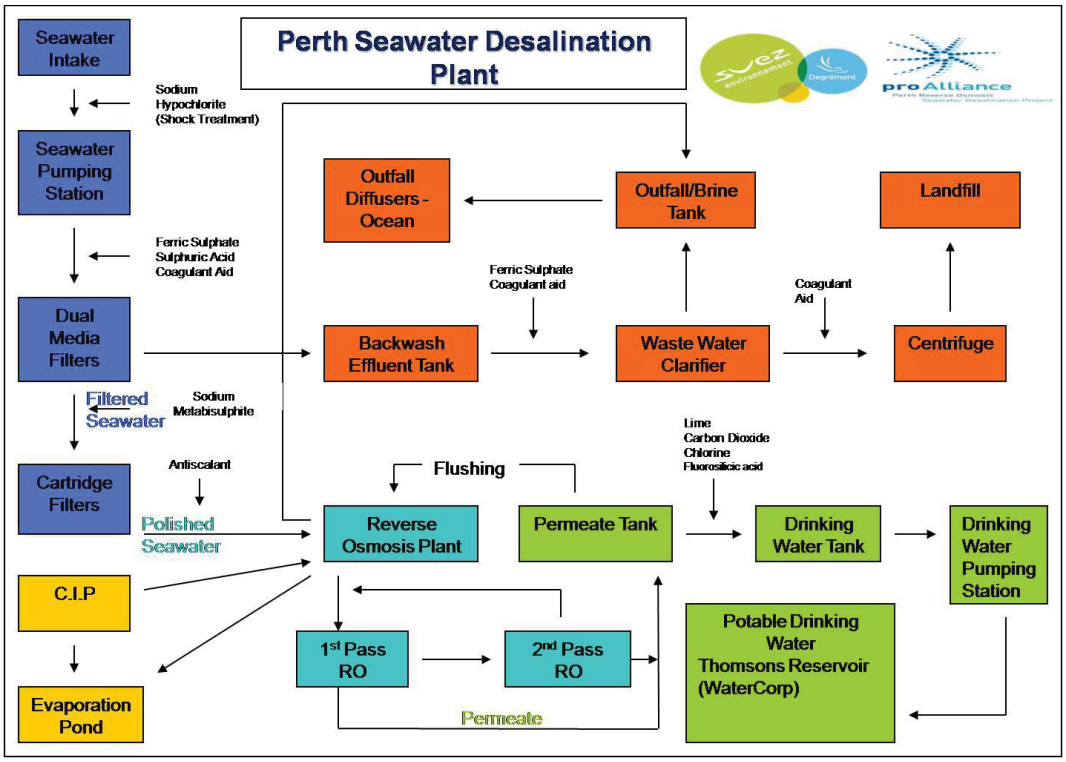


Figure 2.4 The Perth (Australia) SWRO plant.

2.2.3 SWRO issues

In the RO process the osmotic pressure is overcome by applying external pressure higher than the osmotic pressure on the seawater. Thus, water flows in the reverse direction to the natural flow across the membrane, leaving the dissolved salts behind with an increase in salt concentration. No heating or phase separation change is necessary. The major energy required for desalting is for pressurizing the seawater feed.

When used for RO in the seawater applications, more consideration is required. This is because the major foulants in seawater are quite different compared to those present in the surface water and wastewater. The high salt concentration in the seawater might also influence the interaction forces between the membrane and foulant as well as the interactive forces between foulants that have different properties. All these effects would result in potentially different fouling mechanisms. Thus, different fouling reduction strategies must be applied (Fane et al., 2005).

2.2.4 Seawater Organic Matter (SWOM)

Previous studies indicate that there is approximately 1 to 3 mg of dissolved organic material per liter of seawater (Bader et al., 1960; Preston, 2005). Previous data on the chemical composition of SWOM have been obtained either from direct analysis of selected classes of compound in seawater, or from using hydrophobic resins to isolate a chemically fractionated component. Only 1-15% of the total DOC pool can be accounted for by these methods, and isolated samples are not likely to be chemically representative of the entire SWOM mixture. Chemical analyses of resin isolates in particular have contributed to a long-held perception that the bulk of SWOM in the world's oceans is a refractory, high-molecular-weight humic-like substance with little dynamic role in biological cycling. At least, part of the organic compounds present is proton acceptors with the highest capacity existing in the pH range between 7.8 and 9.0 (Bader et al., 1960). The biochemical compounds which are most likely to contain replaceable hydrogen atoms are the carboxylic acids and amino acid salts. Because of the strong buffering effect of the organic material in the concentrates it was thought that these materials could be functional in calcium carbonate solubility relationship. Dissolved organic material in seawater is involved in carbon dioxide equilibrium relationships and must be taken into account in any attempt to understand the kinetics of the carbon dioxide system. Organic component analysis in seawater is considered from sample collection through bulk or individual class analysis to individual component analysis (Preston, 2005).

The MW fraction of organic matter in seawater represents biopolymers (polysaccharides and proteins), humic substances (or fulvic acid), building blocks (hydrolysates of humic substances), and low molecular weight (LMW) acids, respectively (**Table 2.1**, Huber et al., 2011).

Table 2.1 Chemical composition of organics in seawater (by LC-OCD) (Modified from Huber et al., 2011).

Fraction	Molecular weight	Properties	Description
Biopolymers	> 20,000 Da	Not UV-absorbable, hydrophilic	Polysaccharides and proteins, biogenic organic matter
Humic Substances	800 - 1,000 Da	Highly UV-absorbable, hydrophobic	Calibration based on Suwannee River standard from IHSS.
Building Blocks	350 - 600 Da	UV-absorbable	Breakdown products of humic substances.
Low Molecular Weight Acids	> 350 Da	Negatively charged	Aliphatic and low molecular weight organic acids, biogenic organic matter
Low Molecular Weight Neutrals	> 350 Da	Weakly or uncharged hydrophilic, amphiphilic	Alcohols, aldehydes, ketones, amino acids, biogenic organic matter

2.3 PRETREATMENT

2.3.1 General

Seawater pre-treatment is an integral part of every SWRO desalination plant. Pretreatment removes particulates, debris, micro-organisms, suspended solids and silt from the seawater. Ideally, after pre-treatment the only solids left in the seawater would be the dissolved minerals. If the seawater treatment system is operated in a manner that avoids minerals from precipitating on the membrane surface, the SWRO membranes could operate without any cleaning for a very long time. Fouling can be averted by periodic cleaning of the SWRO, however in some cases, membrane fouling could be irreversible and cleaning may not recover productivity, which may require the replacement of some or all of the SWRO membranes. A pretreatment strategy is therefore necessary to ensure that feed water will not cause excessive fouling on the SWRO. The main disadvantages of the conventional pretreatment such as flocculation, deep bed filtration and cartridge filter are the intensive consumption of chemicals and inconsistency in operation (Teng et al., 2003). For example, Chua et al. (2003) reported that the quality of the filtrate produced by the deep bed filter was inferior and highly inconsistent. Leparc et al. (2007) discovered that dual media filters and cartridge filters did not reduce the SWOM content. Advanced pretreatments such as microfiltration (MF) and ultrafiltration (UF) have recently become more important due to the negligible amounts of chemicals used. They are also operationally stable compared to the conventional pretreatment.

2.3.2 Coagulation/Flocculation

Coagulation (neutralization of the particles' charge) and destabilized particle aggregation occur during flocculation. It has also been reported that aggregates produced under sweep floc conditions were more compressible than for charge neutralization conditions, resulting in compaction when the membrane filtration system was pressurized (Antelmi et al., 2001; Cabane et al., 2002; Choi and Dempsey, 2004). Lee et al. (2000) reported that the specific resistance was smaller with charge neutralization than with sweep floc. This is due to the formation of less compressible and more porous cake former. Lee et al. (2000) also reported that the coagulated suspension under either charge-neutralization or sweep floc condition showed similar steady-state flux under the cross-flow microfiltration mode.

Flocculation achieves three objectives: firstly, eliminating the penetration of colloidal particles into the membrane pores; secondly, increasing the critical flux; and thirdly, modifying the characteristics of the deposit (Mietton and Ben aim, 1992; Teng et al., 2003). Effective conventional coagulation conditions produced larger particles and this reduced fouling during membrane filtration by reducing adsorption in membrane pores, increasing cake porosity, and increasing transport of foulants away from the membrane surface (Hwang and Liu, 2002). Bian et al. (1997, 1999) suggested that the combination of high flux and good water quality were achieved when a lower dose of coagulant was used prior to membrane filtration.

Despite the high salt content of seawater, particles of colloidal nature do not tend to coagulate and settle. The main components of particulate matter that may be found in coastal water are microorganisms, detritus, quartz and clay minerals. There is enough surface-active organic matter to be adsorbed on the surface of the particles, thus keeping particles discrete. So far coagulation/flocculation combined with dual-media filtration is

the most common pre-treatment in the SWRO plant. Traditionally, filtration is used as a pretreatment for the removal of particulate matter from seawater. Most of plants utilize either in-line (contact) coagulation or conventional clarification as a destabilization means prior to the filtration step. The use of an efficient in-line flocculation strategy leads to compact treatment plant designs compared to conventional systems. In-line flocculation was found to have similar removal efficiencies at significantly shorter hydraulic retention times (HRT) compared to conventional flocculation. For either method, preliminary testing of flocculants is highly recommended (Adin and Klein-Banay, 1986).

2.3.3 Adsorption

Adsorption is another physico-chemical pretreatment method which can remove dissolved organic matter, thereby reducing membrane fouling. Adsorbent (such as powder activated carbon; PAC) addition shows various behaviors in a bulk solution, within the membrane module or near the membrane surface. Carbon particles can react with natural organic matter (NOM) or metals in the bulk solution. In addition, PAC forms a cake layer combined with colloids, metals and NOM, providing an adsorption zone for further removal of NOM or a hydraulic resistance layer to permeation. Thus, the probable PAC reaction and with the newly formed cake layer within the integrated membrane system is likely to improve the performance of the integrated membrane with PAC adsorption (Oh et al., 2006; Ye et al., 2010).

Suzuki et al. (1998) found that in the membrane adsorption hybrid system, a large portion of organics, mainly humic substances, with a size smaller than the micro-pores in the MF membranes were absorbed by PAC which was then completely separated by the membranes. Moreover, decline of the membrane permeability was slower in this system, which may have resulted from the reduction of the organic loading to the

membrane due to the adsorption of organics on PAC prior to their contact with the membrane. Fouling of membranes by NOM is further complicated by the presence of PAC particles. Although the removal of NOM is enhanced by the addition of PAC during the membrane process (Adham et al., 1991, 1993; Jacangelo et al., 1995), the presence of PAC increased the fouling problem and flux decline as reported by some researchers (Lin et al., 1999a; Carroll et al., 2000; Han et al., 2002) but was reported to prevent flux decline by others (Lin et al., 1999b). Overall, the importance of PAC in flux enhancement is due to the effect of physical scouring of the membrane surface, lowering of specific cake resistance, or adsorption of fine colloids and dissolved organics.

The removal of PAC adsorbed organics from seawater was enhanced by a combination of adsorption and coagulation. The additional advantage of such a process is a greater effectiveness in removing humic acids removal compared to adsorption conducted without coagulation. The PAC added to the treated solution acts not only as an adsorbent for organics but also enhances the settleability of flocs formed (Tomaszewska et al., 2004).

2.3.4 Membrane Technology

Seawater is traditionally pre-treated using process such as filtration and cartridge filters prior to RO application. More recently, membrane filtration has been deemed an alternative solution to these conventional pretreatment methods. All reported seawater membrane clarification pre-treatment tests used ultra-filtration (UF) membranes operating at instant fluxes less than 100 $L/m^2 \cdot h$. Long-term seawater pilot testing (Carmen, 1937) has highlighted the ability of the 0.1 μm Microza hollow-fiber module in providing clarified water for RO desalination systems. It has been shown that both

seawater pre-treatment and the reagent used during backwashes have an effect on the rate of decrease of the permeability the RO membrane as well as on the filtrate quality.

UF/MF has gradually gained acceptance as the preferred pretreatment to RO in recent years (Baig and Al-Kutbi, 1999). It provides an absolute barrier to particles, and produces consistent quality of treated water with a variable feed source. For seawater sources, feeds with low to medium salinity have benefits of improved RO performance resulting in reducing the RO operating cost. For high salinity feeds of 38,000 ppm TDS and above, higher RO flux and recovery may be limited, but operating cost benefits can still justify the use of UF/MF pre-treatment. UF/MF provides improved security and stream time to the RO system (Pearce, 2007).

UF can remove all suspended particles and some dissolved organic compounds, with the removal rating depending on their molecular mass and the molecular mass cutoff of the membrane. The typical removal capability of UF used for general water treatment is 0.01-0.02 micron. Some new materials even provide 0.005 micron filtration. MF typically operates at a particle size in order of magnitude coarser than UF, e.g. approx 0.1–0.2 micron. UF therefore has the advantage over MF of providing a better disinfection barrier, since the pore size of UF excludes viruses (Baig and Al-Kutbi, 1999).

2.3.5 Membrane Hybrid System

A combination of membrane filtration with physico-chemical processes such as coagulation and adsorption, can improve the quality of the produced water and membrane permeability (Maartens et al., 1999).

The addition of coagulant prior to MF or inside the membrane reactor is often called the submerged membrane coagulation hybrid system (SMCHS). Coagulation improves the

filtration characteristics of MF by reducing cake resistance of the deposit on the membrane (Cho et al., 2006). One of the expected benefits of the membrane process is a reduction of coagulant demand. Removal in membrane filtration differs from those in conventional technologies, ultimately affecting coagulant dosages, points of application, type of coagulant applied, etc. The combination of coagulation, flocculation, and membrane filtration is also an efficient and reliable treatment option for surface waters with high NOM concentrations at relatively low coagulant concentrations. It enables operations under optimal pH conditions (Guigui et al., 2002).

More efficient virus retention can potentially be expected when coagulation/flocculation is combined with membrane filtration where microbes are adsorbed to or included in larger flocs that are retained by the membrane (Guo et al., 2008).

Powdered activated carbon (PAC) adsorption has been widely applied as a pretreatment method to assist low-pressure driven membrane filtration processes such as MF to remove dissolved organic solutes from polluted water. In submerged membrane systems, air bubbles are injected to the tank to provide mixing and introduce shear at the membrane surface to prevent particle deposition. In this hybrid system the organics are adsorbed onto the PAC, and the organic-laden PAC is eventually separated by the membrane (Guo et al., 2004).

The submerged membrane adsorption hybrid system (SMAHS) has many advantages when it is operated on a long-term basis. PAC initially acts as an adsorbent. After the growth of microorganisms on the PAC surface, the organic would be biodegraded by the microorganisms and thus the PAC can be used for a long time (Guo et al., 2008). The membrane is also free from fouling (or very little fouling) and thus can be used for long time without cleaning. The submerged membranes do not become clogged as

almost all organics are removed by the PAC and the role of the membrane is only to retain the PAC and other suspended solids. The energy requirement is very low (as low as 0.2 kwh/m^3) and there is no major sludge problem (Vigneswaran et al., 2007).

The pre-adsorption of organics onto the PAC could help to firstly, reduce the membrane fouling and secondly, maintain a consistent permeate flux. The PAC replacement in a submerged membrane adsorption bio-reactor (SMABR) could stimulate both biological activity and adsorption, as well as optimize the operation of the hybrid system. Guo et al. (2008) reported that with PAC replacement, the organic removal efficiency of the system was more than 90%.

2.4 BIOFOULING REDUCTION STRATEGIES

As discussed in **section 2.1.4**, biofouling strategies can be divided into control and prevention. Prevention includes membrane modification, water disinfection, biochemical and feed water pretreatment while control is mainly associated with membrane cleaning. Here, biofouling reduction strategies are broadly clarified into direct methods and indirect methods to membrane (**Table 2.2**).

2.4.1 Direct methods (to membrane)

In "Direct methods", biofouling is controlled from when membrane modules are manufactured and is effectively removed during the operational phase. The immediate method is to control biofouling *in situ* by applying antifouling agents to the membrane directly. Effective cleaning of the fouled RO membrane extends of the RO membrane's life and thus results in reduced operation costs.

2.4.1.1 Membrane modification

Membrane modification improves the physico-chemical properties of membrane such as roughness, functional group, charge and membrane hydrophilicity which influences membrane fouling. Various antifouling materials have recently been used in membrane modification (Louie et al., 2006, Chae et al., 2009; Malaisamy et al., 2010; Miller et al., 2012).

It could improve the RO flux by reduction of bacterial adhesion on the membrane surface and inactivation of microbes. Smooth membranes can reduce the rate of microbial attachment on the membrane's surface (Louie et al., 2006). Adjustment of the surface charge to a negative charge can also reduce biofouling since most microorganisms have a negative charge in solution state (Hori and Matsumoto, 2010).

However, this can cause the deposition of negatively charged foulants onto the membrane.

Increase of hydrophilicity can reduce the attraction of microbes on the membrane. The enhancement of hydrophilicity can induce more organic fouling caused by the hydrophilic components in surface water (Kwon et al., 2004). Biosurfactants can also reduce surface and interfacial tensions in both aqueous solutions and hydrocarbon mixtures. They have several advantages over chemical surfactants, such as less toxicity, higher biodegradability, better environmental compatibility, higher foaming, high selectivity, and specific activity at extreme temperatures, pH, and salinity; and the ability to be synthesised from renewable feed stocks (Desai and Banat, 1997; Chapman Wilbert et al., 1998).

Although, this modification can prevent microbial adhesion effectively in the short term, there are some drawbacks. It is relatively costly and only some microbes can overcome the new conditions of the modified membrane surface since they have a tendency to easily develop adhesion under different environmental conditions (Hori and Matsumoto, 2010). Thus, when modification methods are used consequent reduction of the concentration of microorganisms in the feed solution of the RO membrane is required.

2.4.1.2 Membrane cleaning

Many studies have focused on effective chemical cleaning conditions. Most reduction in membrane performance can be overcome by cleaning the membrane (Sadhwani and Vesa, 2001; Madaeni and Mansourpanah, 2004). It was reported that cleaning efficiency depends on the cleaning agent, concentration, pH, temperature, and cleaning time. In general, cleaning is applied when the permeate yield drops by about 10%, or feed pressure increases by about 10% and/or differential pressure increases by 15–50% (Al-

Amoudi and Farooque, 2005). In most of the RO desalination plants, around 5–20% of the operating cost is used for membrane cleaning (Fane, 1997).

The mechanical stability of biofilms can be overcome by: i) weakening of the biofilm matrix by employing appropriate chemicals that interfere with the bonding; and ii) removal of the biofilm from the membrane surface by shear forces (Flemming, 2002). Sodium hypochlorite (NaOCl) (Subramani and Hoek, 2010) and sodium hydroxide (NaOH) (Kim et al., 2011) are used as biofouling control agents and a NaOH cleaning for 20 min showed a biofouling reduction efficiency of more than 95%. However, these methods of cleaning are not effective in controlling biofouling since biomass is not removed from the module completely (Kim et al., 2009). It can therefore cause rapid bacterial regrowth to occur (Vrouwenvelder et al., 2003; Bereschenko et al., 2011). Also, these kinds of cleaning techniques lead to problems such as less permeate production due to system shutdown, damage to the membrane and causing waste pollution (Kang et al., 2007; Khan et al., 2010).

Table 2.2 Comparison of biofouling reduction strategies on RO membrane.

Biofouling strategies		Description	Advantages	Disadvantages
Direct methods to membrane	Membrane modification	Modification to improve the physico-chemical properties of membrane	Prevention from microbial adhesion	Costly, microbes can develop new condition on the membrane and lead to additional fouling
	Membrane cleaning	Recovery of reduced membrane performance by adding cleaning agents	High and immediate effect on the performance	System shutdown, damage of membrane; and additional waste
Indirect methods to membrane	Feed water treatment	Production of feed water with reduced fouling potential	Subsequent removal of microbes and nutrients	Membrane fouling, backwashing and cleaning
	Biochemical methods	Regulating different biological activities for microorganisms	Environmentally friendly	Costly, low efficiency and industrial limitation
	Water disinfection	Inhibition of the adhesion of microorganisms to the membrane	Deactivate the microorganisms before entering them into RO membrane unit	Chemical: Disinfection by-Products (DBPs) production and mutagenic agents Thermal: Limitation on location and climate UV: Low performance

2.4.2 Indirect methods (to membrane)

Indirect methods include physical removal of bacteria from the feed water of membrane systems such as microfiltration (MF) and ultrafiltration (UF) and metabolic inactivation of bacteria by applying biocide (biochemical) or disinfectant.

2.4.2.1 Feed water pretreatment

Pretreatment systems to RO are designed to produce feed water with a reduced fouling potential, and they do this by removing particulates, micro-pollutants and micro-organisms as well as preventing the formation of inorganic scales. From previous experience, pretreatment is one of the most important processes for successful operation of RO since it reduces the organic substances and bacteria which may cause membrane biofouling (Kumar et al., 2006). Low concentrations of microorganisms present in the RO feed can reduce the possibility of microbial adhesion to the membrane.

Pretreatment is carried out using either conventional physico-chemical methods or MF/UF membrane processes. The former is composed of coagulation/flocculation or adsorption, dissolved air flotation and granular media filter (or dual media filter).

2.4.2.1.1 Conventional filtration

The use of filtration techniques for biofouling control in the RO system includes a conventional filtration technique using granular media filtration and non-conventional filtration techniques using pressure driven membranes. The granular media filtration technique can be applied in three arrangements: single, dual and mixed media. Increasing the number of the media involved in the filtration process can improve the coarse-to-fine filtration process of the granular filter (Prihasto et al., 2009). When contaminated water passes through a granular filter, microorganisms and other

contaminants get adsorbed to the filter media or to initially attach contaminants on their surface (Jegatheesan and Vigneswaran, 1997). There are a number of factors that determine the capacity of a granular filter such as operational parameters, size and kind of filter media.

Achieving a stable RO water quality with conventional pretreatment systems with complex feedwaters is difficult. To control biofouling, different pretreatment regimes such as coagulation and dual media filtration were applied and these configurations reduced the bacterial number in the feed by 32–100% (Chua et al., 2003). In most cases the coagulation and filtration effectively removed a large portion of the total bacterial mass (82%) in the feed (Al-Tisan et al., 1995).

In spite of the acceptable level of biofouling control achieved by applying filtration techniques (Sadr Ghayeni et al., 1998), these techniques still face some challenges. For example, high concentrations of microorganisms and nutrients can pass through the granular filter during the period between the backwash and before it gets the ideal level of filter compactness (Chua et al., 2003), microorganisms may have the opportunity to pass through and colonize membrane surface and build a biofilm. Similarly, the efficiency of membrane filtration pre-treatment processes deteriorates significantly due to the problems of fouling and biofouling (Subramani and Hoek, 2008).

2.4.2.1.2 Membrane filtration

Membrane filtration is known as a more effective pretreatment than the conventional one since membrane pretreatment systems generally require less space and chemicals compared to conventional pretreatment systems (Brehant et al., 2002; Valavala et al., 2011). As membrane costs are becoming competitive, the economics of operating a membrane plant are perhaps favorable.

The mechanism of membrane filtration technology in detaining microorganisms is a combination of two phenomena: firstly, the effect of physio-chemical interactions between the membrane and microorganisms; and secondly, the sieving effect (Van der Bruggen et al., 1999; Kosutic and Kunst, 2002). The microorganisms that are larger than the pore size of the membrane are retained, and in a similar way the membrane that is negatively charged retains the microorganisms through the repelling force.

The filtration and membrane pretreatment system mainly reduces the formation of biofouling by removing the available nutrients for microorganisms in the feed stream of the RO system. When installing filtration techniques ahead of a RO system, the filter can form a barrier that retains the available nutrients in the passing water, leaving the microorganisms in the RO feed water in a starvation condition (Flemming, 1997a). Starvation can compromise the reproducibility of microorganisms and their ability to produce dense and widespread biofilm (Al-Juboori et al., 2012).

2.4.2.2 Biochemical method

The robust structure of biofilm can be degraded by using biochemical substances such as enzymes, bacteriophage and signaling molecules (Flemming, 2011). Bacteriophage can be defined as viruses that infect the bacteria (Fu et al., 2010). Signaling molecules (quorum sensing inhibition) are specific biomolecules that regulate different biological activities for microorganisms such as cell-cell communication activity in the bacterial communities of the biofilm (Davies and Marques, 2009). These techniques are usually applied to removing the already formed biofilm on surfaces. Applying biochemical techniques for removing the established biofilm on a surface is limited by some drawbacks such as the high cost associated with producing the biochemical substance (limitation on industrial scale) and unstability and low efficiency (low sensitivity) in

detaching the adhered microorganisms from substrates (Richards and Cloete, 2010; Flemming, 2011).

2.4.2.3 Water disinfection method

The use of disinfection as pre-treatment to the RO membrane system is an effective way of inhibiting the adhesion of microorganisms to the membrane (Hori and Matsumoto, 2010). Disinfection techniques have the potential to deactivate the microorganisms before the attachment takes place. The water disinfection process includes using of a wide spectrum of treatment methods ranging from conventional treatment techniques such as chemical and thermal treatments, to non-conventional treatments such as ultraviolet (UV) light treatments, electrical treatments, mechanical treatments and ultrasound treatments.

Chemical treatments for water disinfection include the addition of chemical agents such as chlorine and ozone to the water that have the potential to deactivate the existing microorganisms in the water. In spite of the advantages of chemical methods, such as low cost and the capacity to deactivate a wide range of microorganisms effectively, these techniques have some shortcomings related to Disinfection by-Products (DBPs) production and mutagenic agents which attack the materials of the RO membrane and mass transfer limitation (Gogate, 2007; Hulsmans et al., 2010; Kim et al., 2009).

For this reason, thermal treatment such as solar energy (Davies et al., 2009) has emerged as an alternative option. Solar disinfection is regarded as a low-cost water disinfection technique, yet its efficiency depends on the geographical location and climate conditions which may restrict its feasibility (Davies et al., 2009).

UV light treatment is an alternative treatment technique (Schwartz et al., 2003). In spite of this the use of UV light as a disinfectant has some limitations such as low

performance in the light scattering (Parker and Darby, 1995) and absorbing solutions (Harris et al., 1987).

The use of ultrasound technology for water disinfection is a very valuable application, due to the environmentally friendly effect of ultrasound and its ability to deactivate and disintegrate clusters of the pathogenic microorganisms (Joyce et al., 2003; Gogate and Kabadi, 2009). The potency of ultrasound for disintegrating microorganisms lies in the simultaneous effects of acoustic cavitation. Acoustic cavitation is defined as the process of generation, growing and subsequent collapse of the bubbles as a response for the passage of ultrasound waves through a liquid body (Vichare et al., 2000; Gogate, 2007).

2.5 DETECTION OF FOULING

Deposition and accumulation of foulants such as particulate and organics on the membrane surface not only cause permeate flux decline with time, but also deteriorates the permeate quality in many situations (Hoek and Elimelech, 2003; Ng and Elimelech, 2004). Although membrane fouling is affected by the operating conditions such as flux and recovery (Chen et al., 2004), the more fundamental cause for membrane fouling is the properties of feedwater. This is known as the fouling potential (Kremen and Tanner, 1998; Vrouwndvlder et al., 2003).

2.5.1 Organic matter (OM) in seawater

A major constraint is organic fouling associated with bulk organic matter (OM). However, the classification of organic fouling overlaps those of colloidal fouling and biofouling. In addition to macromolecules, organic foulants can include organic colloids.

Moreover, biofouling can be considered as a biotic form of organic fouling while OM derived from microbially-derived cellular debris is considered to be an abiotic form of biofouling (Amy, 2008).

Table 2.3 presents the OM measurements and characterization of feed water samples.

Researchers have developed new analytical tools for better OM characterization. Not only fundamental OM characterization but also new techniques are being employed to improve our knowledge of OM present in seawater.

XAD resins have been largely used to characterize and to concentrate NOM from seawater (Amador et al., 1990; Lara and Thomas, 1994; Lepane, 1999). A more specific protocol using adsorption onto XAD8 and XAD4 resins has been described by Martin-Mousset et al. (1997) to fractionate dissolved organic matter in three categories of

polarity namely, hydrophobic (HPO), transphilics (TPI which is an intermediate or transitional polarity) and hydrophilic (HPI). LC-OCD is the combination of a size exclusion chromatography with continuous analysers able to quantify DOC, DOC and UVA254 (Huber and Frimmel, 1994; Huber et al., 2011). The fluorescence EEM (F-EEM) is convenient tool for distributing NOM over different fractions following their chemical nature from seawater (Coble, 1996; Sierra et al., 2005).

Table 2.3 Various OM measurements and characterization of feed water samples (Amy, 2008).

Measurement category	Protocol
Dissolved organic carbon (DOC)	The amount of OM
Dissolved organic nitrogen (DON)	The nitrogen content of OM
UVA absorbance @ 254 nm (UVA254)	The aromatic character of OM
Specific UVA (SUVA = UVA254/DOC)	The relative amounts of humic OM (higher SUVA) vs. non-humic OM (lower SUVA)
Molecular weight (MW) distribution by size exclusion chromatography with on-line DOC detection (SEC–DOC)	OM in terms of chromatographic peaks corresponding to high molecular weight (MW) polysaccharides (PS), medium MW humic substances (HS) consisting of humic and fulvic acids, and low MW acids (LMA); this technique is conceptually equivalent to LC–OCD, liquid chromatography with organic carbon detection
Hydrophobic/transphilic/hydrophilic (HPO/TPI/HPI) DOC distribution	XAD-8/XAD-4 resin adsorption chromatography, revealing a polarity distribution of OM
3-dimensional spectra Fluorescence excitation–emission matrix (3D-FEEM)	Distinguishing between humic-like and protein-like OM as well as providing a fluorescence index (FI) that is related to OM source (i.e., terrestrial or microbial)
Pyrolysis gas chromatography/mass spectrometry (Py-GC/MS)	OM biopolymer composition in terms of polyhydroxy aromatics, polysaccharides, proteins, and amino sugars (NOM isolate characterization)

2.5.2 Parameters characterizing biomass

Parameters to measure biomass include adenosine 5'-triphosphate (ATP), total direct cell count (TDC) and heterotrophic plate count (HPC) (Vrouwenvelder and van der Kooij, 2001). The higher concentrations of biomass increased normalized pressure drop (NPD) and/or declined normalized flux (MTC) operating parameter values (Vrouwenvelder et al., 2001). ATP, which is a quick and simple method, gives an indication of the total amount of active biomass in seawater systems. Its concentration was measured by an enzymatic reaction using luciferin and firefly luciferase. Light production was determined and the ATP concentration was derived from the linear relationship between light production and reference ATP concentrations. TDC values are determined with epifluorescence microscopy using dyes such as SYTO, acridine orange and 4'-6-diamidino-2-phenylindole (DAPI). However, those fluorochromes stained all bacterial cells that have got into the samples. Therefore, both live cells and dead cells in samples are measured. HPC can be obtained by spreading of the water sample on R2A plates and incubating at 20 or 28 °C for 5–7 d to enumerate the heterotrophic bacteria found in biomass suspension samples (Vrouwenvelder et al., 2000; Schneider et al., 2005;; Veza et al., 2008; Vrouwenvelder et al., 2008). TDC was better at assessing the pretreatment plant performance than HPC, but the quantification of cells delivered in the form of aggregates was not satisfactory with either counting methods. ATP analysis is much more accurate and distinctive, thus, the combination of ATP and cell number analysis is a suitable biomass parameter to the membrane element and feedwater.

In addition to the microbial quantity in seawater, diverse bacterial communities can severely affect the pre-treatment step in the desalination process (Schneider et al., 2005). Many different species of bacteria are present in seawater. Understanding the abundance

of different bacterial species is important for designing a proper pretreatment strategy in the desalination process. As discussed earlier, dominant groups or specific bacteria may increase the concentration of high molecular weight organics or microbial EPS (or biopolymers) (Cottrell and Kirchman, 2000; Frias-Lopez et al., 2002).

2.5.3 Fouling potential of water

2.5.3.1 Particulate fouling potential

It is necessary to establish a reliable method to measure and predict the particulate fouling potential of feed water to membrane filtration systems (Boerlage et al., 2003). It can be used at the design stage to assess the pretreatment required and to monitor the effectiveness and performance of a pretreatment system during a plant's operation.

The silt density index (SDI) and the modified fouling index (MFI) are the most widely applied methods. Initially, microfilter (0.45μm) (MF-MFI) was used to evaluate the particulate fouling potential but Moueddeb et al. (1996) demonstrated the limits of the MF-MFI for seawater. Boerlage et al. (2003) introduced the UF-MFI test as a water quality monitor and this test can be used to measure the fouling potential of a single given feed water type, and register a change in feedwater quality before membrane installation.

2.5.3.2 EPS (Extracellular polymeric substances)

Both adhesion of microorganisms to inanimate surfaces and cohesion of biofouling layer are performed by EPS, which are composed of polysaccharides, protein, glycoprotein, lipoproteins and other macromolecules of microbial origin. These form a slime matrix which "glues" the cells onto the surface and keep the biofilm together.

Especially, transparent exopolymer particles (TEP) were recently introduced as a major indicator of biofilm formation in RO systems which could potentially lead to biofouling (Berman, 2010). TEP are highly sticky and can easily accumulate on RO membranes, thereby initiating biofilm development in the system. Many studies reported that significant percentages (up to 68%) of total bacterial population found in seawater were attached to TEP (Alldredge et al., 1993; Passow and Alldredge, 1994). TEP acts not only as an indicator but also plays a crucial role in enhancing microbiological growth in the system. Thus, monitoring the presence of TEP in the feed water of RO plants is necessary to better understand their contribution to membrane fouling (Villacorte et al., 2009).

2.5.3.3 Biofouling potential

The biofouling potential is determined by ubiquitous microorganisms and the availability of nutrients. These must be considered as potential biomass. The biofilm accumulation depends on different factors: i) nutrient concentration, type and availability; ii) shear forces; and iii) mechanical stability of the biofilm matrix (Flemming et al., 1997b). A reliable monitoring of biofouling potential is applied may save large amounts of biocides (Vrouwenvelder et al., 2000, 2007, 2011).

The level of biodegradable organic matter (BOM) is the limiting nutrient for bacterial growth (LeChevallier et al., 1991). Thus, BOM concentration is quantified as assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC). Both are bacterial regrowth potential indicators. Moreover, AOC has actually been correlated with bacterial counts in water samples (Hambsch and Werner, 1996). DOC and BDOC are typically more related to higher molecular weight compounds (e.g. humic acids), while lower molecular weight compounds are quantified as AOC (e.g. acetic acids and amino acids).

2.5.3.3.1 Assimilable Organic Carbon (AOC)

AOC refers to a fraction of the total organic carbon (TOC) which can be utilized by bacteria, resulting in an increase in biomass concentration that is quantified. AOC typically comprises just a small fraction (0.1-9.0%) of the TOC. In the AOC assay, bacterial growth is monitored in water samples by colony counts. The average growth (Navg) observed during the incubation is converted into AOC by using a growth yield of the bacteria from calibration curves derived from standard concentration of organic compounds. Van der Kooij (1992) showed that heterotrophic bacteria did not increase when AOC levels were less than 10 μg/L. Conventional AOC methods and newly developed methods are discussed in **sections 5.1** and **6.1** of **Chapters 5** and **6**, respectively and in more detail.

2.5.3.3.2 Biodegradable Organic Carbon (BDOC)

The BDOC content represents the fraction of DOC that is assimilated and/or mineralized by a heterotrophic microflora (Servais et al., 1987). The inoculum for the test consists of environmental bacteria, suspended or alternatively fixed on a support, such as sand or porous beads. BDOC is the difference between initial DOC of the water sample and the minimum DOC observed during the incubation period of 28 days for suspended indigenous bacteria or 5-7 days for bacteria attached to sand. However, a study by Van der Kooij (1992) suggested that BDOC could not be used to predict the level of regrowth because no significant correlation was observed between counts of heterotrophic bacteria and BDOC concentration. Moreover, its detection limit was 0.1 mg/L which could detect the AOC level. Recently, the determination of BDOC has been used in water treatment as a measure of biodegradability.

2.5.3.3.3 Biomass Production Potential (BPP)

Biomass production potential (BPP, ATP_{max}/mg product or liter of water) test is performed by determining the maximum concentration of ATP of the indigenous bacterial population in a water sample with incubation at 25 °C (Vrouwenvelder et al., 2000). This test is useful when a biodegradable chemical that is present in the water sample cannot be utilized by the strain used in the AOC test.

2.5.3.3.4 Biofilm Formation Rate (BFR)

The biofilm formation rate (BFR) value was determined utilizing an on-line operated biofilm monitor at a continuous linear flow rate of 0.2m/s. The accumulation of active biomass (ATP) on the surface of glass rings in this monitor was determined as a function of time and the BFR value is expressed as $pgATPcm^2$/day (Van der Kooij et al., 1995).

2.5.4 Membrane characterization

Fouled membrane characterization is significant for understanding both organic and biofoulants and their influences on membrane properties (**Table 2.4**).

This includes the observation of fouling layer and biofilm structure. When fouling is complex and poorly understood, membrane autopsy is a powerful diagnostic tool which can help to enhance the system's performance. Effective control of fouling requires a good diagnosis of the foulant present (Vrouwenvelder et al., 2003). Many methods have been carried out to identify the foulants on the RO membrane (Lawrence et al., 2003; Schneider et al., 2005; Tansel et al., 2006; Xu et al., 2010). The best autopsy approach today is also to develop more *in situ* tools which engage non-destructive analysis of the membrane materials (Ponte et al., 2005).

Table 2.4 Fouled membrane characterization.

Measurement category	Protocol
Pure water permeability (PWP)	
Pore size or molecular weight cut-off (MWCO)	
Contact angle (°)	An index of hydrophobicity
Zeta potential (mV)	An index of surface charge
Surface roughness	
Atomic force microscopy (AFM)	Foulant layer morphology in terms of (membrane) surface topography and pore distribution
Confocal Laser Scanning Microscopy (CLSM)	The presence and the viability of the biofilm consortium and biofilm/substrata interactions
Infrared spectrophotometry (FTIR)	Foulant layer composition in terms of organic functional groups including amines (proteins), carbohydrates (polysaccharides), and carboxylic acids (humic substances)
Magnetic Resonance Imaging (MRI)	Sequences of NMR measurements in the presence of magnetic fields with linear gradient
Optical coherence tomography (OCT)	Optical signal acquisition and processing method allowing extremely high-quality, micrometer-resolution, 3D image from within optical scattering media (or reflecting structure)
Scanning electron microscopy (SEM)	Foulant layer morphology
Transmission electron microscopy (TEM)	Cross-section information about the spatial relationships of microorganisms within the biofilm matrix.

CHAPTER 3

University of Technology Sydney

Faculty of Engineering& Information Technology

EXPERIMENTAL INVESTIGATIONS

This chapter introduces the study's experimental materials and applied analytical methods. The experimental set-up is also explained in detail. The specific details on different experiments and analyses used for different pretreatments are discussed in **Chapters 4** to **7**.

3.1 EXPERIMENTAL MATERIALS

3.1.1 Seawater

Pretreatment experiments related to adsorption, membrane adsorption bioreactor, flocculation and deep bed filtration were conducted with seawater drawn from Chowder Bay, Sydney, Australia. Seawater was pumped from 1 m below the sea surface level and filtered using a centrifuge filtration system to remove any large particles. The characteristics of the seawater are presented in **Table 3.1**.

Table 3.1 Characteristics of seawater in Chowder Bay in Sydney, Australia.

Analysis category	Measurement value
pH	8.2
Conductivity (mS/cm)	51.8–55.5
TSS (mg/L)	3.6
Salinity (g/L)	35.5
UF-MFI (s/L^2)	15,848
Turbidity (NTU)	0.41
UV254 (/cm)	0.026
DOC (mg/L)	1.29

Table 3.2 Characteristics of seawater in Kijang, Busan, Republic of Korea.

Analysis category	Measured value	Analysis method	Analysis category	Measured value	Analysis method
pH	8.13	pH meter	SUVA	0.466	(UV_{254}/TOC) X100
Conductivity (mS/cm)	53.61	Conductivity meter	COD_{Mn} (mg/L) (0.2~3)	0.93	UV detector
Salinity (PSU)	34.37	Salinity meter			
Turbidity (NTU)	0.99	Turbidity meter	B (mg/L)	4.375	ICP/MS (Heavy metal)
TSS (mg/L)	2.7	Standard method	Al (mg/L)	-	
TDS (mg/L)	35,160	Standard method	Si (mg/L)	0.137	
Ca^{2+} (mg/L)	411	IC (Cation)	Cr (mg/L)	-	
Na^{+} (mg/L)	11,031		Mn (mg/L)	-	
Mg^{2+} (mg/L)	1,400		Fe (mg/L)	0.013	
K^{+} (mg/L)	448		Ni (mg/L)	-	
F^{-} (mg/L)	-	IC (Anion)	Cu (mg/L)	-	
Cl^{-} (mg/L)	19,225		Zn (mg/L)	-	
SO_4^{2-} (mg/L)	2,680		As (mg/L)	0.002	
NH_4^{+} (mg/L) (0.03~1)	-	UV detector	Sr (mg/L)	7.131	
NO_3^{-}(mg/L) (0.1~2)	0.005		Cd (mg/L)	-	
Alkalinity (HCO_3^{-}, mg/L)	130	Titration method	Ba (mg/L)	0.004	
UV_{254} (/cm)	0.01	UV spectrometer	Total cell number (cells/mL)	5.1(±1.3) x 10^6	Culture-Independent
DOC (mg/L)	2.38 (± 0.15)	TOC analyzer	Coliform group (MPN/ml)	43.2	Colilert kit (Enzymatic)
TN (mg/L)	-	TN analyzer	Chlorophyll a (mg/m^3)	1.083	Dye Extraction

For RO test, experiment was carried out in Republic of Korea. The seawater used in this test was collected from Kijang, Busan, Republic of Korea. It was taken from 7 meters below sea level and filtered through the centrifuge filtration system to remove the large particles. The seawater characteristics are given in **Table 3.2**. The dissolved organic carbon (DOC) value of collected seawater was 2.38 ± 0.15 mg/L. The total number of bacterial cells in the untreated seawater was 5.1 ± 1.3 x 10^6 cells/mL. After sampling, it was kept refrigerated at 4.0°C before been utilized as feed water for the RO test unit.

The values of pH, turbidity (NTU), conductivity (mS/cm) and salinity (g/L) were measured by a pH meter (HANNA, HI902), a turbidity meter (HACH, 2100P) and a conductivity and salinity meter (WTW, LF330) respectively at room temperature (25 ±1.0°C). The analysis of total suspended solids (TSS) was carried out in the laboratory according to the Standard Methods procedure (APHA/AWWA/WEF, 1995).

3.1.2 Microfiltration (MF) membrane

The membrane used in this study was a hollow fibre microfiltration (MF). The hollow fibre MF (Cleanfil®-S, Polysulfone, Polyethersulfone, PVDF of 0.1 μm, Kolon membrane) was vertically submerged directly into a reactor. The U-type membrane length was 47.0 cm - 48.5 cm with an outer diameter of 2 mm. The combined surface area of the hollow fibre membrane was 0.044 m^2 - 0.1 m^2.

3.1.3 Coagulants

3.1.3.1 Ferric chloride ($FeCl_3$)

In the pretreatment of seawater, ferric salts, particularly $FeCl_3$, are recommended because their equilibrium solubility of Fe with amorphous ferric hydroxide in seawater is low over a wide range of pH and temperature conditions. Ferric chloride is very insoluble, leaving residual dissolved Fe in the water after pretreatment and it causes

only a minor scaling effect on the RO membrane. Buffer intensity is also relatively low and therefore it requires only a small addition of strong acids. For natural ranges of pH (7.5 to 8.0) and temperature (20 to 35 °C), there would be high fractions of positively charged Fe as $Fe(OH)^{2+}$ available for charge neutralization coagulation reaction. Some NOM can easily make a complexation with positively charged Fe and get absorbed to flocs.

3.1.3.2 Poly ferric silicate (PFSi)

PFSi was modified to improve coagulation performance in terms of organic removal, and coagulant dose and coagulated sludge reduction. The preparation of modified poly ferric silicate (PFSi-δ) consisted of three processes: (i) preparation of polysalicic acid (PSiA) (ii) preparation of poly ferric silicate (PFSi) and (iii) modification of PFSi (PFSi-δ).

Firstly, PSiA was prepared by acidification of sodium silicate (Na_2SiO_3) containing 26.6% SiO2. Diluted hydrochloric acid of 20% was poured slowly into Na_2SiO_3 solution while the mixture was stirred with a magnetic stirring apparatus at room temperature (25°C). In order to obtain good polymerisation of silicate, diluted hydrochloric acid was added until the pH decreased to 1.8.

To obtain PFSi, 3.1M solution of $FeCl_3$ was then mixed rapidly with the PSiA solution at 40-60°C. In this study, the ratio of Fe to Si was kept at 1. The PFSi was produced in a brown-yellow gel-type solution.

Finally, PFSi was modified to become PFSi-δ by diluting it with deionised water 40 times in order to decrease the iron content in the final solution.

3.1.3.3 Titanium tetrachloride ($TiCl_4$)

The application of Ti-salt flocculant in water treatment was first investigated by Upton and Buswell (1937). Since then it has led to more research into the treatment of seawater. The advantages of Ti-salt coagulation are: i) it is required at lower dosage; ii) it is active at low water temperatures; iii) it facilitates short sedimentation time; iv) it removes organic/inorganic materials more effectively; and v) it generates a valuable by-product.

3.1.4 Activated carbon

Powdered activated carbon (PAC, wood based, James Cumming & Sons Pty Ltd) was used as an adsorbent in a submerged membrane adsorption hybrid system. The characteristics of PAC are shown in **Table 3.3**.

Table 3.3 Characteristics of powdered activated carbon (PAC) used in this study.

Specifications	PAC-WB
Moisture content maximum (%)	5.0
Bulk density (kg/m^3)	290–390
Surface area (m^2/g)	882
Organic adsorption capacity (q_m, mg/g)*	23.1
Nominal size (μm) 80% min finer than	75
Mean pore diameter (Å)	30.61
Mean diameter (μm)	19.71
Product code	MD3545WB powder

*: Maximum organic adsorption capacity (q_m) estimated by the Sips isotherm model.

3.2 EXPERMENTAL METHODS

3.2.1 Membrane Hybrid System (MHS) as a Pre-treatment

Low pressure driven membrane processes, such as microfiltration (MF) and ultrafiltration (UF), are excellent techniques for eliminating or removing suspended solids so that colloidal particulate fouling is alleviated. Energy consumption in MF is relatively low. MF generally provides good quality feed water for RO compared to untreated seawater. Further improvements can be obtained by using UF where microorganisms, macromolecules and colloids can also be removed. Due to higher applied pressure UF is more expensive than MF, but still competitive with conventional pre-treatment. On the other hand the UF permeate used as RO feed significantly improved the RO performance. Recent studies proved that hybrid membrane processes (coupling coagulation/flocculation and/or adsorption and/or ion exchange resins with membranes) are efficient in simultaneously reducing membrane fouling and improving water quality (Chinu et al., 2010; Guo et al., 2008; Shon et al., 2009).

3.2.1.1 Submerged Membrane Coagulation Hybrid System (SMCHS)

The schematic diagram of the experimental set-up of SMCHS used in this study is shown in **Figure 3.1**. In-line coagulation with different doses of $FeCl_3$ and filtration experiments was carried out using hollow fibre MF (See **section 3.1.2**) in column type reactor. The effective volume of this reactor was 6 L and the aeration rate that was injected from the bottom of reactor was 1 L/min (1.36 m^3/m^2 membrane area · h) at a pre-determined flow rate. Permeate was pumped out using a peristaltic pump at constant flux. After each experiment, chemicals were used to clean the membrane, which was then placed into 0.2% NaOH and 0.2% NaOCl (total volume was 2 L) solution using a horizontal shaker at 60 rpm for 3 h. The data for the permeate flow rate was recorded

automatically. The trans-membrane pressure (TMP) was recorded using data logger every 5 min.

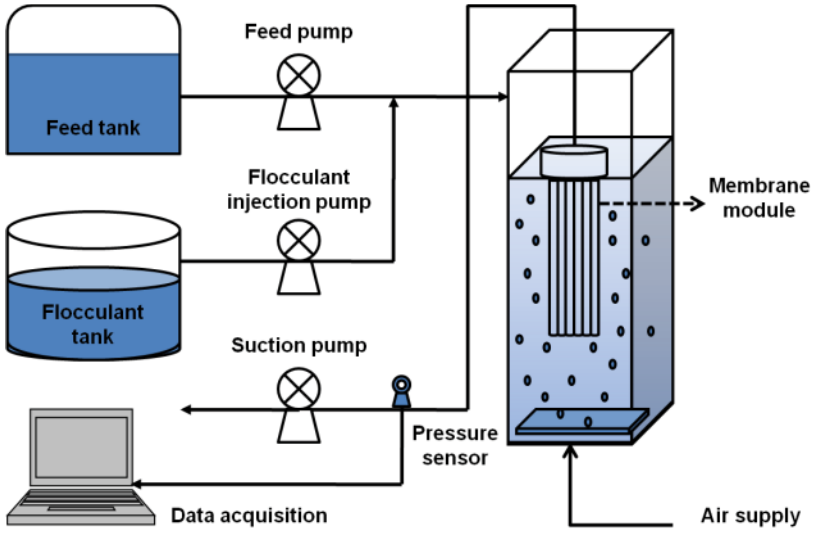


Figure 3.1 Schematic diagram of the submerged membrane coagulation hybrid system (SMCHS).

Continuous micro-filtration experiments were conducted without stoppage and cleaning. For TMP measurements in this study, the permeate flow velocity was kept approximately constant at 33.3 mL/min (corresponding to a constant flux of 20 L/m^2·h). The temperature was maintained at 25°C.

3.2.1.2 Submerged Membrane Adsorption Hybrid System (SMAHS)

The schematic diagram of the submerged membrane adsorption hybrid system is shown in **Figure 3.2**. The experiments were carried out using hollow fibre MF in column type reactor with and without adding PAC. The effective volume of square-column type reactor was 6 L and aeration rate was 1 L/min (1.36 m^3/m^2 membrane area · h). The membrane used in this study was hollow fibre microfiltration (MF, see **section 3.1.2**). Permeate was pumped out using a peristaltic pump at constant flux. The data of permeate flow rate was acquired to panel automatically to monitor trans-membrane

pressure (TMP) once every 5 min. A thorough cleaning of the unit at the beginning and the end of every experiment was conducted. Before every experiment, the MF reactor and MF membrane were disinfected and thoroughly cleaned to remove trace organic impurities by applying the following steps: (1) membrane was placed into 0.2% NaOH and 0.2% NaOCl solution using a horizontal shaker at 60 rpm for 3h; (2) rinsing the unit several times with DI water (heterotrophic count of the DI water was less than 10 bacterial cells per mL) to eliminate chemical residues, and (3) sterilizing MF membrane modules with DI by increasing flux (flux test).

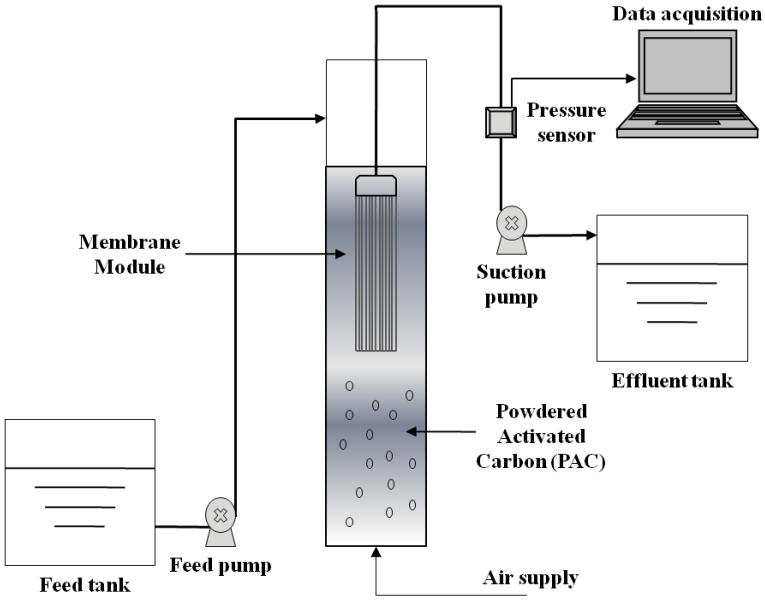


Figure 3.2 Schematic diagram of the submerged membrane adsorption hybrid system (SMAHS).

3.2.2 Reverse Osmosis (RO) test unit set-up

A flat sheet polyacrylamide RO membrane (Woongjin chemical, Republic of Korea) having an effective area of 140 cm^2 was used. It was soaked in de-ionized (DI) water at 4.0 °C for 24 hr prior to usage. The test set-up (part no. 1142819, GE Osmonics) consists of a spacer connected to a 10 L feed-tank with a feed-water volume capacity of 7 L. Fouling tests were conducted at a constant flux mode (at a pressure of 5.5 MPa and crossflow velocity of 1.2 L/min at 25°C). Both permeate and retentate were circulated back to the feed reservoir to enhance the bacterial growth during the short periods of conducted batch tests (**Figure 3.3**).

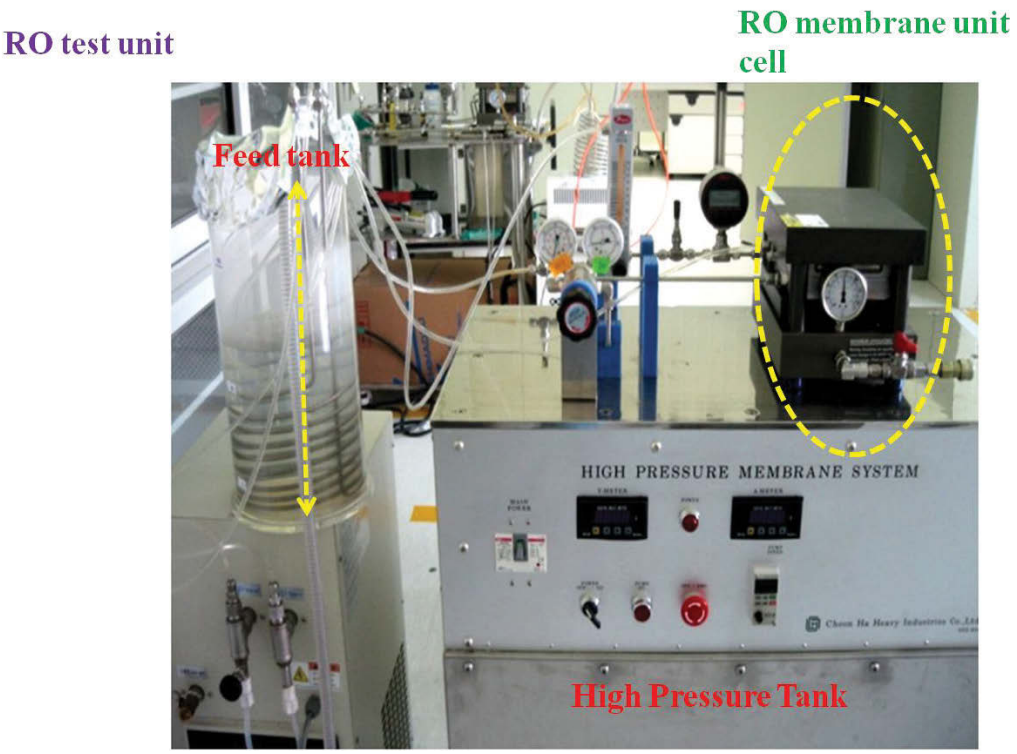


Figure 3.3 Experimental set-up of RO test unit.

The RO test unit (without membrane) was disinfected before each experiment. Before inserting the RO membrane, the RO unit was disinfected and thoroughly cleaned to remove trace organic impurities using the following procedure: (i) recirculation of 0.5% sodium hypochlorite for 2 h; (ii) cleaning trace organic matter by recirculation of 5 mM ethylenedi-aminetetra-acetic acid (EDTA) at pH 11 for 30 min; (iii) additional cleaning of trace organic matter by recirculation of 2 mM sodium dodecyl sulfate (SDS) at pH 11 for 30 min; (iv) sterilizing the unit by recirculation of 95% ethanol for 1 h; and (v) rinsing the unit several times with DI water to eliminate ethanol residues. The RO membrane then went through compaction with DI water at a pressure of 3.5 MPa after the sterilisation and cleaning phases (Herzberg and Elimelech, 2007). This membrane was not influenced by disinfection since it was not placed in the unit during the cleaning process. Furthermore the disinfection efficiency was tested in terms of the number of microbes after cleaning was completed. It indicated the acceptable range of bacterial number of less than 10^1cells/mL.

3.2.3 Modified Fouling Index (MFI)

The MFI was established by Schippers and Verdouw (1980) to evaluate the membrane fouling mechanism. The schematic diagram and figure of MFI experimental set-up is shown in **Figure 3.4**. MFI is determined at standard reference values of 207 ± 3 kPa, a feed water temperature of 20°C and ultrafilter (UF) with a 47 mm diameter and molecular cut-off of 17.5 kDa. The ultrafilter - modified fouling index (UF-MFI) can indicate whether coagulation was effective in reducing the membrane's fouling potential.

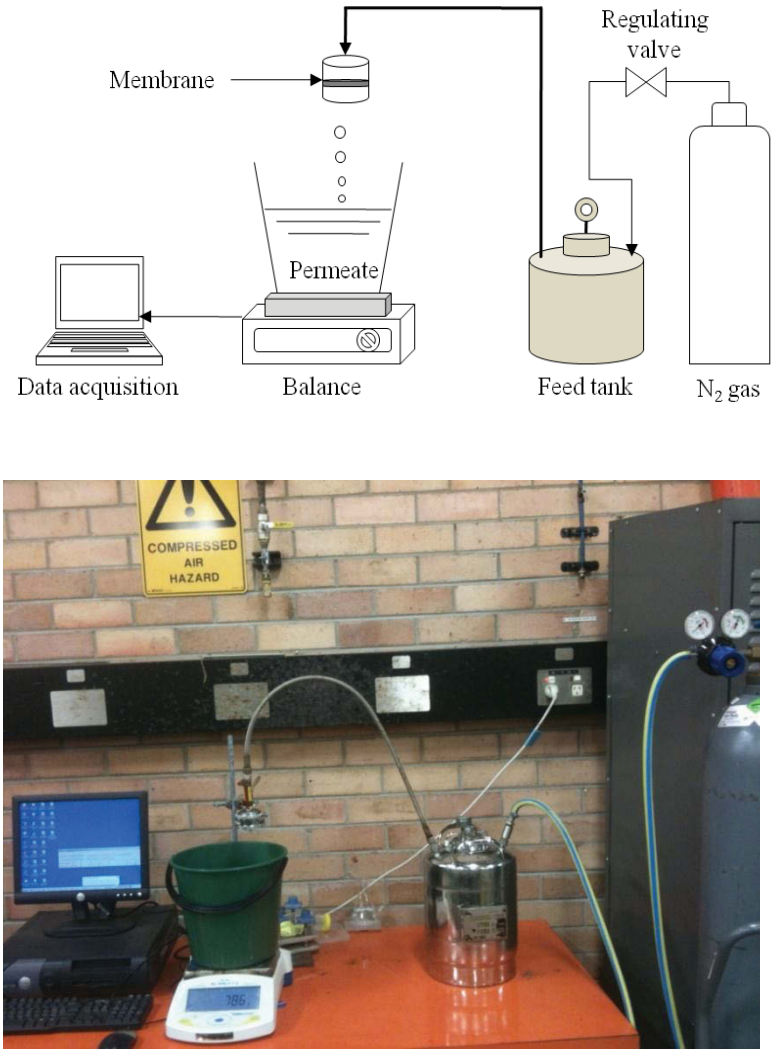


Figure 3.4 UF-MFI experimental set-up.

3.3 EXPERIMENTAL ANALYSES

Experimental analyses can be divided into seawater and foulant characterisation, and membrane autopsy. However, seawater and foulant characterisation methods were similar. The characterisation can be further classified into organic and biological features based on their origin. Detailed organic matter in seawater (seawater organic matter; SWOM) characterisation was done through the fractional and structural study after isolation from seawater. Summary of experimental analyses is given in **Table 3.5**.

3.3.1 Seawater (water samples) and Foulant characteristics

3.3.1.1 Organic characterization

3.3.1.1.1 Dissolved Organic Carbon (DOC)

Dissolved organic carbon (DOC) and detailed organic fractions were measured using DOC-LABOR Liquid Chromatography - Organic Carbon Detector (LC-OCD) (**Figure 3.5**). The LC-OCD system consists of a size exclusion chromatography column, which separates hydrophilic organic molecules according to their molecular size. The separated compounds were then detected using two different detectors: a UV detector (absorption at 254 nm) and a DOC detector (after inorganic carbon purging). Depending on the size of the molecules, the different fractions of the organic matter can be identified and quantified.

LC-OCD measurement was made at least in duplicate and their deviation was less than 5%. Thus mean value was reported in the thesis.

In this LC-OCD analysis, a Toyopearl TSK HW50S column (TOSOH Bioscience GmbH, Stuttgart, Germany) was utilized with phosphate buffer mobile phase of pH 6.4 (2.6 g/L KH_2PO_4 and 1.5 mol/L Na_2HPO_4) at a flow rate of 1.1 mL/min. Injection

volumes and retention time were 1,000 μL and 120 min, respectively. The chromatographic column was a weak cation exchange column based on polymethacrylate.

3.3.1.1.2 Detailed organic fractions

Organic matter was divided into two parts by LC-OCD. In LC-OCD system, hydrophobic organic carbon (HOC) was calculated from the difference of dissolved organic carbon (DOC) and chromatographic DOC (CDOC). All organic matter retained in the column was defined as hydrophobic. This could be either dissolved hydrocarbons or micro particulate including humics. CDOC is calculated from the area enclosed by the total chromatogram.

Figure 3.5 DOC-LABOR Liquid Chromatography-Organic Carbon Detector.

Natural organic matter (NOM) in seawater mainly contains biopolymers (BP), humic substances (HS or humics), building blocks (BB) and low molecular weight neutrals (LN).

BP has a very high molecular weight (20,000-100,000 g/mol) representing compounds such as polysaccharides amino sugars, polypeptides, proteins, "extracellular polymeric substances", hydrophilic fraction and not UV-absorbing. In surface water, BP exists as colloidal transparent exopolymeric particles (TEP) and polysaccharide. Humic substances (HS) represent compounds with molecular weights approximately 1000 g/mol. Building Blocks (BB) is defined as HS-hydrolysates, sub-units of HS with molecular weights between 300-450 g/mol. There are mainly weathering and oxidation products of HS. Low molecular weight neutrals (LMW Neutrals; LN) are the only low-molecular weight weakly charged hydrophilic or slightly hydrophobic "amphiphilic" compounds such as alcohols, aldehydes, ketones and amino acids.

3.3.1.1.3 Biopolymers (or EPS)

Determination of EPS compositions of raw seawater and pretreated seawater sample was performed in terms of biopolymer and transparent exopolymeric particles (TEP) using LC-OCD and spectrophotometric method (Villacorte et al., 2009). Protein concentration was measured by bicinchoninic acid (BCA) assay (Lee, 2010).

-Transparent Exopolymeric Particle (TEP) - *Estimation using LC-OCD*: Biopolymers are high molecular weight (>20,000 Da) biologically derived polymers that are present in surface waters. These organic substances often consist mostly of polysaccharides but may also contain significant amounts of proteins. The organic carbon concentration of protein in biopolymers can be estimated based on its organic nitrogen content. According to the ROEMPP chemical encyclopedia, protein compounds normally contain 15–18% nitrogen and 50–52% carbon (molar content basis). Assuming that all organic nitrogen in biopolymers originates from proteins, the C : N ratio of the latter can be estimated as 3 : 1. Polysaccharide concentrations (C_{PS}) were computed by

subtracting protein (C_{PR}) from biopolymers (C_{BP}) in terms of organic carbon concentrations by using the following equations:

$$C_{PS} = C_{BP} - C_{PR} \quad [mg\text{-}C/L] \tag{3.1}$$

$$C_{PR} = 3N_{BP} \quad [mg\text{-}C/L] \tag{3.2}$$

Where N_{BP} = organic nitrogen content of biopolymers (mg-N/L).

- ***Spectrophotometric method***: A volume of 5ml of water sample without colloids or reference solution was transferred to a 10ml volumetric flask. Then, 0.5 ml of 0.06% (m/v) alcian blue solution was added and the volume was made up with 0.2 mol/L acetate buffer solution (pH 4). The volumetric flask was stirred for 1 min. The resulting suspension was then centrifuged at 3000 rpm for 30 min and the absorbance of the supernatant (alcian blue solution in excess) was measured at 602 nm.

- Carbohydrate and Protein - *Carbohydrate* assay was done using modified phenol-sulphuric acid. *Protein assay*: BCA acts as the Folin reagent in the Lowry assay, namely to react with complexes between copper ions and peptide bonds to produce a purple end product. The advantage of BCA is that the reagent is fairly stable under alkaline conditions, and includes the copper solution to make a one-step procedure possible. A molybdenum/tungsten blue product is produced as with the Lowry method.

3.3.1.2 Assimilable Organic Carbon (AOC)

AOC assays typically measure growth of an inoculum in a water sample from which the natural bacterial community has first been removed and inactivated through sterilization. The inoculum grows until stationary phase ($\mu = 0$), with the principle that the growing bacteria have assimilated all the AOC in the water. The net growth of the bacteria is measured and then converted to an AOC (or AOC-equivalent) concentration.

A newly developed rapid bioluminescence AOC method is explained and discussed in **section 6.1**of **Chapter 6** in detail.

3.3.1.3 Microbial characterization

Heterotrophic plate count was done on marine agar to suit the seawater condition. *Plate count* was used to assess total direct cell count of raw seawater and samples after pretreatment. Serial dilutions of samples were prepared (using phosphate buffer solution). Marine agar plate is inoculated from the dilution (which has been thoroughly mixed), using a 0.1 mL inoculum. *Total direct cell counts* (TDC values) were performed to quantify the number of bacterial cells in the water samples. The TDC value was measured by using confocal laser scanning microscope (CLSM; Olympus FV1000) after staining the bacterial cells with 4'-6-diamidino-2-phenylindole (DAPI). As TDC does not distinguish active and not active cells so the number of *live and dead cells (cell viability)* in the samples was also measured. After staining samples with SYTO9 and propidium iodide (PI), fluorescent image was also captured by a CLSM system (Olympus FV1000). Quantitative analysis was conducted of fluorescent signal on captured image. *Microbial activity (active biomass)* was determined by measuring the adenosine triphosphate (ATP) concentration of microbes on foulants. ATP was measured using the Molecular Probes' ATP determination kit (A22066) and 96-well luminometer (Dynex Technologies) at room temperature within 15 min. Reagent preparation and analysis were according to the manufacturer's guidelines.

3.3.1.4 Quantitative analysis of SWOM

3.3.1.4.1 XAD fractionation

XAD fractionation was carried out by passing the seawater sample through XAD 8 and XAD 4 resins. Seawater samples were filtered through (Washed by MQ water) 0.45 μm

PVDF syringe filter (Millipore) and acidified with 2N hydrochloric acid to a pH of less than 2 before passing through the XAD resins. XAD-8 and XAD-4 resins were used for fractionating organic matter into hydrophobic (HPO) (XAD-8 absorbable; mostly hydrophobic acids with some hydrophobic neutrals) and transphilic (TPI) (XAD-4 absorbable; hydrophilic bases and neutrals) components. The final filtrate emanating from both XAD resins contained only hydrophilic (HPI) organic compounds. XAD resins (with adsorbed HPO and HPI) were washed using Milli-Q water flowing at a rate of 2.0 mL/min for 20 min and eluted by 0.1N sodium hydroxide (NaOH) at a lower flow rate (1.0 mL/min) for another 40 min. Dissolved organic carbon (DOC) concentration of the acquisition was measured using a carbon analyzer (TOC-V, Shimadzu Corp., Japan). The samples were filtered through a 0.45 μm PVDF syringe filter (Millipore) and acidified with 5.0 % H_3PO_4.

3.3.1.4.2 HP-SEC (High Pressure Size Exclusion Chromatography)

High pressure size exclusion chromatography (HP-SEC, Shimadzu Corp., Japan) with a SEC column (Protein-pak 125, Waters Milford, USA) was used to determine the MWD of organic matter. A UV detector was used at 254 nm. Standard solutions of different polystyrene sulfonates (PSS) with known MW (PSS: 210, 1,000, 4,600, 8,000 and 18,000 Da) were employed to calibrate the equipment. After filtering through a 0.45 μm filter, the samples' pH was adjusted with 0.1N hydrochloric acid to a pH of less than 7.0 before the measurement.

3.3.1.4.3 3D-FEEM (Three dimensional-fluorescence emission excitation matrix)

Three dimensional-fluorescence excitation emission matrix (3D-FEEM) fluorescences can distribute the fluorescent organic matter based on their properties by changing excitation and the emission wavelength simultaneously. The fluorescence signals are

basically attributed to protein-like fluorophores and humic-like fluorophores (Coble, 1996; Jiang et al., 2008).

Table 3.4 presents the representative fluorescent components of seawater organic matter. It can be seen that five characteristic peaks were observed in EEMs including two protein-like peaks B and T, and three humic-like peaks A, M, and C. Protein-like peaks (peaks B and T) represent materials containing tyrosine-like (4-hydroxyphenylalanine which is used by cells to synthesize proteins) and tryptophan-like. These are probably the metabolic products (biopolymers) from bacterial and phytoplankton activities. Peaks A and M are indicative of humic-like compounds (mainly humic and fulvic acids) which are the main components leading to bioactivity.

Table 3.4 Major fluorescent components of seawater organic matter.

Peak designation	Ex_{max} (nm)	Em_{max} (nm)	Chemical functionality
B	270-280	300-310	Tyrosine-like, Protein-like
T	270-280	320-350	Tryptophan-like, Protein-like
A	250-260	380-480	UV-humic-like
M	290-320	380-420	Visible marine humic-like
C	330-350	420-480	Visible humic like

Prior to optical analysis, the seawater samples were first allowed to warm to room temperature after filtration through a 0.45μm membrane filter. Organic matter in seawater fluorescence measurements were carried out using a Hitachi F-2500 spectrofluorometer. EEMs were recorded by scanning emission wavelengths from 250

to 600 nm repeatedly at excitation wavelengths scanned from 220 to 450 nm. The excitation and emission bandwidths were both set at 5 nm. The fluorometer was set at a speed of 3000 nm/min, a PMT voltage of 700 V and a response time of 2 s. Instrumental biases were corrected using the excitation spectra of 8 g/L Rhodamine B solution (in ethylene glycol) and emission spectra of a ground quartz diffuser (as recommended by the manufacturer). No changes in the lamp intensity during the measurement showed with comparison of the integrated Raman spectra of Milli-Q water over excitation wavelengths (Ex=350 nm). The fluorescence spectra were Raman calibrated by normalizing to the area under the Raman scatter peak (Ex=350 nm) of a Milli-Q water. Finally, a Raman normalized Milli-Q EEMs was subtracted from the data to remove the Raman scattering.

3.3.1.5 Structural analysis of SWOM

3.3.1.5.1 Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy

Proton nuclear magnetic resonance (^{1}H-NMR) was employed for the structural characterization of seawater organic matter. Isolated SWOM sample was freeze-dried at -40°C. ^{1}H-NMR were collected on JNM-LA300WB FT-NMR (300 MHz) (JEOL, Japan) spectrometer at a temperature of 25°C. All solidified SWOM samples were dissolved in dimethyl sulfoxide-d_6 (DMSO-d_6) solvent (4.5 to 7.0 mg/ml equate to 3.2 to 4.9mg) for one dimension liquid NMR measurements. To calculate chemical shifts, tetramethylsilane was used as a reference.

3.3.1.5.2 LCMS-IT-TOF (Liquid-chromatography-mass spectroscopy-ion trap-time of flight)

Liquid-chromatography-mass spectroscopy-ion trap-time of flight (LCMS-IT-TOF) was used for elemental analysis in seawater organic matter. The LCMS system used in this

study consisted of an LC-20AD (Gemini 5 μm C18; 50 mm Length. × 2.0 mm I.D.). Prominence liquid chromatography (Shimadzu Corp., Japan) which is connected to a hybrid mass spectrometer liquid chromatography mass spectroscopy-ion trap-time of flight (LCMS-IT-TOF) equipped with an electro-spray ionization source (Shimadzu Corp., Japan). This system was equipped with a vacuum degasser (DGU-20A3), binary pumps (LC-20AD), auto-sampler (SIL-20A), column oven (CTO- 20A), UV/VIS detector (SPD-20A) and a communications bus module. Instrument control, data acquisition and processing were accomplished using Shimadzu LCMS solution version 3.41 for the LCMS-IT-TOF system. The mobile phase system consisted of HPLC grade methanol (solvent A) and HPLC grade water (solvent B). Both solvents were injected into the MS detector at a flow rate of 0.20 mL/min. The IT-TOF mass spectrometer was operated using an electro-spray ionization (ESI) nano interface in positive mode as follows: probe voltage of +4.5 kV, both the curved de-solvation line (CDL) temperature and the block heater temperature of 200°C, CDL voltage of +25 V, drying gas pressure of 200 kPa, and nebulising gas flow of 1.5 L/min. Sample injection volume was 5 μm and acquisition m/z ranged from 100 to 2,000 Dalton.

3.3.1.5.3 Pyrolysis-GC/MS (Pyrolysis-Gas chromatography mass spectrometry)

Pyrolysis-Gas chromatography mass spectrometry (Pyrolysis-GC/MS) was applied to study the precursor of seawater organic matter in the solute state. The Curie point Pyrolysis-GC/MS system consisted of the 7890A GC system (Agilent Technology, USA) and 5975C inert MSD with triple-Axis detector (Agilent Technology, USA). DB-5MS was used as column in GC/MS. Lyophilic powders (0.1 to 0.5 mg) of seawater and pretreated seawater were pyrolysed at 590°C (heating rate of °C per 0.16 sec, hold time of 5 sec and purging gas of He) using portable pyrolyzer (JCI-22, Japan Analytical Industry Inc., Japan).

3.3.2 Foulant characterization

The foulants on the RO membrane were extracted using mild sonication for a short time to prevent organic matter from denaturing and biological modification. Prior to each experiment starting, the cleaned membrane was tested using DI water and it indicated nearly the same pure water permeability as that of virgin membrane. This ensures that this method extracted the majority of foulants. This extraction method has also been used in recent studies (Nghiem and Schäfer, 2006; Lee and Kim, 2011).

The relationship between organic and bio foulant on membrane and organic matter remaining in the effluent after SMHSs was investigated. Seawater organic matter (SWOM) has been regarded as an important RO foulant. Organic foulant (as a nutrition source) could also be assimilated by microorganisms. This resulted in enhanced membrane biofouling (Khan et al., 2010). Specific biofoulants were characterized. The fouled membrane surface and its layer structure, which may be crucial to the formulation of pertinent fouling control strategies, were also examined.

3.3.2.1 Organic foulant

Dissolved organic carbon (DOC) concentration of the extracted foulant was measured using a carbon analyzer (TOC-V, Shimadzu Corp., Japan). The samples were filtered through 0.45 μm PVDF syringe filter (Millipore) and acidified with 5% H_3PO_4 prior to DOC measurement. The MWD of extracted foulant was measured using high pressure size exclusion chromatography (HP-SEC, Shimadzu Corp., Japan) with a SEC column (Protein-pak 125, Waters Milford, USA). This equipment was calibrated using polystyrene sulfonates (PSS: 210, 1,800, 4,600, 8,000 and 18,000 Da) MW standards.

Fluorescence excitation–emission matrix (F-EEM) was measured using fluorescence spectroscopy (Hitachi F-2500 spectrofluorometer). The procedure is presented in

section 3.1.4.3. The fluorescence of organic compounds such as humic and protein-like materials was characterized, and furthermore these materials may be associated with biological activity in seawater (Liu et al., 2011). Their spectral regionalization was done by varying the excitation and emission wavelength simultaneously. EPS compositions were measured using modified carbohydrates assay (see **section 3.1.1.3**) while EPS protein concentration was measured using a Micro BCA protein kit (Cat no. 23235; Thermo Scientific Pierce, USA), with EPS extract prepared from foulants' extract.

3.3.2.2 Biological foulant

In this study we tested the hypothesis that initial organic foulants' adhesion could have accelerated the bacterial accumulation on RO membrane surface and eventually on the formation of biological (or bio) fouling, even though the RO was run only for a short time. Microbial counts on membrane were measured in terms of total direct cell count (TDC value) and cell viability. For the TDC, bacterial cells were stained with 4'-6-diamidino-2-phenylindole (DAPI). The TDC was measured using a confocal laser scanning microscope (CLSM; LSM5, Zeiss, Germany) after filtering the sample through a 0.2 μm-pore size black polycarbonate membrane. To determine the cell viability, a LIVE/DEAD BacLight staining kit was used to enumerate the proportion of live and dead cells in the samples. A staining procedure was performed with two different dyes of SYTO9 for live and dead cella and propidium iodide (PI) for dead cella. CLSM was used to capture the fluorescent image and signals on the captured image were quantified using image analyzer software (isolution/Lite, *i*MTechnology, Republic of Korea).

3.3.3 RO membrane autopsy

After RO operation, fouled membranes were washed with milli-Q water several times and dried in a conical tube by refrigerating them at 4.0°C.

Field Emission Scanning Electron Microscope (FE-SEM S-4700, Hitachi Corp. Japan) was used to investigate the clean and fouled membrane morphology and to observe the membrane fouling. The voltage used was 10 kV and the working distance was 13.3 mm. The magnification was 20k times. Only top views of the membrane were made in this study. SEM images were investigated by coupling with energy dispersive spectroscopy (EDX) to discover whether there is any chemical precipitation on the membrane surface.

The virgin (clean) and fouled RO membrane surfaces were analyzed for functional groups using attenuated total reflection - fourier transform infrared spectroscopy (ATR-FTIR). Spectrum of each foulant was collected between 4000 $cm^{-1}$and 400 cm^{-1} wavelength ranges by FTIR (660-IR, Varian, Australia) equipped with an ATR accessory. In order to estimate the index of hydrophobicity of membrane surface, the contact angle of membrane surface was measured by sessile drop method using a goniometer (model 100, Ramé-Hart, Montrian Lakes, USA). The images were captured and interpreted by DROP Image Advanced software. A volume of 2 μL of milli-Q water was dropped onto the dried membrane surface. Measurements were repeated 10 times to calculate the average contact angle and standard deviations.

Membrane surface charge was monitored using the electrophoretic light scattering system (ELS-8000, Otsuka Electronics Co. Ltd, Japan). Flat-type board cell was used to measure the zeta potential of membrane surface. 10mM KCl solution was used as the solution for mobility of standard monitoring particle provided by the manufacturer. The

measurements were performed under the identical pH and temperature and repeated 5 times for each membrane sample.

Membrane surface morphology and roughness was monitored using atomic force microscopy (AFM) (XE-100, Park System, Republic of Korea). AFM was operated under the non-contact mode with PPP-NCHR 5M cantilever (Park System, Republic of Korea). Five scanning points for each membrane sample were randomly selected and the measured images were processed using XEI software.

Table 3.5 Summary of experimental analyses used in this study.

Clarification		Objective	Method	Notes
Seawater and foulant characteristics	Organic	DOC	LC-OCD	Quantification of organic in the seawater, pretreated seawater
		Detailed organic fraction	LC-OCD	Detailed fractionation of organic content
		Fractionation of organic	XAD resin	XAD-8 and XAD-4 resins; to obtain HP DOC (XAD-8 isolate), TP DOC (XAD-4 isolate), and HL DOC (effluent from XAD-8 followed by XAD-4)
		Modified fouling index (MFI)	MFI filtration test	Colloidal and organic fouling potential using MF, UF and NF
		Biopolymers	CH and PN	Colorimetric method and LC-OCD
			TEP	LC-OCD estimation and Alcian blue method
		Molecular weight distribution (MWD)	HP-SEC	A chromatographic method in which molecules in solution are separated by their size
		Fluorescence characteristics	3D-FEEM	Semi-quantifications of protein-like, fulvic-like and humic-like organic matters
		Structural study	NMR, py-GC/MS and LC/MS-IT/TOF	After isolation of organic matter in seawater

	Biological	Bacterial regrowth or biofouling potential	AOC	Bioluminescence method using *Vibrio fischeri*
		Total cell number	HPC and TDC	Plate count and CLSM using DAPI
		Cell viability	Live/Dead cell	CLSM using PI and SYTO dye
		Active biomass	ATP	ATP assay kit and Luminescence spectrophotometer
Membrane Autopsy		Membrane structure and chemical composition	FE-SEM with EDX	
		Membrane surface morphology and roughness	AFM	
		Functional groups	ATR-FTIR	
		Electrostatic interaction	Zeta potential	
		Hydrophobicity	Contact angle	

CHAPTER 4

University of Technology Sydney

Faculty of Engineering& Information Technology

EFFECT OF COAGULATION AND ADSORPTION AS PRETREATMENT

This chapter presents physico-chemical pretreatment methods such as coagulation and adsorption in five sub-chapters (**Sections 4.1** to **4.5**).

The first part of this chapter introduces the typically used coagulant, ferric chloride ($FeCl_3$) in submerged membrane coagulation hybrid system (**Section 4.1**). This is followed by a quantitative prediction of DOC removal by $FeCl_3$ coagulation using a conceptual mathematical model (**Section 4.2**). The third part investigates the effect of flocculation on the performance of MF in submerged membrane coagulation hybrid system (SMCHS) using modified poly ferric silicate (PFSi-δ) (**Section 4.3**). The fourth part compares titanium tetrachloride ($TiCl_4$) as flocculant with $FeCl_3$ in the removal of organic matter in seawater **(Section 4.4).** The last part highlights the effect of powder activated carbon (PAC) in a submerged membrane adsorption hybrid system (SMAHS) in removing organic matter from seawater (**Section 4.5**).

<Publications related to this chapter>

– Jeong, S., T.V. Nguyen, S. Vigneswaran. (2011) Submerged membrane coagulation hybrid system as pretreatment to organic matter removal from seawater. Water Science and Technology: Water Supply 11(3): 352-357.

– Jeong, S., A. Sathasivan, G. Kastl, W.G. Shim, S. Vigneswaran. (2013) Dissolved organic carbon removal from seawater by $FeCl_3$ coagulation: Experiment and modeling (*In preparation*).

– Jeong, S., F. Nateghi, T.V. Nguyen, S. Vigneswaran, T.A. Tu. (2011) Pretreatment for seawater desalination by flocculation: Performance of modified poly ferric silicate (PFSi-δ) and ferric chloride as flocculants. Desalination 283: 106–110.

– Jeong, S., Y. Okour, T.V. Nguyen, H.K. Shon, S. Vigneswaran. (2012) Ti-salt flocculation for dissolved organic matter removal in seawater. Desalination and Water Treatment (DOI: 10.1080/19443994.2012.672179).

4.1 FERRIC CHLORIDE ($FeCl_3$) COAGULATION

4.1.1 INTRODUCTION

Pretreatment of feed water is an effective and necessary method for reducing membrane fouling. To ensure the expected quality of feed water to the RO process, more researchers are currently considering the use of membrane-based pretreatment coupled with conventional pretreatment which includes coagulation/flocculation (Ma et al., 2007; Choi et al., 2009; Shon et al., 2009).

Coagulation is a pretreatment method that can improve the permeate flux of membrane while removing particles and colloids. Coagulation can achieve three objectives: (a) eliminate the penetration of colloidal particles into the low pressure MF/UF membrane pores used as pretreatment, (b) increase the critical flux, and (c) modify the characteristics of deposit (Visvanathan and Ben Aim 1989).

Previous coagulation studies have shown the importance and the superiority of $FeCl_3$ due to the trivalent ferric ions (Fe^{+3}). Fe^{+3} readily undergoes hydrolysis, complexation/polymerisation and precipitation in aqueous solution (Visvanathan and Ben Aim 1989; Chapman et al., 2002). Brehant et al. (2002) showed that an in-line injection of 1 mg/L of $FeCl_3$ with UF could help in controlling fouling by reducing the silt density index (SDI_5) of surface seawater from 13-25 to below 1.

In this study, a commonly used ferric chloride was used as a coagulant for removing organic compounds from seawater. SMCHS was also experimentally investigated as pretreatment for RO.

4.1.2 MATERIALS AND METHODS

4.1.2.1 Determination of optimum dose

$FeCl_3$ was used as a coagulant and its optimum dose was determined by employing standard jar tests. The seawater (see the **Table 3.1**) was placed in 1 L beakers and predetermined amounts of coagulant were added. The samples were then stirred rapidly for 2 min at 120 rpm, followed by 20 min of slow mixing at 30 rpm, and 30 min of settling. The supernatant was taken and analysed for DOC to determine the effects of the coagulant in the removal of organic matter.

4.1.2.2 Submerged membrane coagulation hybrid system (SMCHS)

The schematic diagram of the submerged membrane coagulation hybrid system experiments used in this study is presented in **Figure 3.1**. In-line flocculation and MF experiments were carried out using hollow fibre MF (see **section 3.1.2**) in a column-type reactor. The effective volume of the reactor was 6 L, the total membrane area was 0.1 m^2 and air was injected from the bottom of reactor at a predetermined aeration rate of 1 L/min (1.36 m^3/m^2 membrane area·h). Permeate was pumped out using a peristaltic pump at constant flux. After each experiment, the membrane was cleaned by placing the membrane into a 0.2% NaOH and 0.2% NaOCl solution and shaking the content using a horizontal shaker at 60 rpm for 3 h.

4.1.3 RESULTS AND DISCUSSION

4.1.3.1 Jar test experiments

Table 4.1 presents the variation of turbidity and pH as a function of coagulant concentration. pH of seawater after coagulation slightly decreased when the dose of $FeCl_3$ increased to 4.0 mg/L. Surprisingly, the turbidity of seawater increased after coagulation and this phenomenon was similar to the one observed by Chinu et al. (2010). The jar test experiment also shows that there was no floc if the concentration of coagulant was below 1.0 mg/L (in terms of Fe^{+3}).

The addition of ferric chloride may generate ferric hydroxide and ferric oxide which caused an increase of turbidity after coagulation. The increase of turbidity was noted for all $FeCl_3$ doses (**Table 4.1**). Thus, an optimum dose of $FeCl_3$ cannot be determined in terms of turbidity.

Table 4.1 The turbidity and the pH after coagulation.

	Raw seawater	Fe^{+3} (mg/L)				
		0.5	1.0	2.0	3.0	4.0
pH	7.98	7.53	7.41	7.25	7.22	7.16
Turbidity (NTU)	0.41	1.26	1.83	1.33	1.43	1.65

The analyses of organic fractions of seawater by LC-OCD showed that the DOC of seawater used in this study was 1.29 mg/L in which 33% of total DOC was hydrophobic.

The humic substances with molecular weight about 1,000 Da account for more than half of hydrophilic part (51% of hydrophilic). The percentage of bio-polymers (MW > 20,000 Da), building block (MW >> 300-500 Da), and low molecular weight of neutrals (MW < 350 Da) were 15, 23, and 11%, respectively.

Table 4.2 The changes of turbidity, pH, DOC fractions and removal efficiencies of seawater by coagulation with $FeCl_3$.

	Seawater		$FeCl_3$									
as Fe^{3+} (mg/L)	0		0.5		1.0		2.0		3.0		4.0	
Turbidity	0.41		1.26		1.83		1.33		1.43		1.65	
pH Initial	7.98		-		-		-		-		-	
Final	-		7.53		7.41		7.25		7.22		7.16	
	mg/L	%[a]	mg/L	%[b]	mg/L	%[b]	mg/L	%[b]	mg/L	%[b]	mg/L	%[b]
DOC	1.29	100	0.65	50	0.66	49	0.69	47	0.56	57	0.69	47
Hydrophobic	0.43	33	0.03	93	0.01	98	0.11	74	0.02	95	0.16	63
Hydrophilic	0.86	67	0.62	28	0.65	24	0.58	33	0.54	37	0.53	38
Biopolymer	0.13	10	0.08	38	0.07	46	0.06	54	0.05	69	0.04	69
Humic	0.44	34	0.37	16	0.39	11	0.37	16	0.36	18	0.34	23
Building blocks	0.20	16	0.17	15	0.15	20	0.13	30	0.14	30	0.13	30
Neutrals	0.09	7	0.00	100	0.03	67	0.01	89	0.00	100	0.01	89

[a] Composition of the different organic fractions in seawater.

[b] Removal efficiencies of the different organic fractions in seawater after flocculation.

Table 4.2 presents the variation of DOC removal efficiency as a function of concentrations of Fe^{+3}. It can be seen that the more than 57% of DOC was removed at the optimum dosage of 3.0 mg Fe^{3+}/L. At lower doses, the DOC removal efficiencies were below 50%. With an increase of Fe^{3+} concentration to 4.0 mg/L, the DOC removal efficiency decreased further. This may be due to the restabilisation of the colloidal particles.

Detailed analyses of organic fractions after coagulation show that coagulation by $FeCl_3$ could remove a majority of hydrophobic fraction. However coagulation was not effective in removing hydrophilic, except neutrals part with molecular weight below 350 Da and bio-polymer with large molecular weight (MW more than 20,000 Da) (**Table 4.2**). This trend was similar to results reported by Shon et al. (2005).

The reduction of the fouling potential of seawater before and after coagulation was also studied using modified fouling index with ultrafilter membrane of 17.5 kDa (UF-MFI). The results showed that the coagulation led to significant decrease of UF-MFI (**Table 4.3**). The UF-MFI reduced about five times from 15,848 s/L^2 to less than 3,209 s/L^2 at all of the studied doses.

Table 4.3 The ultrafilter-modified fouling index (UF-MFI) of seawater before and after coagulation with different $FeCl_3$ doses.

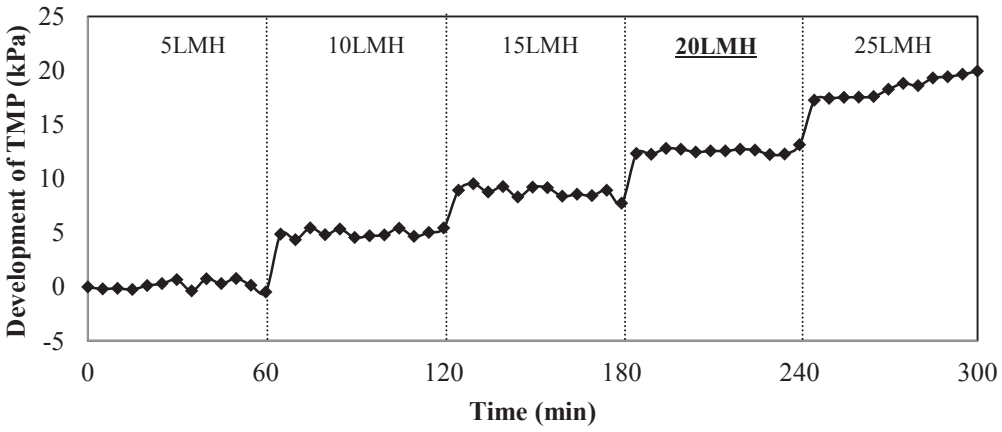
	Raw seawater	Fe^{3+} (mg/L)			
		1.0	2.0	3.0	4.0
UF-MFI (s/L^2)	15,848	3,209	2,238	3,025	2,771

4.1.3.2 Submerged membrane coagulation hybrid system (SMCHS)

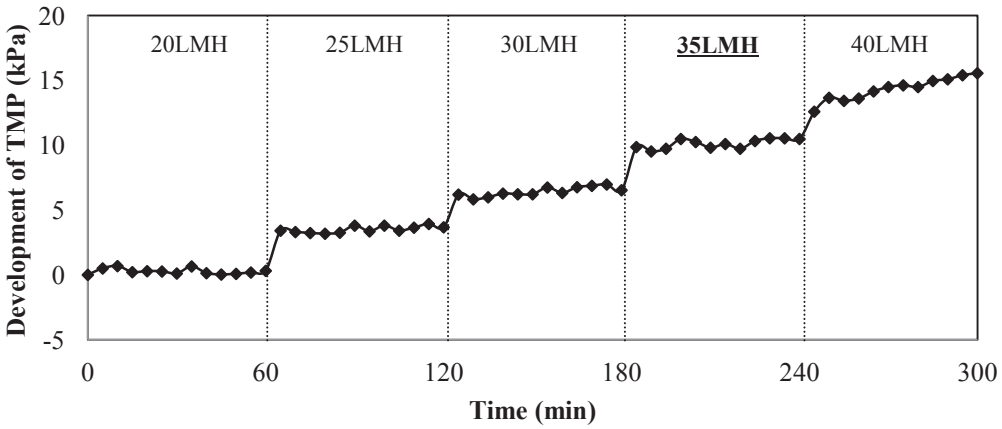
4.1.3.2.1 Critical flux

In this experiment, critical flux was measured quantitatively using a 'flux stepping' method. The membrane reactor was operated at a fixed flux for around 60 min and the TMP was monitored simultaneously. The flux was then increased and operated at a constant flux for another 60 min and so on. As the flux was increased gradually, the critical flux condition was detected where TMP no longer remained steady but increased with time. The maximum flux which showed no increase in TMP was taken as the critical flux. The critical flux of micro-filtration system with seawater (without any coagulation) was only 20 $L/m^2 \cdot h$ (**Figure 4.1(a)**).

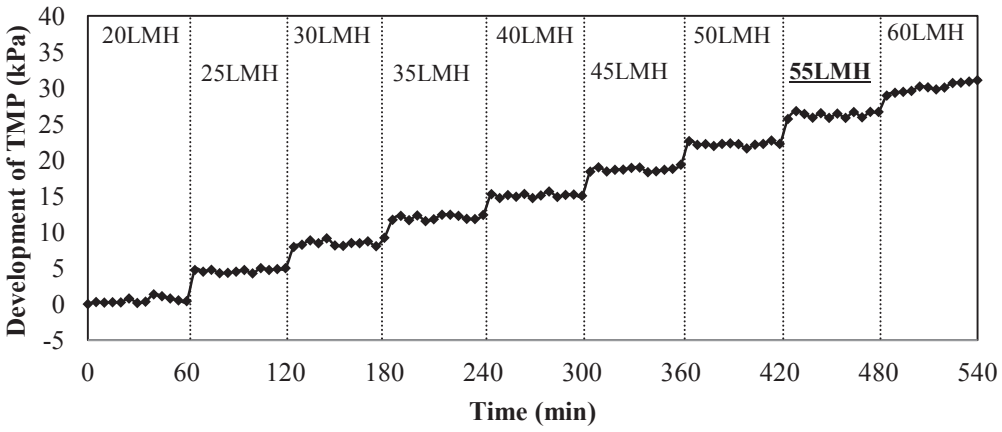
The submerged membrane coagulation system led to increase of critical flux and the increase of critical flux was related with the increase of coagulation doses (**Figure 4.1(b, c)**). The critical flux increased to 35 and 55 $L/m^2 \cdot h$ when 0.5 mg/L and 3.0 mg/L of Fe^{+3} were used as coagulant.



(a) Fe^{+3} doses: 0 mg/L (Without coagulant)



(b) Fe^{+3} doses: 0.5mg/L



(c) Fe^{+3} doses: 3.0mg/L

Figure 4.1 Variation of TMP values (LMH=L/m^2·h).

4.1.3.2.2 Organic removal

It was observed that by SMCHS, more than 57% of hydrophilic compounds could be removed (**Table 4.4**). This value was about 20% higher than that of coagulation alone. As a result, the DOC removal of submerged membrane coagulation system was also higher than that of coagulation alone. On the other hand, when seawater was filtrated by MF alone, DOC removal efficiency was only 18%. The capacity of removal efficiency of hydrophilic compounds could improve nearly 10 times when in-line coagulation was coupled with MF (**Table 4.4**).

Table 4.4 Fraction of organic matter after SMCHS for 24 h (filtration flux 20 $L/m^2.h$, Fe^{+3} doses: 3.0 mg/L).

Feed water	DOC (%)	Hydro-phobic (%)	Hydro-philic (%)	Bio-polymer (%)	Humic (%)	Building blocks (%)	Neutrals (%)
Seawater by MF alone	18	32	6	54	-	16	44
After 2h	70	95	57	62	55	40	100
After 24h	71	95	58	85	66	20	67

The results for both the jar test and in-line coagulation also showed that the removal efficiency of hydrophobic compounds was much higher than that of hydrophilic compounds (**Tables 4.2 and 4.4**). In this study, the hydrophobic compounds of experimental seawater only accounted for a third of NOM. Therefore, for seawater containing more hydrophobic NOM, more DOC removal can be achieved through the coagulation process.

4.1.3.2.3 Trans-membrane pressure (TMP)

The variations of TMP of a conventional membrane system and submerged membrane coagulation system with pre-selected two doses (0.5 mg Fe^{+3}/L and 3.0 mg Fe^{+3}/L) with seawater are presented in **Figure 4.2**.

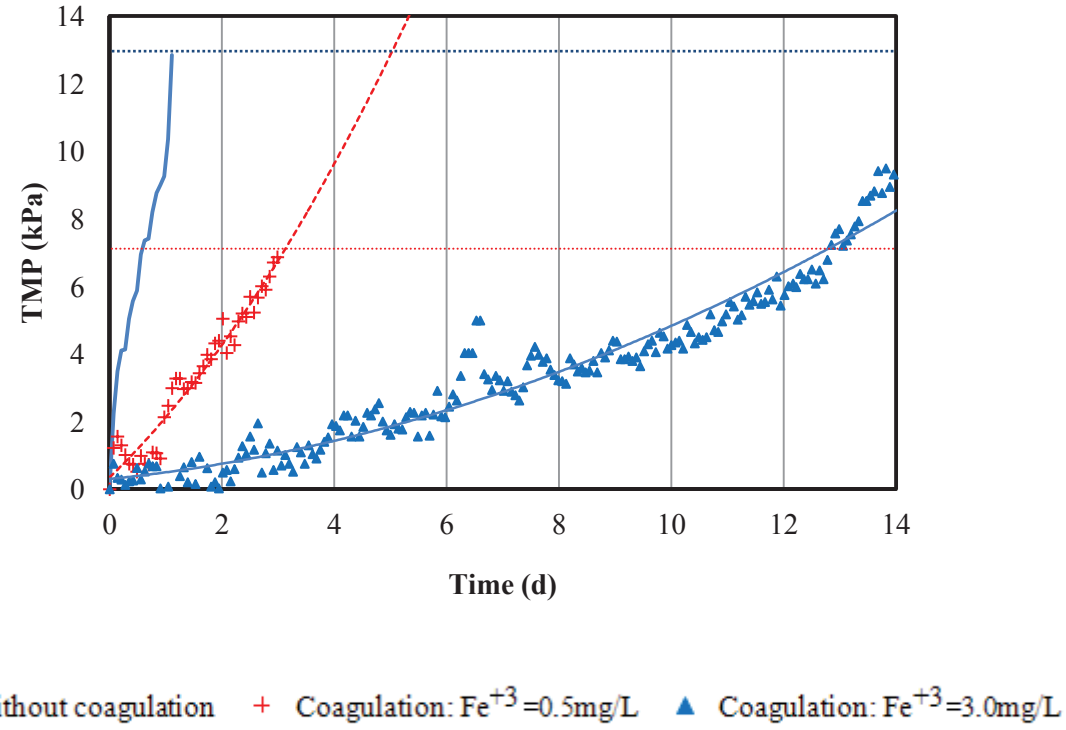


Figure 4.2 The development of TMPs of a submerged membrane coagulation system with and without in-line coagulation (filtration flux =20 L/m^2·h).

As can be seen from **Figure 4.2**, the TMP of a conventional submerged membrane system increased rapidly and reached more than 10 kPa during the first day of operation. The submerged membrane coagulation system helped reduce the increase of TMP and at Fe^{+3} dose of 3.0 mg/L, the development of TMP after 14 days of operation was still lower than that of the conventional submerged membrane system after the first day of operation. $FeCl_3$ accumulated into the reactor during 14 days did not influence the membrane fouling. However, longer operation may lead to additional fouling due to coagulated ferric oxide flocs. This shows that in-line coagulation helped reduce membrane fouling significantly.

4.1.4 SUMMARIZING THE $FeCl_3$ COAGULATION

The results from this study showed that ferric chloride could remove 57% of DOC from seawater collected at Chowder Bay, Sydney, Australia. The removal efficiency of hydrophobic compounds by coagulation was much higher than that of hydrophilic compounds. 95% of hydrophobic compounds and 37% of hydrophilic compounds could be removed at Fe^{+3} dose of 3.0 mg/L. The coagulation also could reduce five times of UF-MFI in batch mode as well as increase three times of the critical flux of submerged membrane system when it was coupled with in-line coagulation. The in-line coagulation coupled with submerged membrane system was found to remove DOC effectively with more than 70% DOC removal.

4.2 FERRIC CHRORIDE ($FeCl_3$) COAGULATION MODELING

4.2.1 INTRODUCTION

The concentrations and types of natural organic matter (NOM) in seawater vary with time and location. Dissolved organic carbon (DOC) is a collective (surrogate) parameter expressed in mg of all carbon in organic molecules in unit volume and it is most widely used to represent the concentration of NOM (Emelko et al., 2011). The DOC of seawater is typically 1-3 mg/L. This dissolved organic matter from algae and humic substances in NOM causes severe fouling of reverse osmosis (RO) membranes by organic adsorption or biofilm growth (Shon et al., 2009). Therefore pretreatment for removal of NOM is essential in seawater RO plant. Coagulation/flocculation is one of the available chemical pretreatment options for removal of colloidal particles and for NOM control (Duan et al., 2002). NOM molecules are complex mixtures of aromatic and aliphatic molecules with organic acid groups, the majority of which are negatively charged at neutral pH. This negative charge and hydrophobic character of NOM can be removed by coagulation and separation of precipitated solids. Metal coagulants such as Al and Fe are used commonly in water treatment at different dose and appropriate pH condition to precipitate as Al- or Fe-hydroxides (Edzwald and Haarhoff, 2011).

The mathematical model enables the selection of an optimal coagulation conditions (i.e. coagulant dose and coagulation pH) through a limited number of experiments. The prediction of the residual DOC will be beneficial for optimization of the treatment process, once the impact of various fractions on the membrane fouling is known. Furthermore, applicable conceptually valid models would provide further understanding of the process and would aid better control (Kastl et al., 2004).

Several empirical and semi-empirical models have been proposed and have been used in prediction of DOC removal during coagulation (Harrington et al., 1992; Moomaw 1992;

Edwards, 1997; van Leeuwen et al., 2005). Tseng and Edwards (1999) showed that the accurate predictions of final DOC by enhanced coagulation was possible using the model developed by Edwards (1997). Kastl et al. (2004) was improved the previous model by Edwards (1997) by conceptually separating the DOC into three fractions: *Non-sorbable* fraction – hydrophilic compounds which cannot be removed at any pH by a given coagulant; *Non-polar* fraction – compounds that can be removed at any pH as it possess neutral charge irrespective of pH; and *Humic acid* fraction – compounds that is capable of dissociating like a weak acid and is assumed that only the neutral form can be removed by adsorption. Similar to Edwards (1997), Kastl et al. (2004) assumed that the removal follows Langmuir adsorption theory. They successfully validated their model against 17 different water sources in Australia and United States (US). Aryal et al. (2011) applied the model of Kastl et al. (2004) to quantitatively prove that biologically activated carbon enhances the removal of DOC by converting non-sorbable organic fraction into sorbable organic fractions.

To date, however, little works have been reported on the DOC removal or its modeling by coagulation in seawater or saline water. The general factors that influence the DOC removal in seawater following coagulation are now well understood and studied, but quantitative formulation and model have been hindered due to complex interplay of seawater organic matter. The salinity and ion product (on the seawater chemistry of significant parameters) can also be affected by chemical hydrolysis and metal-hydroxide solubility reactions during coagulation (Edzwald and Haarhoff, 2011). Thus, seawater could show a different coagulation performance from freshwater. In the pretreatment of seawater, ferric salts, particularly $FeCl_3$, are recommended because the equilibrium solubility of Fe with amorphous ferric hydroxide in seawater is low over a wide range of pH and temperature conditions. $Fe(OH)_3$ is highly insoluble, leaving less residual

dissolved Fe in the water after pretreatment and hence it causes only minor scaling effect on RO membrane. Assuming raw seawater pH is about 8 and Fe dose is low, the buffer intensity is fairly low at pH 7.5 to 8.0 (Edzwald and Haarhoff, 2011). Thus, it requires only a small addition of strong acids in coagulation step.

In this study, standard coagulation jar test was carried out using $FeCl_3$ as coagulant at a wide concentration of 0.5 to 8.0 mg-Fe^{3+}/L. The liquid chromatography-organic carbon detector (LC-OCD) was used to quantify DOC concentration in seawater following coagulation. The use of LC-OCD enabled a more detailed fractionation of DOC compounds in seawater (see **section 3.3.1.1.1**). DOC can be divided into two fractions (hydrophobic and hydrophilic) by LC-OCD. The hydrophobic (HB) DOC (HOC in LC-OCD) is calculated from the difference of DOC and chromatographic DOC (CDOC in LC-OCD or hydrophilic (HF) DOC) (In the modelling study, two DOC terms are simplied hydrophobic to HB and hydrophilic to HF). All organic matter retained in the column is defined as HB DOC. This can be either dissolved hydrocarbons or micro particulate including humics. CDOC is calculated from the area enclosed by the total chromatogram (Huber and Frimmel, 1994). The HF DOC compositions are classified as biopolymer, humics, building blocks, and low molecular weight (LMW) neutrals and acids.

The aim of this study was to develop a quantitative mathematical model of the residual DOC in seawater after coagulation treatment with $FeCl_3$ at different pH and coagulant dose. The model described was used to fit the experimental data for removal of HB and HF DOC fractions by coagulation. It is expected that the data would reduce the number of experiments necessary and enable prediction of benefits achievable by coagulant dose and pH change.

4.2.2 MODEL DESCRIPTION

Kastl et al. (2004) described removal of DOC by enhanced coagulation with aluminum and iron salts for various doses and pHs. They used a Langmuir adsorption theory to model DOC removal onto the metal hydroxide surface. They hypothetically divided DOC into three fractions:

(1) Humic acid fraction which adsorbs in associated form and therefore its adsorption is pH dependent as humic acid is defined as a weak acid with a dissociation constant of K_a.

(2) Neutral component which is absorbed by metal hydroxides and the adsorption is pH independent.

(3) Non-sorbable fraction (Inert organic fraction) the removal by metal hydroxides can be neglected.

In this study, it is intended to describe removal of DOC in the form of hydrophobic (HB) and hydrophilic (HF) fractions and hence modification to the model is needed. This is done by replacing the conceptual non-polar fraction in Kastl et al. (2004) with a hydrophobic fraction which behaves as a weak base and a non-polar hydrophobic fraction (HB_n). In addition the humic acid conceptually assumed in the Kastl et al. (2004) is replaced with a dissociable hydrophilic fraction (HFD) of which the neutral form could only be removed. Non-sorbable fraction in Kastl et al. (2004), which is mostly low molecular hydrophilic compound; it is renamed as inert hydrophilic fraction (HF_i).

DOC is therefore the sum of both fractions:

$$DOC = HB + HF \tag{4.1}$$

Hydrophilic compounds are, for the purpose of modeling, divided into dissociating and inert fraction:

$$HF = HFD + HF_i \tag{4.2}$$

Where HFD is dissociating hydrophilic (HF) compounds, which are adsorbed onto ferric hydroxide in their associated form.

Dissociation of HFD is assumed to progress according to the reaction:

$$HFD = H^+ + FD^- \tag{4.3}$$

This is an equilibrium reaction controlled by the equilibrium constant:

$$K_{HFD} = ([H^+] \times [FD^-]_l) / [HFD]_l \tag{4.4}$$

HB fraction is composed of

$$HB = HBOH + HBn \tag{4.5}$$

Where HBOH is assumed to be a weak base and only its neutral form is assumed to be adsorbed onto ferric hydroxide flocs. The HBn is assumed to adsorb independent of pH, i.e. it doesn't dissociate and hence always adsorbs. The HBn is same as non-polar organic fraction in Kastl et al. (2004).

$HBOH_l$ is assumed to dissociate according to:

$$HBOH_l = HB_l^+ + OH^- \tag{4.6}$$

Here, dissociation constant is expressed using following relationship:

$$K_{HBOH} = ([HB^+]_l \times [OH^-]) / [HBOH]_l \tag{4.7}$$

And only the associated form of HBOH ($HBOH_s$) is assumed to adsorb onto ferric hydroxide surface. In summary, there are three groups which compete for adsorption of ferric hydroxide surface.

$$HFD_s = \alpha_{HFD} \frac{\beta_{HFD} \times HFD_l}{1 + \beta_{HFD} \times HFD_l + \beta_{HBOH} \times HBOH_l + \beta_{HBn} \times HBn} \quad (4.8)$$

$$HBOH_s = \alpha_{HBOH} \frac{\beta_{HBOH} \times HBOH_l}{1 + \beta_{HFD} \times HFD_l + \beta_{HBOH} \times HBOH_l + \beta_{HBn} \times HBn} \quad (4.9)$$

$$HBn_s = \alpha_{HBn} \frac{\beta_{HBn} \times HBn_l}{1 + \beta_{HFD} \times HFD_l + \beta_{HBOH} \times HBOH_l + \beta_{HBn} \times HBn} \quad (4.10)$$

Where HFD_s, $HBOH_s$ and HBn_s are amount of HFD, HBOH and HBn adsorbed onto metal hydroxides respectively; α and β are respective adsorption constants for each component.

In the flocculated seawater,

$$HF_0 = HFD_s + FD_l^- + HFD_l + HF_i \quad (4.11)$$

$$HB_0 = HBOH_s + HB_l^+ + HBOH_l + HBn_l \quad (4.12)$$

Where subscript *l* represents the compound dissolved in liquid.

In the raw seawater,

$$DOC_0 = HF_0 + HB_0 \quad (4.13)$$

$DOC_{remaining}$ (final DOC) can therefore be calculated using the following formula;

$$DOC_{remaining} = DOC_0 - HFD_s - HBOH_s - HBn_s \quad (4.14)$$

These equations were solved using Aquasim® software to find the respective coefficients.

4.2.3 RESULTS AND DISCUSSION

4.2.3.1 DOC fraction depending on different $FeCl_3$ dose and pH

Figure 4.3(a) represents the fractional DOC (HB DOC and HF DOC) at different pH (pH 5~pH 9) after coagulation with 8.0 mg of Fe^{+3}/L. The DOC of raw seawater was 2.720 mg/L comprising of 1.424 mg/L (52.4%) of HB fraction and 1.296 mg/L (47.6%) of HF fraction. More than a third of HF DOC compounds were humic substances (0.478 mg/L) which was the major portion of HF DOC compounds. Building blocks, which are hydrolyzed products of the humic substances, consisted of only 12.7% of the HF DOC compounds in seawater.

In contrast, the removal of NOM in seawater by coagulation improved as pH was increased from pH 5 to pH 9. This could be attributed to different chemistry of seawater (Edwards, 1997; Kastl et al., 2004). The NOM removal in seawater was dominated by HB DOC removal. $FeCl_3$ coagulation removed the HB DOC compounds in seawater with increase of pH as shown as **Figure 4.3(a)**. At pH 9 complete removals of HB DOC compounds was achieved.

In the case of HF DOC compounds, the completely opposite trend was noticed with HB DOC compound removal. When pH was increased from 5 to 9, the removal efficiency of hydrophilic decreased from 62.6% to 54.7%. The removal of humic substances, and building blocks (which are hydrolyzed compounds of humics) led to the HF DOC compound removal at a higher pH. Especially, the removal of humic, which is the major portion of HF DOC compounds, was the highest (60%) at pH 5.

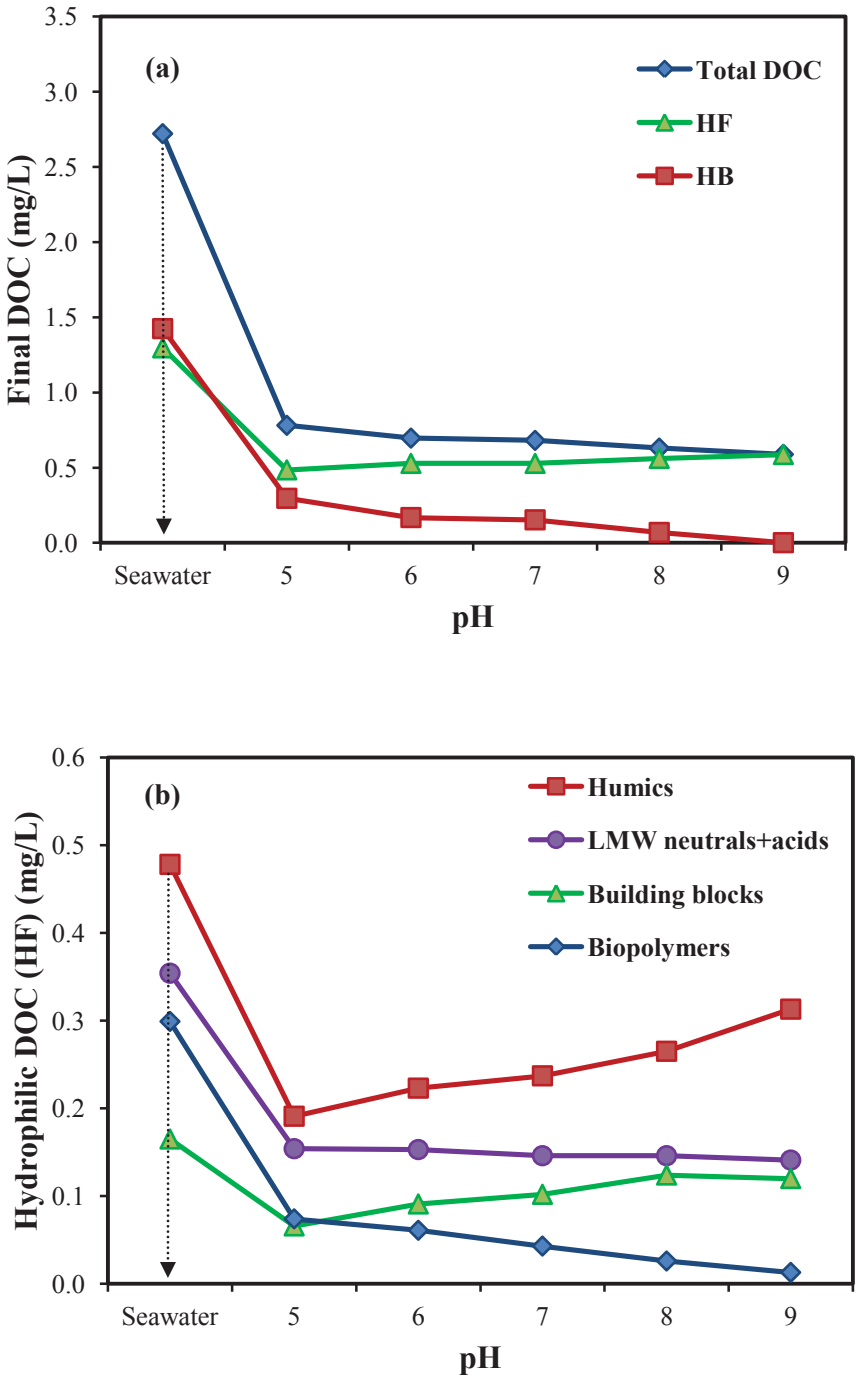


Figure 4.3 Remaining DOC after coagulation with $FeCl_3$ of 8.0 mg/L at different pH: (a) Total DOC and hydrophobic (HB) and hydrophilic (HF); (b) Four different HF fractions (Humics, Low molecular weight (LMW) neutrals + acids, Building blocks and Biopolymers).

In the case of HF DOC compounds, the completely opposite trend was noticed with HB DOC compound removal. When pH was increased from 5 to 9, the removal efficiency of hydrophilic decreased from 62.6% to 54.7%. The removal of different fractions of HF DOC compounds at different pHs was analyzed using LC-OCD. The removal of humic substances, and building blocks (which are hydrolyzed compounds of humics) led to the HF DOC compound removal at a higher pH. Especially, the removal of humic, which is the major portion of HF DOC compounds, was the highest (60%) at pH 5.

On the other hand, as can be seen from **Figure 4.3(b)**, removal of biopolymer in HF DOC fraction increased linearly with the increase in pH. At pH 9, 95.7% of biopolymer in seawater was removed. Meanwhile, removals of LMW neutrals and acids were not affected much by the increase of pH.

4.2.3.2 The removal of hydrophilic and hydrophobic fractions of DOC by $FeCl_3$ coagulation (model fitting)

As can be seen in **Figure 4.4** and **Figure 4.5**, the predicted final HB DOC and HF DOC concentrations are very close to the measured ones at the range of pH 5 to pH 9 with different ferric coagulant doses. It was noted that the removal of HB DOC compound was affected by the pH. An increased removal of HB DOC was noted with the increase in pH. Consequently, HB was completely removed at pH 9 and model predicted likewise. On the other hand, HF DOC showed different removal patterns for each and every component (**Figure 4.3(b)**).

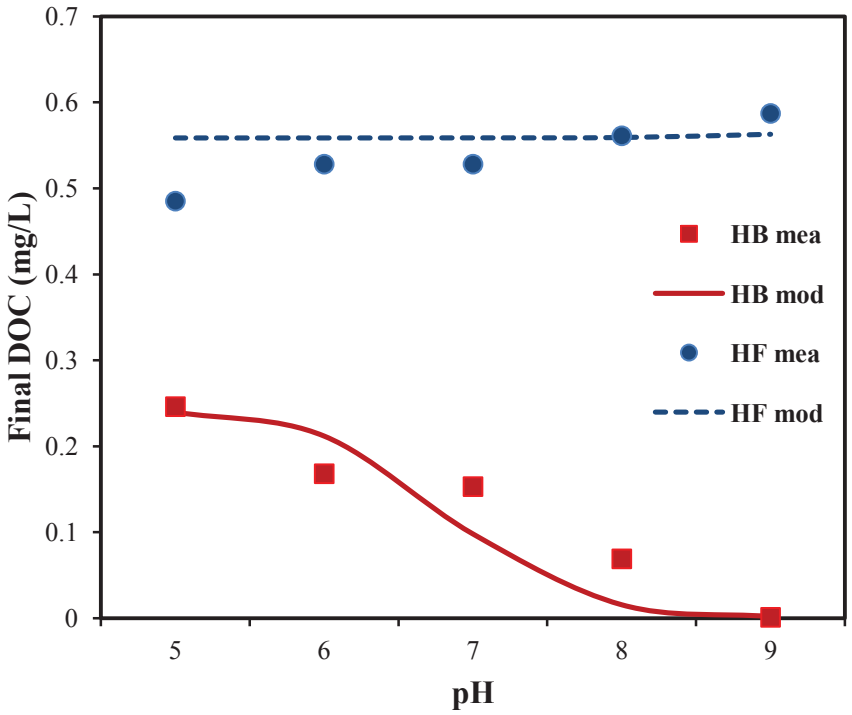


Figure 4.4 The pH dependence of hydrophobic (HB) and hydrophilic (HF) fractions of final DOC when 8.0 mg Fe^{3+}/L of $FeCl_3$ was dosed.

Modeling to all the fractions is complicated and such models are not practically feasible to predict different fractions. Hence the prediction was made for three fractions, namely hydrophobic fractions and non-sorbable/sorbable hydrophilic fractions. The remaining DOC after coagulation at pH 5, 7 and 9, and different ferric doses is presented in **Figure 4.4**. HB DOC removal was not much affected by $FeCl_3$ doses and even at a low dose of 0.5 mg of Fe^{3+}/L, up to 98.5% of HB DOC removal was achieved at pH 9. It shows that HB DOC in seawater requires only a small amount of $FeCl_3$ dose for coagulation. However, HF DOC removal was improved with the increase of ferric doses. A 24% of increase in HF removal was observed from 0.5 mg of Fe^{3+}/L to 8.0 mg of Fe^{3+}/L at pH 5. As noted in **Figure 4.4**, there is a marginally increased removal of HF DOC compounds with pH as also earlier noted by Kastl et al. (2004). For the purpose of model prediction in this paper, the difference was ignored.

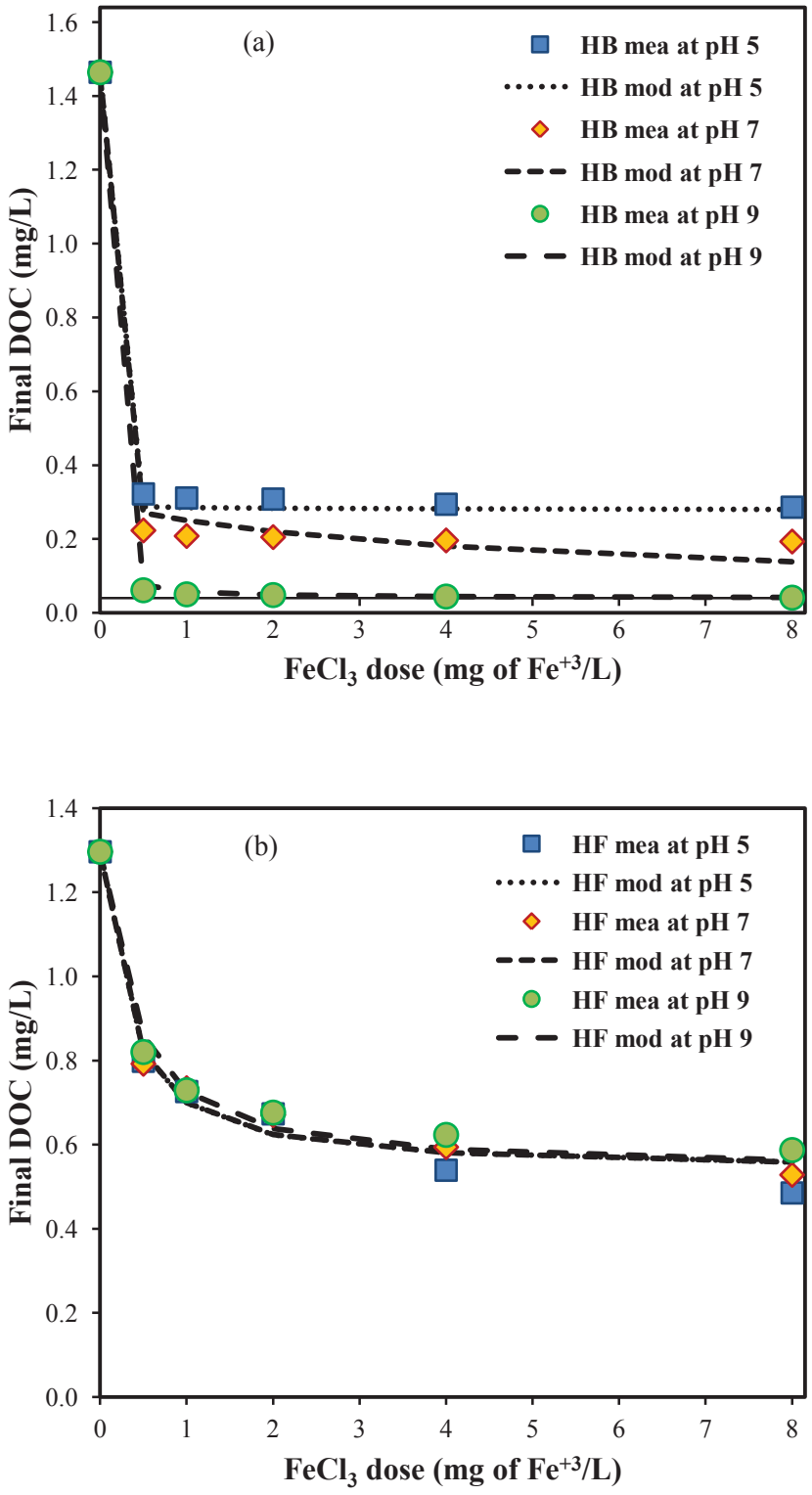


Figure 4.5 Final DOC for different ferric doses in seawater: Model fitting at different pH (pH 5, pH 7 and pH 9).

Experimental data for removal of HF and HB fractions of DOC during coagulation with $FeCl_3$ were fitted to the model. It was possible to describe all experiments (pH 5, 7, and 9 and doses of 0.5, 1, 2, 4 and 8 mg of Fe^{3+}/L) with one set of parameters. The deviation between the model and measured values were minimal (maximum error in prediction=0.053 mg/L of HB and 0.002 mg/L of HF). The model outputs for all experiment are presented in **Table 4.5**.

Table 4.5 Model parameters and errors with model value.

Adsorbing fraction	HFD	HBOH	HBn
α [mg/mg]	9.82	10	30
β [L/mg]	0.4119	24.75	20
Fraction	0.59 (of hydrophilic)	0.171 (of hydrophobic)	0.829 (of hydrophobic)
Dissociation constant	1.85E-10	1.31E-04	n/a
Chi^2	0.0369		

From a practical point of view, DOC removal model can successfully be used to predict the organic removal in seawater by coagulation. More importantly prediction of HB and HF fractions separately will pave the way for better coagulation pH to be adopted.

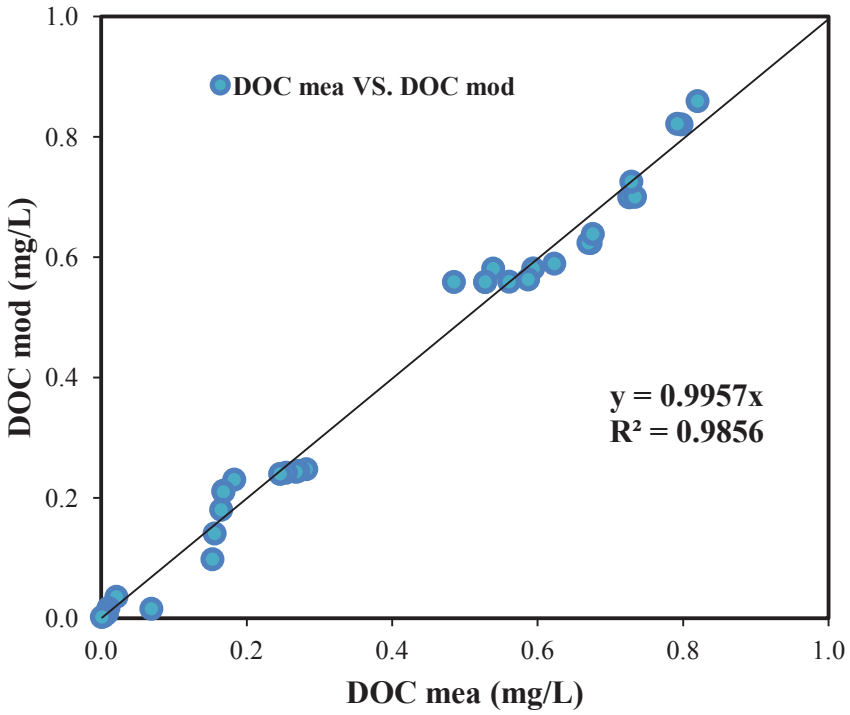


Figure 4.6 Comparison of measured final DOC (DOC_{mea}) and model predicted final DOC (DOC_{mod}) for seawater at different pH.

The prediction of DOC showed a good fit (R^2=0.986, n=34) of DOC obtained from experiment (**Figure 4.6**) when natural organic matter in seawater is conceptually divided into three fractions: hydrophobic, non-sorbable hydrophilic fractions and sorbable hydrophilic fractions.

4.2.4 SUMMARIZING THE $FeCl_3$ COAGULATION MODELING

Coagulation with $FeCl_3$ was carried out with different doses of coagulant and pHs. Measured hydrophobic (HB) and hydrophilic (HF) DOC was fitted successfully with the proposed model. Following are specific conclusions.

(1) Unlike in surface and wastewater, the removal of DOC (HB and HF) in seawater by coagulation improved marginally as pH was increased from pH 5 to 9. This could be attributed to a different chemistry of seawater as compared to surface or waste water.

(2) Collective hydrophobic and hydrophilic fractions showed a completely different behavior, i.e. the removal of hydrophobic fractions increased with pH but that of HF marginally decreased.

(3) The final DOC and fractionated DOC (HB and HF) were successfully fitted by the model proposed. Maximum error between the model (prediction) and measured values were minimal (0.053 mg/L of HB and 0.002 mg/L of HF).

4.3 POLY FERRIC SILICATE (PFSi) COAGULATION

4.3.1 INTRODUCTION

Due to the potential biological toxicity produced by residual aluminium in the effluent, iron-based flocculant has been used as a coagulant. A new kind of iron-based inorganic polymer - poly ferric silicate (PFSi) flocculant- which is a complex compound of positively charged Fe-flocculant and negatively charged polysalicic acid flocculant, is being studied (Wang and Tang, 2001; Fu et al., 2007, 2009).

The aim of this study is to evaluate the performance of modified PFSi (PFSi-δ) as a new flocculant in pretreatment for seawater desalination. The results were compared with $FeCl_3$, a common flocculant for seawater pretreatment. The characteristics of the flocs formed by two flocculants were also examined.

4.3.2 MATERIALS AND METHODS

4.3.2.1 Flocculation test

PFSi-δ and $FeCl_3$ were used as flocculants. Standard jar tests were carried out to determine the optimum dosage and to investigate the characteristics of flocs and DOC removal capacities of both flocculants. The experiments were performed in 1 L beakers by adding a predetermined amount of flocculants (see **section 4.1.2.1**). To examine the effect of flocculants, samples were collected immediately after rapid mixing and settling. The supernatant was taken and analysed for DOC to determine the ability of flocculants to remove organic matter. The flocs also were taken and measured for the size, charge, the amount of them as well as the organic content. The details of SMCHS are given in **section 4.1.2.2**.

4.3.2.2 Characterization of flocculation flocs

After settling (flocculation), the fine particles remaining in the supernatant were analysed for particle size and charge using Malvern Zetasizer 3000. The samples were analysed without dilution or other treatments in triplicate. Malvern Zetasizer 3000 was also used to measure the zeta potential and particle size of raw seawater and the flocculants tested. After 2 min of stabilisation, the data were recorded automatically. Mean value was reported in this study since the deviation beween measured values was less than 5%.

Suspended solids (SS) and volatile suspended solids (VSS) of flocs samples were analysed in the laboratory. The analytical procedures used were in accordance with the standard methods prescribed by the American Public Health Association, American Water Works Association, and Water Environment Federation (APFA/WWA/WEF, 2005).

4.3.3 RESULTS AND DISCUSSION

4.3.3.1 Flocculation performance of PFSi-δ

The results of PFSi-δ flocculation of seawater are presented in **Table 4.6** (The results of $FeCl_3$ flocculation is given in **Table 4.2** of **section 4.1.3.1**).

Table 4.6 The change of turbidity, pH, DOC fractions and removal efficiencies of seawater by coagulation with PFSi-δ.

	Seawater		PFSi-δ					
as Fe^{3+} (mg/L)	0		0.4		0.8		1.2	
Turbidity	1.70		0.74		0.69		0.67	
pH Initial	8.0		-		-		-	
pH Final	-		8.2		8.2		8.2	
	mg/L	%[a]	mg/L	%[b]	mg/L	%[b]	mg/L	%[b]
DOC	1.45	100	0.68	53	0.57	61	0.46	68
Hydrophobic	0.59	41	0.19	68	0.12	80	0.07	88
Hydrophilic	0.86	59	0.49	43	0.45	48	0.39	55
Biopolymer	0.13	9	0.01	92	0.01	92	0.01	92
Humic	0.45	31	0.31	31	0.31	31	0.23	49
Building blocks	0.19	13	0.15	21	0.12	37	0.13	32
Neutrals	0.09	6	0.01	89	0.01	89	0.01	89

[a] Composition of the different organic fractions in seawater.

[b] Removal efficiencies of the different organic fractions in seawater after coagulation.

It is interesting to observe that pH values were stable and did not depend on the concentration of PFSi-δ. As expected, a higher dose of PFSi-δ led to higher turbidity and DOC removal efficiency. After flocculation, pH increased to about 8.2, a suitable range for flocculation, regardless of concentration. At dosage of 1.2 mg Fe^{3+}/L, more than 60% removal of turbidity was observed.

DOC removal efficiency of different fractions of organic matter by flocculation is presented in **Table 4.6**. Compared with $FeCl_3$, PFSi-δ could remove turbidity of seawater effectively. In terms of DOC, the removal efficiency of organic matter by PFSi-δ (with ferric content of 1.2 mg/L) was 68%. This removal efficiency was 11% higher than the highest organic matter removal with $FeCl_3$ as flocculant (57% DOC removal by $FeCl_3$ of 3 mg/L as Fe^{3+}).

The results with PFSi-δ also show that PFSi-δ could remove most of the hydrophobic compounds. Even at a low dose of 1.2 mg Fe^{3+}/L, PFSi-δ could remove more than 88% of hydrophobic compounds. PFSi-δ proved to have better hydrophilic organic matter removal capacity compared with $FeCl_3$. It removed up to 55% of the hydrophilic fraction at a dose of 1.2 mg Fe^{3+}/L. This value is 18% higher than that of $FeCl_3$ at a concentration of 3 mg/L.

The removal efficiencies of biopolymers (MW>>20,000 Da) and low molecular weight of neutrals (MW<350 Da) by flocculation with PFSi-δ were also high with efficiencies of 92% and 89% respectively. However, the removal efficiency of building blocks (MW 300–500) by PFSi-δ was less than 32%.

4.3.3.2 Comparison of the characteristics of flocs

The physical and chemical characteristics of flocs of both flocculants at pre-selected concentration (0.5mg Fe^{3+}/L as lower dose and 3.0 mg Fe^{3+}/L as higher dose) are summarised in **Table 4.7**. The charge of raw seawater induced by organic matter was −1.86 mV.

Table 4.7 The charges of coagulants and particles in supernatant after coagulation, and physical characteristics of coagulated suspended solids.

			$FeCl_3$		PFSi-δ
Concentration	mg (Fe^{3+})/L	0.5	3.0	0.5	3.0
Zeta potential (mV)	Coagulants[a]	3.48	20.0	7.59	13.9
	Raw seawater	-1.86	-1.86	-1.86	-1.86
	Particles (in supernatant)[b]	-4.50	-1.90	-6.20	-0.40
Particle size (Z-average)	(nm)	1878	2468	1757	2245
MLSS	(mg/L)	9.6	20	10	38
VSS	(mg/L)	4.8	2.0	4.4	10.8
VSS/MLSS	(%)	50	10	44	28

[a]: Coagulants itself at a given concentration.

[b]: Particles in supernatant after coagulation and settling.

It can be seen that the charges of particles increased at higher flocculant doses. As PFSi-δ concentration increased to 3.0 mg Fe^{3+}/L, the negative charge fell markedly. With respect to the average particle size, $FeCl_3$ flocs were larger than PFSi-δ flocs at the same ferric contents. At a low flocculant dose of 0.5 mg Fe^{3+}/L, the amounts of flocs of the two flocculants were not much different. However, when the flocculant dose was increased to 3.0 mg Fe^{3+}/L, the amount of flocs with PFSi-δ was twice that of $FeCl_3$.

4.3.3.3 Submerged membrane coagulation hybrid system (SMCHS)

4.3.3.3.1 Critical flux

Detail of critical flux is explained in **section 4.1.3.2.1**. The critical flux for the system with seawater without any coagulant was only 20 L/m^2·h. The submerged membrane coagulation system led to an increase of critical flux (**Figure 4.7**). Since the pore size of MF was large, reversible fouling was dominant due to the deposition of low MW weight organic matter on the internal pores of the membrane. After chemical cleaning, flux recovery test showed that the fouling on MF with flocculated seawater is reversible. Flux was recovered completely with chemical cleaning. Lee et al. (2008) found that medium to low MW component of organic matter (300–1000 Da) was responsible for the initiation of fouling (Lee et al., 2008). In this study, both $FeCl_3$ and PFSi-δ could remove a majority of neutrals (MW<350 Da) and some parts of the building blocks (MW≈300–500 Da) from the hydrophilic compounds. Thus, removal of these fractions of organic compounds led to an increase in the critical flux.

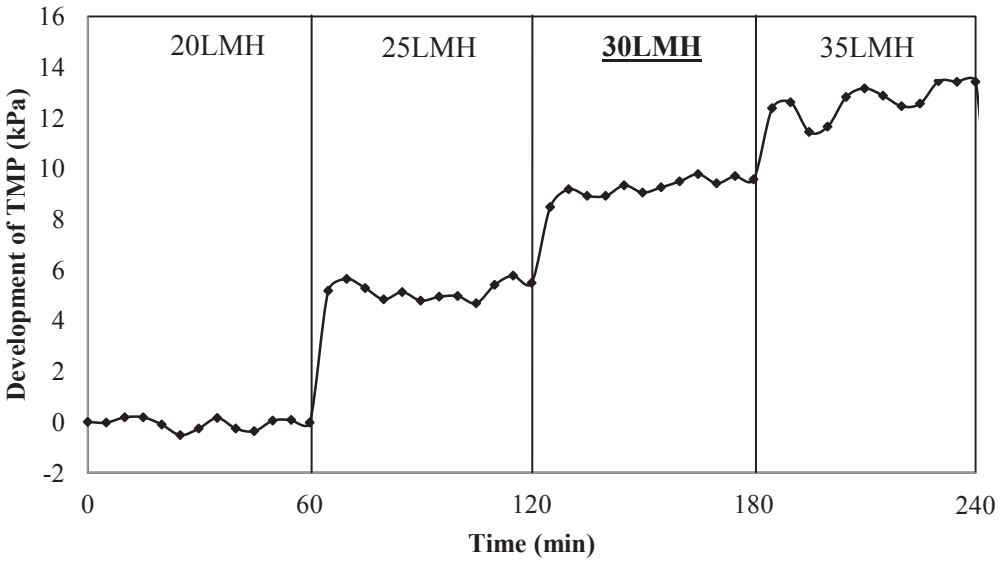
The experimental results show that critical flux increased to 55 L/m^2·h (**Figure 4.7(b)**) when $FeCl_3$ with concentration of 3.0 mg Fe^{3+}/L was used. Although the DOC removal efficiency by PFSi-δ of 1.2 mg Fe^{3+}/L was higher than that by FeCl3 of 3.0 mg Fe^{3+}/L, the critical flux by PFSi-δ of 1.2 mg Fe^{3+}/L was only 30 L/m^2·h (**Figure 4.7(a)**). The

difference in sizes and amounts of flocs produced from these two flocculants may be the reason for this phenomenon. As can be seen from **Table 4.8**, with the same ferric content, PFSi-δ generated larger amounts of flocs and they were smaller than flocs obtained from ferric chloride.

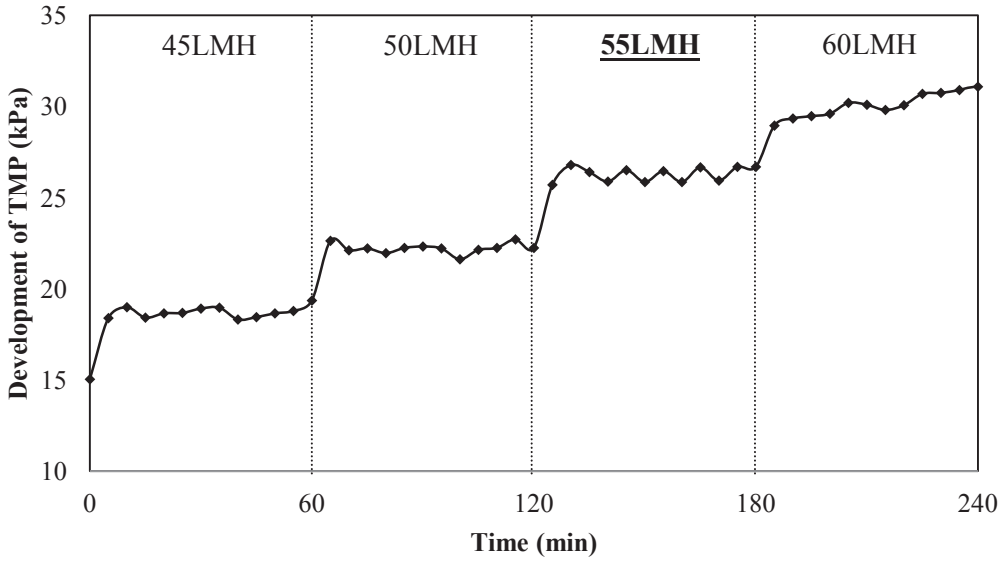
4.3.3.3.2 Organic removal

It was observed that by SMCHS, up to 58% of hydrophilic compounds could be removed at a dose of $FeCl_3$ 3.0 mg/L (as Fe^{3+}) (**Table 4.8(a)**). This value was 21% higher than that of coagulation alone. The submerged membrane coagulation system also led to 71% organic matter removal, 14% higher than that of coagulation alone.

The result from MF filtration coupled with in-line flocculation with PFSi-δ shows that 77% of DOC could be removed after 6 h (**Table 4.8(b)**). This value was 9% higher than that of coagulation alone. In particular, biopolymer and neutrals were removed completely by SMCHS. Compared with $FeCl_3$, these results show that by coupling with MF, PFSi-δ at a lower concentration of ferric (1.2 mg/L as Fe^{3+}) could result in a higher DOC removal efficiency. Consequently the DOC removal of the submerged membrane coagulation system was also 14% higher than that of coagulation alone.



(a) PFSi-δ (1.2 mg Fe^{3+}/L)



(b) $FeCl_3$ (3.0 mg Fe^{3+}/L)

Figure 4.7 Variation of TMP values (filtration flux 20 L/m^2.h).

Table 4.8 Fraction of organic matter after SMCHS (filtration flux 20 L/m^2·h).

Feed water	DOC	Hydro-phobic	Hydro-philic	Bio-polymer	Humic	Building blocks	Neutrals
(a) $FeCl_3$ (3.0 mg Fe^{3+}/L) concentration (mg/L)							
Seawater	1.29	0.46	0.83	0.13	0.44	0.20	0.09
Effluent after 2 h	0.39	0.02	0.37	0.05	0.20	0.12	0.00
Effluent after 24 h	0.38	0.02	0.36	0.02	0.20	0.11	0.03
Removal efficiency (%)							
Effluent after 2 h	70	95	55	62	55	40	100
Effluent after 24 h	71	95	58	85	66	20	67
(b) PFSi-δ (1.2 mg Fe^{3+}/L) concentration (mg/L)							
Seawater	1.45	0.59	0.86	0.13	0.45	0.19	0.09
Effluent after 1 h	0.41	0.04	0.37	0.00	0.22	0.15	0.00
Effluent after 2 h	0.41	0.05	0.36	0.00	0.17	0.20	0.00
Effluent after 6 h	0.34	0.02	0.32	0.00	0.20	0.11	0.00
Removal efficiency (%)							
Effluent after 1 h	72	93	57	100	51	21	100
Effluent after 2 h	72	92	58	100	62	10	100
Effluent after 6 h	78	97	63	100	56	42	100

4.3.4 SUMMARIZING THE PFSi-δ COAGULATION

The performance of PFSi-δ and $FeCl_3$ coagulants was studied in both batch mode (using jar test apparatus) and using submerged membrane hybrid system (SMCHS). The results show that both PFSi-δ and $FeCl_3$ were effective in removing dissolved organic compounds in seawater. Higher removal efficiencies of turbidity and DOC were obtained at lower doses of PFSi-δ (1.2 mg/L as Fe^{3+}) in comparison with $FeCl_3$ (3 mg/L as Fe^{3+}). In particular, hydrophilic compounds were removed more effectively by PFSi-δ. It emerged that approximately 55% of hydrophilic compounds in seawater was removed by PFSi-δ 1.2 mg Fe^{3+}/L. However, in comparison with $FeCl_3$, the smaller size and larger amount of flocs with PFSi-δ resulted in higher fouling on the MF membrane and a lower critical flux when PFSi-δ was employed as flocculant.

4.4 TITANIUM TETRA CHLORIDE ($TiCl_4$) COAGULATION

4.4.1 INTRODUCTION

The use of $FeCl_3$ as Fe-salt coagulant is considerably increased due to its high DOC removal efficiency and having no detrimental effect on the living environment compared to aluminium (Al) salt (Qureshi and Malmberg, 1985). Recently, Okour et al. (2009) studied the application of Ti-salt flocculant as a pre-treatment for seawater reverse osmosis (SWRO). They reported that flocculation followed by granular activated carbon (GAC) filtration significantly reduced the turbidity, silt density index (SDI_{15}), dissolved organic carbon (DOC), colour and UV absorbance of flocculated seawater. In addition, $TiCl_4$ coagulation as a pretreatment to SWRO was compared with $FeCl_3$ coagulation with respect to flocculation performance, fouling reduction of RO membranes and sludge recovery after $TiCl_4$ flocculation. The authors found that the residual Ti salts did not cause any severe membrane fouling compared to Fe salts. Zhoa et al. (2011) investigated the flocculation mechanism by $TiCl_4$ and they stated that the flocculation was not only processed by charge neutralisation but also due to a chemical bond. During flocculation, NOM might absorb by hydroxide solid at an optimum pH of 8.0. Floc size by $TiCl_4$ flocculant was larger than that of $FeCl_3$, polyferric sulfate (PES), $Al_2(SO_4)_3$ and polyaluminium chloride (PACl). $TiCl_4$ flocculation has an advantage in application over a wider range of high pH (Zhao et al., 2011). However, no efforts were made to study the organic matter removal in detail by Ti-salt flocculant.

A significant disadvantage of flocculation is the production of a large amount of chemical sludge. The sludge requires an additional treatment and safe disposal in ocean and landfills. Due to serious oceanic contamination and damage of the fragile ecology of the coastal area, disposal of the waste into the ocean has been restricted. Shon et al. (2007, 2009) developed a method to recover multi-functional titanium dioxide (TiO_2)

nanoparticles from the $TiCl_4$ sludge. The prices of Ti-salt coagulation are 5 times higher than those of Al-salt while the sludge recycling and TiO_2 production compensate for the high Ti-salt price and ultimately provide numerous benefits with revenue to promote a water treatment plant (Kim et al., 2011). These benefits of adopting Ti-salt coagulation, sludge recycling and by-product production have been proven during the last 6 years of research studies. Titanium dioxide is used in a number of industries. It is used as white pigment, sunscreen, a thickener in cosmetic and skin-care products and particularly a photo-catalyst under ultraviolet (UV) light. Lee et al. (2009) evaluated on aquatic toxicity of this TiO_2 nanoparticle produced from flocculated sludge of seawater in terms of LC50 and mortality of *D. magna* and EC50 of Microtox® test. They found that $TiCl_4$ coagulant and TiO_2 produced from flocculated seawater sludge had very low toxicity in aqueous condition compared to Degussa TiO_2-P25.

In this study, the flocculation performance of $TiCl_4$ of organic matter in seawater was investigated in terms of NOM fractionations removal. NOM removal of $TiCl_4$ was also compared with that of commonly used $FeCl_3$ flocculant. Finally, TiO_2 recovered from flocculated sludge of seawater was characterised in terms of particle structure and atomic composition to evaluate its use.

4.4.2 MATERIALS AND METHODS

4.4.2.1 Flocculation test

$TiCl_4$ and $FeCl_3$were used as flocculants in this study. $TiCl_4$ was prepared as 10% stock solution and $FeCl_3$ was prepared as 1000mg/L of stock solution using $FeCl_3 \cdot 6H_2O$. The flocculation tests were carried out using standard jar test as indicated below. The seawater was placed in 1 L beakers and predetermined concentrations of titanium (Ti^{+4}) and ferric (Fe^{+3}) of 1.3-6.3 mg/L and 1.0-5.0 mg/L were added respectively. The samples were then stirred rapidly for 2 minutes at 120 rpm, followed by 20 minutes of slow mixing at 30 rpm, and 30 minutes of settling. The supernatant was filtered through 0.45μm micro filter and the filtrate was used for further dissolved organic carbon (DOC) analysis.

4.4.2.2 TiO_2 recovery

The flocculated sludge of $TiCl_4$ was collected, filtered and dried in the oven at 100°C for 3 days to remove the water content. Then it was ground and placed in a furnace at 600°C for 24 h. Following incineration, the colour changed from black to white, indicating the formation of TiO_2.

4.4.2.3 TiO_2 characterization

To identify TiO_2 particle structure, x-ray diffraction (XRD) was investigated using MDI Jade 5.0 (Materials Data Inc., USA). The aggregated particle image and composition of TiO_2 was observed using scanning electron microscopy (SEM, Rigaku, Japan).

4.4.3 RESULTS AND DISCUSSION

4.4.3.1 Organic matter removal

Table 4.9 The removal of DOC after coagulation with $TiCl_4$ and $FeCl_3$.

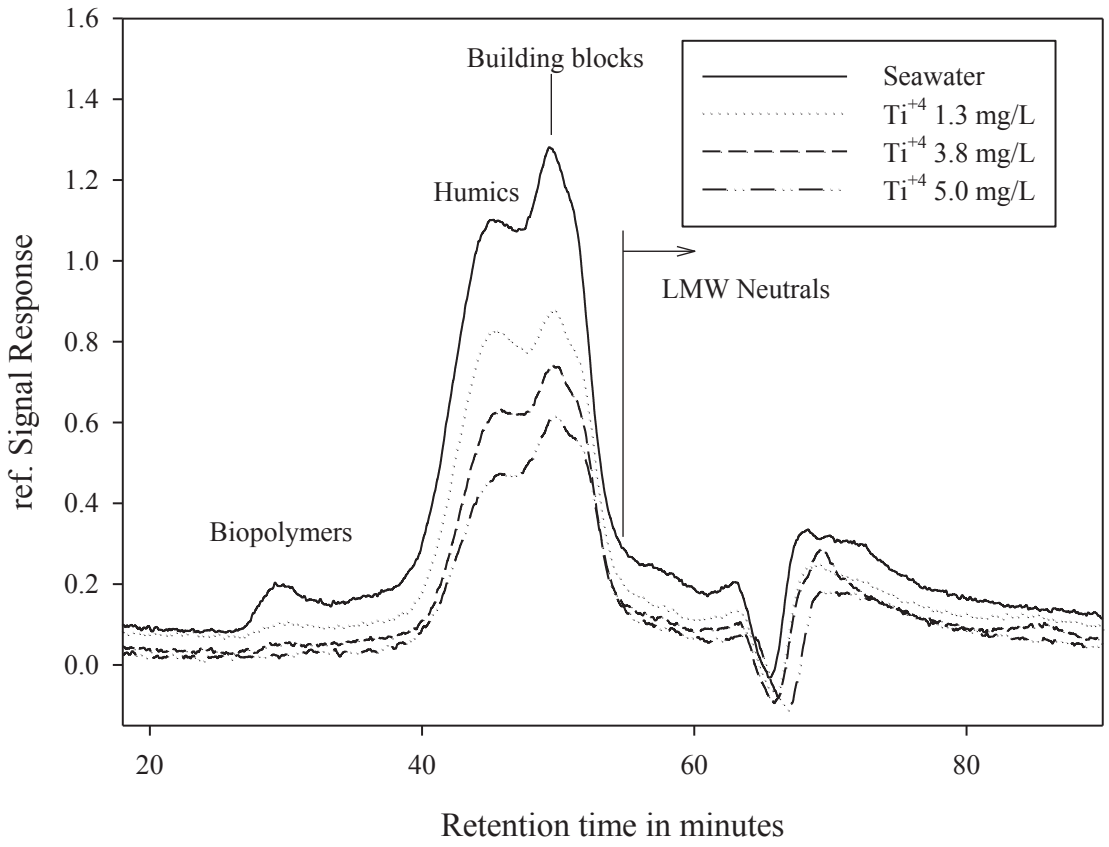
	DOC (mg/L)*	Removal efficiency (%)**	HOC (mg/L)* Hydrophobic	Removal efficiency (%)**	CDOC (mg/L)* Hydrophilic	Removal efficiency (%)**
(a) $TiCl_4$ (as mg of Ti^{+4} /L)						
0.0***	1.45	-	0.59	-	0.86	-
1.3	0.62	57.2	0.15	74.6	0.47	45.3
2.5	0.57	60.7	0.15	74.6	0.42	51.2
3.8	0.52	64.1	0.15	74.6	0.37	57.0
5.0	0.47	67.6	0.15	74.6	0.32	62.8
(b) $FeCl_3$ (as mg of Fe^{+3} /L)						
0.0***	1.30	-	0.33	-	0.97	-
0.5	0.70	46.2	0.05	84.8	0.65	33.0
1.0	0.65	50.0	0.05	84.8	0.60	38.1
3.0	0.60	53.8	0.04	87.9	0.56	42.3
5.0	0.52	60.0	0.02	93.9	0.50	48.5

* Concentrations of the different organic fractions in seawater

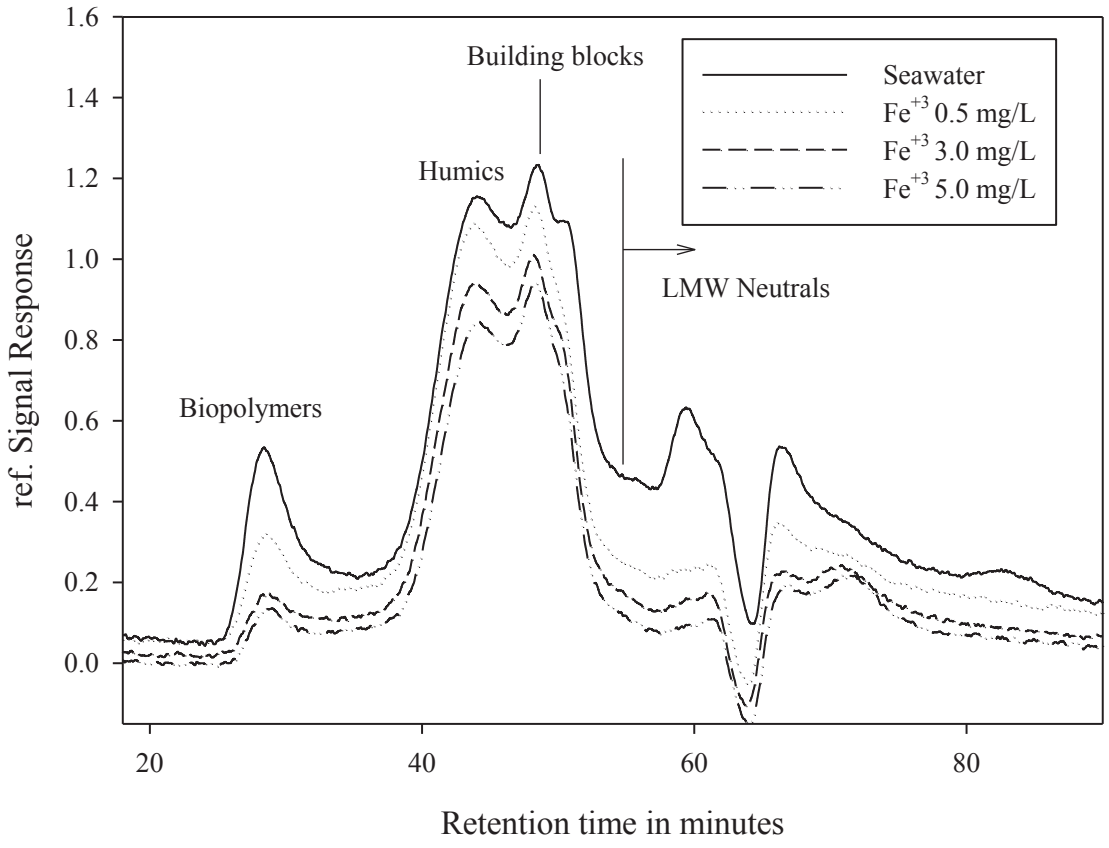
** Removal efficiencies of different organic fractions in seawater after the pretreatment

*** Seawater with no flocculant

In this study, $TiCl_4$ was used as Ti-salt coagulant and its performance was compared with that of $FeCl_3$. **Table 4.9** presents the DOC of flocculated effluent after $TiCl_4$ and $FeCl_3$ coagulation.



(a) $TiCl_4$



(b) $FeCl_3$

Figure 4.8 LC-OCD chromatogram of seawater and pre-treated seawater using $TiCl_4$ and $FeCl_3$.

LC-OCD chromatograms of seawater and pre-treated seawater after $TiCl_4$ and $FeCl_3$ coagulation present in **Figure 4.8**.

Although the seawater samples were taken from the same sampling site, they were collected at different times for $TiCl_4$ and $FeCl_3$ flocculation tests. This explains why the seawater used in flocculation with $TiCl_4$ had more hydrophobic organic matter (40.7%) than that with $FeCl_3$ (25.4%).

The results showed that the DOC removal efficiency increased when flocculant doses also increased. Hydrophobic compound removal was achieved to a significant amount by both flocculants. The removal efficiency of hydrophobic compounds by $FeCl_3$ flocculation was much higher than that of hydrophilic compounds. Most hydrophobic compounds (94%) and some of hydrophilic compounds (49%) were removed at a ferric (Fe^{+3}) dosage of 5.0 mg/L.

In the case of $TiCl_4$, the difference in hydrophobic and hydrophilic compounds removal was only 12% at a dose of 5.0 mg of Ti^{+4}/L. Interestingly, at all experimental concentrations, around 75% of hydrophobic compounds in seawater was removed through $TiCl_4$ flocculation. On the other hand, the removal of hydrophilic compounds did improve significantly as $TiCl_4$ concentration rose from 1.3 to 5.0 mg/L. Similar results were obtained by Okour et al. (2009). They reported that biopolymers, fulvic acids, low molecular weight compounds with molecular weight of 1200, 950, and less than 650 Da were removed by Ti-salt flocculant.

4.4.3.2 Detailed natural organic matter (NOM) fraction

Natural organic matter (NOM) in seawater mainly contains biopolymers (BP), humic substances (HS or humics), building blocks (BB) and low molecular weight neutrals (LN). It was observed that $TiCl_4$ flocculation led to a higher amount of CDOC removal than $FeCl_3$ (**Table 4.10**).

Table 4.10 Amount of different hydrophilic fractions of seawater removed by coagulants of different doses.

	$FeCl_3$ (mg of Fe^{+3} /L)					$TiCl_4$ (mg of Ti^{+4} /L)				
	0.0*	0.5	1.0	3.0	5.0	0.0*	1.3	2.5	3.8	5.0
BP	0.14	0.08	0.07	0.05	0.04	0.09	0.06	0.04	0.01	0.00
HS	0.34	0.27	0.27	0.26	0.25	0.44	0.26	0.24	0.21	0.16
BB	0.21	0.19	0.16	0.16	0.13	0.18	0.13	0.11	0.11	0.10
LN	0.28	0.11	0.10	0.09	0.08	0.15	0.01	0.01	0.01	0.01

* Seawater with no coagulant

4.3.3.2.1 Biopolymers (BP)

BP has very high molecular weight (20,000-100,000 g/mol) and it represents compounds such as polysaccharides amino sugars, polypeptides, proteins; "extracellular polymeric substances", hydrophilic fraction and not UV-absorbing. In surface water, BP exists as colloidal transparent exopolymer particles (TEP) and polysaccharide. These fractions were identified as possible fouling active substances (Laabs et al., 2006; Rosenberger et al. 2006; Villacorte et al., 2009). BP decreased significantly after flocculation with both flocculants (**Figure 4.11 and Table 4.12**). The comparison of LC-OCD chromatograms shows that $TiCl_4$ flocculation retained more organic bio-polymers than the $FeCl_3$ coagulation. BP removal efficiency increased as $TiCl_4$ doses increased with complete removal occurring at a dose of 5.0 mg of Ti^{+4}/L.

4.3.3.2.2 Humic substances (HS)

Humic substances (HS) represents compounds with molecular weights approximately 1000 g/mol. Zazouli et al. (2010) reported that the flux reduction on NF membrane increased with increasing humics concentration in foulants. As can be seen from **Figure 4.9** and **Table 4.10**, HS removal was marginal when using coagulation with $FeCl_3$ (20.6% to 26.5%). On the other hand when $TiCl_4$ dose increased from 1.3 to 5.0 mg/L, the amount of HS removed rose remarkably from 40.9 to 63.6%.

4.3.3.2.3 Building blocks (BB)

Building Blocks (BB) is defined as HS-hydrolysates, sub-units of HS with molecular weights varying between 300-450 g/mol. There are mainly weathering and oxidation products of HS. According to Huber et al. (2011), BB cannot be removed by typical flocculation processes. Flocculants or coagulants as well as flocculated particles sometimes should be considered as another factor in the formation of BB. In the same

manner, in this study not much BB was removed (**Table 4.10**). BB removal slightly decreased as the flocculant doses increased. Removal efficiencies of BB by $FeCl_3$ and $TiCl_4$ coagulants at a dose of 5.0 mg of Ti^{+4}/L were below 38.1% and 44.4%, respectively.

4.3.3.2.4 Low molecular weight neutrals (LMW neutrals or LN)

Low molecular weight neutrals (LMW Neutrals; LN) are the only low-molecular weight weakly charged hydrophilic or slightly hydrophobic "amphiphilic" compounds such as alcohols, aldehydes, ketones and amino acids. Dittmar and Kattner (2003) stated that LMW neutrals could be described as amphiphilic dissolved organic matter (DOM) recalcitrant to biodegradation such as metabolic intermediates and bacterial membranes moieties. Therefore, effective LN removal may reflect the reduction of microbial activity. Some researchers indicated that organic fouling is primarily caused by LN (Hong and Elimelech, 1997).

Both flocculation tests indicated high LN removal efficiencies, particularly with $TiCl_4$. Only trace of LN remained after $TiCl_4$ flocculation with removal efficiency reaching 93.0% (**Table 4.10**).

4.3.3.3 Sludge recovery

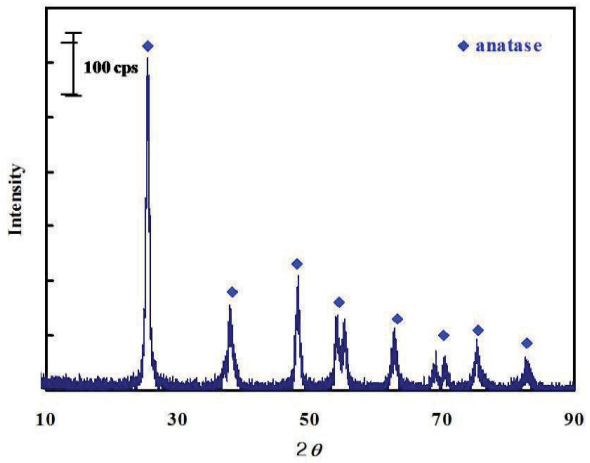


Figure 4.9 XRD pattern of the TiO_2 recovered from$TiCl_4$ flocculation.

During coagulation processes the disposal and treatment of sludge is the major question because of the impact on the natural environment. In order to recover valuable TiO_2 nanoparticle from flocculated sludge, Ti-salt sludge was calcinated at 600°C to remove organic matter.

The XRD pattern of recovered TiO_2 particles is shown in **Figure 4.9**. Recovered TiO_2 was found to have only anatase phase after calcination at 600^{o}C. Many researchers hydro-thermally crystallised titanium dioxide gel and obtained the anatase phase at temperatures less than 600°C (Dachille et al., 1968). However, the incineration temperature of 600^{o}C was suggested in terms of energy consumption and better photo-catalytic activity of TiO_2 produced from Ti-flocculated sludge (Zhao et al., 2011).

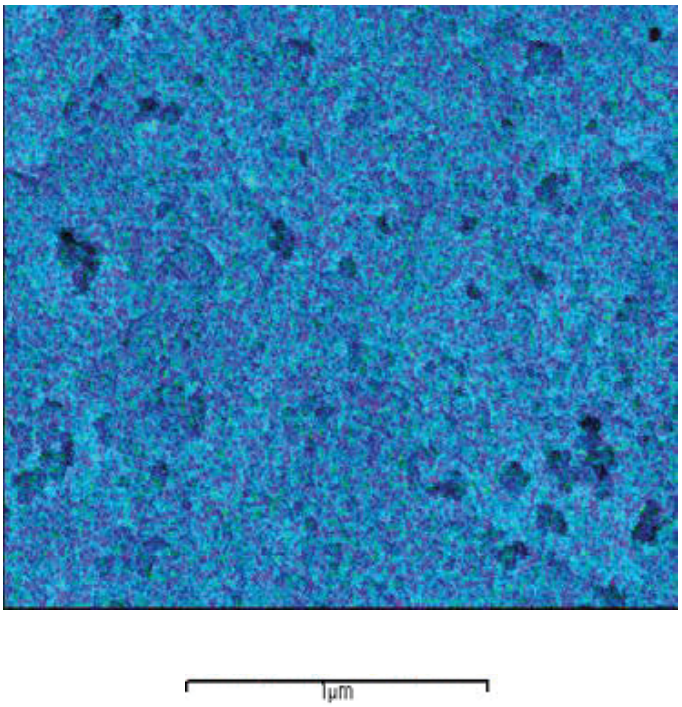


Figure 4.10 SEM image of the TiO_2 recovered from$TiCl_4$ flocculation.

It was observed from SEM image of TiO_2 recovered from $TiCl_4$ flocculation that TiO_2 nanoparticles were doped with Si. Their atomic compositions of Ti, Si and O were 23.8%, 0.2% and 76.0%, respectively. In **Figure 4.10**, violet small-dots and light-blue background represented Si and Ti respectively. Okour et al. (2009) suggested that Si could be diminished through the flocculation process and it was coated with TiO_2.

4.4.4 SUMMARIZING THE TITANIUM TETRACHLORIDE COAGULATION

The performance of Ti-salt flocculation of seawater was compared to Fe-salt flocculation in terms of detailed organic fractionation matter removal. The followings are the findings of the experimental study:

(1) The removal of hydrophilic compounds of seawater by $TiCl_4$ flocculation was superior compared to $FeCl_3$ coagulation and this removal increased significantly as $TiCl_4$ doses increased.

(2) Complete removal of biopolymers of NOM was achieved during $TiCl_4$ flocculation.

(3) Higher HS removal of 63.6% was observed with $TiCl_4$ coagulantion compared to only 26.5% with $FeCl_3$ coagulation.

(4) Both flocculants indicated a poor rate of removal percentage-wise for BB of NOM.

(5) $TiCl_4$ flocculation indicated high LN removal even at low doses. LN is one of the significant compounds causing organic fouling of membranes.

(6) Judging by XRD and SEM/EDX analyses, the recovered TiO_2 nanoparticles from $TiCl_4$ flocculated sludge were found to have a Si-doped anatase structure.

4.5 SUBMERGED MEMBRANE ADSORPTION HYBRID SYSTEM

4.5.1 INTRODUCTION

Incorporating physico-chemical processes with MF for wastewater treatment has proved to be an effective way for reducing membrane fouling as well as improving water quality. Guo et al. (2004) reported that the immersed membrane - adsorption hybrid system could remove a majority of organics while reducing the membrane fouling. The addition of adsorbents into the MF reactor removes organic compounds prior to their entry to the membrane's surface, and these compounds cause membrane fouling. Various additives such as alum, natural zeolite and PAC were used in the submerged membrane reactor for treating wastewater (Guo et al., 2005; Wu et al., 2006; Akram and Stuckey, 2008; Lesage et al., 2008). However, studies are few on the application of PAC into submerged microfiltration with seawater. Another way of reducing MF fouling as well as its operational cost is operating the MF below the critical flux. Adding PAC can reduce the loading of dissolved organic matter on the membrane, improve the permeate flux and thereby reduce membrane fouling.

The objective of this study was to evaluate the performance of PAC on organic removal from seawater through isotherm and kinetic experiments. The effect of PAC on the operation of submerged membrane adsorption hybrid system (SMAHS) in terms of the critical flux improvement and removal of specific organic fractions was also experimentally evaluated.

4.5.2 EXPERIMENTAL METHODS

4.5.2.1 Adsorption isotherm experiment

Isotherm study was conducted at the room temperature of 25°C. In these experiments, different amounts of PAC (0.01 g to 0.5 g) were placed into 250 mL Erlenmeyer flasks containing 100 mL of the seawater. The flasks were shaken at 110 rpm for 48 h by a portable bench top platform shaker (Ratex Instrument Company). After 48 h of contact time, samples from these flasks were taken to analyse the residual organic compounds.

The Freundlich isotherm is an empirical equation developed based on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites, and each site can be modelled by the following equation:

$$q_e = K_F . C_e^{\frac{1}{n}} \tag{4.15}$$

Where K_F: a Freundlich constant indicative of the adsorption capacity of the adsorbent

n: an experimental constant indicative of the adsorption intensity of the adsorbent

The Sips model is another different empirical model representing equilibrium adsorption data. This isotherm model has the features of both the Langmuir and Freundlich isotherm models. The Sips adsorption isotherm model can be written as follows:

$$q_e = \frac{q_m (bC_e)^{\frac{1}{n}}}{1 + (bC_e)^{\frac{1}{n}}} \tag{4.16}$$

Where, q_e is the amount of solute adsorbed per gram of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk of the solution (mg/L), q_m is saturation amount of organic adsorbed (mg/g) and b is a constant (L/mg).

4.5.2.2 Kinetic experiment

In the kinetic studies, 100 mL seawater was transferred to 250 mL Erlenmeyer flasks containing 0.15 g of PAC. The samples were placed on a mechanical shaker and shaken at 110 rpm. Samples were collected at regular time intervals and ana1ysed for residual organic compounds.

Ho's pseudo-second order kinetic model was used to simulate a number of sorption systems (Azizian, 2004). This pseudo-second order model presents the experimental kinetic data for the entire sorption period for most of the systems better than other models. This model has been used extensively by a number of researchers because it simulates and fits experimental kinetic data for the entire sorption period (Kumar and Sivanesan, 2006). The model equation is as follows:

$$q_t = \frac{2k_H q^2 t}{1 + 2k_H q\ t} \tag{4.17}$$

Where: k_H : Ho rate constant for adsorption, function of temperature (g/mg.min); q: the amount of adsorbate at equilibrium (mg/g); and q_t: the amount of adsorbate at any time t (mg/g).

4.5.3 RESULTS AND DISCUSSION

4.5.3.1 Adsorption equilibrium experiment

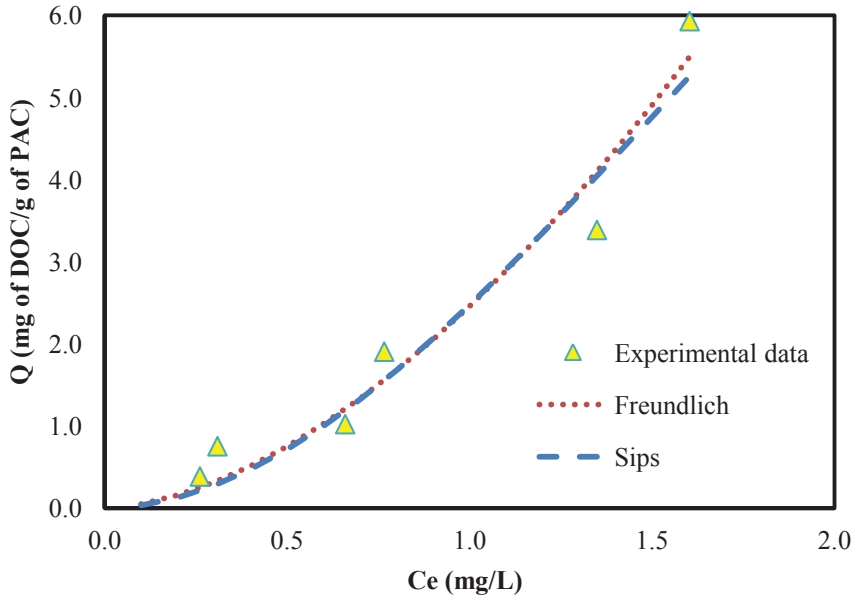


Figure 4.11 Prediction of equilibrium adsorption of organic by different adsorption models (Initial organic concentration = 2.2 mg/L, contact time = 48 h, mixing rate = 110 rpm, temperature = 25°C).

An adsorption equilibrium experiment was conducted to evaluate the adsorption capacity of PAC. The equilibrium results were then fitted with Freundlich and Sips isotherm equations. The adsorption curves simulated by both models fitted well with the observed values. The simulated and the experimental concentrations of the remaining organic are shown in **Figure 4.11**. The model equations and the isotherm parameters are shown in **Table 4.11**.

Table 4.11 Isotherm equations for organic removal using PAC.

Isotherm equations	Parameters	Values
Freundlich	k_F (mg/g)(mg/L)$^{-1/n}$	2.46
	n	0.59
	r^2	0.95
Sips	k_s	0.12
	q_m (mg/g)	23.12
	n	0.52
	r^2	0.94

It can be seen that organic adsorption capacity (q_m) estimated by the Sips model was up to 23.1mg/g. This prediction shows that there is not much difference between these two models in describing the adsorption of organic by PAC. The correlation coefficient (r^2) for both isotherms ranged from 0.94 to 0.95, representing a good fit of the observed data.

4.5.3.2 Fractionation of organic matter

In this study about half of DOC in raw seawater was hydrophilic in which a majority of organic matter had a molecular weight less than 1000 Da. The percentage of humic substances (MW ≈ 1,000 Da), low molecular weight of neutrals (MW < 350 Da) and building blocks (MW ≈ 300-500 Da) in the hydrophilic part were 33%, 27%, and 23% respectively.

These results indicated that at a concentration of 5 g/L, the PAC was able to remove almost all of the hydrophobic compounds (more than 96%) and a significant amount of hydrophilic compounds (78%). The PAC could remove a majority of high molecular weight fractions with 93% removal of biopolymer (MW ≈ 20,000 Da) (**Table 4.12**).

Table 4.12 Removal efficiencies of organic matter fraction by PAC adsorption.

PAC concentration (g/L)	DOC (%)	Hydro-phobic (%)	Hydro-philic (%)	Bio-polymer (%)	Humics (%)	Building blocks (%)	Neutrals (%)
0.10 g/L	27	5	56	54	60	51	74
0.25 g/L	39	15	69	64	66	64	82
0.75 g/L	65	59	71	79	66	72	80
1.50 g/L	70	68	72	81	68	76	85
2.50 g/L	86	92	78	93	76	79	85
5.00 g/L	88	96	78	93	78	84	86

As expected, the DOC removal efficiency was proportional to the PAC doses. However, the effect of PAC dose on removal of different organic fractions was different. Hydrophobic compound removal efficiency strongly depended on PAC doses whereas the removal of hydrophilic compound was not notably affected by the change of PAC doses. PAC even at a very low concentration of 0.1 g/L could remove 60% and 74% of humic substances and low molecular weight of neutrals, respectively. However only a slight increase in the removal efficiency of humic substances and low molecular weight

(LMW) of neutrals was observed when the PAC was increased by 50 times to 5 g/L. This indicates that humic and LMW organics by PAC adsorption is limited on properties of carbon.

4.5.3.3 Fouling reduction

The reduction of the fouling potential of raw seawater before and after adsorption with 1.5 g/L of PAC was also studied using UF-MFI. Following were the values of UF-MFI of seawater before and after the adsorption by PAC (**Table 4.13**).

Table 4.13 UF-MFI of before and after adsorb by PAC.

Sample	UF- MFI (s/L^2)
Seawater	15,848
After adsorb by 1.5 g/L of PAC	3,852

The addition of 1.5 g/L of PAC led to 70% removal of DOC thereby reducing the incidence of membrane fouling. As a result, UF-MFI reduced from 15,848 s/L^2 with raw seawater to 3,852s/L^2 with seawater after adsorption by PAC (**Table 4.13**). The UF-MFI value and the particulate fouling potential decreased with pretreatment due to the removal of particulates from the feedwater. In general, the removal efficiency is for removal of particles larger or equal to the pore size of the membrane. Thus for UF-MFI, particles ≥17,500 Da or estimated pore size of about 1.3 nm. The removal efficiency of the UF-MFI includes the removal of these larger particles plus smaller particles which may or may not be removed from the feedwater. The effect of adsorption by PAC on the particulate fouling potential is difficult to predict. PAC would absorb organic matter, e.g. humic acids into lower molecular weight, more polar and more biodegradable

substances. Therefore the UF-MFI would be expected to increase due to the increased number of particles with a smaller particle diameter. Conversely, some particles may become so small that they can pass the interstices of the cake and the pores of the membrane, resulting in a decrease in the UF-MFI. Moreover, the natural organic matter (NOM) surrounding colloidal particles which stabilises the particle may be hydrophilic, and this may be destroyed or reduced by PAC. More reduction in fouling potential, therefore, can be achieved by employing a higher concentration of PAC.

4.3.3.4 Kinetic experiment

The PAC adsorption amount with time was studied during adsorption kinetics experiments. The results for the PAC adsorption kinetics of organic compounds are presented in **Figure 4.12**.

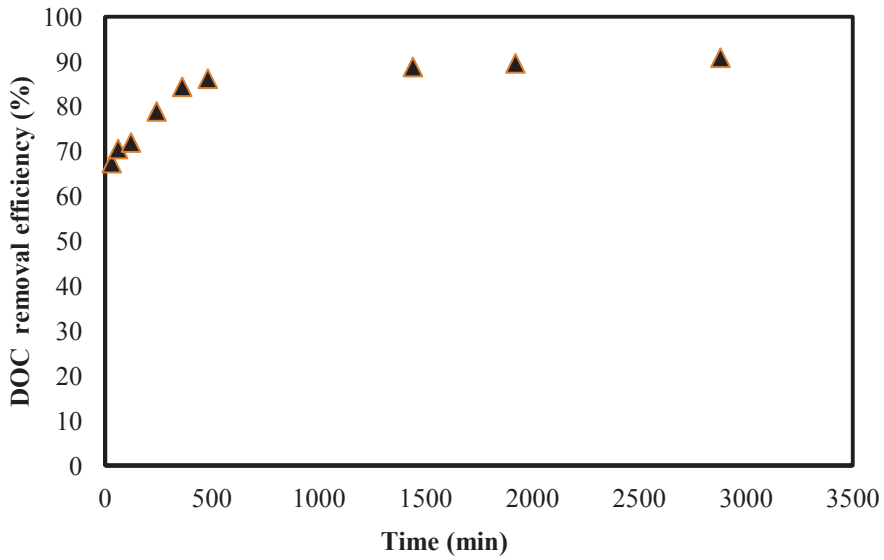


Figure 4.12 DOC removal efficiency as a function of adsorption time (Initial organic concentration = 1.11 mg/L, PAC = 1.5 g/L, mixing rate = 110 rpm, temperature = 25°C).

Organic compounds in the seawater were quickly adsorbed within the first 8 h and then the organic adsorption rate only increased marginally. The results show that PAC could remove 67% of organic within the first 30 minutes of contact with PAC. After 8 h, 86% of organic was adsorbed (with less than 0.15 mg/L of organic matter remaining in the seawater).

The analyses of organic matter fractions from the kinetic experiment also showed that hydrophilic compounds were quickly adsorbed by PAC within the first 30 min. There were not many differences between the removal efficiencies of biopolymer, humic substances, building block and low molecular weight of neutrals after 0.5h and 48h.

The kinetics of PAC adsorption of sea organic matter can be described by the Ho model. With the q and K_H given in **Table 4.14**, the kinetic adsorption data of PAC with synthetic water was also fitted well with the Ho model (**Figure 4.13**).

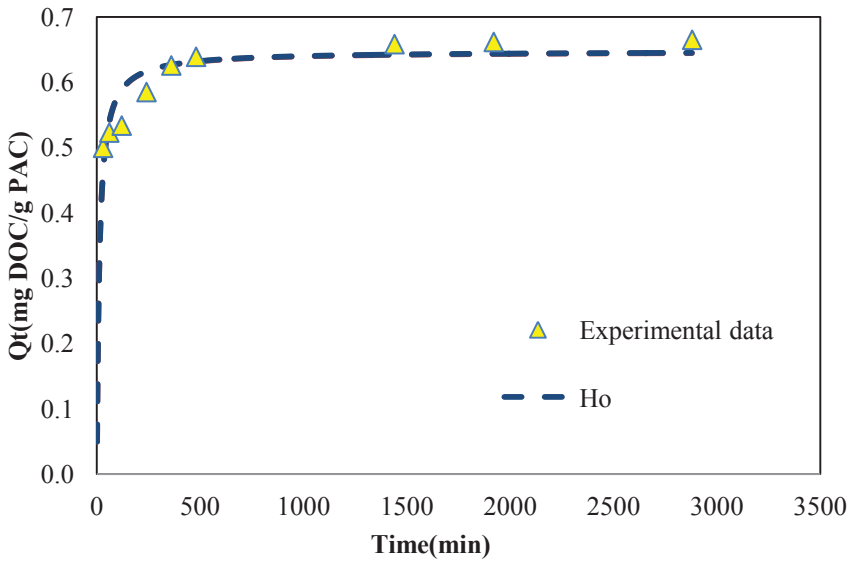


Figure 4.13 Prediction of adsorption kinetics of organic matter by PAC by the Ho model (Initial organic concentration = 1.11 mg/L; PAC = 1.5 g/L, mixing rate = 110 rpm, temperature = 25°C).

Table 4.14 Adsorption kinetics parameters of Ho model for PAC.

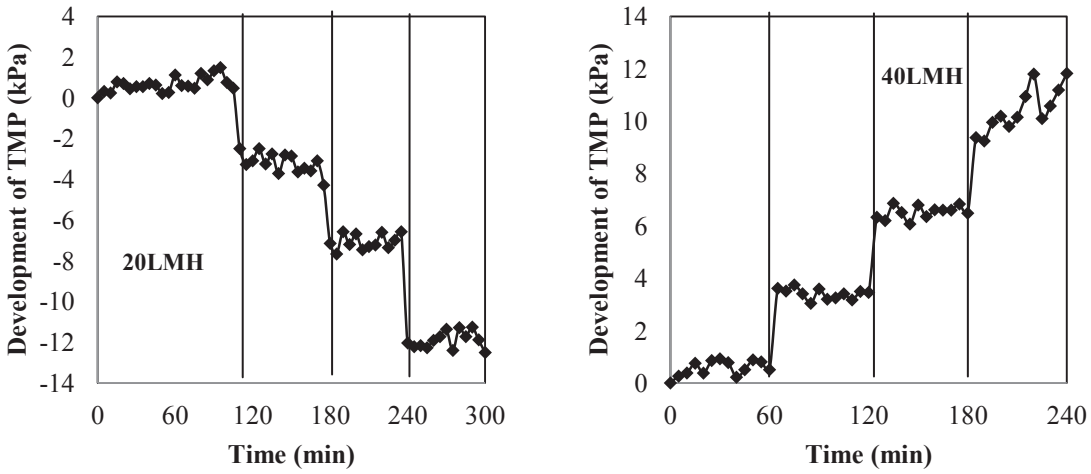
Parameters	Values
K_H	0.064
$q_{e,exp}$ (mg/g)	0.60
$q_{e,cal}$ (mg/g)	0.65
r^2	0.95

The correlation coefficient (r^2) for the modelled plot was more than 0.95 representing a good correlation of the observed data. Thus, the Ho model well describes the adsorption kinetics of organic matter present in seawater.

4.3.3.5 Effect of PAC on operation of SMAHS

Critical flux is the flux above which the membrane gets fouled severely and the trans-membrane pressure (TMP) rises dramatically. In this experiment, critical flux was measured quantitatively by a "flux stepping" method. The detail of the measurement of critical flux is given in **section 4.1.3.2.1**.

The addition of PAC in the submerged membrane reactor led to an increase in the critical flux. The critical flux increased from 20 to 40 L/m^2.h when 1.5 g/L of PAC was added into the submerged membrane reactor (**Figure 4.14**).



(a) Development of TMP without PAC (decreased by 5LMH)

(b) Development of TMP with 1.5 g/L of PAC (Increased by 5LMH)

Figure 4.14 Increase of critical flux by adding of 1.5g/L of PAC (a: seawater only, b: adding of 1.5g/L of PAC).

Furthermore the adding PAC also helped reduce the TMP of the submerged membrane system. At filtration flux 20 L/m^2.h, the TMP of conventional submerged membrane reactor after 1 day of operation was 10 kPa whereas this value was only 1.5 kPa when 1.5 g/L of PAC was added in the submerged membrane reactor. The increase of TMP of submerged membrane reactor with PAC added at a filtration rate of 30 L/m^2.h was also much lower than that of the conventional submerged membrane reactor (**Figure 4.15**).

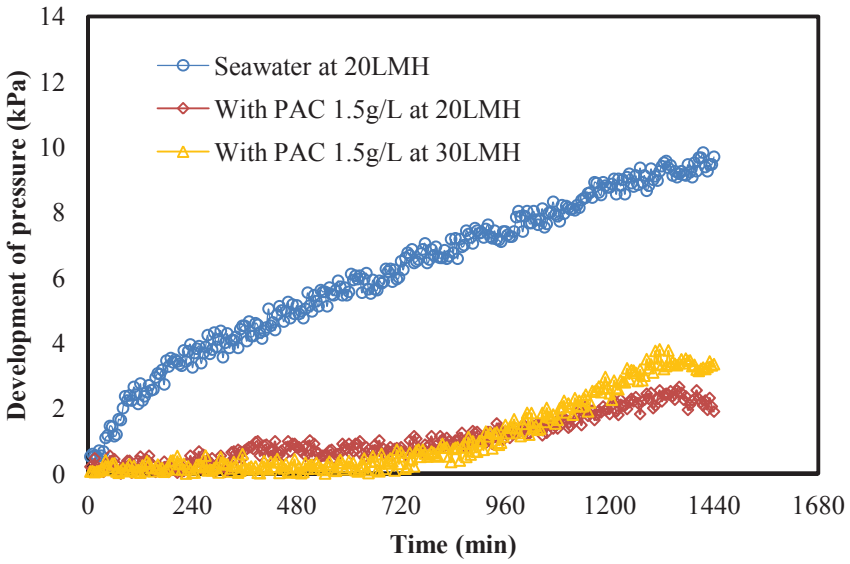


Figure 4.15 Development of TMPs of a submerged membrane reactor with and without adding PAC (PAC dose 1.5 g/L, aeration rate 1 L/min; 1.36 m^3/m^2 membrane area·h).

4.3.3.6 Fractionation of organic matter

Table 4.15 summarizes the DOC removal efficiency of seawater by MF alone and by MF with 1.5 g/L of PAC. PAC was dosed initially once. It is evident that only 15.9% of dissolved organic carbon (DOC) was removed by MF alone. In particular, MF alone could remove only a small percentage of hydrophilic fractions in seawater (5.8%). In contrast, when MF with 1.5 g/L of PAC was used, the DOC removal efficiency increased considerably by 76.6% and about 70% of hydrophilic fraction was eliminated due to the adsorption by PAC. Detailed analysis of the hydrophilic portion showed that the removal efficiencies of biopolymer, humics, building blocks and LMW neutrals were 92.3%, 70.0%, 89.5% and 99.0%, respectively.

Table 4.15 Removal efficiency of organic matter fraction by SMAHS with 1.5g/L of PAC.

Sample	DOC	Hydro-phobic	Hydro-philic	Bio-polymer	Humics	Building blocks	LMW Neutrals
Seawater (mg/L)[a]	1.45	0.59	0.86	0.13	0.45	0.19	0.09
Seawater by MF (%)[b]	15.9	32.2	5.8	53.8	-	15.8	44.4
Seawater + PAC 1.5g/L by MF (%)[b]	76.6	81.4	69.8	92.3	70.0	89.5	99.0

[a] Concentrations of the different organic fractions in seawater

[b] Removal efficiencies of different organic fractions in seawater after treatments

4.5.4 SUMMARIZING THE PAC ADSORPTION

In this study the performance of PAC in removing organic compounds from seawater was experimentally evaluated. The experimental results showed that the PAC adsorption equilibrium with seawater fitted well to the Freundlich and Sips isotherm models. The adsorption capacity of PAC was up to 23.1 mg of organic matter per gram of PAC. Ho's model also well described the adsorption kinetics of organic matter on PAC.

Detailed organic fractions of seawater after adsorption by PAC showed that more than 96% of hydrophobic compounds and 78% of hydrophilic compounds were removed by PAC at 5 g/L. The removal of hydrophobic compounds strongly depended on PAC doses and contact time whereas the removal of hydrophilic compounds was not affected by the PAC dose.

Finally, the addition of PAC in submerged membrane system can improve the critical flux by removing organic matter before it can make contact with the membrane surface. The results also showed that adding PAC could reduce the increasing rate of TMP and remove a majority of both hydrophobic and hydrophilic compounds.

CHAPTER 5

University of Technology Sydney

Faculty of Engineering& Information Technology

MEMBRANE HYBRID SYSTEM AS PRETREATMENT TO SWRO; DETAILED CHARACTERIZATION OF EFFLUENT AND FOULANTS

This chapter introduces three configurations of SMHS namely submerged coagulation hybrid system (SMCHS), submerged membrane adsorption hybrid system (SMAHS) and submerged membrane coagulation–adsorption hybrid system (SMCAHS).

The first part discusses SMHS as a pretreatment in reducing organic fouling and biofouling (**Section 5.1**). This follows with mathematical modelling of SMHS using fouling mechanisms (**Section 5.2**). The third part discusses the advanced organic characterization of SMHS effluent (**Section 5.3**). The last part presents the membrane foulant analyses in detail (**Section 5.4**).

<Publications related to this chapter>

– Jeong, S., L. Kim, S.-J. Kim, T.V. Nguyen, S. Vigneswaran, I.S. Kim. (2012) Biofouling potential reductions using a membrane hybrid system as a pre-treatment to seawater reverse osmosis. Applied Biochemistry and Biotechnology 67(6): 1716-1727.

– Jeong, S., Y.J. Choi, T.V. Nguyen, S. Vigneswaran, T.M. Hwang. (2012) Submerged membrane hybrid systems as pretreatment in seawater reverse osmosis (SWRO): Optimisation and fouling mechanism determination. Journal of Membrane Science 411–412: 173– 181.

– Jeong, S., S.-J. Kim, C.M. Kim, S. Vigneswaran, T.V. Nguyen, H.K. Shon, J. Kandasamy, I.S. Kim. (2013) A detailed organic matter characterization of pretreated seawater using low-pressure microfiltration hybrid systems. Journal of Membrane Science 428: 290–300.

– Jeong, S., S.-J. Kim, L.H. Kim, M.S. Shin, S. Vigneswaran, T.V. Nguyen, I.S. Kim. (2012) Foulant analysis of a reverse osmosis membrane used pretreated seawater. Journal of Membrane Science 428: 434–444.

5.1 ORGANIC AND BIOFOULING REDUCTION USING SMHS AS PRETREATMENT

5.1.1 INTRODUCTION

Biofouling is a significant problem in RO desalination process. It increases operation cost and water production cost due to frequent chemical cleaning. Although various attempts have been made to reduce this problem, it still remains as a challenge due to the complexity of biofouling (Baker and Dudley, 1998). The cause of biofouling is too complicated to understand, but formation of biofouling involves four phases, namely (i) conditioning of the membrane surface with extracellular polymeric substances (EPS) excreted by naturally occurring seawater bacteria, (ii) adhesion and attachment of bacteria, (iii) growth of the bacteria and (iv) partial biomass detachment through erosion and sloughing. On the other hand, organic and colloid fouling and scale formation are easy to identify and control by applying suitable operation based on water chemistry analysis (Flemming, 2002; Lee, 2010).

Bacterial growth is supported by feed water nutrients. Therefore, it is important to eliminate organic foulants by pre-treatment of feed water for SWRO rather than to control biofouling. Traditionally, flocculation and deep bed filtration are used as pre-treatment in SWRO. In new desalination plants, low-pressure membranes are used as pre-treatment. The capability of deep bed filtration and low-pressure membrane filtration in removing dissolved organic matter present in seawaters is limited.

In this study, we used submerged membrane adsorption hybrid system (SMAHS as shown in **section 4.5** of **Chapter 4**) and submerged membrane coagulation–adsorption hybrid system (SMCAHS) in order to reduce dissolved organic matter from seawater which in turn can minimise biological fouling of the RO membrane (Vigneswaran et al., 2003). Membrane hybrid systems based on MF have a number of advantages such as

low energy consumption and high flux operation. When they are incorporated with physico-chemical treatments such as adsorption and coagulation, a superior organic removal can be achieved.

Preliminary tests have investigated on the membrane hybrid systems for seawater in order to reduce the particulates and organics for RO membrane (**sections 4.1** and **4.5** of **Chapter 4**). In this process, small molecular species are adsorbed onto the activated carbon such as PAC or coagulated by $FeCl_3$, which can then be separated easily by the MF process. The effect of PAC on RO membrane fouling reduction was widely studied with the wastewater and surface water. However, it has not been studied much with seawater. The characteristics and organic concentration of seawater are different from those of wastewater or surface water. In seawater RO process, even though the organic concentration is very low (1–3 mg of dissolved organic carbon/L), it still causes severe RO fouling.

There are a variety of methods available to identify and measure the biofouling potentials in both feed water and foulants on RO membrane. Total direct cell count (TDC) and adenosine 5′-triphosphate (ATP) are generally used to quantify the biomass accumulation on the RO membranes and to estimate biofouling potential in the feed water (Veza et al., 2008; Hammes et al., 2010; Lee, 2010). The TDC value is determined via fluorescence microscopy using dyes such as live SYTO 9-stained cells, dead PI-stained cells and 4′-6-diamidino-2-phenylindole (DAPI)-stained cells. ATP gives an indication of the total amount of active biomass. ATP detection involves chemical and/or enzymatic extraction of ATP from bacterial cells, followed by the measurement of light emission derived when the dissolved ATP reacts with the luciferin–luciferase complex.

The assimilable organic carbon (AOC) assay has also been considered as an indicator of the biological growth potential of the water (Van der Kooij et al., 1982; Hammes and Egli, 2005; Hammes et al., 2007). The AOC assay offers a standardised measurement of the heterotrophic bacterial growth potential of treated water. Biodegradable organic matter is used by heterotrophic bacteria for carbon and energy. Vander Kooij's method utilised two bacterial strains (*Pseudomonas fluorescens* P-17 and *Spirillum sp.* Strain NOX) (Van der Kooij et al., 1982).

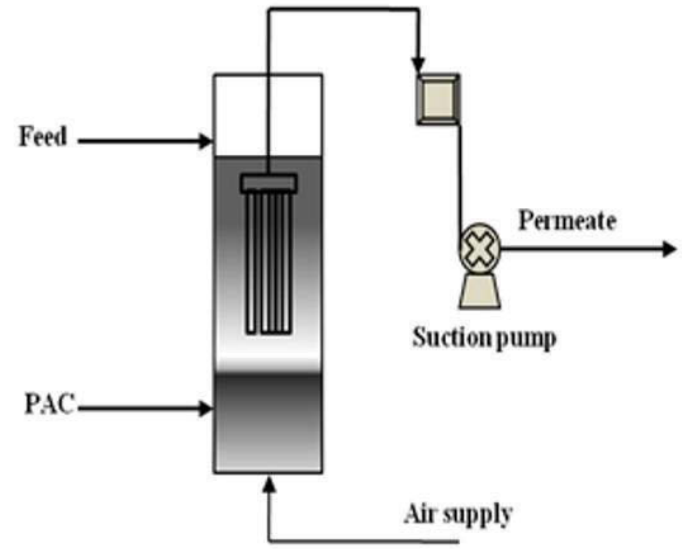
However, previous assays were designed for drinking water and distribution system. AOC measurement for seawater sample requires modification because salt content in seawater is high and microbial ecosystem is different. Modification of AOC method is thus required to measure the parameters governing the growth of bacteria in seawater.

In this study, the effect of SMAHS on the removal of organic foulants was studied in detail. Also, the mitigation of initial biofouling potential was studied through short-term reverse osmosis experiment. In addition, the SMCAHS (addition of coagulation into above SMAHS) was evaluated in view of reducing the adsorbent (PAC) dose and superior biofouling reduction.

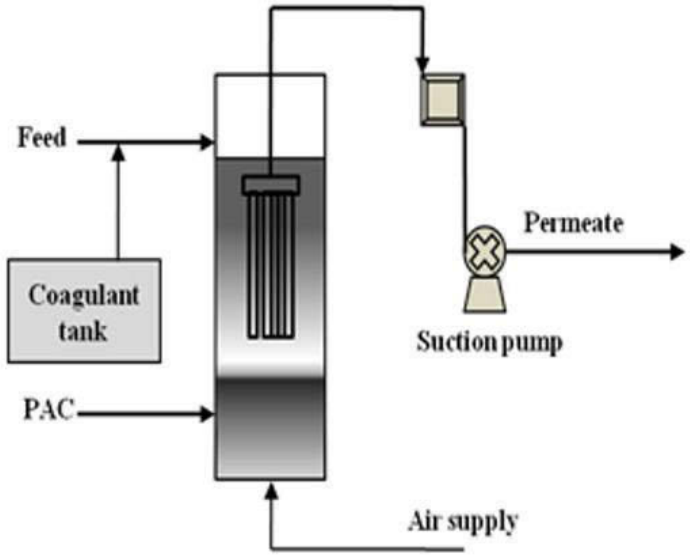
5.1.2 MATERIALS AND METHODS

5.1.2.1 Submerged Membrane Hybrid Systems (SMHSs)

The membrane used in this study was hollow fibre microfiltration (MF as shown in **section 3.1.2**). The schematic diagrams of the two submerged membrane hybrid systems are presented in **Figure 5.1**. In the experiment with SMAHS (**Figure 5.1a**), PAC concentration of 1.5 g/L was added in the membrane reactor. In the case of SMCAHS (**Figure 5.1b**), $FeCl_3$ was used as coagulant at a concentration of 0.5–1.0 mg Fe^{3+}/L. In SMCAHS, a lower PAC dose of 0.5 g/L was found to be sufficient from the preliminary experiments. Feed water to RO was pre-treated by the submerged membrane hybrid systems operated at a permeate flux of 20 $L/m^2 \cdot h$. Compressed air was supplied at the bottom of reactor to provide air scouring and to keep PAC in the suspension.



(A) SMAHS



(b) SMCAHS

Figure 5.1 Submerged membrane adsorption hybrid system (SMAHS) and submerged membrane coagulation–adsorption system (SMCAHS).

5.1.2.2 RO Membrane and Operation of a Cross-Flow Filtration Test Unit

Raw seawater (without any pre-treatment) and pre-treated seawaters by SMAHS (with a PAC dose of 1.5 g/L) and SMCAHS [with a PAC dose of 0.5 g/L and a $FeCl_3$ dose of 0.5 (or 1.0) mg Fe^{3+}/L] were used to evaluate the effect of pre-treatment in alleviating organic and biofouling potentials. The set-up and figure of RO used in this study is given in **section 3.2.2** in detail.

5.1.2.3 Analyses

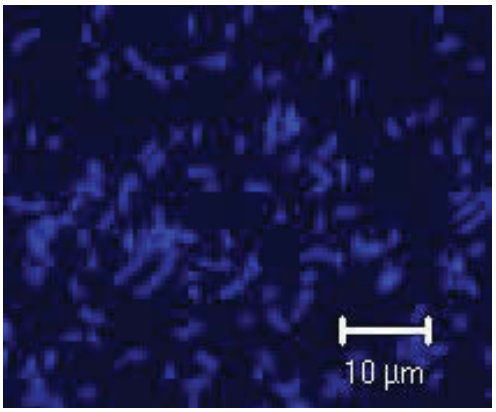
The seawater organic matter (SWOM) analysis is not straightforward. Only a few studies have reported on the specific methods used to measure the organic matter (Amy et al., 2011). In this study, specific organic compounds present in SWOM were measured quantitatively through liquid chromatography–organic carbon detector (LC–OCD), energy-dispersive X-ray spectroscopy (EDX) and EPS analyses. In addition, scanning electron microscope (SEM) and excitation emission matrix (EEM) for the pre-treatment with submerged membrane hybrid system were also carried out.

5.1.2.3.1 Assimilable Organic Carbon (AOC)

The biofouling potential was measured in terms of total and viable cell counts, ATP and AOC analyses. It should be noted that only the initial biofouling was studied. Only a handful of reference is available on these analyses for seawater (Vrouwenvelder et al., 2008), but there is no available reference for the pre-treatment used in this study. Furthermore, AOC test is not developed fully for seawater.

Thus, a new strain (*Pseudomonas sp.* P.60 isolated from the fouled RO membrane in the experimental site) was used this study. Assimilable organic carbon (AOC) is one of the best-known parameters used for the assessment of bacterial re-growth potential in drinking water (Van der Kooij et al., 1982). As an indicator of biofouling potential,

AOC was measured in feed water (seawater) prior to RO process. AOC assays typically measure growth of inoculums in a water sample from which the natural bacterial community has first been removed and inactivated through sterilisation. The inoculums grow until stationary phase (μ=0), with the assumption that the growing bacteria have assimilated all the AOC in the water. The net growth of the bacteria is measured and then converted to an AOC (or AOC equivalent) concentration.



Species	*Pseudomonas sp.* P60
Isolation	From seawater (Busan, Korea)
Nutritional Diversity	Amino acids, carboxylic acids, carbohydrates and ascorbic acid
Growth yield (Y)	3.2 X 10^4 cells/µgC-acetate

Figure 5.2 Model bacteria used in AOC assay.

In this study, AOC method was modified to apply to marine samples. In the modified method, samples were filtered through a 0.45-µm filter to remove particulate organic matters before autoclaving at 70 °C for 30 min to inactivate bacterial community. Then 10^4/mL of *Pseudomonas sp.* P60 isolated from fouled RO membrane (at a concentration of 10^4/mL) was spiked to acetate samples of different concentration (0, 0.1, 0.5, 1.0 and 2.0 µg/mL; stock solution—200 mg/L, 0.1 L) to measure AOC using growth yield factor obtained from standard growth curve (Eq. 5.1 and **Figure 5.2**). The samples were incubated at 25 °C (based on membrane system operation temperature) for 5 days and then monitored over time until peaks become stationary. Total cell number was counted by using DAPI dye and CLSM over the time (0, 12, 24, 36, 48, 60, 72, 96 and 120 h).

5.1.2.3.2 Fouled RO Membrane Characterization

Field emission scanning electron microscope (FE-SEM S-4700; Hitachi Corp., Japan) was used to investigate the clean and fouled membrane morphology and to observe the membrane fouling. The virgin (clean) and fouled RO membrane surfaces were analysed for functional groups using attenuated total reflection–Fourier transform infrared spectroscopy (ATR–FTIR). Details of RO membrane autopsy can be found in **section 3.3.3**.

5.1.3 RESULTS AND DISCUSSION

5.1.3.1 Effect of Dissolved Organic Carbon of Submerged Membrane Systems

Table 5.1 presents the removal efficiency of organic matter fractions by MF alone, SMAHS and SMCAHS from seawater.

Table 5.1 Removal efficiency of organic matter fraction by SMAHS and SMCAHS.

Sample	DOC	Hydro-phobic	Hydro-philic	Bio-polymer	Humics	Building Blocks	LMW Neutrals
Seawater (mg/L)[a]	1.45	0.59	0.86	0.13	0.45	0.19	0.09
Removal efficiency by MF(%)[b]	16.6	32.2	17.4	53.8	2.2	15.8	44.4
Removal efficiency by SMAHS (%)[b] (PAC 1.5g/L)	76.6	81.4	73.3	92.3	70.0	89.5	88.9
Removal efficiency by SMCAHS (%)[b] (PAC 0.5g/L + $FeCl_3$ 0.5 mg/L)	83.9	83.8	85.0	100.0	89.0	92.5	87.8

[a]: Concentrations of the different organic fractions in seawater.

[b]: Removal efficiencies of different organic fractions in seawater after the pretreatment.

The results show that MF alone removed only 16.6% of DOC. In particular, only a small portion of the hydrophilic organic matter was removed. The submerged membrane adsorption hybrid system (with 1.5 g/L of PAC addition), on the other hand, could remove 76.6% of DOC. Majority of hydrophilic fraction (73.3%) was found to be removed by SMAHS. The detailed analysis of hydrophilic portion showed that the removal efficiency of biopolymer, humics, building blocks and neutrals were as high as 92.3%, 70.0%, 89.5% and 88.9%, respectively. SMCAHS, which is the combination of coagulation process and SMAHS, led to remarkable improvement of DOC removal efficiency. Almost hydrophilic compounds considered as natural organic matter (NOM) was removed by SMCAHS (85.0%). Interestingly, biopolymer was completely removed from seawater with SMCAHS.

5.1.3.2 Effect of Pre-treatment using Submerged Membrane Hybrid Systems on RO Performance

The RO set-up is given in **section 3.2.2** of **Chapter 3**. The performance of RO membranes without pre-treatment and with pre-treatment (by SMAHS and SMCAHS) was examined in terms of initial permeates flux ($J_{0)}$ and permeate flux decline (J/J_0). The experimental results show that the initial permeate flux of RO did improve marginally by 6.2 L/m^2·h (by SMAHS) and 13.9 L/m^2·h (by SMCAHS) when the seawater underwent pre-treatment using submerged membrane hybrid systems. The flux decline causes membrane fouling which depends on the composition of the feed water and hydrodynamic conditions. In this study, hydrodynamic conditions (pressure, circulation rate and operating temperature) of RO membrane experiments with raw seawater and pre-treated seawater were kept the same. Thus, flux decline is mainly associated with the feed water quality. After 45-h operation, the permeate flux (filtration flux) decreased to about half of initial flux (J/J_0=0.49) when raw seawater was filtered directly. The reduction in permeate flux with pre-treated seawater was found to be much lower (**Figure 5.3**).

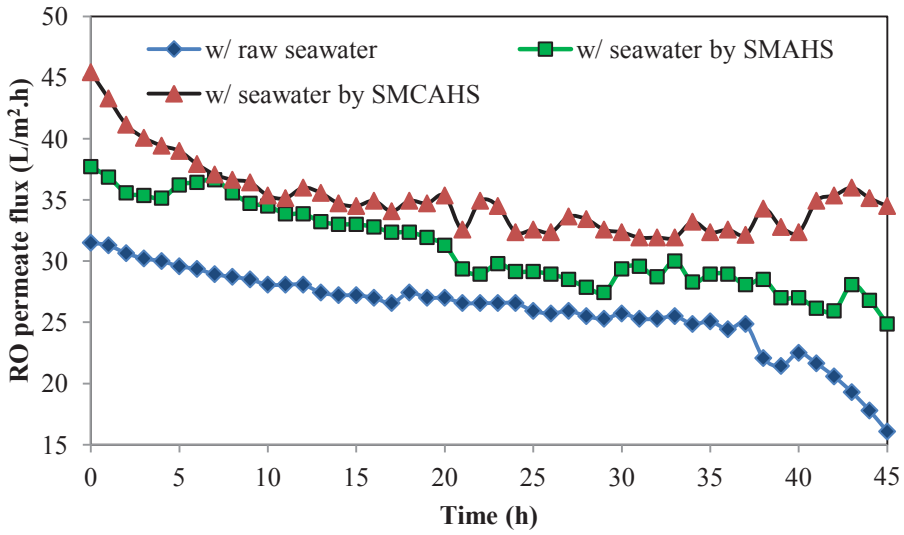


Figure 5.3 RO permeate flux reduction: Initial flux (flux decline; J/J_0) - w/raw seawater = 31.5 $L/m^2.h$ (0.49), w/seawater by SMAHS = 37.7 $L/m^2.h$ (0.34), w/seawater by SMCAHS = 45.4 $L/m^2.h$ (0.24).

This phenomenon can be explained in terms of reduction of DOC. The influence of hydrophilic organic substances such as biopolymers and humics on fouling potential is dominant. The removals of biopolymer and humics were 92.3% and 100%, and 70.0% and 89.0% with the pre-treatments of SMAHS and SMCAHS, respectively. The removals of these substances were only 53.8% and 2.2% with the MF alone as pretreatment (**Table 5.1**).

Since the seawater used in this study has already been filtered through a large pore filtration system (70 μm), the effect of large suspended particles on fouling was little. A parallel fouling index experimental study conducted with seawater collected from Chowder Bay, Sydney with the same pre-treatment of submerged membrane hybrid system showed that the fouling mainly occurred through organic matter (**sections 4.1** and **4.5** of **Chpater 4**). The ultrafilter-modified fouling index (UF-MFI) value of raw seawater was 14,165 s/L^2. It fell to 2,886 and 2,966 s/L^2, respectively, when the

seawater was pre-treated by SMAHS and SMCAHS. When the seawater was filtered directly through submerged microfiltration, the UF-MFI declined to only 7,730 s/L^2. Therefore, the contribution to colloidal matter in the fouling process is only partial.

5.1.3.3 RO Membrane Foulant

After 45 h of operation the RO membrane was cut into small pieces for further analysis. The foulant on the membrane was extracted using mild sonication for a short time to prevent any biological interaction.

EEM spectrum of the foulant indicated the organic matter in samples (see **section 3.3.1.4.3** and **Table 3.4**). In the RO foulant with pre-treated seawater with SMAHS, humic-like peaks (A and M) did not appear and T peak was also relatively weak.

When RO was filtered with seawater pre-treated by SMCAHS, B peak diminished and only T peak was present in foulant (**Table 5.2**). A remarkable organic and biofouling reduction occurred when seawater was used after pre-treatment with SMAHS and SMCAHS.

Table 5.2 EEM peaks descriptions of foulant.

Samples	Peak designation	Chemical functionality
Foulants on RO with raw seawater (without any pretreatment)	A, M, T, and B	UV-humic-like, Visible marine humic-like, Tryptophan-like, Protein-like, Tyrosine-like, Protein-like
Foulants on RO with pre-treated seawater by SMAHS	T and B	Tryptophan-like, Protein-like, Tyrosine-like, Protein-like
Foulants on RO with pre-treated seawater by SMCAHS	T only	Tryptophan-like, Protein-like

ATR–FTIR analysis investigated the functional groups in the foulants on the virgin and fouled RO membrane surfaces. Some peaks which may have originated from the EPS functional group were found in both fouled membranes, but there were differences in patterns. Both fouled membranes had two peaks in common, aliphatic C–H stretching at 2,920 cm^{-1} and OH stretching, N–H stretching at 3,428 cm^{-1}. However, in foulants with raw seawater, there were carboxylic acid (C–O) at 1,258 cm^{-1}, amide I of protein (−C=O) at 1,631 cm^{-1} and N–H stretching vibration at 2,430 cm^{-1}. With seawater pre-treated by SMCAHS, FTIR peaks of foulants were almost similar as those of virgin RO.

5.1.3.4 Microbial Study

5.1.3.4.1 Total Direct Cell / Viability

In raw seawater, the total direct cell was $5.10E^{+06}$ cells/mL but after the pre-treatment of SMAHS, the cell number fell to $3.10E^{+03}$ cells/mL (which corresponds to 99.94% removal).

Pre-treatment by SMAHS and SMCAHS also reduced the cell viability (live cell proportion) in seawater. This cell viability was reduced from 0.56 (live cell:dead cell = $2.90E^{+06}$:$2.20E^{+06}$) in raw seawater to around 0.30 in both pre-treated seawaters. This outcome shows that the seawater after pre-treatment by SMAHS and SMCAHS had less biofouling potential.

5.1.3.4.2 ATP Concentration

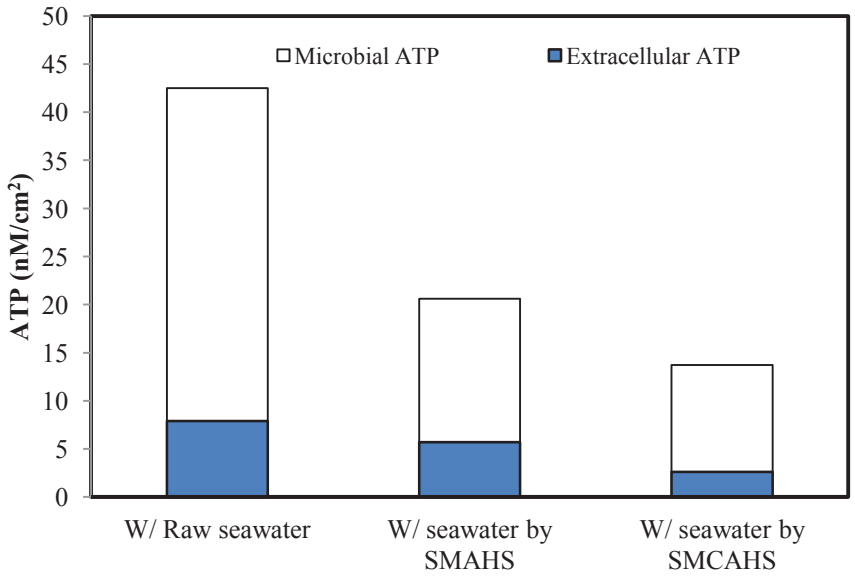


Figure 5.4 ATP concentrations of the RO foulant (Microbial and Extracellular ATP).

ATP is generally considered to indicate live biomass (Veza et al., 2008; Vrouwenvelder et al., 2008). In this study, total ATP was separated into two different portions of microbial and extracellular ATP using sterilised 0.2-μm filter. ATP concentration has a direct correlation with the cell viability in feed water samples. The results show that after pre-treatment by SMAHS, extracellular ATP concentration was similar to that of raw seawater but microbial ATP of pre-treated seawater (0.0582 nM) was less than that of raw seawater (0.0936 nM). The microbial ATP concentrations in the fouled RO membrane with pre-treated seawaters (SMAHS=14.9 nM/cm^2 and SMCAHS=11.1 nM/cm^2) were smaller compared to the fouled membrane with raw seawater (34.6 nM/cm^2) (**Figure 5.4**).

5.1.3.4.3 Modified AOC Test

AOC refers to a fraction of the total organic carbon (TOC) which can be utilised by specific strains or defined mixtures of bacteria, resulting in an increase in biomass concentration that is quantified. A specific bacterium, *Pseudomonas sp*. P60, which was isolated from fouled RO membrane by seawater, was used in this study. *Pseudomonas sp*. P60 was found as one of the dominant culture causing biofouling on RO membrane in seawater (Lee and Kim, 2011). The culture was prepared by incubation in nutrient broth (BD, USA) at 25 °C for 24 h. Seawater and pretreated water samples were pasteurised at 70 °C for 30 min and filtered through a 0.2-um membrane filter prior to use (Advantec, Japan).

Growth yield factor (Y) of *Pseudomonas sp.* P60 was calculated using the following equation:

$$Y\left(\frac{cells}{\mu gC - acetate}\right) = \frac{N_{\max} - N_0}{S_1 - S_0} \tag{5.1}$$

Here, N_0: initial cell concentration, N_{max}: maximum cell concentration, $S_1 - S_0$: consumed substrate concentration.

There is no fixed and representative AOC test for seawater. Consequently it was required to be modified to suit seawater analysis. A new strain of *Pseudomonas sp.* P.60 obtained from fouled RO membrane in the experimental site was used as a preliminary protocol in this study. The growth yield factor was found to be 3.2×10^4 cells/C-acetate. The stationary phase was observed after 3 days. AOC value of raw seawater was 24.2 µg/L C-acetate, and this value reduced to 14.1 µg/L C-acetate after SMCAHS pre-treatment (**Table 5.3**). It should be noted that AOC with milli-Q water itself as a control was 11.1 µg/L C-acetate due to pre-adsorption of nutrients onto bacteria. Therefore this reduction can be considered to be significant. This AOC measurement should be treated as a preliminary step as this method needs to be developed and tested with a wide variety of seawaters.

Table 5.3 Assimilable organic carbon (AOC) concentrations of feed waters.

Feed water samples	AOC (µg/L C-acetate)
Raw seawater	24.2
Seawater by SMCAHS	14.1
Control (Milli-Q)	11.1

5.1.4 SUMMARIZING THE SMHS AS PRETREATMENT

The submerged membrane systems coupled with PAC adsorption and/or $FeCl_3$ coagulation could significantly reduce the organic matter in seawater, especially the biopolymer and humics in hydrophilic parts. This led to a less permeate flux decline in RO operation. A smaller amount of foulants is found on the fouled RO membrane (consisting of a smaller amount of biopolymer) after this pre-treatment. Moreover, after the pre-treatment of submerged membrane hybrid systems, bacteria cell number and cell viability declined significantly by coupling with physico-chemical treatment such as coagulation and adsorption. Based on the microbial ATP, cell activities on the fouled RO membrane were also deactivated by both pre-treatments to a certain extent. The results of this study show the ability of the submerged membrane hybrid system to function as a pre-treatment strategy in reducing the biofouling potential.

5.2 APPLICATION OF THE MEMBRANE FOULING MODEL FOR SMHS USED AS A PRETREATMENT TO SEAWATER DESALINATION

5.2.1 INTRODUCTION

Basically, the small molecular species that are not usually rejected by the MF membrane alone are absorbed by the PAC and coagulated by ferric chloride in the membrane hybrid system. These pretreatments convert dissolved organic matter to a particulate phase ($FeCl_3$ flocs incorporating organics and organic adsorbed onto PAC) which can subsequently be easily rejected by the membranes. This hybrid system can offset the disadvantage of the large equipment size and space requirement where adsorption and coagulation are applied in a traditional way, as membranes provide more efficient separation of treated water than other traditional filtration processes. Moreover, the adsorption and coagulation pretreatments ensure high pollutant removal while the low pressure MF process only requires relatively low energy (Guo et al., 2005; Yang and Kim, 2009). Air bubbling is applied to the hybrid membrane reactor to provide mixing and introduce shear at the membrane surface in order to reduce particle deposition on the membranes. It can minimize reversible fouling and ensure a sustainable operation (Bouhabila et al., 2001; Meng et al., 2008).

In this study, three different configurations of SMHS namely submerged membrane coagulation hybrid system (SMCHS), submerged membrane adsorption hybrid system (SMAHS) and submerged membrane coagulation-adsorption hybrid system (SMCAHS) were tested using real seawater. Their performances were evaluated in terms of trans-membrane pressure (TMP) development; critical flux; ultrafilter modified fouling index (UF-MFI); and dissolved organic carbon (DOC) removal efficiency and detailed organic fractions. Three different filtration models were used to study the fouling behavior of these systems.

5.2.2 EXPERIMENTS

5.2.2.1 Optimum dose of additives

The optimum doses of $FeCl_3$ and PAC were determined in the author's previous studies (**sections 4.1** and **4.5** of **Chapter 4**). Here the suitable doses of additives ($FeCl_3$ and PAC) in SMCAHS were determined in terms of organic removal efficiency. In order to alleviate the adverse effects of chemicals and to increase economic feasibility, relatively low concentrations of 0.5 mg of Fe^{+3}/L, 1.0 mg of Fe^{+3}/L and 1.5 mg of Fe^{+3}/L were trialed. Batch flocculation experiments were conducted by mixing seawater with known concentrations of $FeCl_3$ for 1 minute of rapid mixing at 120 rpm, followed by 20 minutes of slow mixing at 30 rpm, and 30 minutes of settling. The supernatant was taken for a subsequent adsorption experiment with PAC. Different concentrations of PAC (0.5g/L, 1.0g/L and 1.5g/L) were added to the above supernatant sampled after flocculation and they were agitated on the shaker at 120 rpm for 48 h at the room temperature of 25°C.

To study the effect of combining PAC adsorption and ferric chloride flocculation, the above samples after adsorption with PAC were taken for detailed organic fraction analyses using LC-OCD (see the **sections 3.3.1.1.1** and **3.3.1.1.2**).

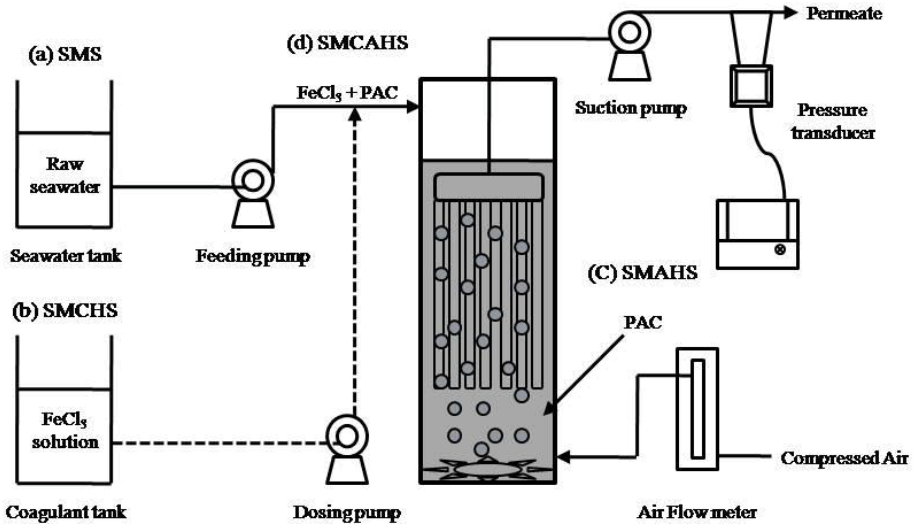


Figure 5.5 The figure of SMHS in TMP studies (a: SMS, b: SMCHS, c: SMAHS and d; b+c: SMCAHS).

Table 5.4 SMHS types and operation conditions.

Types of SMHS	Treatments	Applied flux (LMH)
SMS (a)	MF alone	15 ~ 30
SMCHS (b)	$FeCl_3$ 3.0 mg/L	20, 45 ~ 60
SMAHS (c)	PAC 1.5 g/L	20, 35 ~ 50
SMCAHS (d; b+c)	$FeCl_3$ 0.5 mg/L + PAC 0.5 g/L	20, 35 ~ 75

5.2.2.2 Submerged membrane hybrid systems (SMHSs)

The experiments were carried out using hollow fibre microfiltration submerged in a reactor (**Figure 5.5**). The effective volume of the reactor was 6 L and air was supplied from the bottom of the reactor at a pre-determined aeration rate of 1 L/min. It corresponded to the air flow rate as Specific Aeration Demand (SADm) of 1.36 $m^3/(m^2$ membrane area · h). In this study, the air bubbling has a dual function. The first is to provide the shear stress on the membrane to minimize membrane fouling and chemical cleaning (Judd, 2008). Another purpose is to mix chemicals with seawater in SMHSs (Smith et al., 2005). In the dead-end mode, continuous air sparging may generate a more cohesive cake by transporting biopolymers to the membrane surface. However, it may not have an effect in this study as chemicals are used to protect the membrane surface from the initial cake formation. A number of studies have been done on the impact of aeration rate on membrane fouling (Ueda et al., 1997; Johir et al., 2011). They state that there is no effect of aeration on membrane flux above the critical rate of aeration. The critical aeration rates that have been reported were in the range of 0.0048–0.010 $m^3/m^2 \cdot s$ (for MLSS concentrations varying from 2–10 g/L and flux of 10–20 $L/m^2 \cdot h$). The aeration rate used here was 0.0011 $m^3/m^2 \cdot s$ which is an acceptable value reported in other studies. Here the aeration rate velocity is the aeration intensity which is defined as the air flow/unit floor area in Nm^3 air per m^2 cross-section per s unit time.

Permeate was pumped out using a peristaltic pump at constant flux. A pressure transducer (Cole-Parmer Ins.) was installed on the permeate line to monitor the trans-membrane pressure (TMP) automatically every 5 min. Imposed (applied) flux was increased by 5 $L/m^2.h$ (LMH) each time and it was operated for 4 h (240min) at each flux. Types of treatment, operation conditions and applied fluxes for each treatment are shown in **Table 5.4**.

5.2.3 FILTRATION MODEL

Three membrane fouling models have been used to explain the trans-membrane pressure increase associated with particle deposition during membrane filtration process. They are the pore blockage, pore constriction, and cake formation models (Granger et al., 1985; Ward, 1987). The following two assumptions were used in the model derivation. Firstly, it was assumed that particle deposition occurs only when the operating permeate flux J(t) exceeds the critical flux (J_c). Secondly, only one of the fouling models was predominant in each case. This assumption is justified in the author's study is by determining the major fouling mechanism; the fouling models may be applied using either of two methods. Firstly, the model can be used to find the system parameters including critical flux and the model constant by fitting the model with experimental data. Secondly, from the model parameters and model equation obtained via fitting, the trans-membrane pressure profile can be predicted under various operating conditions. The fouling models' performances were evaluated based on a comparison of the predicted and experimental trans-membrane pressure. Assessment of the fouling models was done based on the most widely used criterion, the root mean square error (RMSE).

5.2.3.1 Pore blockage model

Pore blockage, which contributes significantly to membrane fouling during the blockage of the membrane pores, occurs when the particles are approximately the same size as the membrane pores. When pore blockage is present, the trans-membrane pressure increases rapidly. The separation properties are mainly determined by the membrane. The operating flux can be calculated as a function of total filtration resistance $R_t(t)$ using Darcy's law:

$$J = \frac{\Delta P(t)}{\mu R_t(t)} \tag{5.2}$$

where $\Delta P(t)$ is the trans-membrane pressure and μ is the solution viscosity. In the pore blockage model, the rate of change in the membrane area blocked by particles is assumed to be directly related to the rate of particle convection to the membrane surface. Thus the membrane area blocked by particles is:

$$A_b = \alpha(J - J_c)C_b t \tag{5.3}$$

where A_b is the membrane area blocked by particles, α is the complete blockage model constant, J is the operating flux, J_c is the critical flux, C_b is the concentration of deposits in bulk phase and t is the operating time. Thus, the ratio of the membrane area blocked by particles is:

$$\frac{R_t(t)}{R_t(0)} = \left(1 - \frac{A_b}{A_m}\right)^{-1} = \left(1 - \frac{\alpha(J - J_c)C_b t}{A_m}\right)^{-1} \tag{5.4}$$

where A_m is the initial membrane area. Rearranging Eq. (5.4), $R_t(t)$ is:

$$R_t(t) = R_m\left(1 - \frac{\alpha(J - J_c)C_b t}{A_m}\right)^{-1} \tag{5.5}$$

where $R_m = R_t(0)$ is the intrinsic membrane resistance. Substitution of Eq. (5.5) into Eq. (5.2) yields

$$J = \frac{\Delta P(t)}{\mu R_m}\left(1 - \frac{\alpha(J - J_c)C_b t}{A_m}\right) \tag{5.6}$$

and then rearranging Eq. (5.6), $\Delta P(t)$ is:

$$\Delta P(t) = P_0\left(1 - \frac{\alpha(J - J_c)C_b t}{A_m}\right)^{-1} \tag{5.7}$$

where $P_0 = \mu R_m J$ is the initial trans-membrane pressure.

5.2.3.2 Pore constriction model

Pore constriction is possible only for membranes with relatively large pores that are easily accessible to the particles. Fouling consists of pore constriction involving the adsorption of particles onto the membrane's surface. The extent of this mode of membrane fouling is highly dependent on the morphology of the membrane. In the pore constriction model, a change in deposited mass over time can be derived from the mass balance as:

$$-\frac{1}{\rho_d}\frac{dm_d}{dt} = N\left(2\pi r_p\right)\delta\frac{dr_p}{dt} \tag{5.8}$$

where m_d is the deposited mass of foulants, N is the number of pores on the membrane, δ is the pore length, r_p is the pore radius and ρ_d is the density of the deposit. By integrating Eq. (5.8), the reduction of pore is:

$$\frac{r_p(t)}{r_{p,0}} = \left(1 - \frac{m_d}{\pi N \delta \rho_d}\right)^{1/2} = \left(1 - \beta m_d\right)^{1/2} = \left(1 - \beta(J - J_c)C_b t\right)^{1/2} \tag{5.9}$$

where β is the pore constriction model constant, $r_{p,0}$ is the pore radius before fouling and m_d is assumed to be directly related to the rate of particle convection to the membrane surface.

Using the Hagen-Poiseuille's equation and Darcy's law, the permeate flux is:

$$J = \frac{1}{A_m}\frac{\pi r_{p0}^4 N}{8\mu\delta}(\Delta P(0)) = \frac{\Delta P(0)}{\mu R_t(0)} \tag{5.10}$$

where $\Delta P(0)$ is the initial trans-membrane pressure and $R_t(0)$ is the initial filtration resistance. Thus, the initial filtration resistance $R_t(0)$ is proportional to r_{p0}^{-4}. Thus, the ratio of the filtration resistance is:

$$\frac{R_t(t)}{R_t(0)} = \left(\frac{r_p(t)}{r_{p,0}}\right)^{-4} \tag{5.11}$$

substitution of Eq. (5.9) into Eq. (5.11) yields

$$R_t(x,t) = R_m\left(1-\beta(J-J_c)C_b t\right)^{-2} \tag{5.12}$$

substitution of Eq. (5.12) into Eq. (5.2) yields

$$J = \frac{\Delta P(t)}{\mu R_m}\left(1-\beta(J-J_c)C_b t\right)^2 \tag{5.13}$$

and then rearranging Eq. (5.13), $\Delta P(t)$ is

$$\Delta P(t) = P_0\left(1-\beta(J-J_c)C_b t\right)^{-2} \tag{5.14}$$

5.2.3.3 Cake formation model

Cake formation appears to have a significant effect on the increase in trans-membrane pressure during the formation of cake layers on the membrane surface. This effect tends to occur when the particle forms aggregates. These aggregates are essentially particles that have flocculated and that deposited on the surface of the membrane, forming a cake layer. In the cake formation model the total filtration resistance increased due to the presence of a cake layer on the membrane surface. The total filtration resistance, $R_t(t)$ will be the sum of the intrinsic membrane resistance (R_m) and the cake resistance ($R_c(t)$). Thus, the total filtration resistance is:

$$R_t(t) = R_m + R_c(t) \tag{5.15}$$

substitution of Eq. (5.15) into Eq. (5.2) and then rearranging Eq. (5.2), $\Delta P(t)$ is

$$\Delta P(t) = \mu R_m J + \mu R_c(t) J = P_0 + \mu R_c(t) J \tag{5.16}$$

Based on the concept of critical flux, Eq. (5.16) can be rewritten as follows;

$$\Delta P(t) = P_0 + \mu R_c(t) J (J - J_c) \tag{5.17}$$

The cake resistance, R_c is assumed to be directly related to the rate of particle convection to the membrane surface.

$$R_c(t) = \gamma (J - J_c) C_b t \tag{5.18}$$

where γ is the cake formation model constant. Substitution of Eq. (5.18) into Eq. (5.17) yields

$$\Delta P(t) = P_0 + \gamma (J - J_c)^2 \mu C_b t \tag{5.19}$$

5.2.4 RESULTS AND DISCUSSION

5.2.4.1 The determinations of optimum doses

As shown in **sections 4.1** and **4.5** of **Chapter 4**, $FeCl_3$ as ferric concentration of 3.0 mg/L and PAC concentration of 1.5 g/L were optimum doses for removing organic matter. Adsorption capacity of PAC with DOC estimated by the Sips model was found to be 23.1 mg/g. Details on organic fractions removed by ferric chloride (flocculation) and PAC (adsorption) are reproduced in **Table 5.5**. It can be seen from this result that flocculation by $FeCl_3$ removed most of the hydrophobic organic compounds (95%) whereas hydrophilic organic removal by PAC adsorption was more dominant due to the polar oxygen groups present on the surface of the carbon.

Table 5.5 Organic removals of $FeCl_3$ and PAC at optimum doses.

	Seawater		$FeCl_3$ (3.0 mg Fe^{3+}/L)		PAC (1.5g/L)	
	mg/L	%	mg/L	%	mg/L	%
DOC	1.29	100	0.56	57	0.38	71
Hydrophobic	0.46	36	0.02	95	0.15	68
Hydrophilic	0.83	64	0.54	35	0.23	72
Biopolymer	0.13	10	0.05	69	0.02	85
Humic	0.44	34	0.36	18	0.10	77
Building blocks	0.16	12	0.13	18	0.04	75
Neutrals	0.09	7	0.00	100	0.01	89

The above results suggested that the combination of both flocculation and adsorption could lead to superior removal of both hydrophilic and hydrophobic compounds. In addition, lower doses of flocculant and adsorbent are sufficient when both flocculation and adsorption are applied simultaneously. Thus, here the lower concentrations of ferric chloride were 0.5, 1.0 and 1.5 mg of Fe^{3+}/L followed by PAC doses of 0.5, 1.0 and 1.5 g/L were tested.

Table 5.6 Concentration of different organic matter fractions after coagulation by $FeCl_3$ followed by adsorption by PAC.

Fe^{3+} dose (mg/L)	PAC dose (g/L)	DOC (mg/L)	HOC (mg/L) hydro-phobic	CDOC (mg/L) hydro-philic	Bio-polymer (mg/L)	Humic (mg/L)	Building blocks (mg/L)	LMW Neutrals (mg/L)
Sea Water	0	1.35	0.49	0.86	0.13	0.45	0.19	0.10
0.5	0	0.66	0.04	0.62	0.06	0.41	0.09	0.00
	0.5	0.23	0.04	0.19	0.01	0.13	0.04	0.00
	1.0	0.22	0.04	0.18	0.01	0.13	0.03	0.00
	1.5	0.19	0.03	0.16	0.01	0.13	0.02	0.00
1.0	0	0.64	0.04	0.60	0.06	0.42	0.04	0.00
1.5	0	0.61	0.03	0.58	0.05	0.41	0.03	0.00

The results of the combined flocculation and adsorption experiment with seawater are presented in **Table 5.6**. It was found that the DOC removal did not improve significantly with the Fe^{+3} doses when it was increased in the range of 0.5-1.5 mg/L. The DOC removal efficiency varied from 51.1 to 54.8% when the concentration of ferric increased from 0.5 mg/L to 1.5 mg/L. Most of the hydrophobic compounds (more than 91.8%) were removed at low concentration of ferric (**Table 5.6**).

After the addition of PAC, hydrophilic compounds of seawater reduced significantly. In particular a majority of biopolymer and humic substances which were not removed by flocculation were then removed by the adsorption with PAC. With low $FeCl_3$ and PAC concentrations of 0.5 mg/L and 0.5 g/L respectively, 83% of DOC of seawater was removed. The removal efficiency increased only slightly to 85.9% when the $FeCl_3$ dose was increased three-fold, from 0.5 mg/L to 1.5 mg/L. Thus, a $FeCl_3$ dose of 0.5 mg of Fe^{+3} /L and a PAC dose of 0.5 g/L were selected as suitable dosage in the subsequent experiment.

5.2.4.2 Organic removals by SHMS at different flocculation and adsorption conditions

Figure 5.6 shows the LC-OCD chromatograms with different submerged membrane hybrid systems at 20 LMH of filtration (permeate) flux. The detailed organic fractions are given in **Table 5.7**. The seawater used in this study comprises more hydrophilic compounds (more than 67% of seawater) than hydrophobic compounds. When the submerged membrane was used alone, as expected, there was almost no removal of DOC at 20 LMH. However, at 20 LMH, SMCHS led to a large amount of hydrophobic removal (71.1%). Also, a 60% removal of the neutral part (in **Figure 5.6**) with low molecular weight of less than 350 Da was observed. The SMAHS, on the other hand, could remove a larger amount of DOC (83.1% of hydrophobic and 61.3% of

hydrophilic compounds). The removal efficiencies of biopolymer, humics and building blocks by SMAHS were 84.4%, 76.6% and 71.4% respectively. When coagulation (by $FeCl_3$) and adsorption (by PAC) was dosed together, the removal efficiency of both hydrophobic and hydrophilic compounds was superior. The results indicated that SMCAHS was able to completely remove biopolymer (96.9%) and significant amount of humics (80.9%) and building blocks (75.0%) even with a smaller dose of $FeCl_3$ of 0.5 mg of Fe^{+3}/L and PAC of 0.5g/L.

The results show that ultrafilter modified fouling index (UF-MFI) values decreased remarkably. With SMS alone, UF-MFI decreased by only 45.4%, from 14,165 to 7,730 s/L^2. When SMCAHS was used, a much lower fouling was observed with a UF-MFI value of 2,966 s/L^2. As can be seen from **Table 5.7** and **Figure 5.6**, the difference between MF filtration and UF filtration by SMCAHS was marginal.

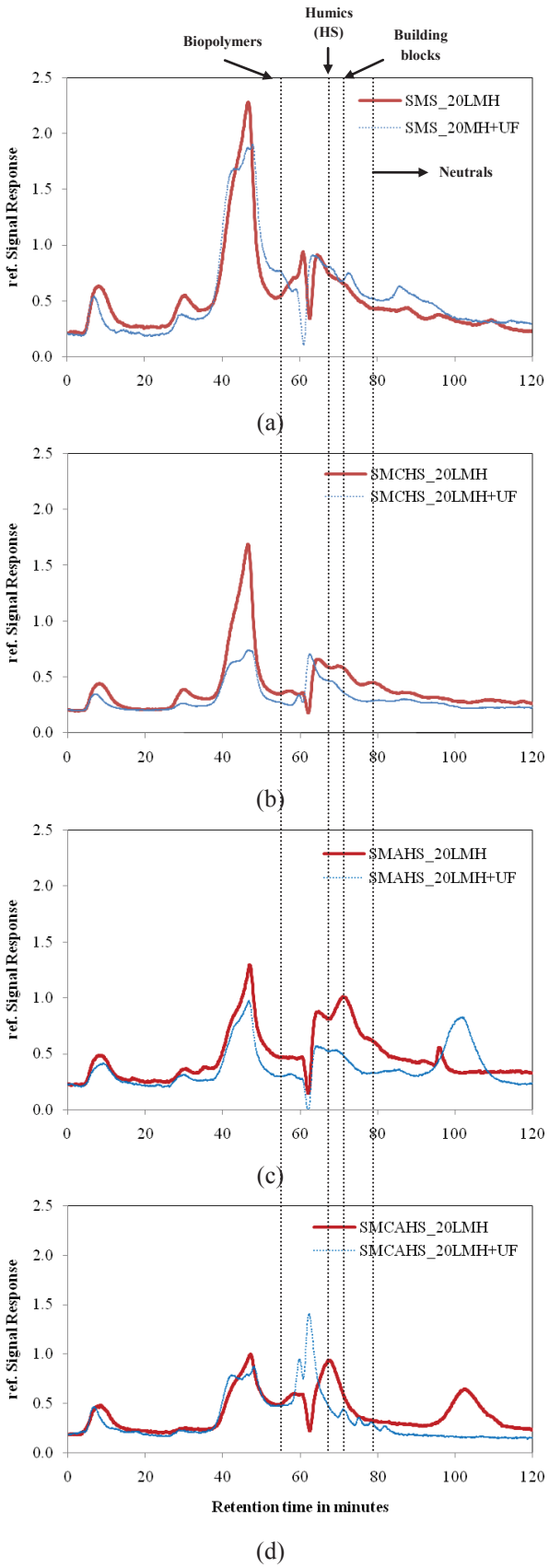


Figure 5.6 LC-OCD chromatograms at different SMHSs and after UF filtration (a: SMS, b: SMCHS, c: SMAHS and d: SMCAHS).

Table 5.7 The UF-MFI values and organic fractions after SMHSs at 20 LMH (a: SMS, b: SMCHS with Fe^{+3} of 3.0 mg/L; c: SMAHS with PAC of 1.5g/L; and d: SMCAHS with Fe^{+3} of 0.5 mg/L and PAC of 0.5 g/L).

Methods		UF-MFI (s/L^2)	DOC (mg/L)	Hydro-phobic (mg/L)	Hydro-philic (mg/L)	Bio-polymer (mg/L)	Humics (mg/L)	Building blocks (mg/L)	LMW Neutrals (mg/L)
Seawater	-	14,165	2.53	0.83	1.70	0.32	0.47	0.28	0.63
SMS	Conc.	7,730	2.26	0.72	1.54	0.30	0.47	0.20	0.57
	R %*		10.7	13.3	9.4	6.7	-	28.6	9.5
SMCHS	Conc.	3,241	1.06	0.24	0.82	0.14	0.32	0.11	0.25
	R %*		58.1	71.1	51.8	56.3	31.9	60.7	60.3
SMAHS	Conc.	2,886	0.79	0.14	0.65	0.05	0.11	0.08	0.38
	R %*		68.8	83.1	61.8	84.4	76.6	71.4	39.7
SMCAHS	Conc.	2,966	0.71	0.16	0.54	0.01	0.09	0.07	0.32
	R %*		72.0	80.7	68.2	96.9	80.9	75.0	49.2

*R%: Removal efficiency.

Figure 5.6 (a) shows the effluent quality after MF (or SMS) and after the MF and UF systems. This outcome indicated that the organics that were not removed by MF could not be significantly removed by subsequent pretreatment of UF. As such, UF did not play any major role in organic removal from seawater. On the other hand, the microfiltration (MF) hybrid systems themselves removed a significant amount of

organics. Organic removal by the hybrid system did not achieve much that was different when the UF was also employed (**Figure 5.6 (b), (c), (d)**). Due to low energy requirement and higher permeate flux, the experiment was restricted to the MF hybrid system. Especially, the UF filtration is not necessary to remove the remaining DOC when SMCAHS was used.

5.2.4.3 Fouling mechanism

In recent research it has been recommended to operate the membrane process under critical flux for filtration with no TMP development so that better stable water quality can be produced (Bonnélye et al., 2008). In this study, TMP development of each SMHS was measured with an increase of flux. In order to analyze the filtration characteristics of the MF membrane as a seawater desalination pretreatment in the presence of coagulant ($FeCl_3$) and absorbent (PAC), three kinds of membrane fouling models were tried to fit with the experimental results. In this study, FeCl3 and PAC were accumulated into reactor during operation but there was no effect of them since it was short-run. As was mentioned previously, critical flux (*Jc*) and the model constants were obtained by fitting the model with experimental data. Each system was operated at constant flux. The best fit was decided in terms of RMSE. The model parameters and RMSE values are presented in **Table 5.8**. *Jc* presents the critical flux estimated from model equation and α, β and γ represents the measure of the pore blockage efficiency, the pore constriction efficiency and specific cake resistance, respectively.

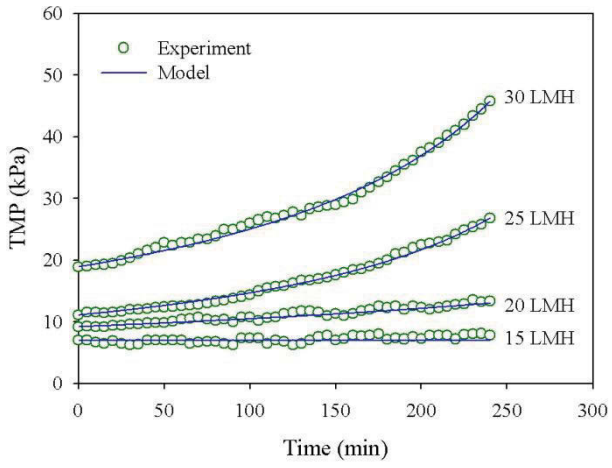
Firstly, models were applied to the MF filtration of seawater without any coupling of flocculation and adsorption with MF. **Figure 5.7** shows the experimental data and model predictions for SMS with seawater alone. The predominant membrane fouling mechanism was analysed in terms of RMSE. The results show that the pore blockage model matched well with the experimental data but pore constriction and cake

formation models could not fit the experimental data in an adequate manner. As shown in **Table 5.8**, the pore blocking model constant α, Jc and RMSE were determined as 129 m^4/kg, 15 LMH, and 1.78, respectively.

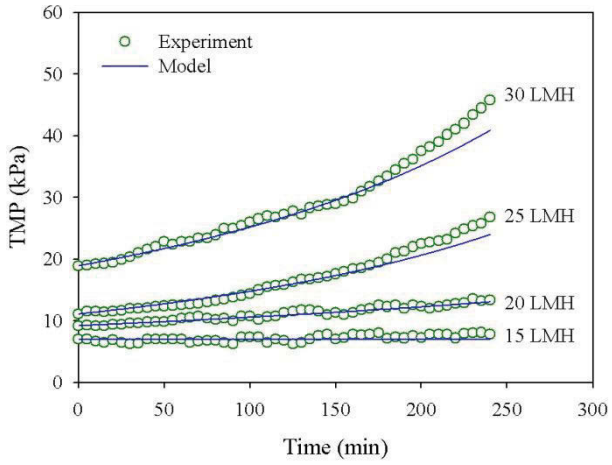
Figure 5.8 shows the experimental data and model fits for SMCHS (seawater with $FeCl_3$ coagulation). Contrary to the previous results with SMS alone with seawater, the cake formation model matched the experimental data better than standard blocking and complete blocking models. This result can be explained by increasing size of the particle (flocs) after the flocculation process. As shown in **Table 5.8**, the cake formation model showed the highest level of agreement among the three models. Cake formation model constants, γ and Jc and RMSE were determined to be $4.90x10^{16}$ m/kg, 56 LMH, and 1.90, respectively.

Table 5.8 Comparison of the model parameters.

		SMS	SMCHS	SMAHS	SMCAHS
Pore blockage	α (m^4/kg)	129	54.0	0.95	2.80
	J_c (LMH)	15	56	46	71
	RMSE	1.78	3.35	3.13	4.08
Pore constriction	β [m^2/kg]	1600	700	12.4	37.7
	J_c (LMH)	15	56	46	71
	RMSE	2.72	2.89	2.72	3.48
Cake formation	γ (m/kg)	$2.84x10^{16}$	$4.90x10^{16}$	$7.40x10^{14}$	$2.90x10^{15}$
	J_c (LMH)	15	56	46	71
	RMSE	5.01	1.90	1.65	2.20



(a)



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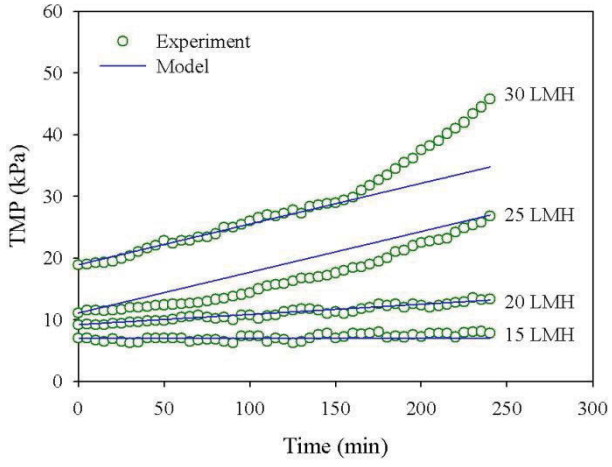


(c)

Figure 5.7 Comparison of the experimental data and model fits for SMH. (a) Pore blockage model; (b) Pore constriction model; and (c) Cake formation model

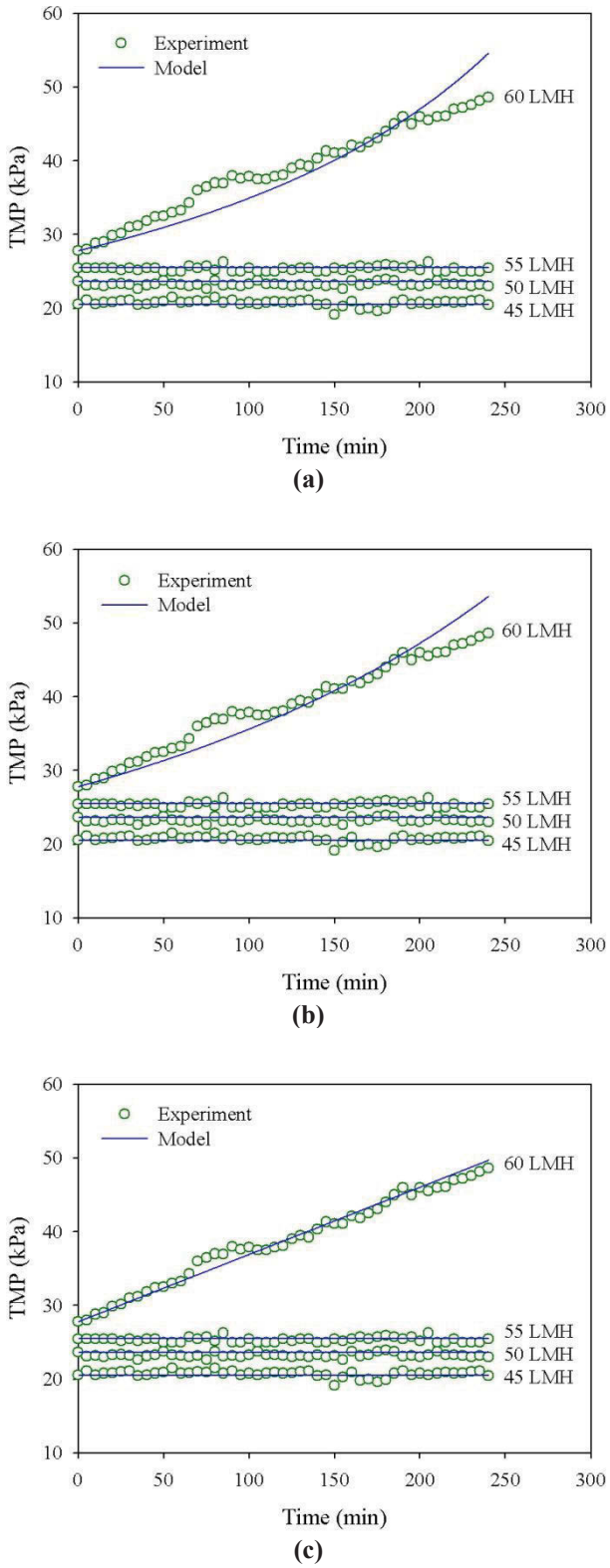
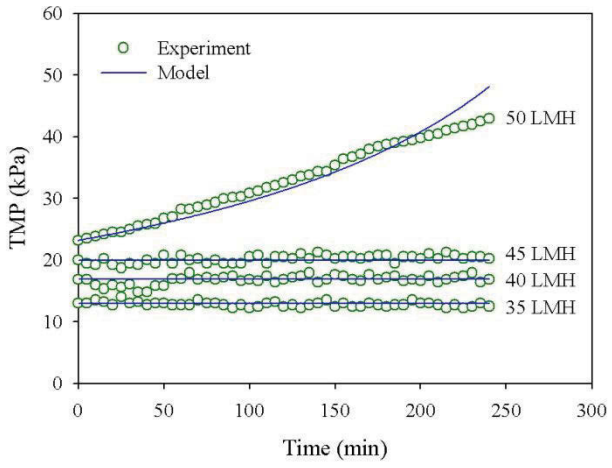


Figure 5.8 Comparison of the experimental data and model fits for SMCHS. (a) Pore blockage model; (b) Pore constriction model; (c) Cake formation model



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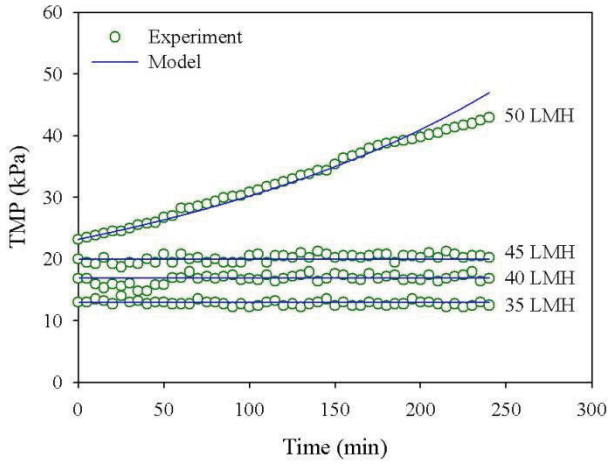

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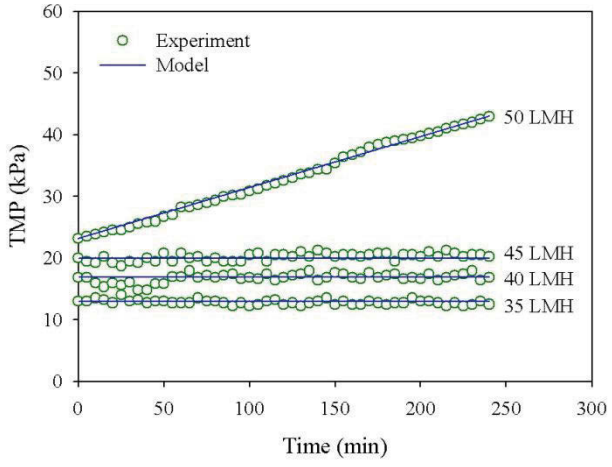
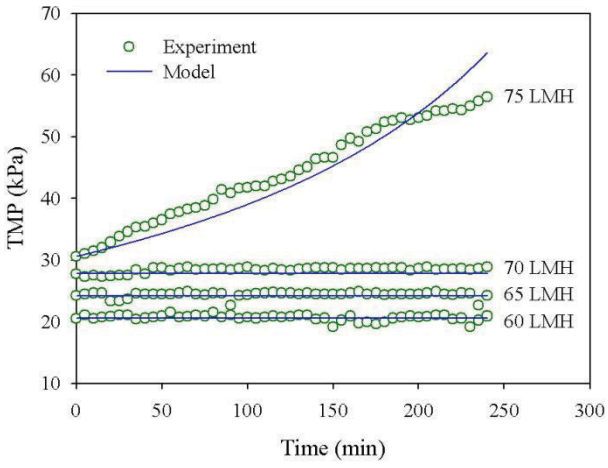
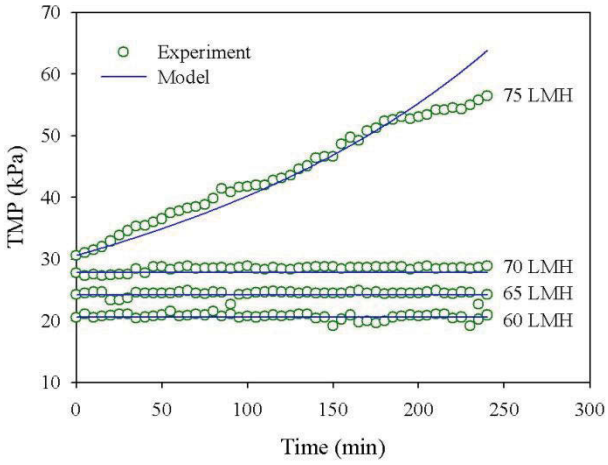


(c)

Figure 5.9 Comparison of the experimental data and model fits for SMAHS. (a) Pore blocking model; (b) Pore constriction model; (c) Cake formation model



(a)



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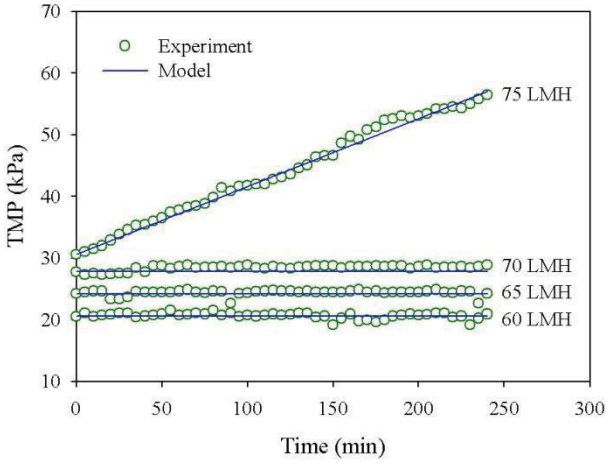


(c)

Figure 5.10 Comparison of the experimental data and model fits for SMCAHS. (a): Pore blocking model; (b): Pore constriction model; (c): Cake formation model

Figure 5.9 presents the model fitting results together with the experimental results of SMAHS. As expected, PAC absorbed the organics from seawater before the water came into contact with the MF which in turn reduced the pore blocking potential. Here too, cake formation model was the best with model constants, γ and J_c and RMSE were $7.4x10^{14}$ m/kg, 46 LMH, and 1.65, respectively.

Figure 5.10 shows the experimental data and model fits for SMCAHS (seawater with $FeCl_3$ and PAC). Again the cake formation model fitted the experimental data well. The cake formation model constants, γ and J_c and RMSE were determined to be $1.39x10^{12}$ m/kg, 71 LMH, and 3.67, respectively.

The difference in fouling mechanisms might have been also caused by the property of membranes surface (Lee et al., 2008). The membrane used in this study was hydrophobic PVDF and slightly hydrophilic by coating. Small particles and macromolecules in hydrophilic foulants in seawater such as biopolymer of more than 20,000 Da. could be attached on the membrane surface or pore itself. The pore size of this membrane was 0.1 μm so some of the foulants may not have passed through the membrane pores and may have blocked the pores of the membrane. Hong et al. (Hong et al., 2009) found that the membrane fouling could be explained by pore blockage and pore adsorption when the major foulants were smaller than the membrane pore size. When flocculation was used as a pretreatment, $FeCl_3$ could have entrapped the organics in the floc structure. At pH 8, the reduction of DOC by $FeCl_3$ coagulation was due to the attachment of humic macromolecules with the ferric hydrolysed species. Increase of particle size might be attributed to competition between re-conformation of humic chains around $FeCl_3$ species and collision of destabilised humic material (Jung et al., 2006; Sharp et al., 2006). This phenomenon could prevent pore deformation such as blockage and constriction. On the other hand, the adsorbent of PAC could absorb the

small organic molecules. This led to cake formation on the MF surface. PAC cake layer formation was affected by small particulates and metal ions in raw feedwater. Larger PAC could easily move the small particles in raw seawater into the void space in the PAC cake. The organics also become associated with the PAC particles due to the bridging effect, which in turn boosts the PAC cake fouling on the membrane surface (Zhao et al., 2005). As can be seen from the organic removal, PAC could alleviate a portion of hydrophilic fraction of organics in seawater. This led to fouling reduction on MF. According to the modelling results, incorporation of PAC and $FeCl_3$ simultaneously into the membrane tank could increase the critical flux as high as 71 LMH.

In order to present the superior performances of SMHSs used in this study calculated close to critical flux from the modelling, SMHSs were operated under the critical flux of each system. The performances were compared with SMS in terms of DOC removal and UF-MFI values. Based on the TMP experiments, it is clear that SMHSs can operate at a much higher critical flux (**Table 5.9**). Submerged membrane system (SMS) alone led to low critical flux of 20 LMH, inferior effluent quality and higher fouling potential (**Table 5.7**) while the hybrid systems (SMCHS, SMAHS, and SMCAHS) led to higher critical flux with superior quality permeate even at 45-65 LMH. The hybrid systems also led to less fouling potential.

Table 5.9 The UF-MFI values and organic fractions for each SMHS obtained close to critical flux (SMCHS with Fe^{+3} of 3.0 mg/L; SMAHS with PAC of 1.5g/L; and SMCAHS with Fe^{+3} of 0.5 mg/L and of PAC of 0.5 g/L).

Methods		UF-MFI (s/L^2)	DOC (mg/L)	Hydro-phobic (mg/L)	Hydro-philic (mg/L)	Bio-Polymer (mg/L)	Humics (mg/L)	Building blocks (mg/L)	Neutrals (mg/L)
Seawater	-	14,165	2.53	0.83	1.70	0.32	0.47	0.28	0.63
SMCHS at 55LMH	Conc.	5,595	1.58	0.32	1.26	0.19	0.39	0.20	0.30
	R %*	60.5	37.5	61.4	25.9	40.6	17.0	28.6	49.3
SMAHS at 45LMH	Conc.	3486	1.10	0.14	0.96	0.03	0.19	0.03	0.44
	R %*	72.8	56.5	83.1	43.5	90.6	59.6	89.3	30.2
SMCAHS at 65LMH	Conc.	3673	1.08	0.22	0.86	0.08	0.41	0.17	0.11
	R %*	71.3	57.3	73.5	49.4	75.0	12.8	39.3	82.5

5.2.5 SUMMARIZING THE FOULING MODELS

Submerged microfiltration hybrid system (SMHS) was trialled with $FeCl_3$ coagulation, PAC adsorption and combination with both coagulation and adsorption. Their performances were evaluated in terms of organic removal; ultrafilter modified fouling index (UF-MFI); and TMP development. The results led to the following conclusions:

(1) When $FeCl_3$ coagulation and PAC adsorption were combined, both hydrophobic and hydrophilic compounds could be removed at low doses of flocculant and adsorbent. In this study, the suitable doses of $FeCl_3$ and PAC were found to be 0.5 mg of Fe^{3+}/L and 0.5 g/L, respectively.

(2) After pretreatment by SMCAHS, more than 72% of DOC was removed, particularly a large amount of biopolymer and humics were removed even at low chemical doses. This led to significant reduction of the fouling potential.

(3) Among the three filtration models, cake formation was found to be dominant on SMHS. Very high critical flux was observed for the hybrid membrane system through TMP experiments and it could be predicted by the model.

(4) The application of the three afore mentioned fouling models based on the critical-flux concept created a better understanding of the membrane fouling characteristics of the MF membrane for seawater desalination pretreatment.

5.3 ORGANIC MATTER CHARACTERIZATION OF SMHS EFFLUENT

5.3.1 INTRODUCTION

Seawater organic matter (SWOM) is removed effectively by membrane hybrid systems; however, there is only limited information on the specific properties of SWOM in pretreated water by membrane hybrid systems. Dissolved organic matter which is ubiquitous in seawater is a mixture of compounds including humic substances, carbohydrates, proteins and a variety of acidic and lower molecular weight species (Huber et al., 2011). Different sophisticated analytical methods have been used during the last decades where insights into the compositions of SWOM have been developed. The characteristics of organic matter in seawater are different from those of wastewater or surface water. In the SWRO process, even though the organic concentration is very low (1-3 mg of dissolved organic carbon/L), it still causes severe RO fouling.

Since the early 1990s, fluorescence techniques (excitation-emission matrix; EEM) have been used to study the nature of seawater, drinking water and sewage (Sun et al., 2007; Wang et al., 2009). The prominent advantage of EEM fluorescence spectroscopy is that information regarding the fluorescence characteristics can be completely obtained by changing the excitation and emission wavelength simultaneously. Since DOM includes organic molecules with chromophoric (light absorbing) and fluorophoric (light emitting) moieties, EEM fluorescence spectroscopy is very useful for studying the physico-chemical characteristics of SWOM (Coble, 1996; Jiang et al., 2008).

In addition, if data on the structural features of SWOM are also available, one can understand the pretreatment process much better. For molecular and structural analysis, adequate extraction, isolation and separation techniques are important (Dittmar et al., 2008). Nuclear magnetic resonance (NMR) spectroscopy such as proton nuclear

magnetic resonance (^{1}H-NMR) has been used for decades to study the functional groups in SWOM (Ruggiero et al., 1980; Hatcher et al., 1980). The NMR technique is especially useful in combination with elemental composition, apparent molecular weight or infra-red spectroscopic data of identified SWOM. A recent innovation to the OM structure research is the introduction of high resolution liquid chromatography/ mass spectrometry (LC/MS). LC/MS such as quadrupole-time of flight and ion trap-time of flight is a technique that combines the physical separation capabilities of LC with the mass analysis capabilities of MS (Gonsior et al., 2011; Matilainen et al., 2011). The possibility of coupling the LC to an advanced technique called electrospray ionisation (ESI) with MS makes the requirement for derivatization of OM unnecessary. The ESI-MS is a better and more sensitive method in the characterisation of OM. For structural analysis using pyrolysis, macromolecules in SWOM are thermally broken down into more analytically available fragments. Pyrolysis combined with gas chromatography/ mass spectroscopy (Py-GC/MS) is a useful technique for obtaining structural information about molecular building blocks of SWOM (Andrew and Michael, 1985; Zen and Hatcher, 2002). Consequently the structural study of the pyrolysates can be of great importance.

The overall aim of this study is to characterize SWOM before and after pretreatment by SMHSs though advanced analytical techniques. In this study, different fractions and molecular weight distributions (MWD) of SWOM were measured using XAD resin, fluorescence spectroscopic and size exclusion methods. After proper SWOM isolation from salt, structure of SWOM was determined by using ^{1}H NMR, LC/MS-IT-TOF and Py-GC/MS. The results obtained from the characterization using different advanced analysis techniques can provide additional useful information and help in selecting suitable pretreatment methods.

5.3.2 MATERIALS AND METHODS

5.3.2.1 Submerged membrane hybrid systems (SMHSs)

In this study two submerged membrane hybrid systems (SMHSs) were used as pretreatment (**Figure 5.11**). In the submerged membrane coagulation hybrid system (SMCHS), $FeCl_3$ at a concentration of 3.0 mg of Fe^{+3}/L was added to the submerged membrane reactor. In SMCAHS system, both $FeCl_3$ (at a lower concentration of 1.0 mg of Fe^{+3}/L) and PAC (at a dose of 0.5 g/L) were added. The chemical doses were optimized as had been done in previous studies (**sections 4.1** and **4.5** of **Chpater 4**). $FeCl_3 \cdot 6H_2O$ was used as a coagulant and PAC served as an adsorbent in the SMHSs. The detailed characteristics of PAC can be found in **Table 3.3**. The detail of MF membrane used in this study is given in **section 3.1.2** of **Chapter 3**. Aeration was used to mix the chemicals with seawater before making contact with the membrane surface. The results of the preliminary study conducted showed that more than half of organic removal can be achieved at low $FeCl_3$ concentration (of 0.5 or 1.0 mg Fe^{+3}/L) (See **section 4.1** of **Chapter 4**). Hence, this study adopted a smaller dose of $FeCl_3$ in SMCAHS. The SMHSs were operated at a filtration (permeate) flux of 20 L/m^2h (LMH).

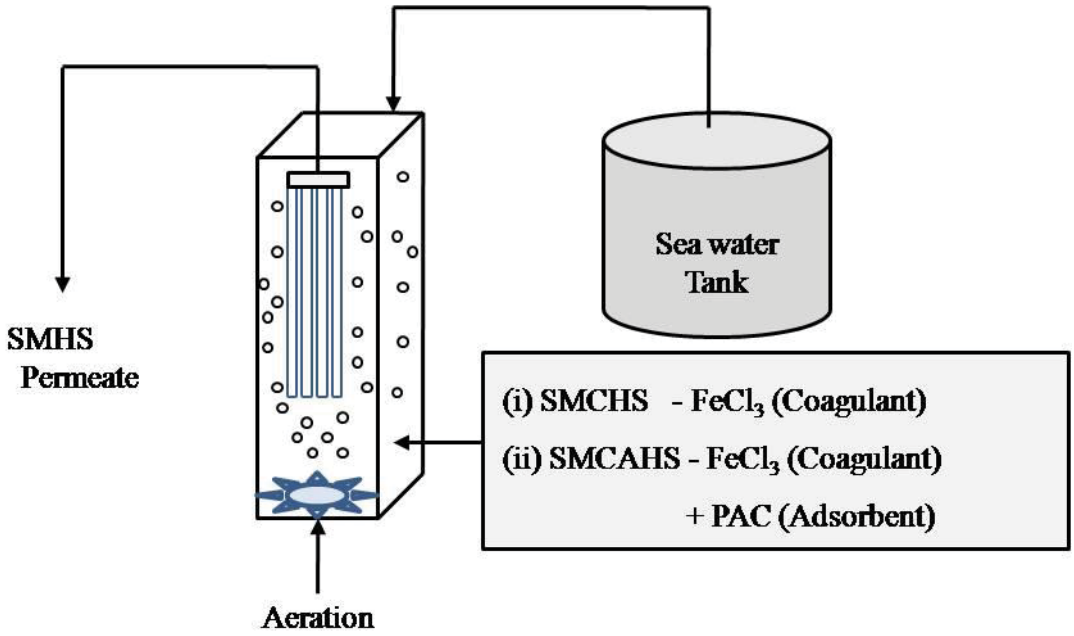


Figure 5.11 Flow diagram of SMHSs (SMCHS; submerged membrane coagulation hybrid system and SMCAHS; submerged membrane coagulation-adsorption hybrid system).

The pretreatment experiments were repeated and the values of organic characterization of effluents had a deviation of less than 5%. Therefore, mixed water samples were used for RO operations in this study. Additionally, all analyses (except for XAD fractionation) were triplicated and the mean values were used in this paper. Here again the deviation was less than 5%.

5.3.2.2 Isolation of SWOM

In order to obtain salt-free and concentrated samples for detailed analysis, SWOM was isolated using solid phase extraction (SPE). The isolation method suggested by Dittmar et al. (2008) was used with modification. This modification is not expected to show any adverse impact on the characterization of the SWOM compared to the established method. Samples were pre-filtered with 0.2 μm filter cartridges (Whatman). In order to prevent organic leaching from the membrane the filter was washed using MQ water several times prior to use. The filtrate (1 L) was acidified with hydrochloric acid (p.a. grade, Merck) to pH 2 and pumped through a 6.0 mL predetermined SPE cartridge (C18 Sep-Pac Vac, 6cc, 1.0g) at a flow rate of less than 2.0 mL/min. C18 Sep Pak used in SPE method was selected through the preliminary test with three different solvents such as Oasis HLB, C18 and silica. They were tested in terms of removal of salt and concentration of concentrated organics. Salt concentration was measured in terms of total dissolved solids (TDS) meter and it showed 99% removal. Organic concentration was determined using chemical oxygen demand (COD) for rapid checking. COD in concentrated SWOM was more than 40 times as that in raw seawater. The cartridges were then washed using acid (with pH 2 of HCl) and ultrapure water (Milli-Q). Immediately after extraction, SWOM was eluted with 6.0 mL methanol (Merck; LiChrosolv) into pre-combusted (5 h, 550°C) glass ampoules at a flow rate of 1.0 mL/min. The samples were stored in sealed ampoules under a nitrogen atmosphere at -18°C in a dark environment. Through this process around 99% salt rejection was achieved and more than 80 times concentration of SWOM.

5.3.3 RESULTS AND DISCUSSION

5.3.3.1 SWOM characterization of the pretreated seawater

The XAD resin fractionation result showed that a majority of hydrophilic compounds were composed of SWOM. The hydrophilic (HPI) was a dominant fraction (59.6%) in raw seawater (SW) of 2.38 mg DOC/L before treatment using SMHSs. The transphilic (TPI) and hydrophobic (HPO) fractions accounted for 26.5 % and 13.9% in raw SW, respectively.

5.3.3.2 SWOM fraction by XAD

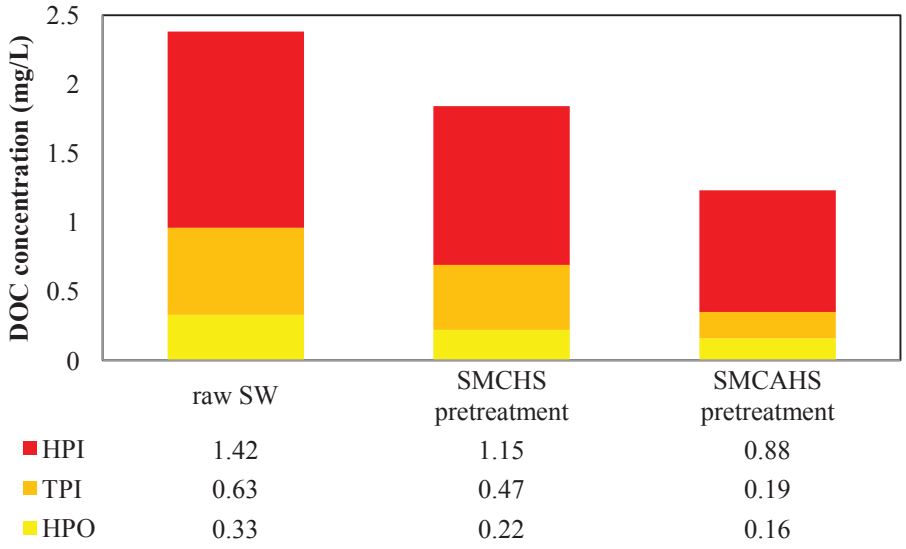


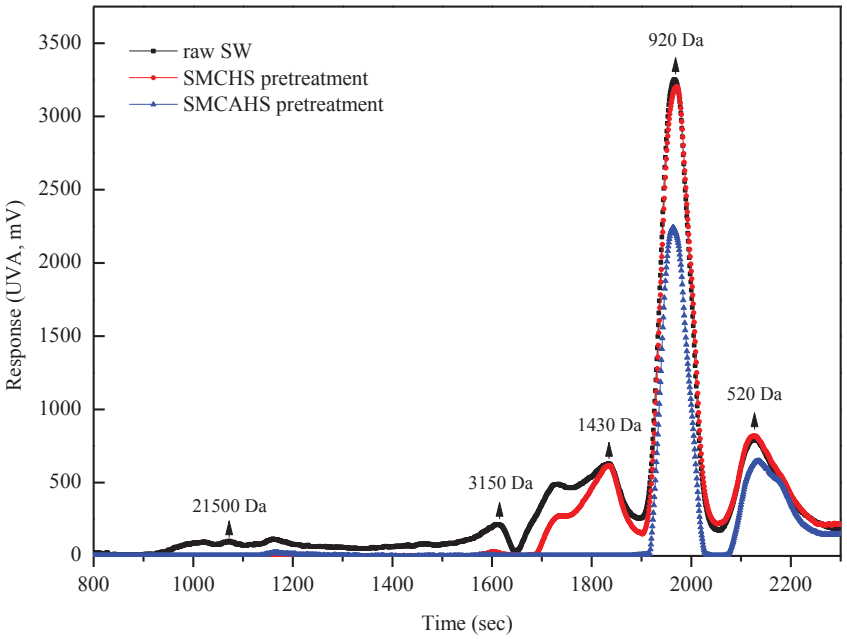
Figure 5.12 XAD fractionation of seawater and pretreated seawater (HPI: Hydrophilic, TPI: Transphilic, and HPO: Hydrophobic) (dissolved organic carbon concentration: raw SW = 2.38 mg/L, SMCHS pretreatment = 1.84 mg/L and SMCAHS pretreatment = 1.23 mg/L).

The HPI, TPI and HPO fractions of the SMHS effluents were investigated. The SWOM was reduced from 2.38 mg/L for raw SW to 1.84 mg/L and 1.23 mg/L after pretreatment using SMCHS and SMCAHS, respectively. This corresponds to a removal of 23% and 48% in each respective case. The PAC addition in SMCAHS led to an additional organic removal of 25%. XAD fractions of raw SW and pretreated SW are presented in **Figure 5.12**. The HPI fraction of raw SW was removed significantly at 19% and 38% respectively by SMCHS and SMCAHS pretreatment. Only 25% of TPI was removed by SMCHS whereas SMCAHS led to an appreciable TPI reduction of 70%. The HPO removal was 52% through SMCAHS pretreatment.

The removal trend for different molecular weight of organics was studied using liquid chromatography-organic carbon detector (LC-OCD) in a previous study (Penru et al., 2001). The difference of LC-OCD and XAD (as fractionated method of organic matter) is presented in **sections 3.3.1.1.1** and **3.3.1.4.1**. HPO are mainly composed of humic-like substances rich in aromatic moieties, whereas TPI and HPI are composed of low aromatic molecules with lower UV-absorbing character. Low molecular weight (LMW) neutrals and biopolymers were found to be exclusively hydrophilic (HPI). The proportion of HPO and HPI in humics was 21% and 62%, respectively. Building blocks comprised 89% of HPI and the remaining (11%) was TPI. Based on this observation the previous studies (see **sections 4.1 and 5.1**) in LC-OCD fractionation concluded that TPI was 15% of the total DOC. Based this finding, SMCAHS could remove a small amount of HPI containing LMW neutrals, biopolymers and some of humics and building blocks. In particular the building blocks and humics, which are mainly TPI portions, declined when PAC was added.

5.3.3.3 Molecular weight distribution (MWD)

To better understand the membrane fouling caused by SWOM and evaluate the performance of the pretreatment by SMHSs, it is essential to analyze the MWD of SWOM before and after the pretreatment by SMHSs. The MW peaks of raw SWOM ranged from approximately 21,500 Da. to 520 Da. with the highest fraction at around 900 Da. (**Figure 5.13**). After pretreatment by SMHSs, the SWOM of MW above 900 Da. declined noticeably and this led to a lower weight average value of the MW from about 10,579 Da. (for raw SW) to less than 1,075 Da. and 788 Da. after pretreatment by SMCHS and SMCAHS, respectively (**Figure 5.13**). The calculation procedure of number average (Mn) and weight average (Mw) of MW, and poly-diversity (Mw/Mn) can be found elsewhere (Huber and Frimmel, 1994). Natural organic matter (NOM) in seawater mainly contains biopolymers, humic substances (or humics), building blocks and low molecular weight neutrals (Shon et al., 2006). Generally, biopolymers represent extracellular polymeric substances which are not UV-absorbed and have very high MW of around 20,000 Da. After the pretreatment by SMCHS and SMCAHS, the peak at 21,500 Da completely disappeared. This indicated that most of the biopolymers were removed by these pretreatments. Humic substances (including fulvic acid) represent compounds with MW of around 1,000 Da. Only a small portion of the humics was removed by SMCHS. SMCAHS, on the other hand, could remove these compounds (humics or fulvic acid) very well (1,430 Da. and 900 Da.). After the pretreatments by SMCHS and SMCAHS, the poly-diversity of MW in seawater diminished from 5.4 to 1.3 and 1.2, respectively. These results show that when the submerged MF was used as a pretreatment with coagulation and/or adsorption, large molecular weight organic compounds with MW from 21,500 Da. to around 1,000 Da. were removed.



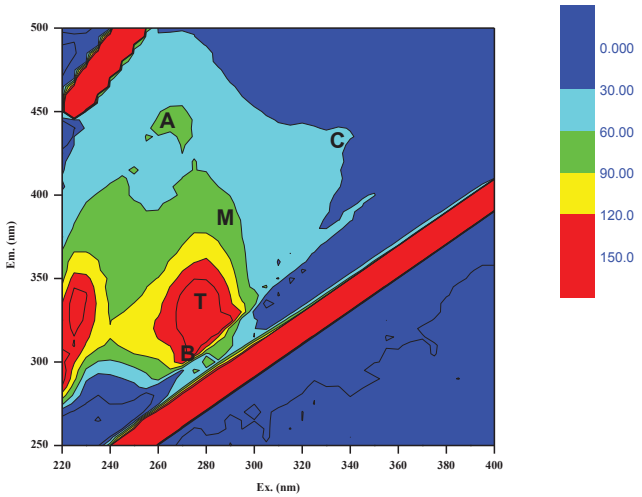
	raw SW	SMCHS pretreatment	SMCAHS pretreatment
Mn (Number average)	1955.8	842.5	665.5
Mw (Weight average)	10579.9	1074.8	788.4
Mw/Mn (Poly-diversity)	5.4	1.3	1.2

Figure 5.13 Average molecular weight (MW) values of SWOM in seawater and pretreated seawater.

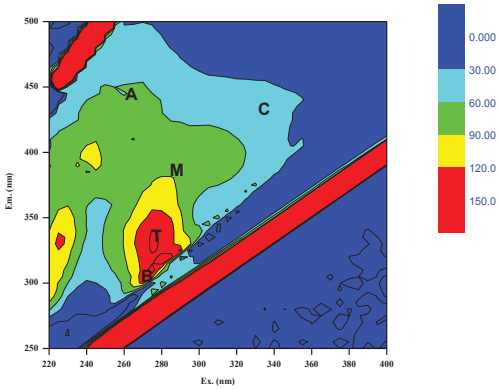
5.3.3.4 Fluorescence by 3D-EEM

The spectral data of EEM of the SWOM before and after pretreatment by SMHSs are given in **Table 5.10**. A typical EEM contour plot can be also found in **Figure 5.14**. It can be seen that five characteristic peaks were observed in EEMs including two protein-like peaks B and T, and three humic-like peaks A, M, and C. Protein-like peaks (peaks B and T) represent materials containing tyrosine-like (4-hydroxyphenylalanine which is used by cells to synthesize proteins) and tryptophan-like (Jiang et al., 2008).

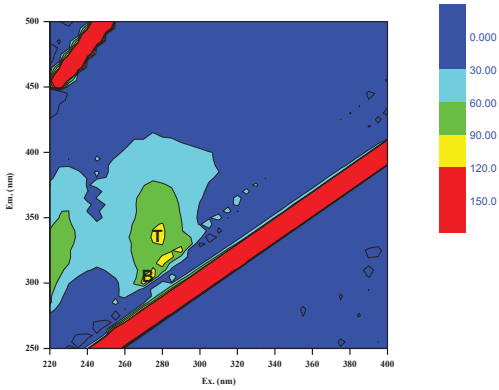
The fluorescence intensities of the tyrosine-like portion of the protein-like peak (peak B) were the strongest in the seawater sample. The C peak (visible humic-like) is not discussed in this thesis as it was too weak to be considered since the main part of the compounds in seawater are based on florescence intensity. In the pretreated seawater using SMCHS, the florescence intensity of B peak decreased significantly. In the case of pretreated seawater when SMCAHS was employed, humic-like peaks (A and M) disappeared and B and T peaks were also relatively weak. The distinguishing structural characteristic of tryptophan is that it contains an indole functional group which is an essential amino acid as demonstrated by its impact on the growth of microorganisms (Mopper and Schultz, 1993; Sierra et al., 2005). Specifically, a decrease in Peak M (which is indicative of microbial activity) could be seen clearly following SMCAHS pretreatment. This indicates the effect of pretreatment in reducing the biofouling potential because organic matter induced by microbes was limited by an adding of PAC.



(a) raw SW



(b) SMCHS pretreatment



(c) SMCAHS pretreatment

Figure 5.14 3D-FEEM spectra of seawater and pretreated seawater.

A humic-like relative to protein-like compounds (the ratio of intensity of peak B and peak M; I_B/I_M) in effluent is known as an indicator that evaluates the removal efficiency of fouling potential (Baghoth et al., 2011; Liu et al., 2011). After the SMHSs pretreatment, the I_B/I_M value (average value) fell from 12.7 to 1.41-2.31. Sun et al. (2007) stated that the humic substance property in surface sediment samples can be

determined by the intensity ratio of peak A and peak M (I_A/I_M). In the present study, this ratio has been applied to seawater sample. The I_A/I_M value was 1.34 in seawater whereas it was decreased by pretreatment to 0.88 (SMCHS) and 0.74 (SMCAHS). Peak M is often implicated as being ubiquitous, relatively stable and high molecular weight aromatic fulvic-like matter (McKnight et al., 2011; Sierra et al., 2005). Therefore the decrease of I_A/I_M value in pretreated samples indicates an increase in the humic substances' aromaticity.

In summary, EEM fluorescence spectra indicate that there is a decrease in protein-like substances and changes occur in the properties of humic-like substances in pretreated seawater samples.

Table 5.10 EEM peaks description and intensities of seawater and pretreated seawater.

				raw SW			SMCHS pretreatment			SMCAHS pretreatment		
Peak	Ex (nm)	Em (nm)	Chemical functionality	Ex/Em	Int. $(I)_{max}$	Int. $(I)_{Ave}$	Ex/Em	Int. $(I)_{max}$	Int. $(I)_{Ave}$	Ex/Em	Int. $(I)_{max}$	Int. $(I)_{Ave}$
B	270-280	300-310	Tyrosine-like, Protein-like	275/305	1072	591	275/310	168	100	275/305	109	67.7
T	270-280	320-350	Tryptophan-like, Protein-like	280/325	258	171	280/320	155	141	280/335	93.1	85.5
A	250-260	380-480	UV-humic-like	250/380	72.5	62.6	250/390	87.2	62.6	260/380	38.6	21.6
M	290-320	380-420	Visible marine humic-like	290/380	71.8	46.7	290/380	88.8	70.8	290/380	47.8	29.2
C	330-350	420-480	Visible humic-like	300/420	33.3	26.5	330/420	45.5	29.3	330/420	15.9	7.9
I_A/I_M					1.01	1.34		0.98	0.88		0.81	0.74
I_B/I_M					14.9	12.7		1.89	1.41		2.28	2.31

*: Ave. is mean value of intensities in Ex/Em range of each peak

5.3.3.5 Structural study of SWOM

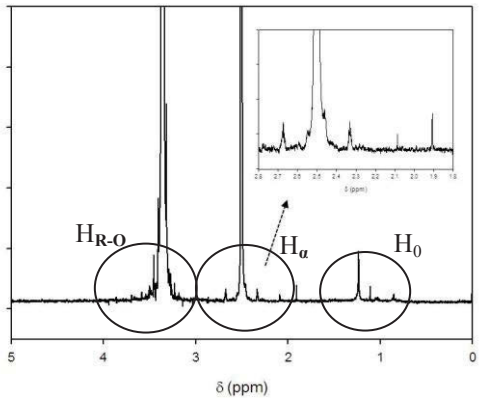
The fractionation and distribution of SWOM using the XAD resin and the fluorescence spectroscopic method, and MWD using size exclusion technique were investigated in bulk states. It provides some information associated with the physico-chemical properties of SWOM. A deeper understanding of molecular organic matter behavior in the pretreatment process can only be achieved through a structural study of SWOM.

5.3.3.5.1 NMR study

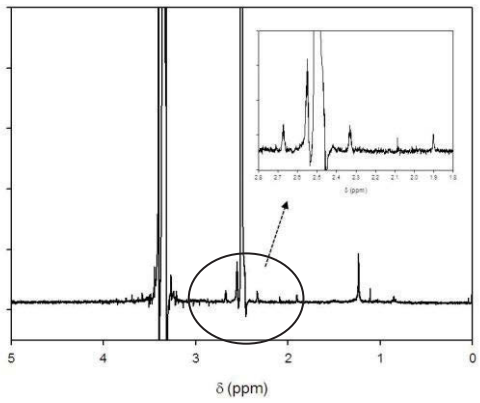
The ^{1}H-NMR spectra of SWOM isolated from raw SW and pretreated seawater (SMCHS and SMCAHS) are shown in **Figure 5.15**. The spectra of ^{1}H-NMR consisted of three main regions (H0, Hα and HR-O) (Ruggiero et al., 1980; Hatcher et al., 1980).

Both types of seawater pretreated by SMHSs and raw SW appeared to have a roughly similar structure in their NMR spectra. The alkyl region (H_0, 0.5-1.8 ppm) of all samples contained three sharp resonances at 0.85, 1.11 and more prominently 1.23 ppm. The signals at 0.85 and 1.23 ppm were due to methyl and methylene resonances, respectively. The resonances for the H_α regions of SMCHS and SMCAHS pretreatment effluent differed from that of raw SW. The signal was weaker at 1.91 ppm and the prominent resonances centered at around 2.49 ppm but they were resolved into one more region at 2.55 ppm after SMHSs pretreatment. The weakened signal at around 1.91 ppm in the spectrum of the isolated SWOM pretreated by SMCHS and SMCAHS indicated protons attached mostly to carbon α to a carboxyl or amide grouping. This may be due to structures such as amino acid driven peptides or uronic acids associated with polysaccharides.

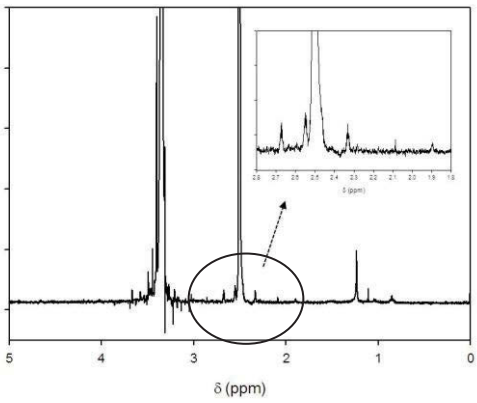
δ (ppm)	Major regions of ^{1}H-NMR
0.5-1.8	Alkyl protons attached to carbons removed from aromatic rings or carboxylic groups, H_0
1.8-3.0	Protons attached mostly to carbon α to aromatic rings and carboxylic groups, H_α
3.0-4.7	Alcohol and ether protons attached to carbon α to oxygen, $H_{R\text{-}O}$



(a) raw SW



(b) SMCHS pretreatment



(c) SMCAHS pretreatment

Figure 5.15 ^{1}H-NMR spectra of SWOM isolated from seawater and pretreated seawater and divided major regions.

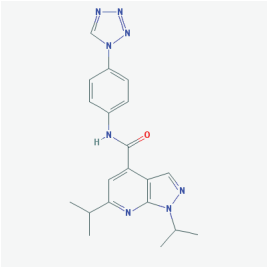
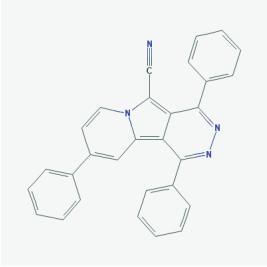
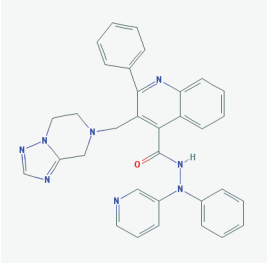
This scenario implies that these structures associated with biopolymers were humified by SMHSs. In other words the carboxyl and amino functional groups may have been de-polymerized into a variety of other carbon frames. An additional resonance at 2.67 ppm was found. The alcohol and ether region, 3.0-4.7 ppm, contained a prominent resonance at approximately 3.35 with spilt peaks. These divided resonances at around 3.44 ppm after pretreatment indicated the possible presence of a specific group of oxygenated compounds. This peak in pretreated seawater samples may be attributed to carbohydrate, ether bond, and amino acid or peptide protons, and infer a slight change in the bonding structure.

NMR data provides only limited structural information of SWOM as it is heterogeneous and complex. In this study rough structures and the possibility of transformation of SWOM could be identified from a NMR study. In order to get more detailed elemental composition data of SWOM (obtained from the pretreated seawater), isolated organic matter was characterized by LC/MS-IT-TOF.

5.3.3.5.2 LC/MS-IT-TOF

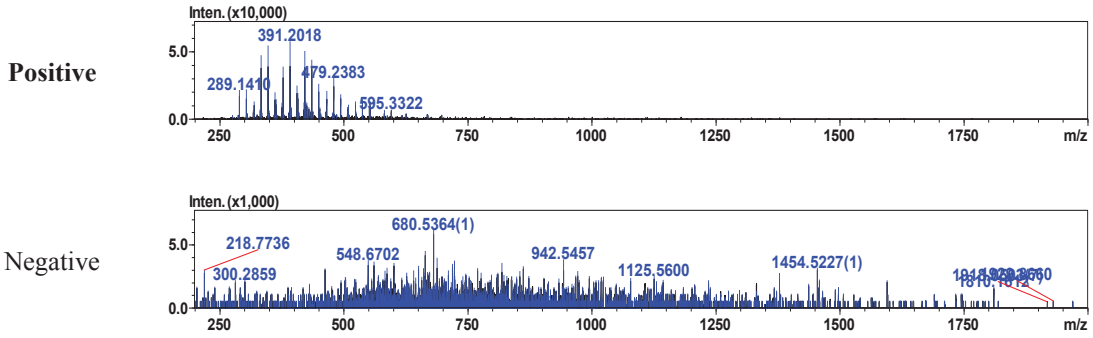
The elemental composition of SWOM is mainly carbon (C), hydrogen (H), oxygen (O) and nitrogen (N) and the other elements having relatively less abundance (Mawhinney et al., 2009). The LC/MS-IT-TOF technique is capable of very high-resolution and this allows most isobaric isotopes or species of SWOM to be clarified. A summary of the LC/MS-IT-TOF results including H/C, O/C and N/C ratio, formulas, IUPAC name and structure of each sample, which occurred in unique fractions (prominent peaks), is presented in **Table 5.11**.

Table 5.11 Summary of LC/MS-IT-TOF: H/C, O/C and N/C ratio, formulas, IUPAC name and structure of seawater and pretreated seawater, which occurred in unique fractions (prominent peaks).

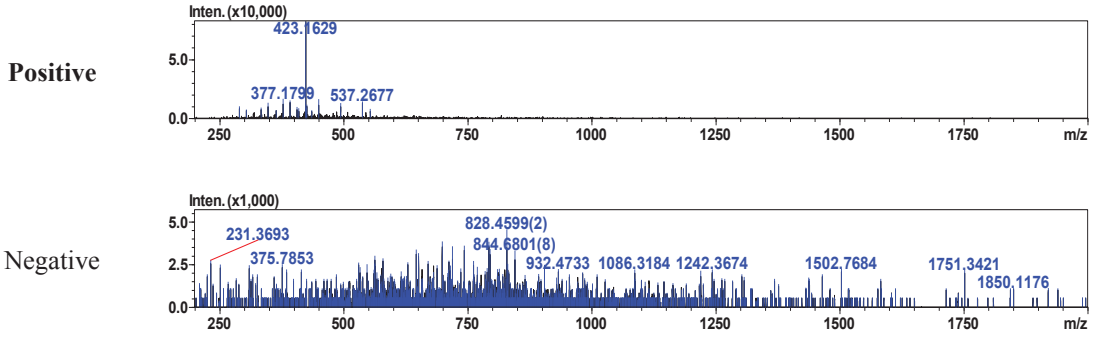
Samples	H/C	O/C	N/C	Prominent peaks (m/z)	Formulas	Name IUPAC	Structures
raw SW	1.38	0.14	0.30	391.2015	$C_{20}H_{22}N_8O$	1,6-di(propan-2-yl)-N-[4-(tetrazol-1-yl)phenyl]pyrazolo[3,4-b]pyridine-4-carboxamide	
SMCHS pretreatment	1.43	0.14	0.29	423.1629	$C_{29}H_{18}N_4$	1,4,9-triphenylpyridazino[4,5-a]indolizine-5-carbonitrile	
SMCAHS pretreatment	1.48	0.11	0.24	553.2713	$C_{33}H_{28}N_8O$	3-(6,8-dihydro-5H-[1,2,4]triazolo[1,5-a]pyrazin-7-ylmethyl)-N',2-diphenyl-N'-pyridin-3-ylquinoline-4-carbohydrazide	

LC/MS chromatograms of each sample can be found in **Figure 5.16**.

(a) **raw SW**



(b) **SMCHS pretreatment**



(c) **SMCAHS pretreatment**

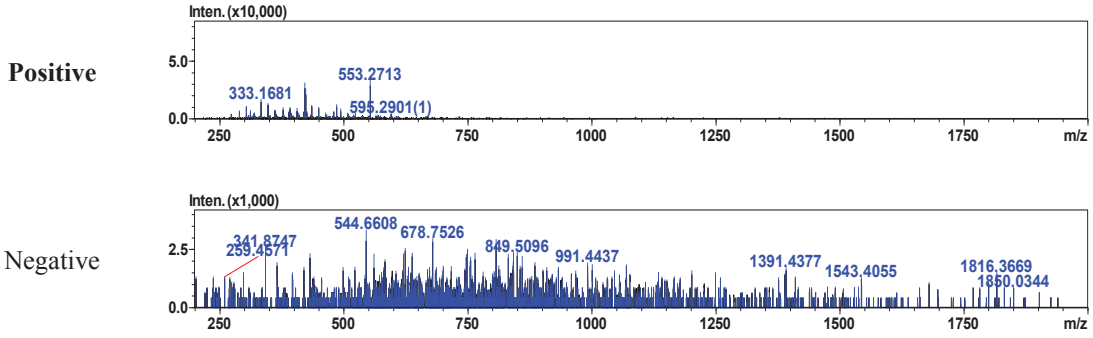


Figure 5.16 Liquid chromatography (LC) mass spectra of seawater and pretreated seawater.

Table 5.12 Specific compounds calculated from positive peaks in LC mass spectra.

Compounds	raw SW (m/z)	SMCHS pretreatment (m/z)	SMCAHS pretreatment (m/z)
$C_{13}H_{16}N_6O_2$	289.1410	289.1661	-
$C_{19}H_{18}N_4$	303.1468	-	303.1633
$C_{26}H_{20}$	333.1630	333.1709	333.1678
$C_{22}H_{22}N_2O_2$	347.1767	347.1690	347.1684
$C_{18}H_{18}N_8O$	363.1711	363.1776	-
$C_{25}H_{20}N_4$	377.1764	377.1799	377.2125
$C_{20}H_{22}N_8O$	391.2015	391.2056	391.1818
$C_{21}H_{24}N_8O_2$	421.2074	-	421.2107
$C_{29}H_{18}N_4$	423.1612	423.1629	423.1640
$C_{18}H_{14}N_{10}O_2$	425.1210	425.1217	-
$C_{26}H_{28}N_4O$	435.2152	435.2328	435.2174
$C_{17}H_{155}N_3O_2$	449.2317	449.2558	449.2214
$C_{24}H_{32}N_{10}O_2$	493.2440	493.2558	493.2782
$C_{28}H_{34}N_8O_2$	537.2827	537.2677	-
$C_{33}H_{28}N_8O$	553.2546	553.2465	553.2713

The detailed LC/MS data and calculated formulas are provided in **Table 5.12**. Generally, OM has similar configurations across the molecular weight range, where each nominal mass is made up of multiple components with varying empirical formulas. Components

with the same empirical formula most likely consist of multiple isomers. Their mass spectra are separation and this is based on the nominal mass-to-charge ratio (*m/z*) and charge is divided into negative and positive. The negative peaks on the LC/MS spectra are too complex and broad to distinguish and analyze. Only the positive peaks in each sample were sorted out and compared. The accurate mass measurement values were generated from LC/MS and based on these data; the corresponding empirical formulae were also calculated. This study concentrated only on common compounds observed. LC/MS-IT-TOF measurement results showed that SWOM after pre-treatment by SMHSs had different element compositions.

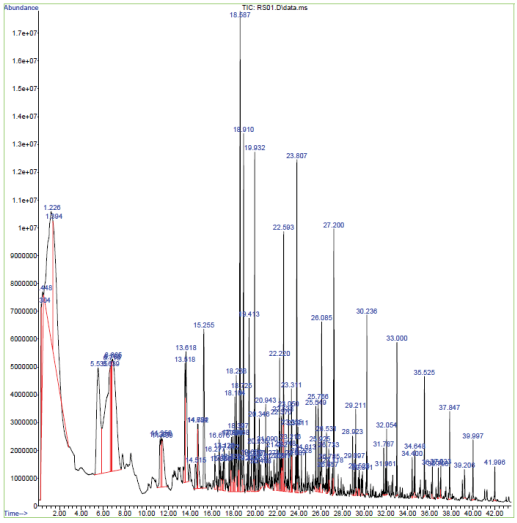
Following the SMCAHS pretreatment, the number of carbon atoms slightly increased (239 to 262 estimated from LC-MS data). The N/C and O/C ratio declined from 0.14 to 0.11 and from 0.30 to 0.24 respectively after SMCAHS pretreatment. This implies that protein-like SWOM was removed by SMCAHS since nitrogenous compounds are generally believed to be derived from protein. Differences in predicted unique compounds were also found. The *m/z* of the prominent peak for seawater and pretreated seawater was different; raw SW = 391.2015 ($C_{20}H_{22}N_8O$), SMCHS pretreatment = 423.1929 ($C_{29}H_{18}N_4$), and SMCAHS pretreatment = 553.2713 ($C_{33}H_{28}N_8O$). The predicted compound from the prominent peak for raw SW was a kind of amide whereas those for SW-SMCHS and SW-SMCAHS pretreatments effluent were nitrile and azide species, respectively. It is clear from the mass spectra of SWOM samples that the intensities and peaks for *m/z* were varied. These mass spectra results additionally indicated that samples accounted for by different in number of carbon atoms, hydrogen to carbon (H/C), oxygen to carbon (O/C) and nitrogen to carbon (N/C) ratio of each SWOM samples are different characteristics. In summary, SWOM composition decreased the number of carbon atoms by SMCHS pretreatment compared to raw SW.

SMCAHS could decrease the number of nitrogen atoms and oxygen atoms significantly and it might be indicated that protein-like organic matters had declined. Possibility of variation in SWOM structure associated with protein-like was observed on two different pretreated SWOM.

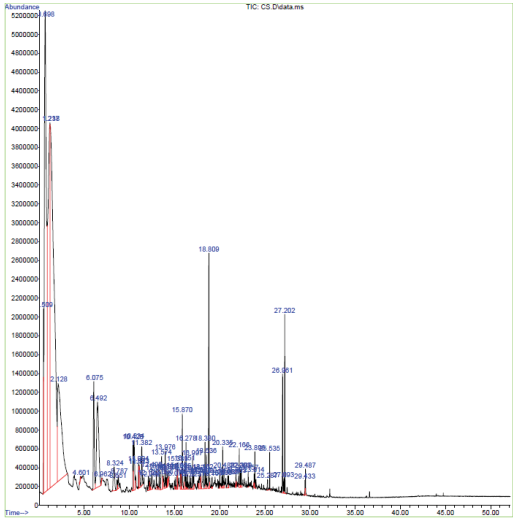
5.3.3.5.3 Pyrolysis GC/MS

Pyrolysis is a useful technique for breaking the complex macromolecules. It enables the pyrolysed SWOM fragments to be detected by GC/MS. A detailed analysis of specific pyrochromatograms is required for more advanced structural analysis. Selected pyrochromatograms produced by pyrolysis GC-MS analyses of raw SW are presented in **Table 5.13**. Two different pretreated seawaters with SMCHS and SMCAHS are shown in **Table 5.14**.

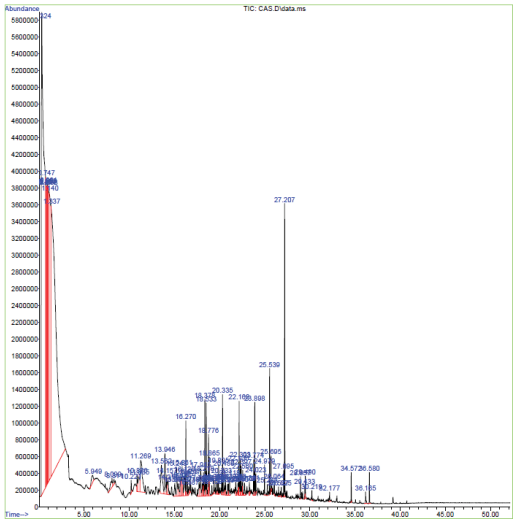
The GC/MS pyrochromatograms of each sample can be found in **Figure 5.17**.



(a) raw SW



(b) SMCHS pretreatment



(c) SMCAHS pretreatment

Figure 5.17 Pyrolysis GC mass spectra of seawater and pretreated seawater.

The relationship between pyrolysis products and the organic matter driven from biopolymers is discussed briefly in this thesis for raw SW and pretreated SW. The relative abundance of pyrolysed SWOM (before pretreatment) was much higher and not comparable to that of pretreated seawater samples.

Table 5.13 Py-GC/MS pyrochromatograms of raw seawater.

Samples	Types	Groups	Pyrolysis fragment
raw SW	Carbohydrate	Furan (1)	Furan, 2,5-dihydro-
		Aldehyde (2)	Cyclopropanecarboxaldehyde, Cyclopropanecarboxaldehyde, 2-methyl-2-(4-methyl-3-pentenyl)-, trans-(.+-.)-
		Ketone (5)	Ethanone, 1-cyclohexyl-, 4-Isopropyl-1,3-cyclohexanedione, Bicyclo[3.1.1]heptan-3-one, 2,6,6-trimethyl-, (1.alpha.,2.alpha.,5.alpha.)-, n-Nonenylsuccinic anhydride, 4,8-Dimethyl-nona-3,8-dien-2-one
	Protein	Amide (4)	1-(tert-Butyl)-3-cyclohexylcarbodiimide, Cyanamide, dibutyl-, 13-Docosenamide, (Z)-, 9-Octadecenamide, (Z)-
		Nitrogen-containing (1)	Benzene, 2,4-dichloro-1-nitro-
	Aliphatic carboxylic acids (2)		n-Hexadecanoic acid , (+-)-3-(2-Carboxy-trans-propenyl)-2,2-dimethylcyclopropane-trans-1-carboxylic acid,[1.alpha., 3.beta.(E)]-
	Cyclic (9)		Cyclohexane, 1,2-diethyl-3-methyl-, Cyclopentane, propyl-, Bicyclo[3.1.1]heptane, 2,6,6-trimethyl, Cyclododecane, Cyclohexane, 1,2-diethyl-3-methyl-, Cyclohexane, 1,2,4-trimethyl-, Cyclohexane, 1,2,4,5-tetraethyl-, (1.alpha.,2.alpha.,4.alpha.,5.alpha.)-, Cyclohexane, 1-ethyl-2-propyl-, Cyclopentane, 1-pentyl-2-propyl-
	n-alk-l-enes, *n*-alkane (15)		2,4-Dimethyl-1-heptene, 4-Octene, 2,3,6-trimethyl-, 1-Dodecene, 1-Hexene, 3,3-dimethyl-, 2-Undecene, 4-methyl-, 3-Octene, 2,2-dimethyl-, 1-Tridecene, 2,2-Dimethyl-3-heptene trans, 2-Tetradecene, (E)-, Tetradecane, Pentadecane, 1-Hexadecene, 1-Heptadecene, 1-Nonadecene, Octadecane
	Unassigned (8)		4,4-Dimethyl-non-5-enal, Cyclopropanemethanol, 2-methyl-2-(4-methyl-3-pentenyl)-, Bacchotricuneatin c, E-14-Hexadecenal, (1R-(1Alpha,3beta,4beta))-1-isopropenyl-4-methyl-1,3-cyclohexanediol 3-acetate, (2,4,6-Trimethylcyclohexyl) methanol, Aspidospermidin-17-ol, 1-acetyl-19,21-epoxy-15,16-dimethoxy-, 11-Dodecen-1-ol, 2,4,6-trimethyl-, (R,R,R)-

Table 5.14 Py-GC/MS pyrochromatograms of pretreated seawater by two different SMHSs.

Samples	Types	Groups	Pyrolysis fragment
SMCHS pretreatment	Carbohydrate	Furan (1)	Benzofuran, 2-methyl-
		Aldehyde (3)	Furfural, 2-Furancarboxaldehyde, 5-methyl-, 2-Furancarboxaldehyde, 5-(hydroxymethyl)-
		Ketone (2)	2-Cyclopenten-1-one, 2-methyl-, Acetophenone
	Protein	Amide (1)	Benzenesulfonamide, N-butyl-
		Nitrogen-containing (6)	2-Octanamine, Pyridine, Styrene, Benzyl nitrile, Hydrazine, 1-methyl-1-phenyl-
	Aromatic hydrocarbons (4)		Benzene, 1,2,3-trimethyl-, Naphthalene, Phthalic anhydride, Naphthalene, 2,6-dimethyl-, Diethyl Phthalate
	Aromatic carboxylic acids (2)		Benzenecarboxylic acid, Benzoic acid, 4-chloro-
	Cyclic (2)		Cyclodecane, Cyclododecane
	n-alk-l-enes, *n*-alkane (13)		4-Nonyne, 1-Dodecene, Dodecane, 1H-Indene, 4,7-dimethyl-, 1-Tridecene, 1,2,3-Trimethylindene, 1-Tetradecene, Tetradecane, 1-Pentadecene, Pentadecane, 1-Hexadecene, 1-Heptadecene, Octadecane
	Phenol (3)		Phenol, Phenol, 2-methyl-, Phenol, 2,4-bis(1,1-dimethylethyl)-
	Unassigned (2)		Pentanal, E-15-Heptadecenal

	Carbohydrate	Ketone (1)	1H-Inden-1-one, 2,3-dihydro-
		Amide (1)	Benzenesulfonamide, N-butyl-
	Protein	Nitrogen-containing (5)	Imidazole-5-carboxylic acid, 2-amino-, Benzyl nitrile, 1H-Pyrazole, 4,5-dihydro-3-phenyl-, Dodecanenitrile, Oleanitrile
	Aromatic hydrocarbons (6)		Naphthalene, Phthalic anhydride, Benzene, 1-butyl-4-methoxy-, Naphthalene, 2,6-dimethyl-, Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-, Dibutyl phthalate
SMCAHS pretreatment	Aliphatic carboxylic acids (3)		n-Decanoic acid, n-Hexadecanoic acid, Octadecanoic acid
	Aromatic carboxylic acids (2)		Benzenecarboxylic acid, Benzoic acid, 3-chloro-
	Cyclic (1)		Cyclodecane, methyl-
	n-alk-l-enes, *n*-alkane (14)		2,4-Dimethyl-1-heptene, 1-Undecene, 1-Dodecene, Dodecane, 1-Tridecene, 1-Tetradecene, Tetradecane, 1-Pentadecene, Pentadecane, 1-Hexadecene, Hexadecane, 1-Heptadecene, 1-Octadecene, Octadecane
	Phenol (6)		Phenol, Phenol, 4-methyl-, Phenol, 3,4-dimethyl-, Phenol, 2-(1,1-dimethylethyl)-, Phenol, 2,4-bis(1,1-dimethylethyl)-, Phenol, 2,5-bis(1,1-dimethylethyl)-
	Unassigned (5)		Cyclobutanol, 1-Undecanol, 11-Dodecen-1-ol, 2,4,6-trimethyl-, (R,R,R)-, E-15-Heptadecenal, 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester

***-SW*:** Most pyrolysed products in raw SW are derived from carbohydrates, proteins, aromatic hydrocarbons, aliphatic carboxylic acids, cyclic, n-alk-l-enes, n-alkane and unassigned materials. Carbohydrate assumed compounds may be due to the decay of terrestrial plants and sugars from phytoplankton. Furan (i.e. 2, 5-dihydro-furan) commonly exists as a pyrolytic degradation product of carbohydrate, hence the origin of the furans in pyrograms is proposed to be carbohydrate-type material. Aldehyde and ketone are the typical thermal degradation products of carbohydrates, monosaccharide and polysaccharides. Most aldehydes in SW are composed of cyclic compounds. Various amides and nitrogen containing pyrolysis products are generally believed to be derived from proteins. They are assumed to be representative of organic matter from aquatic micro-organisms. Moreover, amides were found in the pyrochromatograms and these could be marine humic material derived from peptidoglycans (amino-sugars) in microbial cell walls (Fabbri et al., 2005). The large number of cyclic hydrocarbon compounds in the pyrograms indicates the presence of large amounts of major biochemical groups of compounds such as proteins and carbohydrates. However, these substances are assumed to be associated with molecules of an aromatic nature probably held together by relatively weak linkages. This indicates that the aromatic structures are not the 'building blocks'. Compounds produced from lipids are commonly found in many algal materials. Aliphatic carboxylic acids,*n*-alk-l-enes and*n*-alkane are associated with the occurrence of lipid-like material. Typical pyrolysis products from polysaccharides and lipids are known to be present as predominant compounds in seawater. In the spectra of seawater samples, *n*-alk-l-enes and *n*-alkane were absent and they are also usually identified in pyrochromatograms of a terrestrial humic material (Andrew and Michael, 1985). In the marine environment, uncommon species (which are not generally identified materials as SWOM) such as lignin, protein (tyrosine residues)-

carbohydrate derivatives, algal polyphones are also detected. Several pyrolysates such as alkyl chain (methyl, ethenyl, ethyl and propenyl) and an oxidized alkyl chain are attributed to the aerobic degradation of lignin components (Fabbri et al., 2005).

***-SMCHS and SMCAHS*:** After pretreatment by SMHCS (submerged MF combined with $FeCl_3$ coagulation) and SMCAHS (SMCHS followed by PAC adsorption), various types of changed fragments were noticed. The carbohydrate associated compound in the pretreated seawater by SMCHS was benzofuran which is the heterocyclic compound consisting of fused benzene and furan rings. In the case of aldehyde group, furan carboxaldehyde was present instead of cyclic carboxaldehyde. Carbohydrate-like compounds disappeared after the pretreatment by SMCAHS. In the raw SW, protein-like compounds was mostly present as amide types. The nitrogen-containing benzene ring such as pyridine, styrene and benzyl nitrile and aromatic organics composed of nitrogen such as imidazole and pyrazole; and N-butyl-benzenesulfonaminde as amide containing sulfur (S) functional group were present. The unique structural change caused by the pretreatment of SMCHS and SMCAHS was the formation of aromatic organic compounds. New aromatic pyrolysis products containing benzene, naphthalene, phthalic anhydride and diethyl phthalate (as aromatic hydrocarbons) and benzenecarboxylic acids and benzoic acid (as aromatic carboxylic acids) emerged after the pretreatment by SMCHS and SMCAHS. They may have derived from the poly-hydroxisation of cyclic humic substances. Moreover, the cyclic compounds present as dominant compounds in raw SW largely disappeared after pretreatment. Instead, phenol compounds such as phenol, phenol, 2-methyl-, phenol, 2, 4-bis (1, 1-dimethylethyl) - were present in pyrochromatograms. Phenols may have been derived from the hydrolysis or pyrolysis of proteins and polycarboxylic acids presents in SW. They may also have originated from the hydrolysis reactions of carbohydrates. Aromatic

hydrocarbons and phenols could have been formed by the elimination of electron-withdrawing substituent on polycarboxylic aliphatic acids, leading to poly-conjugated chains which will readily cyclise.

5.3.3.6 Significance of organic characteristics in pretreated SW by SMHSs

So far, organic characterization in seawater has been used to study the removal of DOC and EPS concentration. For this study, DOC concentration in raw SW was 2.38 mg/L. Raw seawater was composed of 0.34 mg/L of carbohydrate and 0.54 mg/L of protein as main EPS composition. As expected, SMHSs could also remove protein and carbohydrate. Both protein and carbohydrate declined slightly even though 23% of total DOC was removed by SMCHS. On the other hand, a large amount of both were restricted by SMCAHS pretreatment and this means pretreatment can be assessed and selected based only on this information. However, more specific organic characteristics and a detailed understanding for it will enable us to develop an approach where pretreatment options can operate more precisely. As discussed before, SMCHS is coupled with the coagulation process using $FeCl_3$ and SMCAHS. It was added PAC adsorption process to SMCHS. In bulk analyses, XAD fractionation results revealed that SMCAHS could remove more than a half hydrophobic (HPO) organic compound. In hydrophilic organic compounds, 38% and 70% of HPI and TPI fractions respectively were removed from raw SW. SMCHS indicated relatively less removal efficiency than SMCAHS. In particular, the removal of the transphilic compound which mainly consisted of building blocks was poor. Based on the MWD measurement after SMCHS pretreatment, 21,500 Da. of MW, which is generally presented as biopolymers, was completely removed. On the other hand, humic and fulvic acids representing ranges of MW (1,430 to 900 Da.) were excluded by SMCAHS pretreatment. Significant removal of protein-like organic matter in raw SW was observed in the EEM analyses. These

large molecular weight of biopolymers which include protein and humic wield an influence on RO membrane performance. It has been proven in a recent study.

SMCAHS could mitigate biofouling potential by removing humic-like SWOM and changing their properties. A basic structural study using proton NMR showed main frames consisted of SWOM after SMHSs pretreatments. However, detailed results indicated that a structure associated with biopolymers may be humidified, de-polymerized and partially oxidized by SMHSs. Advanced liquid chromatographic measurement of SWOM made it possible to observe the change in elemental compositions, especially for nitrogenous compounds. Through the prediction of prominent peaks in positive MS data, SMCHS and SMCAHS led to the transformation from amide of raw SW to nitrile and azide in protein-like SWOM, respectively. This might be due to dehydration by a combination of chloride (ferric chloride or NaCl in raw SW) and humics in SWOM and oxidization by Fe-oxidant (which is intermediated by coagulation) and PAC. These findings are proved by the study of the pyrolysed precursor. Most carbohydrate-like compounds had disappeared and the amide group of protein-like compounds in raw SW was presented to the aromatic groups containing compounds in pretreated SW by SMHSs. One of the biggest differences between raw SW and pretreated SW was the aromatic organic compounds. Cyclic structural compounds in raw SW had mostly disappeared whilst new aromatic compounds were formed. These new compounds may have been derived from the poly-hydroxisation of cyclic humics and hydrolysis of protein and polycarboxylic acid. Further research and analyses are necessary to obtain more conclusive information.

5.3.4 SUMMARIZING THE ORGANIC CHARACTERIZATION

The organic matter was characterized in much detail in terms of seawater and treated seawater by SMHSs. The following conclusions were obtained. The analyses were repeated and any deviation was less than 5% in all cases:

(1) The seawater investigated in this study is mainly composed of hydrophilic matter (57±3.2%). SMHSs removed a significant amount of organic matter, especially the hydrophilic and transphilic compounds.

(2) SMHSs could remove effectively organic compounds of larger MW of more than900Da. These compounds represent biopolymers and humics.

(3) The EEM fluorescence showed a removal of humic-like materials by SMHSs. Following SMHSs pretreatment, a humic-like relative to protein-like compounds was reduced from 12.7 to 1.41-2.31 but the aromaticity of humic increased.

(4) NMR analysis showed that peaks corresponding to carbohydrate and amino acid or peptide structural bonds were slightly changed.

(5) Changes in SWOM element composition caused by the pretreatment used were observed using liquid chromatographic technology. The pretreatment of SMCAHS removed the protein-like SWOM.

(6) Low pressure membrane hybrid system hydrolyzed or oxidized the biopolymers and transferred them into aromatic structural compounds.

(7) SMHSs were effective in improving the RO performance leading to higher RO permeate flux, and lower permeate flux decline. The pretreatment also reduced

the amount of foulants on the RO membrane.

Overall, detailed SWOM characteristics, which have an impact on the SMHSs pretreatment, were attempted based on bulk analysis and structural study. This will help us to understand the SMHSs pretreatment.

5.4 FOULANT CHARACTERIZATION

5.4.1 INTRODUCTION

Inorganic scale can be easily alleviated by addition of anti-scalants and acid prior to the SWRO process. However, organic fouling has a more severe effect on the RO membrane. It is caused by humics, fulvic acid, carboxylic acid and extracellular polymeric substances (EPS). It also acts as a precursor to biological growth which leads to biofouling (Al-Ahmad et al., 2001; Vrouwenvelder and van der Kooij, 2001; Bereschenko et al., 2011; Khan et al., 2011). The key steps in biofouling on the RO membrane are as follows: adsorption of organic matter to membrane surface, continuous adhesion of microorganisms, growth of adhered cells, and subsequent formation of biopolymer matrix. Thus organic and biofouling developments are mutually related. Even low concentrations of appropriate carbon sources can readily lead to substantial bacterial re-growth on membrane. Only a few studies (Flemming, 2002; Meylan et al., 2007; Flemming and Wungender, 2010) have simultaneously analysed of the OM foulant characterization and its effect on the microbial fouling on the RO membrane. Further, the limited data available in the literature means that only a tentative conclusion can be made on initial fouling development on RO in terms of organic and biological fouling.

The efforts to alleviate the organics which are more likely to absorb on the membrane surface have to be preceded. In doing so the reduction in bacteria growth potential could be achieved simultaneously. In other words, in order to control the bio-film development at the surface of the membrane, the pre-treatment prior to the RO unit has to be carefully optimised to remove microbial cells and growth promoting compounds (nutrients and electron donors) from the feed water.

Increasingly, researchers are applying the use of membrane based pretreatment to meet the expected quality of feed water (Meylan et al., 2007; Bonnelye et al., 2008; Prihasto et al., 2009). Low-pressure membranes such as microfiltration (MF) and ultrafiltration (UF) are being used. They can remove suspended solids, colloids and microorganisms effectively which result in higher RO flux, less fouling and chemical dose reduction. MF alone as a pretreatment cannot remove dissolved organic matter (DOM) in seawater (Shon et al., 2009). On the other hand, when MF is combined with adsorption and coagulation, DOM in the seawater can be removed. In addition, MF has a number of advantages such as low energy consumption, and high flux operation when it is coupled with physico-chemical treatment such as adsorption and coagulation. Previous studies indicated the small molecular species that are not usually rejected by the MF membrane alone could be absorbed by the PAC and coagulated by the $FeCl_3$ in the submerged membrane hybrid systems (SMHSs) (**sections 4.1** and **4.5** of **Chapter 4**). However, details on the biofouling and its relationship with organic controls on RO membrane fouling at initial stage have not been studied and reported. This study deals with the characterization of foulants on submerged membrane coagulation and adsorption hybrid system as a pretreatment to seawater reverse osmosis.

Membrane foulant characterization (on the fouled RO membrane) is very effective for evaluating pretreatment and investigating fouling behavior on the RO membrane (Xu et al., 2010). It also assists in determining the suitable process for pretreatment to control the fouling. The physico-chemical characteristics of organic foulant such as molecular weight distribution (MWD), EPS and fluorescence analysis provide valuable information for understanding the complex interactions of organics that occur in the RO membrane. However, seawater organic foulants analysis is not straight forward. Only a few recent studies have suggested specific methods to measure the organic foulants

(Amy et al., 2011). This present study gives the quantitative values of specific groups of organics and detailed information on foulant characterization. This information is essential to assess the initial organic and biofouling. There are a number of simple microbial methods to identify and measure biofoulants, and the following methods have been used for RO membrane processes: total direct cell (cell/mL or cell/cm^2) and live/dead cells (cell viability). The measurement of adenosine triphosphate (ATP) has also been proposed as an indicator of biomass content on the fouled RO membrane, since ATP is a bimolecular material which exists in all living cells. There are only a few references on the fouling analyses especially for seawater (Vrouwenvelder et al., 2008) and they were not undertaken for the pretreatment system used in this study. The experimental protocols adopted provide the practical information on foulants and some useful information on organic and biofouling.

In this study two submerged membrane hybrid systems (SMHSs), firstly submerged membrane coagulation hybrid system (SMCHS) and secondly, submerged membrane coagulation adsorption hybrid system (SMCAHS) were used as pretreatment strategies. The effect of pretreatment on the performance of a RO unit was evaluated by examining the fouled RO membrane. Detailed investigations on organic and biological foulant were done using representative analytical methods.

5.4.2 MATERIALS AND METHODS

5.4.2.1 Pretreatment method

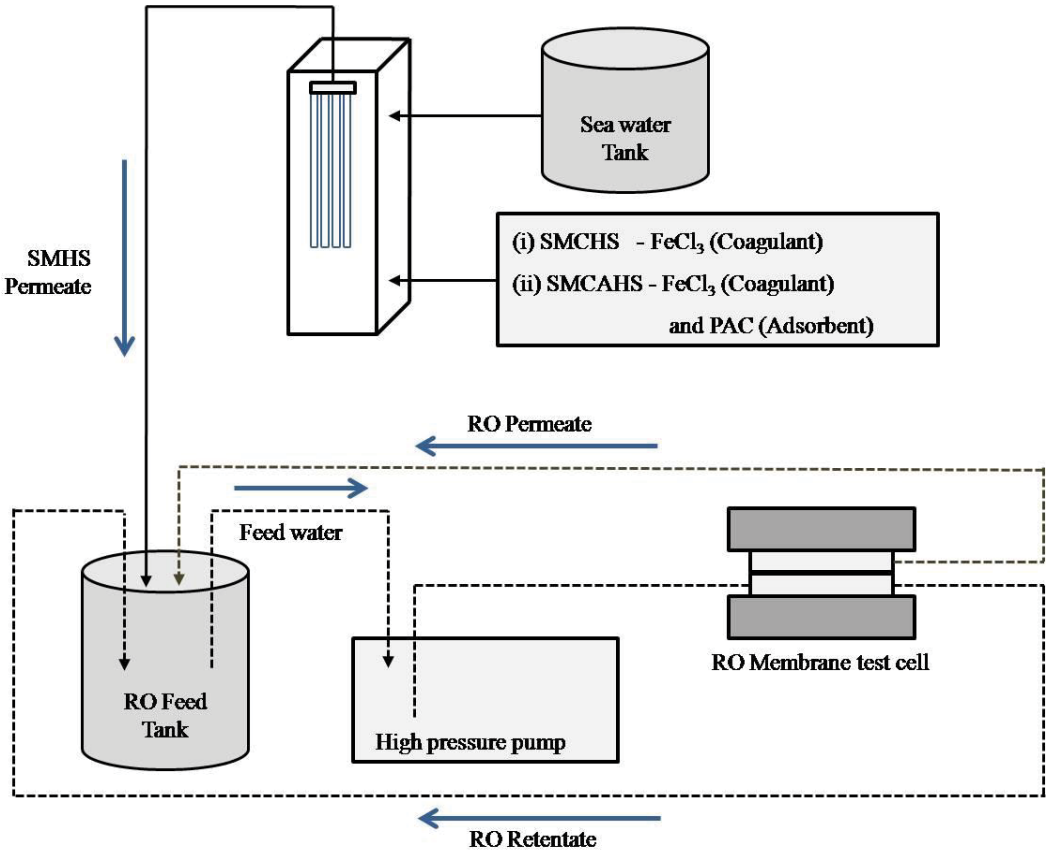


Figure 5.18 Overall flow diagram of SMHSs and RO test unit.

In this study SMHSs were used as pretreatment methods for the RO. The impact of SMHSs was assessed in terms of the fouling performance and behavior on the RO membrane. Untreated seawater (raw SW- prefiltered by 0.45µm to minimize the effect of particulates in raw seawater) and seawater pretreated with SMHSs (at predetermined conditions) were used as the feed solutions for the RO membrane test unit. In the SMHSs set-up submerged-type of hollow fibre MF membranes (see **section 3.1.2**) were used. The SMHSs were operated at a constant permeate flux mode of 20 $L/m^2 \cdot h$ (LMH). The filtered seawater through SMHSs was used as feed solution in a lab-scale cross-

flow RO membrane test unit (**Figure 5.18**). $FeCl_3$ and PAC (**Table 3.3**) were used as a coagulant and an adsorbent respectively in the SMHSs. A high concentration $FeCl_3$ of 3.0 mg Fe^{+3}/L dose was used for the SMCHS while a smaller one (1.0 mg Fe^{+3}/L) was employed for the SMCAHS. In addition to the coagulation, 0.5 g/L of PAC was dosed at the initial in the SMCAHS. Details on the adsorbent and membrane set-up are given in **Table 3.3** and **section 3.2.1.2**, respectively.

The figure of RO set-up and the method for foulant extraction used in this study are given in **section 3.2.2** of **Chapter 3** in more detail.

5.4.3 EXPERIMENTAL RESULTS

5.4.3.1 RO performance with pretreated samples by different SMHSs

The performance of RO was studied in terms of permeate flux and decline in permeate flux during 45 h operation with pretreated seawater samples (by different SMHSs). Pretreatment improved the initial permeate flux (J_i) and reduced the flux decline (J_f/J_i) rate (**Figure 5.3** of **section 5.1**). At 5.5 MPa the RO test unit with raw SW (untreated seawater) had an initial flux value of 31.5 LMH. In comparison the pretreated seawater by SMCHS and SMCAHS showed better initial permeate flux of 36.0 LMH and 45.4 LMH, respectively. Furthermore, when pretreated seawater treated with SMCHS and SMCAHS was used, flux decline decreased to about half after 45 hours, from 49% (J_f/J_i=0.51) with raw seawater to 26% (J_f/J_i=0.74) with SMCHS pretreatment and 24% (J_f/J_i=0.76) with SMCAHS pretreatment. Here the control was the raw seawater filtered through 0.45 μm filter to minimize the effect of particles. These results imply that SMHS as a pretreatment strategy was effective in improving the RO performance because it resulted in higher initial permeate flux and less permeate flux decline.

The submerged membrane system coupled with PAC adsorption and $FeCl_3$ coagulation (SMCAHS) was found to significantly reduce organic matter in seawater (from 2.38 mg/L of raw seawater to 1.23 mg/L by SMCAHS). In particular it removed the biopolymer and humics in hydrophilic portions (see **Figure 5.6** and **Table 5.7** of **section 5.2**). The SMHS as pretreatment led to a lower organic fouling on the RO membrane. In addition to this the foulant had different characteristics. Thus this study dealt with both organic and biological foulants extracted by mild sonication. Fouled RO membranes were also characterized after RO operation with pretreated seawater by SMHSs.

5.4.3.2 Organic foulant characterization

The amount of organic foulant extracted from fouled RO membrane was measured by TOC analyzer. The amount of foulant with raw SW was 23.5 μg-C/cm^2 while foulant with the pretreatment of SMCHS decreased slightly to 21.6 μg-C/cm^2. On the other hand, SMCAHS showed a significant reduction of approximately 40% in the organic foulant of SW (14.8 μg-C/cm^2). These amounts of organic foulant are consistent with the removal of organic matter by SMHSs. Pretreatment by SMHSs was helpful in reducing the initial organic accumulation on the RO membrane.

5.4.3.2.1 MWD

The MWD of organic foulant was measured after extracting the foulant from the fouled RO membrane. The MWD was analyzed using the response (mV) of ultraviolet absorbance (UVA) of HP-SEC with elapsed time. **Figure 5.19** shows the MWD of organic foulant extracted from the fouled RO membrane. The MW of the organic foulant with raw SW varied from high MW of 33.3 kDa and 12.7 kDa to relatively low MW of 1,500 Da, 790 Da, 165 Da, 41 Da, and 21 Da. The four main MW ranges in seawater found are: i) 10 kDa-50 kDa, ii) 1500 Da-800 Da, iii) 800-500 Da, and iv) <250 Da. The compounds in the range of 10 kDa-50kDa are biopolymers; 1,500-800Da is humic substances; 800-500 Da is building blocks and less than 250 Da is low molecular weight (LMW) neutrals and amphiphilics. Here, biopolymers include polysaccharides and proteins; building blocks include hydrolysates of humic substances; LMW neutrals and amphiphilics (slightly hydrophobic compounds) include sugars, alcohols, aldehydes, ketones and amino acids.

On the other hand, after the RO operation with the pretreated seawater, the organic foulant on the RO membrane had a peak of around 24.1 kDa, which is mainly the biopolymer. There were also humic-like foulants ranging from 1,500 Da to 800 Da. Relatively small amounts of MW foulant (building blocks) of 620 Da were observed. Regarding the same sample treated by SMCAHS, MW of 165 Da to 185 Da and 90 Da almost disappeared on the foulant. It indicated that these LMW materials were removed effectively by adding PAC.

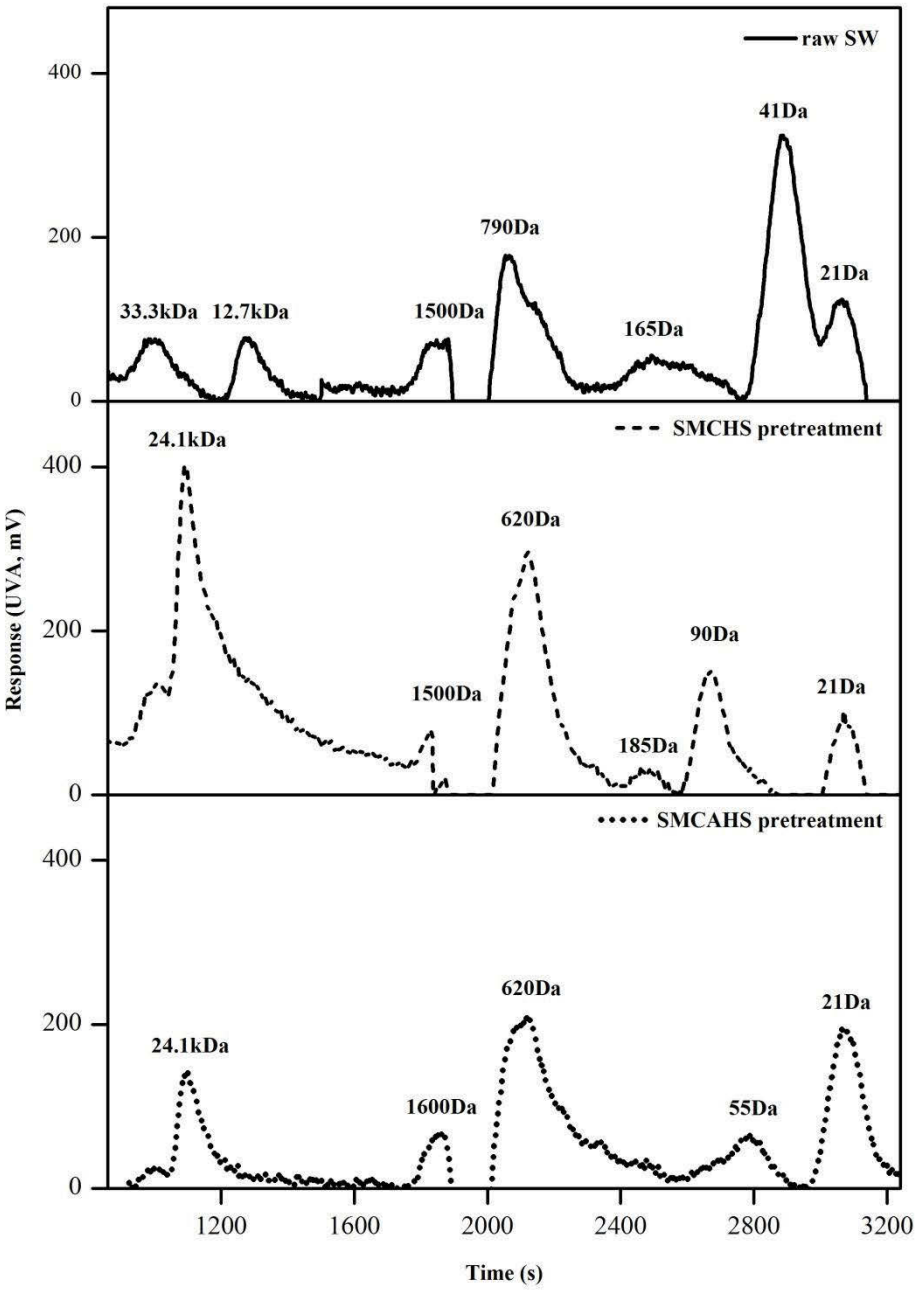


Figure 5.19 MWD of foulants on RO membranes after RO operation with raw SW and pretreated seawater.

Table 5.15 EEM peaks description and intensities of foulants on the RO membrane with pretreated seawater.

				raw SW			SMCHS pretreatment			SMCAHS pretreatment		
Peak	Ex (nm)	Em (nm)	Chemical functionality	Ex/Em	Int. $(I)_{max}$	Int. $(I)_{Ave}$	Ex/Em	Int. $(I)_{max}$	Int. $(I)_{Ave}$	Ex/Em	Int. $(I)_{max}$	Int. $(I)_{Ave}$
B	270-280	300-310	Tyrosine-like, Protein-like	275/305	1329	790	275/305	1100	667	275/305	1408	854
T	270-280	320-350	Tryptophan-like, Protein-like	280/320	330	281	280/320	525	478	280/320	330	281
A	250-260	380-480	UV-humic-like	290/380	194	87.6	290/380	174	76.9	290/380	186	79.1
M	290-320	380-420	Visible marine humic-like	290/380	194	87.6	290/380	174	76.9	290/380	186	79.1
C	330-350	420-480	Visible humic-like	330/430	53.9	38.1	330/420	29.2	29.3	330/440	32.7	28.7
I_A/I_M					0.75	1.05		0.93	1.09		0.90	1.16
I_B/I_M					6.85	9.02		6.32	8.67		7.57	10.8

5.4.3.2.2 FEEM

The spectral data of FEEM of the RO foulant extracted after the operation with seawater (with and without pretreatment) are presented in **Table 5.15**. There were five characteristic peaks in EEMs including two protein-like peaks B and T, and three humic-like peaks A, M, and C. Protein-like peaks (peaks B and T) represent materials containing tyrosine-like (4-hydroxyphenylalanine which is used by cells to synthesise proteins) and tryptophan-like. These are probably the metabolic products (biopolymers) from bacterial and phytoplankton activities. Peaks A and M are indicative of humic-like compounds (mainly humic and fulvic acids) which are the main components of bioactivity.

The fluorescence intensities of the protein-like peak including the tyrosine-like and the tryptophan-like (peak B and T) were stronger than those of humic-like peaks in all foulant samples. EEM peaks of foulant could not be correlated with flux decline on the RO test as fluorescence itself cannot be quantified. However, fluorescence results helped us to understand the chemical properties of protein-like and humic-like organic foulants in a qualitative manner. Of the organic foulants, only the peak C (visible humic, humic-like) had some correlation with RO performance in terms of flux decline. However the peak C showed weaker florescence intensity than other fractions. Tryptophan (peak T) is used in structural or enzyme proteins. It is also occasionally found in naturally produced peptides. The distinguishing structural characteristic of tryptophan is that it contains an indole functional group which is an essential amino acid as demonstrated by its growth effects on microorganisms.

The humic substance property in foulants could be determined by the intensity ratio of peak A and peak M (I_A/I_M). The I_A/I_M value was 1.05 with raw SW whereas it was slightly higher for foulant with pretreatment samples (SMCHS= 1.09 and SMCAHS= 1.16). Here peak A is representative of UV-humic-like. The increase of I_A/I_M value in pretreated samples indicates the decrease in the aromaticity of the humic substance since Peak M is often implicated with ubiquitous, relatively stable and high molecular weight aromatic fulvic-like matter. This indicates that the pretreatment led to less aromaticity of humic substances in the foulant. A tyrosine-like protein-like compounds relative to visible marine humic-like (the ratio of intensity of peak B and peak M; I_B/I_M) in the foulant was not significantly different for seawater and pretreated seawater. However Peak M in foulant with seawater samples pretreated by SMHSs was less than that containing raw SW. The quantification of various peaks and compounds of the foulants with/without pretreatment is not straight forward.

5.4.3.2.3 EPS analysis

The EEM data was also similar to direct EPS measurement (**Figure 5.20**). In EPS, carbohydrate (CH) concentrations were much less than those of protein (PN) in foulant on RO membrane. In other words protein was the dominant EPS content in foulant. Protein content on the RO foulants dropped significantly with pretreatment by SMCHS and SMCAHS to 0.79 μg/cm^2 and 0.24 μg/cm^2, respectively from 1.02 μg/cm^2 (with raw SW). The amount of carbohydrate in the RO foulant was slightly lower in both SMCHS and SMCAHS pretreated effluent (**Figure 5.20**).

In summary, SMHS pretreatments led to a change in the characteristics of organic foulants which reduced the initial biofouling development. This explains why biofouling at the initial stage of RO operation was investigated here. This was further confirmed by measuring microbial fouling.

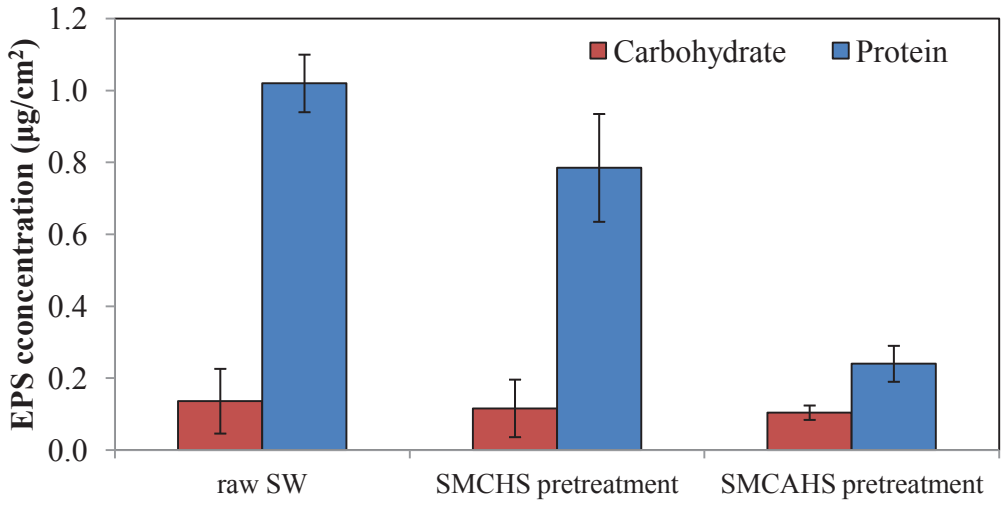


Figure 5.20 Extracellular polymeric substances (EPS) concentrations of foulant on the RO membrane with raw SW and pretreated seawater.

5.4.3.3 Biofouling at the initial stage

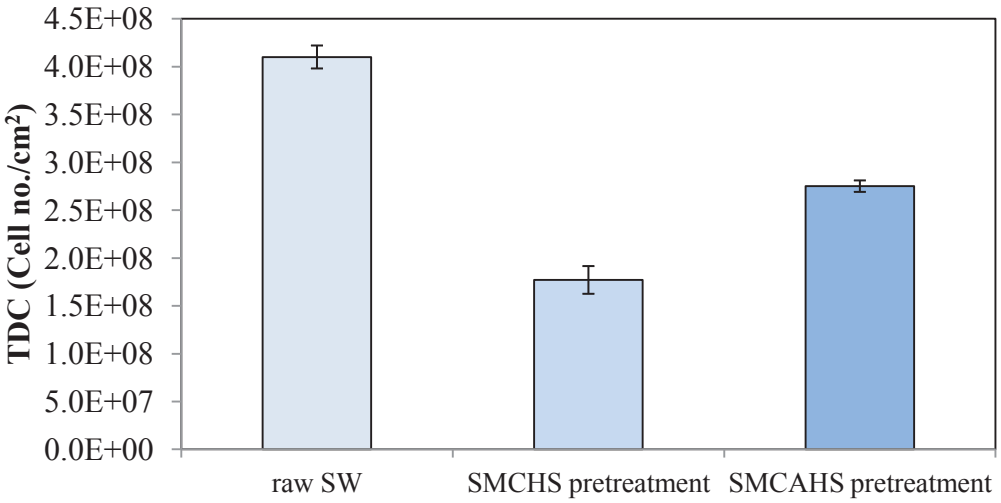
5.4.3.3.1 Total direct cell/cell viability

The total bacterial cell number on the RO foulant with raw seawater (after 45 h of RO operation)was $4.10E^{+08}$cells/cm^2 but with pretreated seawater using SMCHS and SMCAHS, the accumulated cell numbers on the RO membrane fell to $1.77E^{+08}$cells/cm^2 and $2.75E^{+08}$cells/cm^2 respectively (**Figure 5.21 (a)**).

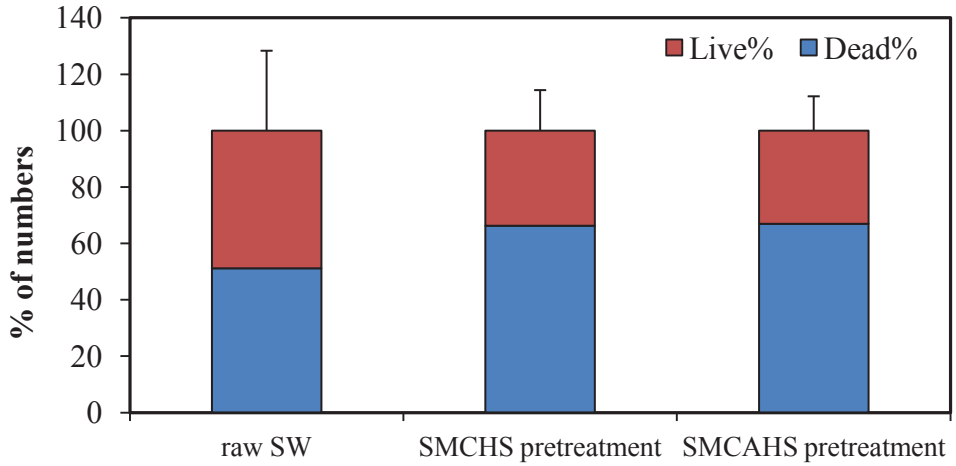
Pretreated samples by SMCHS and SMCAHS also reduced cell viability (i.e. live cell proportion) on the RO foulants. The cell viability in the RO foulant was reduced from 0.5 (with raw SW) to 0.3 (with pre-treated seawater by both SMHSs) (**Figure 5.21(b)**). This outcome shows that after pretreatment by SMAHS and SMCAHS, the biofouling development in the initial stage could be ameliorated.

5.4.3.3.2 ATP concentration

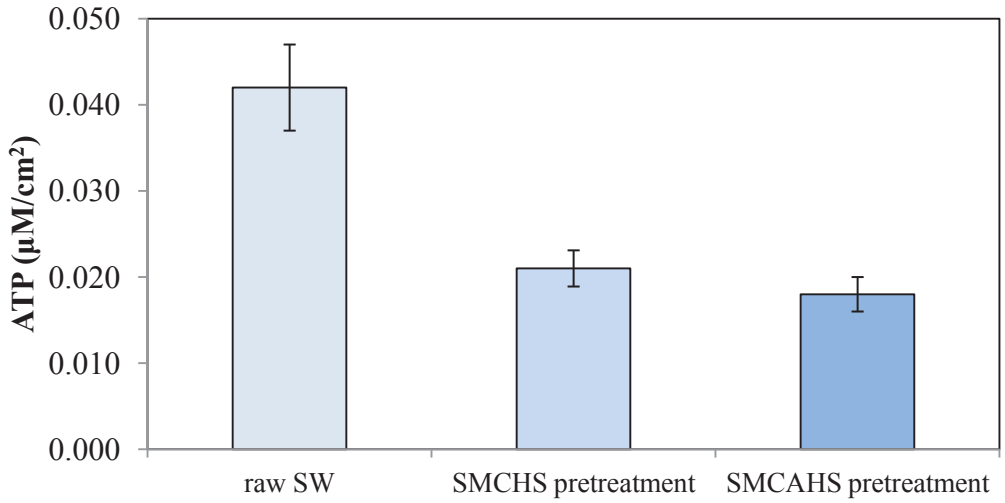
The cell viability results were consistent with ATP concentration measurement. ATP is generally used as an indicator for live biomass. The results on RO foulants show that after pretreatment by SMAHS and SMCAHS, seawater had low biofouling potential. It led to lower biomass activity on RO membrane. Total ATP concentration on foulants with pretreated seawaters (SMCHS; 0.021μM/cm^2 and SMCAHS; 0.018μM/cm^2) was lower than that with raw SW (0.042 μM/cm^2) (**Figure 5.21(c)**).



(a) Biomass accumulation (TDC)



(b) Cell viability (live/dead cell)



(c) Biomass activity (ATP)

Figure 5.21 Biofouling parameters on RO membranes. (a) Biomass accumulation (TDC); (b) Cell viability (live/dead cell); and (c) Biomass activity (ATP)

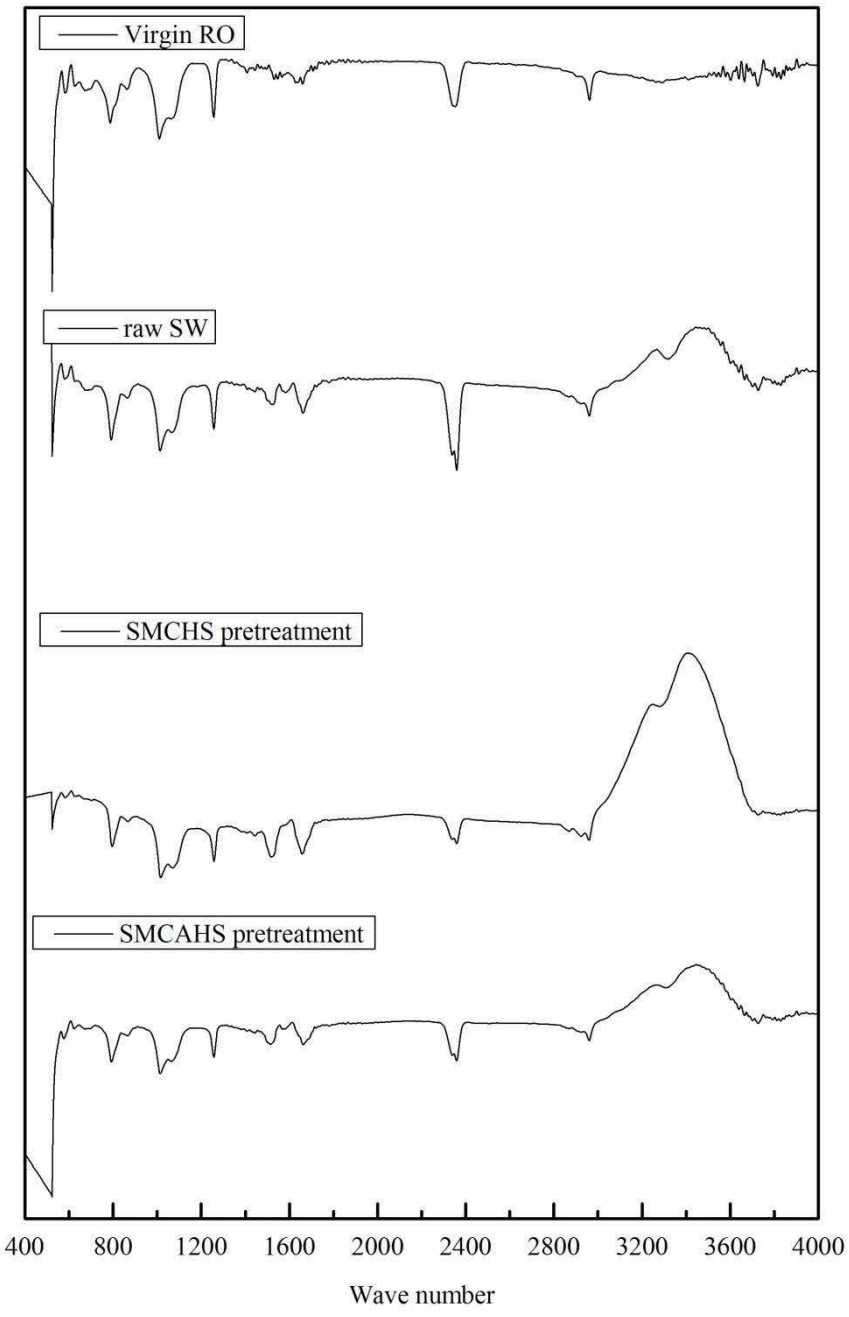


Figure 5.22 ATR-FTIR spectra of fouled membranes with raw SW and pretreated seawater.

5.4.3.4 Fouled membrane characterization

In this study, fouled RO membranes were also characterized as follows: functional group using ATR-FTIR, chemical precipitation on the membrane using SEM-EDX, membrane morphology and roughness using AFM, membrane hydrophobicity using contact angle measurement and membrane surface charge using zeta-potential analysis.

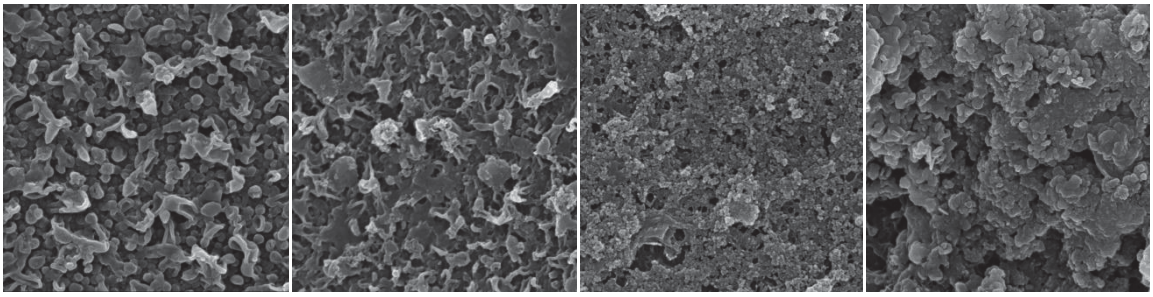
5.4.3.4.1 Functional group

ATR–FTIR analysis investigated the functional (reactive) groups in the organic foulants on the fouled membrane surfaces (**Figure 5.22**). It was especially evident that distinguished molecular functional groups forming the organic matter could be interpreted from the typical IR bands of aliphatic and aromatic groups, and humic substances. They may include biopolymers such as polysaccharide, proteins and humic substances.

Similar frequencies were observed on the fouled RO membrane which, with raw SW, the peak at wave number of 1040 cm^{-1} indicated polysaccharide of aliphatic ether. The wave numbers of 1480 cm^{-1} and 2940 cm^{-1} reflect polysaccharide related to alkane group. All indicative peaks of protein were shown as amides and carboxylic acid (3300 cm^{-1}), alkene in aromatic group or amides (1640 cm^{-1}), secondary tertiary amines (C-N, 1540 cm^{-1}). Wave numbers representing fatty acids are 2950, 2850, 1470, and 1430 cm^{-1}as alkane group. Humic substances were represented by alcohol and alkane at 3400cm^{-1} and 2960 cm^{-1}. On the other hand, the peaks observed for the fouled RO membranes with pretreated SW were (more or less) similar to the clean (virgin) membrane, indicating the RO membrane surface was not much contaminated when pretreated seawater was fed into RO.

5.4.3.4.2 Chemical precipitation

Figure 5.23 shows the SEM image and chemicals on the fouled RO membrane with pretreated SW. Virgin RO (the clean membrane) and fouled RO membranes with raw SW were compared to the RO membrane fed with pretreated seawater. The SEM analysis provides not only distinct morphology information about fouling but also shows clear evidence of chemical precipitation on the membrane surface.



(a) Virgin RO (Clean)	(b) Raw SW (without pretreatment)	(c) SMCHS pretreatment	(d) SMCAHS Pretreatment
Chemicals (weight %)	C:6.90, O:2.12, N 1.47, Na 0.18, Cl 0.12 Mg 0.01, Si 0.01, P 0.10, S 0.09, Mn 1.18, Fe 1.94	C:10.61, O:1.55, Na 0.01, K 0.09, Cl 0.06 Mg 0.05, Si 0.04, P 0.02, S 0.42, Mn 1.20, Fe 0.98	C:0.41, O:0.63 K 0.01, Cl 0.08 Mg 0.00, Si 0.08 P 0.05, S 0.12 Fe 0.56

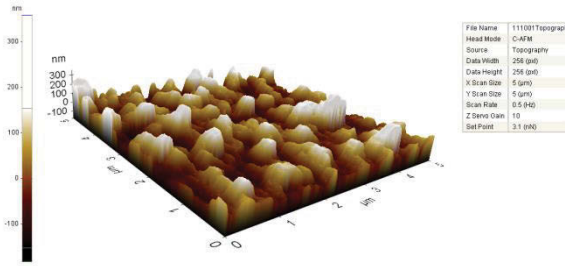
Figure 5.23 SEM images and chemical precipitations by EDX on the fouled RO membrane.

When raw SW was used as feed water to the RO unit, various elements (Na 0.18%, Mg 0.01%, Si 0.01%, P 0.10%, S 0.09%, Mn 1.88% and Fe 1.94%) were observed. Cl and Fe were found in all foulant obtained from raw SW and SMHSs samples. However, N in SMCHS and SMCAHS and Na and Mn in SMCAHS were below detection limits. Contrary to expectations, ferric precipitation decreased when pretreated seawater was used. Ferric fraction in RO foulant was reduced from 1.94% with raw SW to 0.98% with SMCHS and 0.56% with SMCAHS in terms of weight percentage. Thus, ferric precipitation on membrane is marginal when pretreated seawater was sent to the RO unit.

5.4.3.4.3 Morphology and roughness

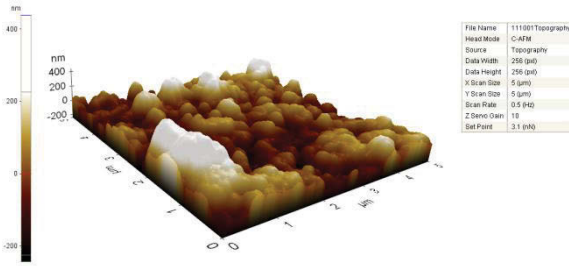
Membrane surface morphology and roughness was determined using the non-contact mode AFM. AFM images of the fouled RO membrane surfaces are presented in **Figure 5.24**. Fouled RO membranes fed with raw SW and pretreated SW were analysed. The unique ridge and valley shape was observed on the virgin RO membrane. The resolution of this image is given in the set with scan area of 5 μm x 5 μm.

The average roughness of the clean membrane surface was 56.24 nm. After pretreatments with raw SW, the roughness increased up to 88.09 nm. With SMCHS and SMCAHS pretreatments the roughness also increased up to 86.12 nm and 81.00 nm, respectively. Thus, the pretreatment by MF coupling with coagulation and/or adsorption could not preserve the membrane surface completely.



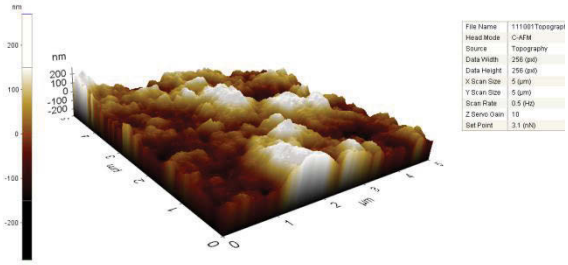
Roughness 56.24 nm

(a) Virgin RO



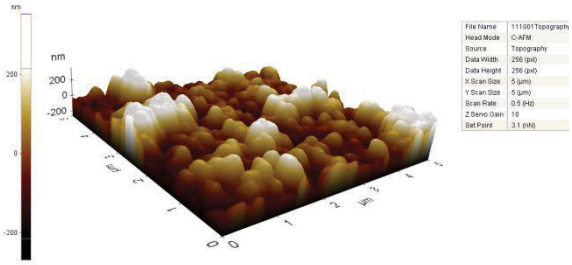
Roughness 88.09 nm

(b) raw SW



Roughness 86.12 nm

(c) SMCHS pretreatment



Roughness 81.00 nm

(d) SMCAHS pretreatment

Figure 5.24 AFM images and roughness on fouled RO membrane with raw SW and pretreated seawater.

5.4.3.4.4 Membrane hydrophobicity and surface charge

Table 5.16 Changes of hydrophobicity and surface charge of Virgin RO membrane and fouled RO membrane with pretreated seawater.

	Hydrophobicity Contact angle (°)	Surface charge Zeta potential (mV)
Virgin RO	64.3 ± 5.1	-41.09
raw SW	61.5 ± 1.7	-33.15
SMCHS pretreatment	72.2 ± 6.1	-20.75
SMCAHS pretreatment	119.8 ± 2.9	-15.65

Contact angle on the clean and fouled membranes after different pretreatments with SMHSs was measured to estimate the hydrophobicity (Table 5.16). A higher contact angle represents higher hydrophobicity of the membrane surface. The result of the contact angle indicates the following order: RO fouled with raw SW (61.5 ± 1.7) <clean (virgin) RO (64.3 ± 5.1°) < RO fouled with SW pretreated by SMCHS (72.2 ± 6.1°) < RO fouled with SW pretreated by SMCAHS (119.8 ± 2.9°). The RO fouled with raw SW exhibited that the lowest contact angle and the fouled RO membrane with pretreated SW showed higher hydrophobicity. It indicates that hydrophobic compounds are deposited on RO membrane with SW pretreated by SMHSs. This suggests that pretreatment with SMHSs led to prevention of absorption of hydrophilic compounds (present in the feed water) on the membrane surface by removing hydrophilic compounds from SW. Table 5.16 presents the variation of zeta potential of clean RO membranes with raw SW and pretreated SW. Zeta potential of fouled RO membrane

with raw SW slightly increased. The zeta potential of fouled membrane with SMCHS pretreated SW also increased. The latter might be due to the adsorption of the iron ions and/or iron hydrolytes on the membrane surface.

5.4.4 DISCUSSION

The factors affecting the SWOM fouling on membrane include membrane feed organic matter characteristics, membrane operating conditions, membrane characteristics and solution chemistry. Hydrophobicity and electrostatic interactions between solute and membrane were also reported to be the dominant factors that affect the extent of SWOM fouling. As various factors influence the process of fouling, it is difficult to distinguish the dominant factors that are responsible for it. Hence this study was done in order to solve this ambiguity and help in the proper selection of configurations of pretreatment and operating conditions to ensure an economical and successful operation.

5.4.4.1 Effect of fouling on RO performance

A potential drawback of RO is membrane fouling, resulting in an increase of normalised pressure drop and/or a decrease of normalised flux. All types of fouling except biofouling and organic fouling are controllable. Organic fouling and biofouling are irreversible. Biofouling, in particular, is difficult to quantify because to date, no univocal quantification method linking biofouling and operational problems are described (Vrouwenvelder et al, 2009b). In this study, pressure drop was measured during the RO operation and the pressure drop declined was less with pretreated seawater since pretreated seawater had a lower organic matter content. Specifically protein-like and humic-like materials in biopolymer contents that have high molecular weight (approximately 20 kDa) were removed by SMHSs.

Pressure drop has been generally used as an indicative parameter to evaluate fouling in various studies. An increase in pressure drop, however, is not directly linked to fouling because other factors including inorganic salts and organics accumulation or adsorption

may also influence pressure drop. Flemming (1993) stated that the pressure drop measurement may not be sensitive enough for (early) detection of fouling.

Detailed foulant characterization showed that hydrophilic organic compounds and high MW protein and/or humic-like substances evidently fouled the RO membrane used. The colloidal NOM (biopolymers) was further analysed and found to be composed of polysaccharides, amino sugars, proteins as well as humics from the IR spectra. Colloidal materials that are not removed by the pretreatment play a critical role in causing/contributing to severe fouling of the RO membrane. Therefore selecting the pretreatment method is significant as organic matter remaining after pretreatment is responsible for development of initial biofilm on the RO membrane. However, SMHS could remove these main organic foulants effectively. For example, a considerable reduction of high molecular weight (33.3kDa and 1,500Da) represents the removal of biopolymers.

5.4.4.2 Relationship of organic and biological (bio) fouling

Bacterial growth occurs in the presence of small organic molecules such as low molecular weight acids and neutrals that are easily assimilated by microorganisms (Van der Kooij, 1992; Hammes et al., 2006). Low molecular weight (LMW) organic matter in the feed water caused bacterial growth and re-growth on the RO membrane. According to previous research (Xu et al., 2010) SMCAHS removed almost of hydrophilic compounds in seawater. About 88% of LMW neutrals were removed when SMCAHS was used. In this study, when seawater pretreated by SMHS entered into the RO unit, a majority of LMW organic foulants in the MW range of 165 Da to 40 Da disappeared in the RO foulant (**Figure 5.19**). After RO operation with the pretreated seawater, the organic foulant was observed to have a peak around 24.1 kDa, which is mainly the biopolymer. Humic substances with a molecular weight of 1,500 to 1,600 Da were also

present in the foulant. These substances are known to exhibit relatively highly specific UV absorbance (SUVA) values and contain relatively large amounts of aromatic carbon. Here SUVA is defined as UV absorbance at 254 nm/dissolved organic carbon. Meanwhile, microbial by-products, from either algae or bacteria, generally have relatively low SUVA values. Microbial by-products are composed of acids with a relatively high charge density (Croue et al., 1999). This finding is consistent with the research by Park et al. (2006). They stated that colloidal NOM with molecular weight cut-off (MWCO) of 3,500 Da contained relatively polar amino sugars which might have exhibited high membrane fouling potential due to its neutrality.

The fluorescence analysis showed a reduction of humic-like relative to protein-like compounds and aromaticity of humics in the foulants of RO with pretreated seawater. The two peaks (T and M) can be assumed to represent or indicate biofouling potential. The intensity of peak T in the foulant on RO membrane with SMCHS pretreated seawater decreased to almost half of that with raw SW. Peak M in foulant with seawater samples pretreated by SMHSs was also less than that when using raw SW. Thus, the reduction of organic matter in the RO foulant with pretreated water proved semi-quantitatively through the EEM.

The organic matter in feed water and/or the accumulation of organics on the membrane also led to the development of biological foulant at the initial stage. The combination of ATP and TDC analyses (and cell viability) in a membrane element is a representative for diagnosis of biofouling (Vrouwenvelder et al., 2008). Cell viability is the ratio of the number of live and dead cells whereas ATP represents bacterial activity in foulant in terms of ATP concentration per unit membrane area ($\mu M/cm^2$). ATP concentration depends on TDC (Total direct cell counts) value while cell viability influences only the live and dead cell portions. Thus, ATP value is proportional to live cell % (cell viability)

x TDC value (**Figure 5.21**).The biological foulant characterization results showed that fewer cell numbers and less biomass activity and cell viability were observed on the RO membrane with seawater samples pretreated by SMHSs. Therefore an integral approach (incorporating both organic and biological) is essential in fouling diagnosis and control. The organic and biofouling results obtained prove that the SMHS pretreatments help in producing permeate of superior micro-biologically stable feed to the RO unit. This is because the organic compounds of LMW (the preferred carbon source for microorganisms) were partially removed by SMHS. At the same time the high molecular organics such as biopolymers causing organic fouling were also removed by SMHS. Biofouling leads to microbial growth and production of EPS. EPS-polysaccharides and EPS-proteins are also important components of bacterial biofilms and their function is related to adhesion, aggregation, sorption of organic compounds and inorganic ions together with enzyme activity. Thus, not only does bio-volume but also the distribution of the biofilm components (i.e. protein and carbohydrates) is important. This ultimately affects the membrane permeability. Generally, the membrane biofouling can originate from soluble and suspended material (e.g. NOM, cells, EPS) in the feed water and from cell growth on the membrane.

5.4.4.3 Effect of membrane characteristics

In addition to the feed water quality, characteristics of the membrane also play a significant role in membrane fouling during the initial phase of filtration. This is important in hydrophobic membranes with high permeability. A membrane characterization study also provides useful information on the types of fouling present even though it is not significant during the initial period of RO run. A detailed membrane characterization enables actions for prevention and control of fouling at initial stage (for early warning). To date, despite the substantial effort in understanding

the fundamentals of membrane fouling, information on fouling reduction by a low pressure-based membrane hybrid pretreatment system is limited.

The fouling materials are made of polysaccharides, amino-sugars and proteinaceous structures which had a bacterial origin (living and/or non-living residues, and soluble microbial products) present in the water during operation. The presence of organic materials with amine and amide functional groups on the membrane surface was confirmed from the FTIR analysis.

The surface roughness normally influences the fouling rate for the thin-film membrane which is inherent in interfacially polymerised aromatic polyamide composite membranes (Pontié et al., 2007). However, in this study, we did not observe significant change in the membrane roughness from AFM analyses. This may be due the fact that RO run was only for 45 hours. Generally, the rejection rate of hydrophilic fractions (i.e. non-humic substances) by a negatively charged membrane surface was considerably lower than that of hydrophobic fractions because of their charge characteristics.

Non-humic substances were easily deposited on the negatively charged RO membrane surface. It significantly decreased the surface charges of the RO membrane. Due to the relatively high charge repulsion between the humic substances and the RO membrane surfaces, the hydrophobic fractions of SWOM might have covered the fouling layers with polysaccharide-like and protein-like substances. It may have resulted in the increase of the contact angle. The latter effect might be considered the most important factor in enhancing the subsequent fouling formation of the RO membranes.

5.4.5 SUMMARIZING THE FOULANT ANALYSES

Evaluation of organic fouling and biofouling characterization of RO membrane on lab-scale cross flow RO test unit with seawater samples pretreated by SMHSs led to the following conclusions:

(1) Pretreatment by SMHSs helped to reduce the organic concentration in the RO feed and in turn reduced the organic foulant on RO.

(2) Less high molecular weight organic content (biopolymers and humics) in the RO feed by SMHS pretreatment helped to reduce the flux decline by organic foulants on the RO membrane(from 31.5 LMH with raw SW to 36.0 LMH with SMCHS and 45.4 LMH with SMCAHS).

(3) SMHSs also led to less deposition of low molecular weight organic matter on the RO membrane which in turn resulted in lower initial biomass accumulation (from $4.10E^{+08}$cells/cm^2 with raw SW to $1.77E^{+08}$cells/cm^2 with SMCHS and $2.75E^{+08}$cells/cm^2 with SMCAHS) and microbial activity (from 0.5 with raw SW to 0.3 with pre-treated seawater by both SMHSs).

(4) During the initial stage, it was difficult to directly link changed membrane characteristics to membrane performance. However, pretreated seawater reduced the hydrophilic organic foulants and preserved the membrane surface.

It can be stated that these various approaches can help to select a hybrid membrane system's optimal configuration.

CHAPTER 6

University of Technology Sydney

Faculty of Engineering& Information Technology

TESTING OF A NEW PRETREATMENT OF MEMBRANE ADSORPTION HYBID SYSTEM WITH A NEW RAPID AOC METHOD

This chapter introduces a newly developed the assimilable organic carbon (AOC) method to rapidly evaluate biofouling potential (**Section 6.1**). This is followed by a submerged membrane adsorption bioreactor (SMABR) as sustainable pretreatment to control biofouling on RO membrane (**Section 6.2**). The new AOC method is also tested.

<Publications related to this chapter>

– Jeong, S., G. Naidu, S. Vigneswaran, C.H. Ma, S.A. Rice. (2013) A rapid bioluminescence-based test of assimilable organic carbon for seawater. Desalination 317: 160-165.

– Jeong, S., G. Naidu, S. Vigneswaran. (2013) Submerged membrane adsorption bioreactor as a pretreatment in seawater desalination for biofouling control. Bioresource Technology (DOI: http://dx.doi.org/10.1016/j.biortech.2013.01.021).

6.1 NEW RAPID BIOLUMINESCENCE-BASED ASSIMILABLE ORGANIC CARBON TEST

6.1.1 INTRODUCTION

Biofouling imposes a significant economic burden on the operation of reverse osmosis (RO) desalination systems and results in greater operating pressures, the frequent need for chemical cleaning, membrane deterioration and compromised water quality (Martin et al., 2011). It has been suggested that early biofouling prediction (or warning) has the potential to significantly reduce operating and membrane costs by having remediation steps implemented earlier (Vrouwenvelder et al., 2011). For example, early warning of biofouling potential could lead to selecting the best pre-treatment method and better monitoring of the effectiveness of the pretreatment process. The potential annual savings of an early prediction of biofouling is anticipated to be USD 2 million based on a seawater reverse osmosis (SWRO) plant operating at 10,000 m^3/h capacity (Vrouwenvelder et al., 2011).

Assimilable organic carbon (AOC) refers to a fraction of “labile” or “bio-available” dissolved organic carbon (DOC) that is readily assimilated and utilized by microorganisms resulting in an increase of biomass. Thus, the concentration of AOC can influence biological fouling (biofouling) in water treatment systems and distribution processes by promoting growth of fouling organisms. Indeed, a high level of AOC is directly linked with rapid biofilm formation and loss of performance in membrane processes (Hambsch and Werner, 1996). Therefore, assays that quantify AOC can be used as an indicator of the relative fouling potential of specific samples, such as seawater entering an RO plant.

To date, the available methods for quantifying AOC are rather laborious and time-consuming to complete. Many AOC assays typically measure the growth of an inoculum in a water sample which the natural bacterial community has first been removed and inactivated. The inoculum grows until stationary phase ($\mu = 0$), based on the principle that the growing bacteria have assimilated all the AOC in the water sample. The net growth of the bacteria is measured by various methods, and then converted to an AOC (or AOC-equivalent) concentration (Van der Kooij et al., 1982). This cell growth based method can take up to 3-7 days to complete after which time it is often too late to take action to control the AOC levels. AOC test investigated in **section 5.1** also required 5 to 6 days to be completed. This made a strong motivation to develop rapid AOC method. In addition, the methods adopted from previously published research are especially tailored for quantification of AOC in freshwater and drinking water (Hammes and Egli, 2005; Hammes et al., 2007; Van der Kooij et al., 1982). While two studies have reported AOC methods using different *Vibrio* strains, which can be used for marine water samples, these methods are still time consuming and not suited for informing plant operation (Orange County Water District Fountain Valley, 2005; Weinrich et al., 2011). Therefore, this study focused on the development of a new rapid and sensitive method for easy applicable measurement of AOC in seawater (marine) samples.

In this study, *Vibrio fischeri* MJ-1 (*V. fischeri*) strain was used (Nealson, 1977). A direct bioluminescence measurement method was applied as an instantaneous indicator of cell number and AOC concentration. This was feasible because the strain constitutively produces bioluminescence, which can be directly related to biomass density. The bioluminescence can consequently be correlated to the AOC in the

seawater sample. In order to further substantiate the applicability of the selected method, this study was applied for pretreated seawater samples by biofiltration.

6.1.2 MATERIALS AND METHODS

6.1.2.1 *Vibrio fischeri* MJ-1 (*V. fischeri*)

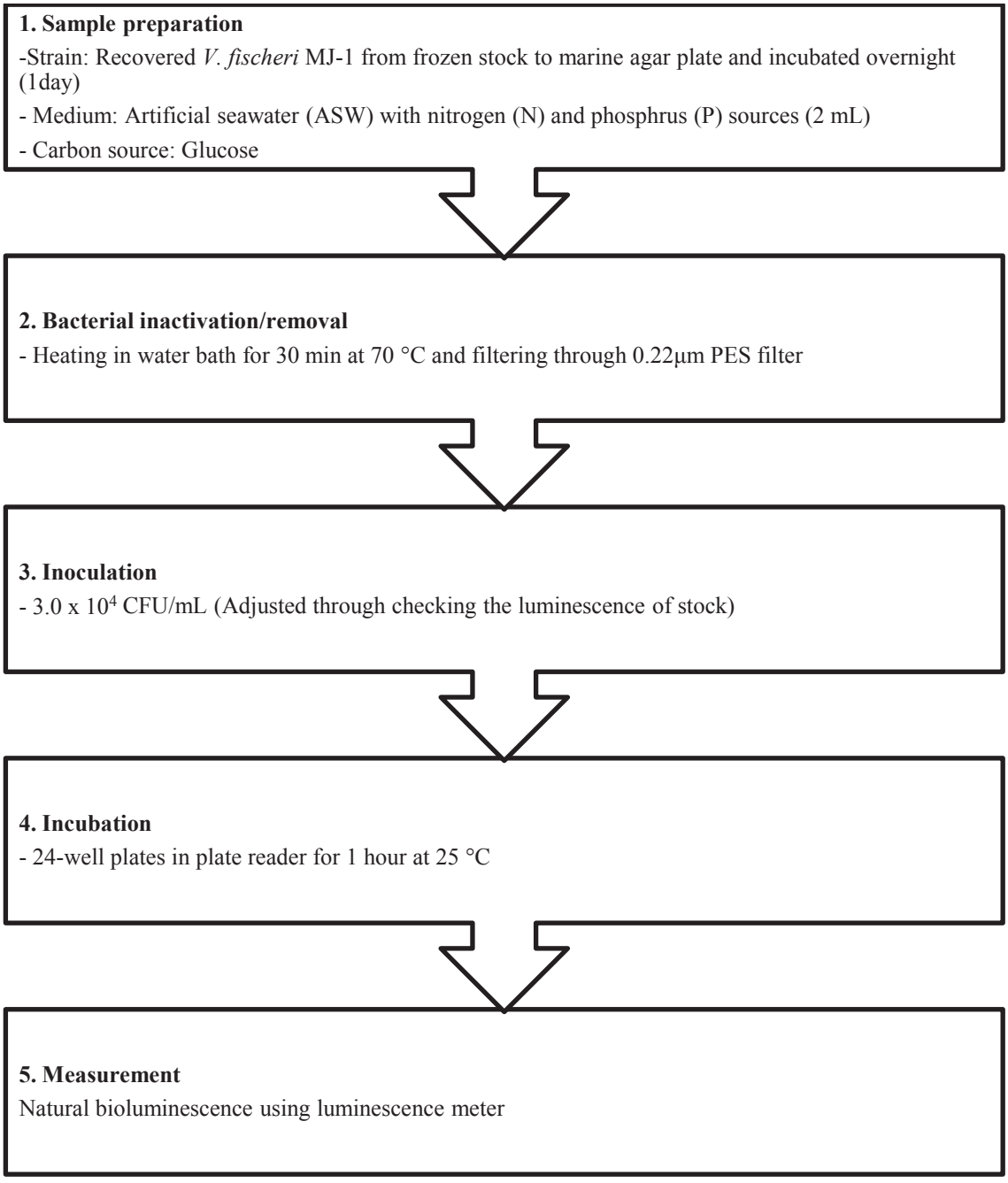
V. fischeri was provided by Dr. Diane McDougald at University of New South Wales, Australia. It was recovered from stocks that were kept frozen at -80°C in marine broth and 10% glycerol by streaking onto marine agar containing (per liter) 37.4 g marine broth and 15.0 g bacto agar (Difco™ and BBL™), and incubated (room temperature 25°C) overnight. To prepare the stock for AOC test, colonies were re-suspended from the marine agar plate into artificial seawater (ASW) and concentrated for inoculation. ASW was prepared by dissolving (13.5 g NaCl, 1.96 g Na_2SO_4, 0.107 g $NaHCO_3$, 0.33 g KCl, 0.053 g KBr, 2.5 g $MgCl_2 \cdot 6H_2O$, 0.55 g $CaCl_2 \cdot 2H_2O$, 0.0107 g $SrCl_2 \cdot 6H_2O$ and 0.0107 g H_3BO_3 and adjusted to pH 7.5) in 1,000 ml Milli-Q water. The ASW medium was fortified with 9.52 mM NH_4Cl and 1.32 mM K_2HPO_4.

6.1.2.2 AOC test

A 24-well multiwell, tissue culture treated plate (353047 - BD Falcon™) was used for the AOC test and was covered with parafilm to minimize the evaporation. ASW was inoculated with 3.0 x 10^4 CFU/mL of *V. fischeri* from a concentrated (3.0 x 10^6 CFU/mL) stock solution (initial luminescence was set at approximately 1.0 x 10^6 counts per second (CPS)). Upon checking the luminescence, the strain was transferred to a 2 mL tube for washing with culture media three-times. Luminescence was measured using a Wallac 1420 VICTOR2™ plate reader (PerkinElmer Inc., US). To prepare the seawater samples for AOC quantification, the samples were filtered to remove large particles (0.45 μm PES filter), bacteria were inactivated at 70 °C for 30 min, and the

seawater samples were then filtered (0.22 μm PES filter). Predetermined cell numbers of each bacterium was spiked to the sample (2 mL). For the standard curve, glucose was added to the ASW as a sole carbon source at a range of concentrations (0, 10, 25, 50 and 100 μg-C/L; stock solution-100 mg-C/L). A general carbon source; glucose was used as a better cell growth was obtained with glucose even at low concentration. Previous research has shown that *V. fischeri* cells are able to metabolize a variety of compounds. Specifically, it has been highlighted that a high bioluminescence production can be achieved with glucose between the sensitivity ranges of 5-100 μg/L (Orange County Water District Fountain Valley, 2005). The plates were then incubated at 25°C in the plate reader and bioluminescence was measured automatically every 5-10 min for 2 h. In this study, all the measurement was triplicate at least. The detailed procedure of AOC test is given in **Table 6.1**.

Table 6.1 Procedure of *V. fischeri* AOC method.



6.1.2.3 CLSM observation

Direct observation of *V. fischeri* cell was trialed using confocal laser scanning microscopy (CLSM). This is in order to ensure and validate the cell growth of *V. fischeri*. For this purpose, the *V. fischeri* cells were filtered onto 0.2 μm-pore sized black polycarbonate membrane (Millipore) for quantification of cell number. The number of

live and dead cells in the samples was also measured after staining samples with SYTO9 and propidium iodide (PI). Samples were analyzed by collecting images and quantifying cells using image analyzer software. CLSM (Olympus FV1000) was equipped with excitation (Ex) and emission (Em) wavelengths for the two channels (Ex: 420nm/Em: 580nm for SYTO9 and Ex: 488nm/Em: 640nm for PI) used.

6.1.2.4 Application and validation of the new AOC method

Deep-bed biofilters have been used as a conventional pretreatment method to remove organic matter from feedwater. In a deep-bed biofilter, organic matter is firstly removed by adsorption. Subsequently microbes, which have absorbed onto the filter medium, utilize the labile dissolved organic carbon or AOC as a carbon source for their growth and metabolism. This can ensure biological stability of the treated water (Boon et al., 2011). The bioluminescence based AOC method developed in this study was validated by measuring the AOC concentration in raw seawater and biofilter-treated seawater. Granular activated carbon (GAC) was used as a packing medium in a deep-bed biofilter.

6.1.3 RESULTS AND DISCUSSION

6.1.3.1 Correlation between bacteria number and bioluminescence

In order to develop a rapid assay, the relationship between bioluminescence and cell number of *V. fischeri* was determined (**Figure 6.1**). A correlation between these two measurements would mean that bioluminescence can be used to represent cell number, saving time for extraction and quantification steps. For this purpose, *V. fischeri* cells were diluted from a single stock culture and the bioluminescence was quantified. Across the range of CFUs tested, from 10^3 to 10^5, a linear correlation (R^2=0.999) between the CFUs and bioluminescence was observed. This suggests that bioluminescence can be used to estimate cell numbers of *V. fischeri* since cell numbers increase as a function of available carbon substrate. Thus bioluminescence should be a suitable indicator of AOC concentration in samples as well as to estimate CFU/ml. *V. fischeri* (at 10^5 cells per mL) produced a high level of bioluminescence (32,033 CPS).

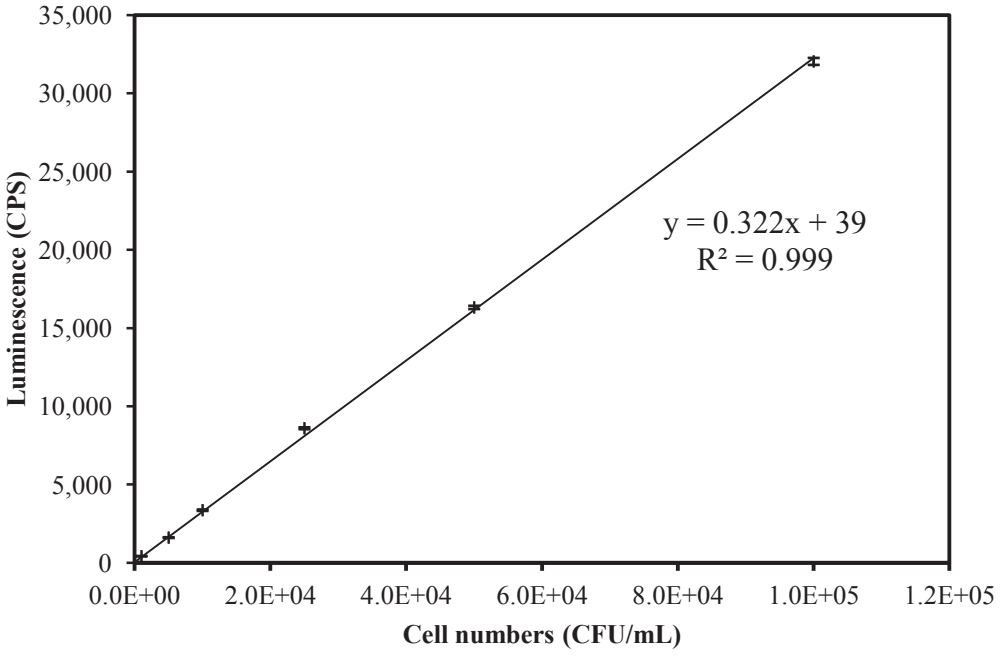


Figure 6.1 Correlation of luminescence and cell number of *V. fischeri*.

6.1.3.2 Bioluminescence response as a function of AOC concentration

The bioluminescence output of *V. fischeri* was quantified for a range of glucose concentrations (0, 20, 40, 60 & 100 µg-C/L) at 5 min intervals for duration of 2 h (**Figure 6.2**). This is to determine the correlation between bioluminescence responses of *V. fischeri* to glucose concentration over a short time frame, enabling it to be suitable as a rapid AOC test. For all concentrations, the bioluminescence response reached its maximum within the first 30 min, and the total counts declined to almost undetectable levels after 6 h. This is an added advantage of using *V. fischeri* for the AOC test as the analysis can be conducted within a short span of time. Previous researches (Herring, 2002; Karen et al., 2012) also reported that the doubling time of growth of *V. fischeri* was short of 30 min to 1 h. In this study, the doubling time of *V. fischeri* was found to be around 30 min. After 30 min, bioluminescence produced by *V. fischeri* decreased drastically. This may be attributed to the limited nutrients at high population densities (around 10^5 cells). Thus, it can be assumed that all the glucose was consumed when the strain growth reached the generation time (doubling time).

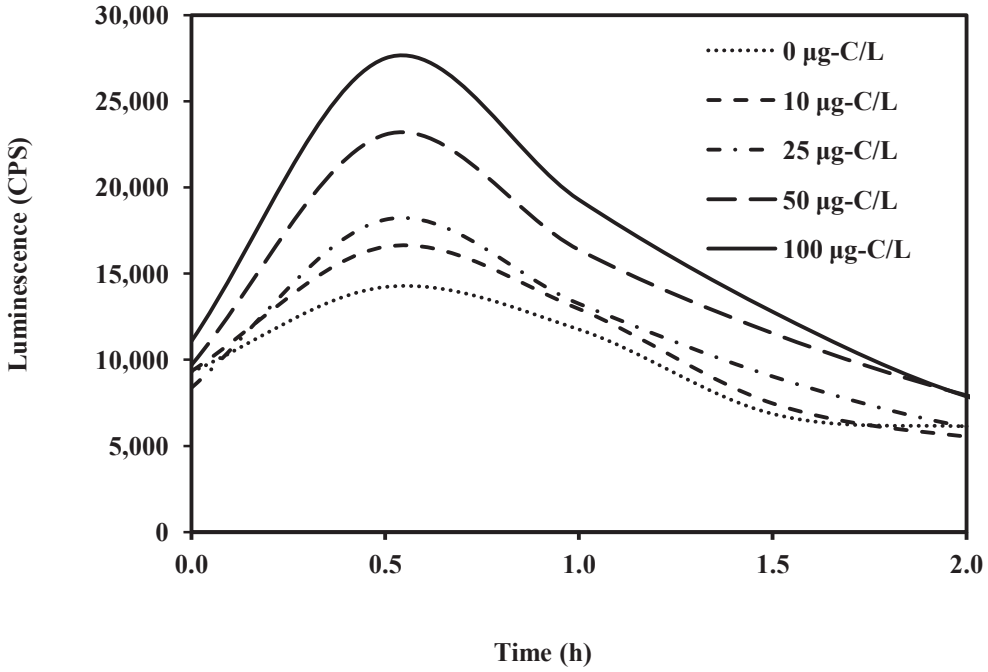


Figure 6.2 Variation of bioluminescence of V. fischeri on different glucose concentrations.

Also glucose concentration used in this assay was only less than 100 µg-C/L. Therefore one could assume that the consumed glucose concentration is an accurate representation of the actual AOC compound. The bioluminescence output was directly related to glucose concentration, whereby at the highest concentration (100 µg-C/L), the luminescence was 27,508 CPS while at the lowest concentration (0 µg-C/L) the luminescence was 14,221 CPS (**Figure 6.2**).

By plotting the maximum bioluminescence (at 30 min) against glucose concentration, it is clear that there is a strong and linear correlation between the two measurements (R^2=0.978) (**Figure 6.3**). Based on this relationship, it was possible to estimate the AOC concentration of samples based on the bioluminescence response of *V. fischeri*. For practical reasons, the bioluminescence at zero glucose concentration was adjusted to zero by subtracting the background luminescence value.

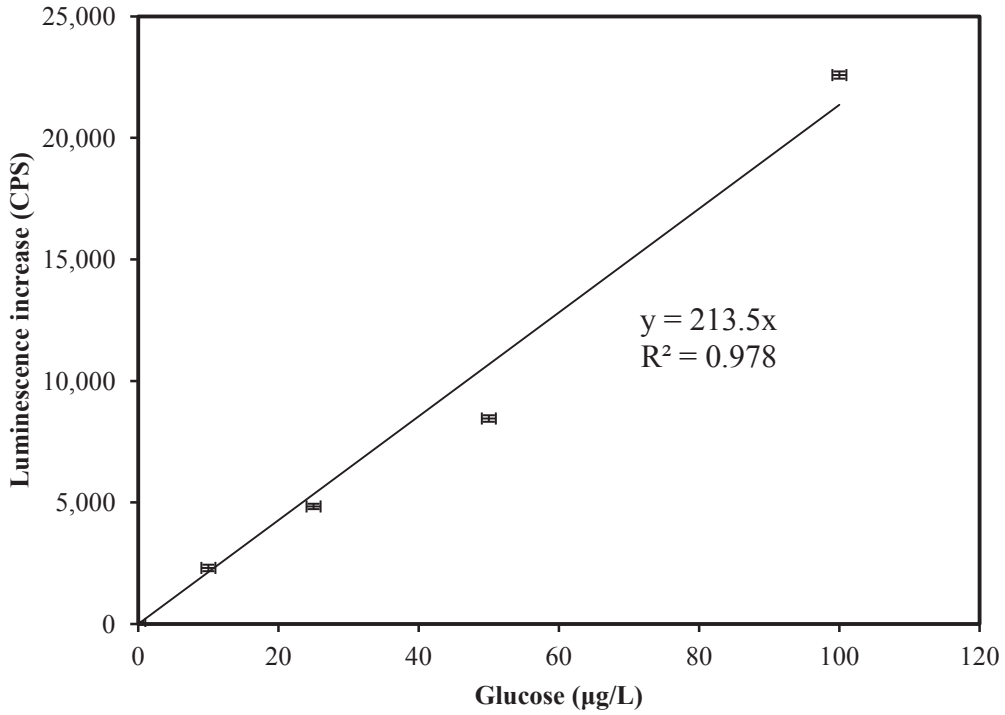


Figure 6.3 Measured bioluminescence of *V. fischeri* at different glucose concentrations after 30 min incubation (the luminescence value at 0 µg/L of glucose concentration was adjusted to zero by subtracting the background one).

6.1.3.3 Cell viability and bioluminescence

The cell growth of *V. fischeri* was observed using self-produced bioluminescence and further validated through staining of live and dead cells by CLSM (**Figure 6.4**). A significant decrease in live cells was observed between 20 and 40 min (around 30 min in the bioluminescence reading) and was associated with an increase in the number of dead cells. This observation further substantiates that luminescence produced from *V. fischeri* can be related directly with their growth and density of live cells. The specific number of live/dead cell did not counted in this study since this CLSM observation was carried out to validate the change of bioluminescence depending on the live/dead cell portion of *V. fischeri*.

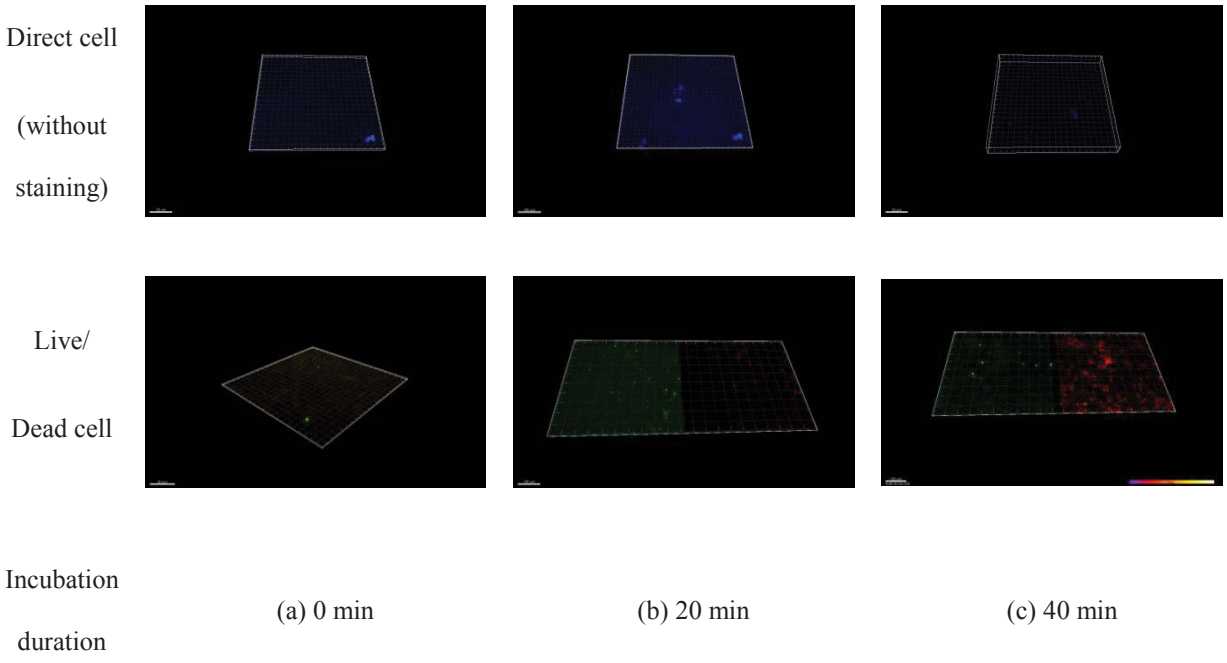


Figure 6.4 Direct observation of *V. fischeri* and variation of cell viability.

6.1.3.4 Quantification of AOC in seawater samples

The *V. fischeri* AOC assay was used to quantify the AOC concentration in raw seawater and effluent from a GAC biofilter. The AOC concentration in the raw seawater was in the range of 11.2-26.4 μg-C glucose equivalents/L. The value of AOC concentration in raw seawater was similar to previously reported values (Van der Kooij et al., 1982; Boon et al., 2011). Filtering raw seawater through a GAC biofilter significantly reduced the AOC concentration from 1818.0 to 0.2 μg-C glucose equivalents/L after 15 days of operation (**Figure 6.5**) (the X-axis in **Figure 6.5** represents the average value during the given period).

The results showed the capability of GAC biofilter to reduce AOC and the potential for the seawater to reduce microbial growth and biofouling on RO based seawater desalination. This also further validated the accuracy of the new AOC assay in determining the AOC concentration in seawater samples. The AOC in the untreated seawater (which was drawn from 1 m below the surface level of the sea and filtered to remove the large particles) showed changes with time, which may be due to metabolism

by endogenous bacteria in the seawater. These data suggest that the biomass formed on the GAC filter media has potential to remove AOC. This serves as a good selection criterion in considering biofilter as a pretreatment to control biofouling. As shown in **Figure 6.5**, the *V. fischeri* method was able to detect a low concentration of AOC (0.2 µg-C glucose equivalents/L) with a deviation of less than 5.0 %. The total time required to measure the AOC using the new method was less than 2 h, from the initial time of spiking the *V. fischeri* cells to the seawater samples to the final generation of a standard curve and plotting of the data. Therefore, this method is suitable to be applied to measure AOC concentration for pretreated seawater samples in current operating plants.

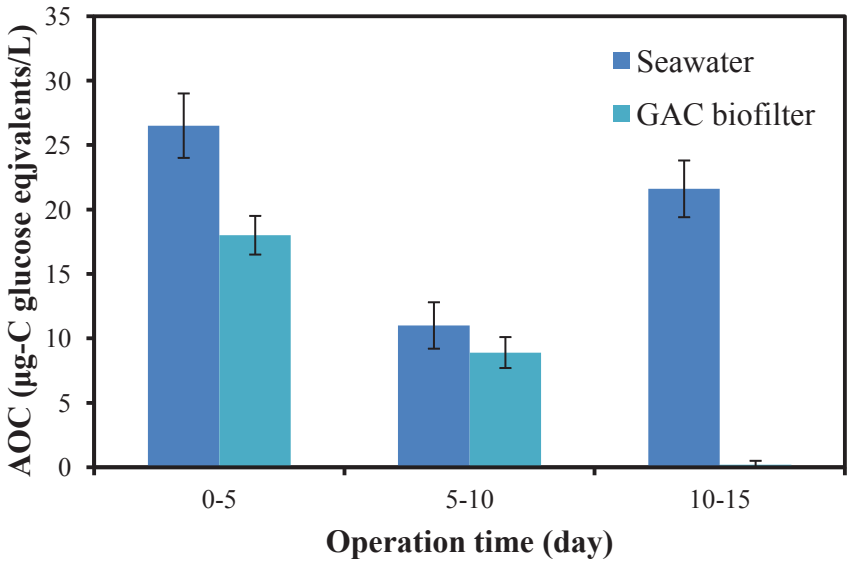


Figure 6.5 AOC concentrations of effluents through GAC media biofilter.

6.1.3.5 Comparison of AOC methods

6.1.3.5.1 Rapid Analysis

Studies have previously linked AOC directly to microbial re-growth and biofilm formation in water distribution systems (Van der Kooij 1992; Chien et al. 2007). The

implication is that, if it is possible to monitor AOC levels, it may be possible to apply methods that will reduce AOC and hence control biofouling. Despite the importance of AOC as an indicator of fouling potential, this measurement is not practiced routinely in the water industry. One of the contributing reasons to AOC not being routinely measured is that the existing assays are time-consuming (up to 14 days) and ultimately becomes retrospective measurements (Van der Kooij et al. 1982; LeChevallier et al. 1993). More recent improvements on this method have reduced the detection time to 3 to 4 days (Hammes and Egli 2005; Hammes et al. 2007) or to 1 to 2 days using a *Vibrio harveyi* based bioluminescence-based method (Orange County Water District Fountain Valley, 2005; Weinrich et al. 2011) (**Table 6.2**). Despite the significant improvement in time, an assay that provides a result after 5 days does not allow for remediative measures to be implemented. The new AOC method developed using *V. fischeri* can quantify the AOC concentration within 30 min. This would make it possible for operators to take prompt actions to control the AOC in the influent at the right time, enabling to reduce subsequent biofouling. Moreover, the highlighting point of this method is considerable saving of time and labor to measure AOC concentration.

6.1.3.5.2 Sensitive/ low detection limit

The results showed that the luminescence detection approach enabled to achieve small standard deviation of less than 10 % on triplicate measurements. Compared to plate counting (Van der Kooij et al., 1982; LeChevallier et al., 1993) and turbidity (Hambsch and Werner, 1996), the AOC method based upon luminescence was more sensitive (approximately 30,000 CPS per 10^5 cells). That apart, pure culture (*V. fischeri*) is well characterised and generally display uniform growth behaviour.

Other variations of the AOC assays have adopted flow cytometric quantification as a means of cell quantification (Hammes and Egli, 2005). In comparison to plate counting,

both the luminescence and flow cytometry are rapid, easy and sensitive techniques for measurement total cell concentration (Hammes et al., 2008). However, the flow cytometry cannot detect lower cell numbers (less than 10^2 cells/mL) which is possible with the luminescence method. The luminescence enumeration is also advantages to the flow cytometry due to the simple approach of luminescence detection. On the other hand, the more flow cytometric parameters that are taken into account, the more complex it gets to analyze the results (Karen et al., 2012). Another setback of flow cytometry is the reliability of the results as it is highly subjective to the handling and interpretation of the flow cytometry patterns. Further, a flow cytometer can cover only a small size range of microbes from 0.5 to 40 μm in diameter (Karen et al., 2012). Moreover it is not cheap, which is an important consideration. Flow cytometers normally cost between $100,000 to $250,000 including the machine, accessories and reagents. Furthermore, the flow cytometer typically requires a dedicated, skilled operator and is not readily used by non-skilled operators. This means that measuring cell number using flow cytometer is very expensive and not readily accessible.

In terms of the bacteria, strain chosen for the new AOC method using *V. fischeri* MJ-1 showed relatively high correlation of cell number and luminescence at even low carbon concentration of less than 50 μg/L, in comparison to the *V. harveyi* stain (Weinrich et al., 2011). A further advantage of the *V. fischeri* method developed here is that, since this bacterium is a marine isolate, it is adapted to high salt conditions and its metabolism is therefore suited for testing the AOC concentration in marine samples.

As with all methods there are some points that must be taken into consideration when using this method to quantify AOC in seawater sample. We have developed and validated the method here using artificial seawater and glucose as a carbon source to estimate AOC in real samples. While acetate gives a similar concentration dependent

increase in bioluminescence, it is not as strong as we observed for glucose (data not shown) and hence the AOC values are estimates, based on our standard curves using glucose. It is however, not possible to model all potential carbon sources and hence, glucose was used here to validate and standardise the method. Users should also consider the source water, in particular if it contains contaminants that might interfere with the bioluminescence response, such as organic pollutants, which might damage bacterial membranes, which would inhibit ATP production necessary for bioluminescence. Interesting, the method developed here can actually give an indication that source waters contain inhibitors since their presence would result in low or no bioluminescence relative to controls. This could further be tested and controlled for by spiking source waters with glucose and comparing the bioluminescence response with the standard curve.

Table 6.2 Comparison of AOC methods.

Method	Target (Volume, mL)	Culture	Sterilization	Inoculation	Incubation		Cell counts	Substrate	Detection limits	Ref.
					Temp. (°C)	Time (day)				
Van der Kooij	Drinking water (600)	*Pseudomonas fluorescence* strain P-17 and *Spirillum* strain NOX	70 °C, 30 min	500 CFU*/mL	15	7-9	Nutrient agar plate	Acetate	10 µg/L acetate C equivalents	[4]
Dutch standard	Tap water	P-17 and NOX	70 °C, 30 min	N.A.*	15	2-14	ATP analysis + plate	Acetate	N.A.*	[11]
Werner & Hambsch	Sterile nutrient salt solution (250 mL)	Natural community	0.22µm filter	50000 cells/mL	22	2-4	Turbidity	Acetate	10 µg/L acetate C equivalents	[3]
Eawag	Tap water	pre-cultured natural microbial community	0.2 µm syringe filter	10^4 CFU/mL	30	2-3	Flow cytometry	Acetate	10 µg/L	[5]
V. harvey	Saline water	*V. harvey*	N.A.*	N.A.*	30	<1	Luminescence	Acetate	<10 µg/L	[8]
V. fischeri	Seawater (2mL)	*V. fischeri*	70 °C, 30 min 0.22µm filter	3 x 10^4 CFU/mL	25	< 1h	Luminescence	Glucose	1 µg/L	This study

*N.A: Not available.

6.1.4 SUMMARIZING THE RAPID AOC TEST

A new AOC method was developed for seawater based on bioluminescence using *V. fischeri*. In comparison to previously developed methods, a more accurate and significantly time-saving measurement method was achieved. *V. fischeri* AOC method was rapid (within 1 h), and sensitive (R^2 = 0.978) for seawater. Reproducibility (<10% of standard deviation) of the method was evaluated through biofiltered seawater sample. This bioluminescence-based AOC method can be effectively used as an indicator for biofouling potential in seawater.

6.2 SUBMERGED MEMBRANE ADSORPTION BIOREACTOR

6.2.1 INTRODUCTION

The major types of fouling in RO membranes are crystalline (scaling), organic, particulate (or colloidal) and microbiological. The first three types of fouling can be reduced to a great extent through pretreatment while biofouling can be difficult to control, since deposited microbial cells can grow, multiply and relocate. Biofouling is mainly the accumulation of microorganisms accompanied with agglomeration of extracellular materials on the membrane surface. When a microorganism adheres to the membrane surface, it starts building up aggregates in the form of biofilm matrix (Al-Juboori and Yusaf, 2012). Even if 99.99% of all bacteria are eliminated by pre-treatment (e.g. microfiltration or biocide application), a few surviving cells will enter the system, adhere to surfaces, and multiply at the expense of biodegradable substances dissolved in the bulk aqueous phase. Therefore, membrane biofouling has been found to occur extensively on RO membranes even after significant periodic direct cleaning of membranes and continuous upstream application of biocides and disinfectants such as chlorine (Flemming et al., 1997a). Further, polymeric membranes are sensitive to oxidizing disinfectants and hence continuous biocide addition from the usage of disinfectant and biocide can affect the growth of resistant strains of bacteria (Kang et al., 2007; Shannon et al., 2008).

Thus the removal of biodegradable organics as well as microbial inactivation at the same time would be effective to control the biofouling. A promising option to control biofouling is membrane bio-reactor (MBR). The removal of organics and nutrients (such as ammonia, nitrate and phosphorus) for wastewater by MBR was achieved through the microbial decomposition of these materials. The MBR system can also

effectively treat saline water such as blackish water and seawater (Ahmad et al., 2010; Lay et al., 2010; Chen et al., 2011; Johir et al., 2011; Tian et al., 2011).

A few initial studies have been conducted on the use of MBR to treat saline water. Visvanathan et al. (2002) conducted experiments with MBR to investigate the effects of biodegradable organic content removal in biofouling control. Their results showed that MBR was able to remove 78% of dissolved organic carbon (DOC). They also reported that effluent from MBR increased the RO permeate flux by 300% more than the untreated seawater. Yogalakshmi and Joseph (2010) studied the effect of sodium chloride (NaCl) shock loading on the removal efficiency of chemical oxygen demand (COD) on a bench-scale aerobic submerged MBR operated at a steady state oxygen uptake rate (OUR) of 3.6 g of COD/L/d and hydraulic retention time (HRT) of 8 h. They found almost 95% of COD was removed with a sodium chloride shock loading of 5–30 g/L. The removal efficiency of COD at a NaCl shock of 50 and 60 g/L was 77% and 64% respectively. From the above studies, it is evident that MBR technology can be effectively applied as a pre-treatment of seawater with high salt concentration.

Lay et al. (2010) reported that true halophilic microorganisms or halophiles grown in a saline environment required a certain minimum level of salt for continued existence. These groups of microorganisms contained a large number of aerobic heterotrophs that are able to biodegrade organic carbon matter from saline water. Lefebvre and Moletta (2006) also stated that biological treatment of carbonaceous, nitrogenous and phosphorous pollution had proven to be feasible at high salt concentrations but its efficiency depended on proper adaptation of the biomass or the use of halophilic organisms.

Organic pollutant cannot be completely removed by conventional MBR systems (Orem et al., 2011). A submerged membrane adsorption bio-reactor (SMABR), on the other hand is expected to remove a superior amount of organic pollutants (Guo et al., 2008). This is because adsorbent added in a submerged MBR in a small quantity increases the organic pollutant removal capacity. The SMABR system can reduce RO membrane bio-fouling by eliminating biodegradable organic matter (BOM). It is robust, environmentally friendly due to reduced usage of chemicals (coagulants and biocides), and requires little maintenance as well as energy.

The effect of adding PAC on the performance of submerged microfiltration system with seawater was investigated in this study. A short-term study as shown in **section 4.5** of **Chapter 4** showed that the submerged membrane system coupled with PAC adsorption was investigated with 1.5 g/L of PAC added. It showed superior DOC removal (76.6%) and most of the hydrophilic fraction (73.3%) had been removed. The detailed analysis of the hydrophilic portion showed that the removal efficiencies of biopolymer, humics, building blocks and neutrals were as high as 92.3%, 70.0%, 89.5% and 88.9%, respectively. The RO lab-scale cross-flow test showed that the initial permeate flux was improved by 6.2 $L/m^2.h$ when the seawater was pretreated using the submerged membrane system coupled with PAC adsorption (See **Figure 5.3** of **Chapter 5**). This also led to a lower permeate flux decline in RO operation. Apart from this, less foulant was found on the RO membrane (consisting of less biopolymer). Moreover, this system resulted in a significant decline in bacteria cell numbers and cell viability. The positive results obtained from these preliminary studies demonstrated the necessity for a detailed and a long-term study on MBR as a sustainable pre-treatment to reduce biofouling.

In this study, PAC replenishment was optimized to maintain stable bioactivity and produce high quality permeate in terms of organic removal by adsorption and consistent

increase of biomass. The effect of PAC age (residence time) in SMABR to treat seawater was evaluated by comparing optimal PAC replenishment with maximum biological mode. Not only organic removal but also biofouling potential reductions were investigated in terms of assimilable organic carbon (AOC).

6.2.2 MATERIALS AND METHODS

6.2.2.1 Materials

6.2.2.1.1 Seawater

The continuous SMABR study was conducted at Sydney Institute of Marine Science, Chowder Bay, Sydney, Australia. The seawater was pumped from 1 m below seawater surface level and pre-filtered through a 140μm large-pore filtration system to remove the large suspended particles. During the entire operation period, the average pH, turbidity and DOC values of seawater used in experiments were 8.1 (±0.3), 0.65 (±0.15) NTU and 2.15 (±0.85) mg/L, respectively. Total suspended solid in seawater was 3.6 (±0.8) mg/L.

6.2.2.1.2 Powder activated carbon (PAC)

PAC (MDW3545CB powder, coal based) was used as an adsorbent in this study. The mean diameter and the nominal size (80% min. finer than) of PAC were 19.7μm and 75.0μm, respectively.

6.2.2.1.3 Microfiltration membrane

In the SMABR system a hollow fibre microfiltration (MF) membrane (see **section 3.1.2**) was used. The U-type membrane length was 47.0 cm with an outer fibre diameter of 2.0 mm and an inner fibre diameter of 0.8 mm.

6.2.2.2 Optimization of PAC replenishment

PAC replenishment (replacement) needs to be optimized to maintain a stable biological activity in a submerged membrane bio-reactor while achieving consistently high rates of organic removal. A renewed PAC has high capacity to absorb the organic matters but

too frequent replacement leads to low growth of microorganisms. Here, optimal conditions were selected based on high DOC removal and continuous increase of mixed liquor suspended solids (MLSS) by microbes in the reactor.

In order to find the optimal PAC replenishment range, a semi-batch test was carried out for 28 days. This batch experiment was conducted in a carbon-free glass bottle (300 mL) shaked at 150 rpm and 25°C using temperature controlled shake incubator. In order to avoid the evaporation of sample, the top of the bottle was sealed. An initial amount of 5 g/L (1g in 200 mL) of PAC was dosed initially. There was no seeding done at the start. The microbes in the seawater utilized the organic matter in the seawater during incubation (accumulation) period of 28days. Visvanathan et al. (2002) also observed biomass accumulation with seawater without any seeding. Our previous work with biofilter to treat seawater also did not have any prior seeding and a significant biological activity was observed after 15 to 20 d of filter run (Naidu et al., 2013).

PAC with five different amounts was replenished daily and fresh seawater of 100 mL (half of total water volume) was replaced on a daily basis after settlement. MLSS concentration was calculated as suspended solid concentration. The mixed liquor was taken together with PAC particles. The batch reactor was shaked vigorously at 150 rpm when the mixed liquor was taken for MLSS analysis. Thus, it was assumed that the biomass attached on PAC was detached into the suspension. Further, MLSS measurement was triplicated and an average value was taken. At the same time, sampling of supernatant for other measurements was done intermittently. The measurement of MLSS was carried out in the laboratory according to the standard procedures (APHA/AWWA/WEF, 1995).

The residence time of the PAC can be defined as the ratio between the mass of PAC in the bottle and the mass of PAC replaced daily. PAC residence time corresponds to the ratio of PAC replenishment. The replacements of PAC were 0, 1.0, 1.5, 2.5, 5.0 and 20% which correspond to a PAC residence time of ∞, 100, 66, 40, 20 and 5 d respectively.

In SMABR, the age of PAC (δ_{PAC}, in d) is defined as the ratio between the mass of PAC in reactor (m_{PAC}, in g) and the mass of PAC replaced daily. This relationship can be identified with the replaced volume (Q_R, in L/d) and PAC concentration within the reactor (C_{PAC}, in g/L). Also, this equation can be used simply to calculate the replacement % (R, in %) and reactor volume (V_r, in L) as below.

$$\delta_{\mathrm{PAC}} = \frac{\mathrm{m_{PAC}}}{\mathrm{C_{PAC}} \times Q_R} = \frac{V_r}{R/100 \times V_r} \tag{6.1}$$

Thus, PAC age was calculated based on the replaced fraction of PAC as shown in Eq. (6.1).

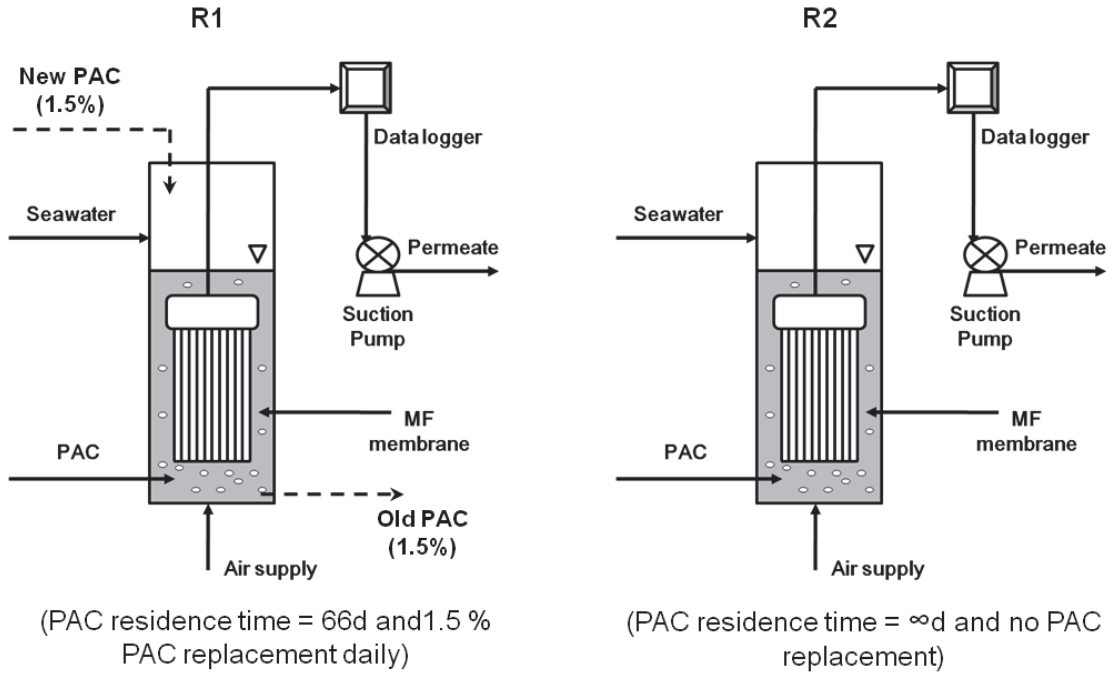


Figure 6.6 Schematic diagram of SMABR set-up in long-term on-site operation.

6.2.2.3 Long-term on-site experimental set-up

Experimental set-up (R1 and R2) of continuous (long-term) SMABR is shown in **Figure 6.6**. Both R1 and R2 are of the same configuration with only differing operational conditions. In R1, 1.5% of PAC was replaced on a daily basis whereas in R2, the PAC was not replaced. Here, R1 is with PAC residence time of 66 d, whereas R2 is with PAC residence time of ∞ d is R2. The operation period was 50d. Initially, 3.0 g of PAC was dosed to 2.0 L volume reactor (totally 1.5 g/L). Air was supplied to the bottom of the reactor using an external aerator. This helped to suspend the PAC and biomass in the reactor, to mix PAC completely with seawater and to reduce the particle deposition on the MF membrane. The aeration rate was 1.36 m^3/m^2h (as a pre-determined rate), but it was increased up to 2.72 m^3/m^2h to help the biomass with PAC in suspension after 14 d. In the long-term operation, the aeration was increased only to suspend the PAC with an increase of biomass concentration. The dissolved oxygen (DO) measurement showed that increased aeration rate did not affect the DO concentration of MBR. The DO was maintained at 4.1±0.2 mg/L. Based on the results for the semi-batch test, optimal PAC residence time emerged as 66d. It corresponds to 1.5 % PAC replacement on daily basis. Permeate was pumped out using a peristaltic pump at constant flux of 20 $L/m^2.h$ (LMH). Correspondingly, HRT of both SMABRs was 2.27 hours. TMP was monitored automatically every 6 h. R1 was backwashed once every two days for 5 min at 40 LMH while R2 was backwashed for 10 min at the same flux daily.

6.2.2.4 Microbial community structure

In this study the changes of dominant species in two SMABRs (PAC age of 66d - R1 and PAC age of ∞d - R2) were investigated during the operation time. Water samples were collected occasionally, and they were spread on the marine agar plate and

incubated for 24 h at room temperature. They were suspended into a nutrient buffer solution Based on the colony morphology, individual colonies (8 isolates) were selected and transferred to a nutrient buffer solution and incubated at 37°C until individual strains were grown. Each sub-cultured cell was gathered using inoculating loops to extract genomic DNA for use in a polymerase chain reaction (PCR). Extracted DNA was amplified using PCR with forward 27F (5' to 3' AGAGTTTGATCATGGCTCAG) and reverse 1492R (5' to 3' GGTTACCTTGTTACGACTT) primers for 16S-rRNA. The PCR conditions were employed as follows: 95 °C for 5 min followed by 30 cycles of 94°C for 0.5 min, 57°C for 0.5 min, 72°C for 0.5 min, followed by 72°C for 5 min. Every amplified 16S rRNA gene was then sequenced and aligned. For identification, the partial 16S rRNA gene sequences were compared with the full sequences available in the GeneBank database using a BLAST search, then registered in Genbank (Lee et al., 2009).

6.2.3 RESULTS AND DISCUSSION

6.2.3.1 Determination of PAC residence time

The suitable (optimal) residence time of PAC was determined in terms of removal of DOC in seawater and the increase of biomass. **Figure 6.7** shows the semi-batch results for the determination of optimal PAC residence time for continuous SMABR experiment. In this experiment, all operation conditions were maintained the same except for PAC residence time.

As can be seen from **Figure 6.7 (a)**, at the initial incubation stage (~7d), there was a significant increase in biomass (MLSS) concentration in the reactor with ∞ d of PAC residence time (i.e. with no replacement). Also, after 28 d of experiment, the batch reactor with 1.5 % of daily PAC replacement (or PAC residence time of 66 d) gave rise to a maximum biomass growth measured in terms of MLSS. On the other hand, the increase of biomass was minimal with the high rate of PAC replacement (20%). Here, 20% PAC replacement corresponds to a PAC residence time of 5d. Further, there was an only a slight increase in biomass concentration when PAC replacement was high (20% replacement). It was only 1,200 mg/L after 28d of operation.

The amount of SS and DOC concentrations were around only 3.6 mg/L and 2.3 mg/L, respectively. The SS and DOC would increase by a maximum of 0.35 mg and 0.23 mg respectively with the change of 100mL of seawater in the batch test reactor (on a daily basis). This is a negligible amount compared to the high concentration of MLSS value (5,000 mg/L to 12,000 mg/L).

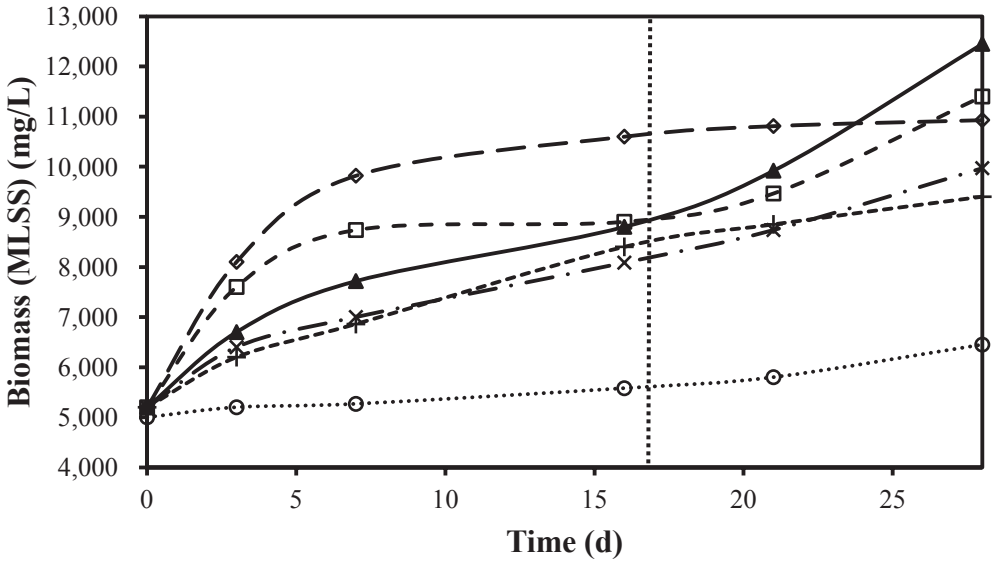
The overall the rate of biomass growth was calculated from the MLSS concentration measured at 28 d and initial value (0 d) using the following formula: Biomass = (MLSS after 28d – initial MLSS) × reactor volume/ 28 d. In this calculation, biomass loss during the replacement of PAC was not considered. After 28 d of incubation, the order

of increase in biomass was 66 d > 100 d > ∞ d > 40 d > 20 d > 5 d. The corresponding biomass growth (in terms of MLSS) in 28 d was 51.8 mg/d > 44.3 mg/d > 40.9 mg/d > 39.3 mg/d > 32.1 mg/d > 10.4 mg/d, respectively. Figure **6.7 (a)** shows that biomass growth was the highest with 66d of PAC residence time after 28 d of incubation. Biomass growth with 66 d of PAC residence time was 24~38% higher compared to those with 40 d and 20 d of PAC residence times. The biomass growth was very low with 5 d of PAC residence time. Too quick replacement of PAC may limit the biomass growth due to low residence time. Considering the economics of PAC replacement and biomass growth, a PAC residence time of 66d was chosen as a suitable value.

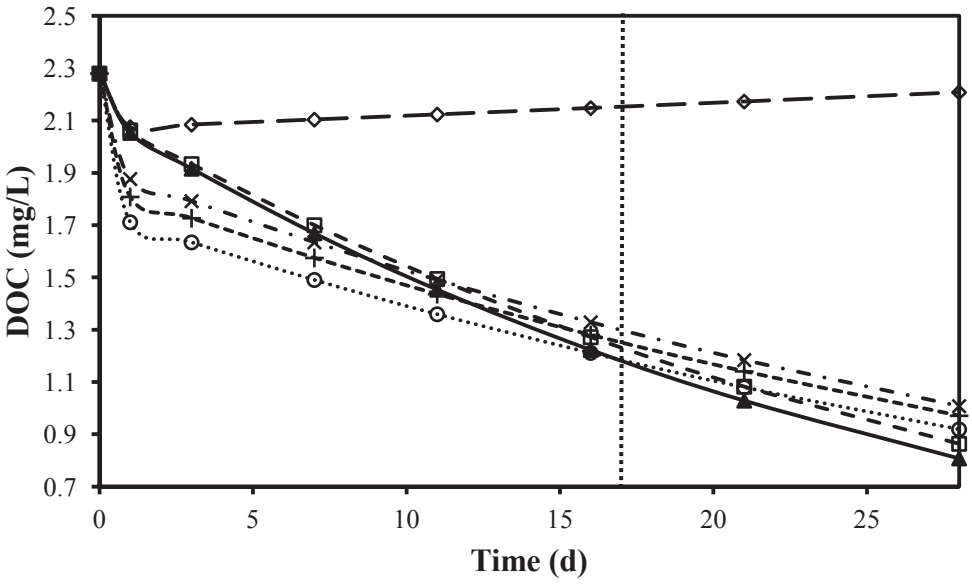
The biological activity (or biodegradation) trend can be explained in terms of DOC removal as both showed a similar pattern (**Figure 6.7 (b)**). Similar to the variation trend during the initial 16d operation, adsorption was dominant in the removal of DOC. This can be found from the initial DOC removal trend showing that the shorter PAC residence times removed more DOC compounds in seawater. A reactor with 5d of PAC residence time showed that much DOC could be removed. Our batch equilibrium test showed an adsorptive capacity of less than 0.2 mg of DOC/g PAC (**Figure 6.9**). Assuming 20% replacement of PAC in a 200 mL batch reactor and 50% exchange of seawater (i.e 100 mL) on a daily basis, the daily amount of dissolved organic matter available for adsorption is 0.23 mg (in terms of DOC) for 0.2 g of PAC available in the batch reactor. Thus, saturation in adsorption is achieved within one day. However, the reactors having relatively longer PAC residence times (100d and 66d) showed better DOC removal efficiencies than the reactors with 40d and 20d of PAC residence times. The DOC removal with PAC residence time of 66d especially started to show significant results compared to the other PAC residence times after 16d of incubation time.

In terms of detailed organic fraction (**Figure 6.8**), hydrophobic DOC and biopolymer was completely removed during the incubation of 28d by the PAC at all retention times. However, lower humics and LMW organics remained within the reactor with 20d (49.3% removal in average) and 66d (64.2% removal in average) of PAC residence time. LMW compounds are used for the growth of microbes. Removing many of these compounds is considered to be an indicator of bioactivity (Hammes et al., 2006) as well as DOC removal on long-term incubation. In this semi-batch test, optimal control of PAC ages (66d and 20d) showed stable LMW compounds removal.

Therefore, a 66d was selected as best PAC residence time in terms of superior DOC removal and increase of biomass for continuous test.



(a)



(b)

Figure 6.7 Semi-batch test results for determination of PAC residence time: (a) Increase of biomass (in terms of MLSS) over the time, (b) Change of DOC concentration over the time (◊: Infinity (0%); □: 100d (1.0%); ▲: 66d (1.5%); x: 40d (2.5%); +: 20d (5.0%); ○: 5d (20%)).

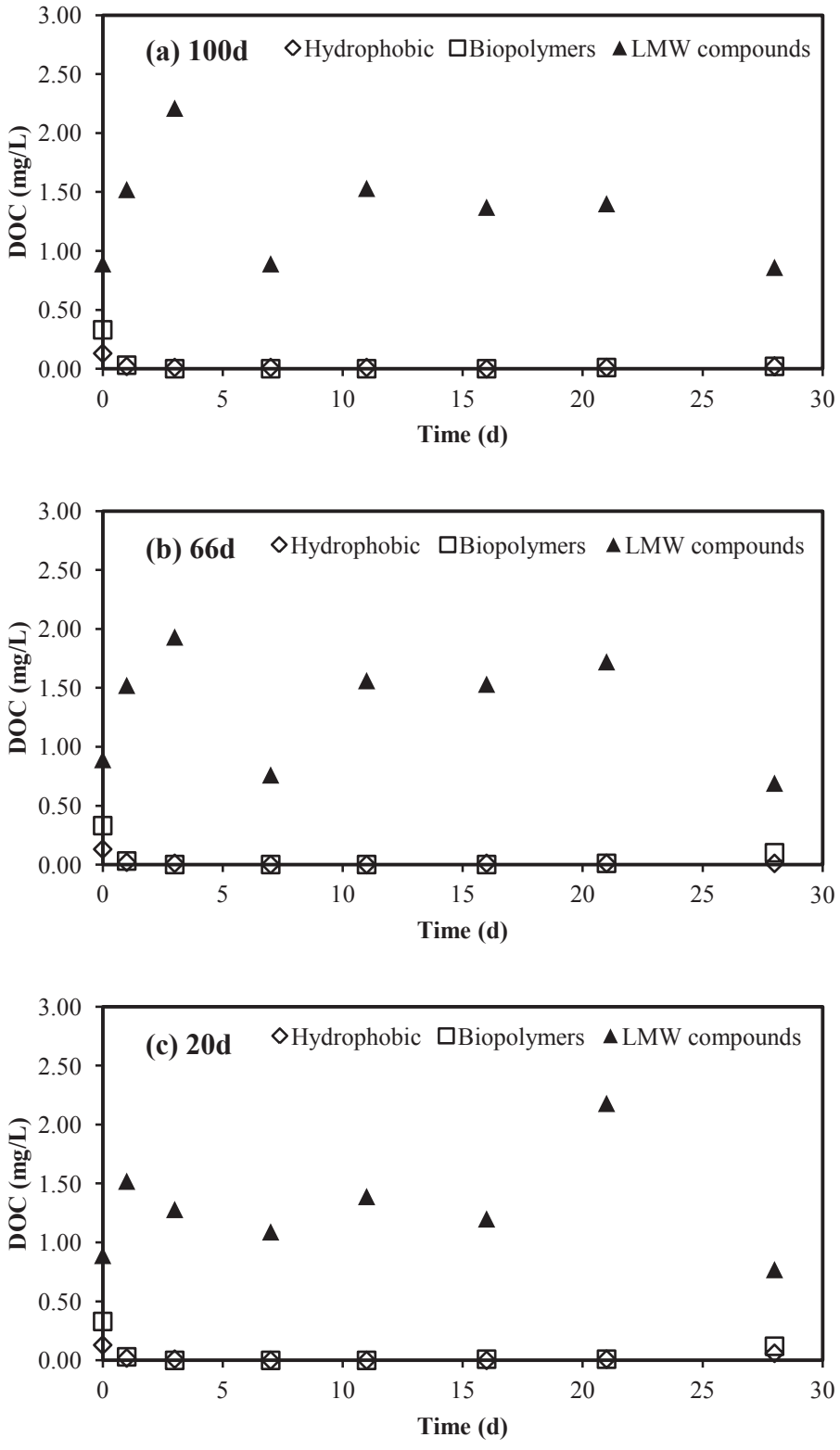


Figure 6.8 Changes of hydrophobic, biopolymers, LMW compounds concentration in supernatant over the time: (a) 100d; (b) 66d; and (c) 20d of PAC residence time.

6.2.3.2 Effect of PAC residence time on SMABR

In SMABR, PAC was mixed directly into the feed water of a submerged MF membrane system. As mentioned earlier, aeration was provided to avoid the PAC settlement and to reduce the incidence of membrane fouling. MBR enables a relatively high concentration of MLSS including PAC to be maintained in the reactor. Since the residence time of PAC can be easily controlled by the replacement, the system can function either under adsorption or a biological mode depending on PAC residence time.

Since the SMABR operation starts with adding only a small amount of PAC, there is no burden of high concentration of MLSS. The preliminary work (**section 4.5**) conducted on the SMABR (at constant flux mode of 20LMH) showed that there was only 5-6kPa of TMP development in SMABR during the first 14d by adding of 1.5 g/L of reactor volume (without any PAC replacement). It should be noted that the addition of PAC was done only at the start of the experiment. On the other hand, the TMP of a conventional submerged membrane system (without any adsorbent addition) with seawater was high even during the first day of operation (around 10kPa of TMP development). Moreover, DOC concentration of seawater is only 1-3 mg/L. It indicates that PAC could remove enough amounts to operate at stable TMP in SMABR. However, a small amount of PAC replenishment can achieve more superior organic removal efficiency and stable biological activity on long-term operation while keeping the cost of PAC replenishment at a minimum.

Continuous SMABR test was done with two different reactors with optimal PAC residence time (66d) and maximum biological mode (∞d, no PAC replacement) as shown in **Table 6.3**. The overall operation period lasted 50d.

6.2.3.3 DOC removal behavior by PAC

Prior to the long-term experiment, to determine the optimal PAC concentration for a continuous test, a PAC adsorption batch test was done for 24h. Almost all of the hydrophobic organic compounds in seawater were removed by 1.5 g/L of PAC (**Figure 6.9**). A slight increase in the removal efficiency of humic substances and biopolymers was observed when the PAC dose was increased. At a PAC dose of 1.5 g/L, DOC removal efficiency was around 76% with biopolymer (81%), humics (78%), building blocks (72%) and LMW neutrals (70%).

The substantial adsorption capacity of PAC of 1.5 g/L of reactor volume with ability of MBR can be expected to remove high molecular compounds (biopolymers and humics) as well as low-molecular and biodegradable organic substances. For these reasons, a dose of 1.5 g/L (of reactor volume) of PAC was maintained in the SMABR experiment.

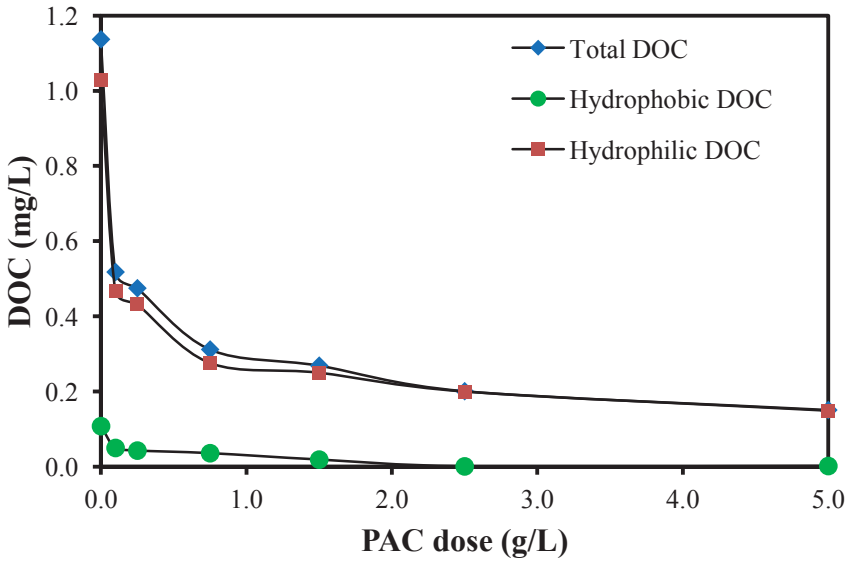


Figure 6.9 Total DOC removal by PAC in seawater.

6.2.3.4 SMABR performance

6.2.3.4.1 TMP development (at 20 LMH)

During the 50d operation, TMP development could be divided into two stages; from initial day to 13d (the stabilization stage) and from 13d to 50d (**Figure 6.10**). No backwashing was provided during the initial 6d. Backwashing was provided once every two days for R1 and once a day for R2 from 13d. This might be because no replacement of PAC resulted in more fouling on the MF membrane (R2). Furthermore, from 13d of operation the aeration rate increased from 1L/min (1.36 m^3/m^2 membrane area. h) to 2L/min (2.72 m^3/m^2 membrane area. h) which helped to keep the solids in suspension (including the PAC with biomass).

During the first 6d, TMP on R2 was increased from 10.9kPa to 13.5kPa while R1 resulted in only 1.1 kPa increase of TMP (from 10.4kPa to 11.5kPa). From 7d to 13d, TMP development was high on R2 of up to 20.5 kPa. This was why backwashing was applied more often and aeration rate increased. However, after the stabilization stage (from 13d) both reactors experienced relatively stable TMP development between the backwashing times. The results of the backwashing on the TMP profiles indicated that the addition of PAC reduced irreversible fouling. This is because after backwashing, the TMP almost recovered to its initial value. Overall TMP development of R1 and R2 was 4.1kPa and 5.9kPa (as mean values) respectively. This also signifies that PAC residence time had an effect on the membrane performance. In other words, stable TMP operation in SMABR with low fouling requires the replacement of PAC.

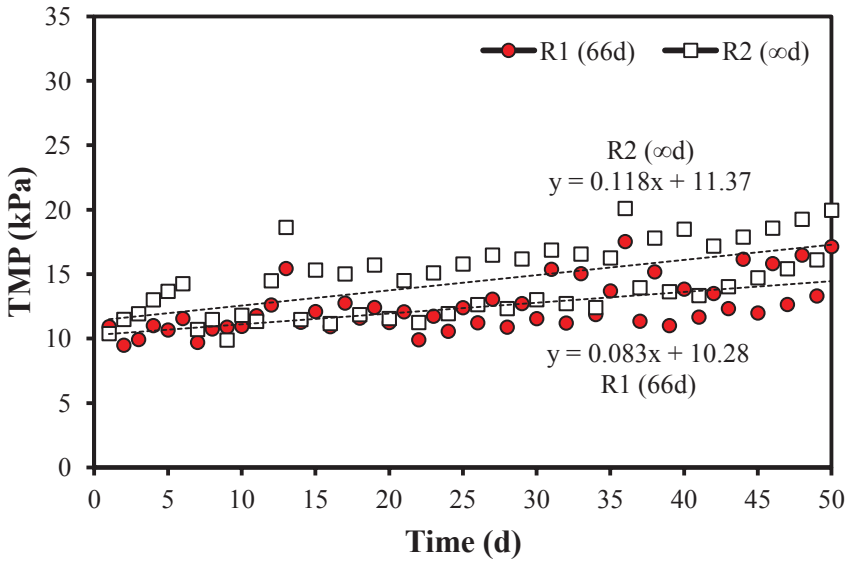


Figure 6.10 TMP developments of SMABRs operated with two different conditions.

6.2.3.4.2 Turbidity & UF-MFI

The turbidity of raw seawater (SW) was 0.75 (±0.12) NTU. After SMABR, the turbidity in the effluents of R1 and R2 was decreased to 0.29 (±0.08) NTU and 0.41 (±0.16) NTU. Turbidity of the R1 effluents was relatively stable while that of R2 effluents increased gradually. Similar trend was observed in UF-MFI value of both SMABR effluents. The UF-MFI value of raw seawater (SW) was 11,826 (±1,523) s/L^2. Both R1 and R2 had a UF-MFI value of 4,395 (±881) s/L^2 and 5,861 (±1,958) s/L^2 indicating low fouling. Turbidity usually expresses the particulate fouling and UF-MFI can be indicative of organic fouling in addition to colloidal fouling. It therefore was found that SMABR could produce feed water having low particulate and organic fouling potential for RO membrane. Here again, the results show that a selection of appropriate retention time of PAC helps to produce better quality effluent from SMABR.

Table 6.3 Organic fraction of seawater (SW) and effluents with the two operating conditions (R1: PAC 66d and R2: PAC ∞d) (Unit: mg/L).

Days	Sample	DOC	Bio-polymers	Humics	Building blocks	LMW Neutrals	LMW Acids
	SW	2.28	0.33	0.75	0.16	0.89	0.02
1	R1	0.62	0.01	0.18	0.05	0.35	0.01
	R2	0.71	0.02	0.22	0.06	0.40	0.01
	SW	2.35	0.25	0.81	0.14	0.84	0.01
6	R1	1.01	0.02	0.30	0.08	0.47	0.14
	R2	1.16	0.09	0.40	0.07	0.46	0.14
	SW	2.65	0.42	0.84	0.20	0.87	0.02
13	R1	1.63	0.08	0.33	0.03	1.10	0.08
	R2	2.44	0.30	0.51	0.06	1.38	0.12
	SW	2.39	0.23	0.81	0.19	0.80	0.02
21	R1	0.86	0.02	0.15	0.16	0.28	0.16
	R2	1.99	0.10	0.79	0.10	0.78	0.12
	SW	2.45	0.25	0.94	0.21	0.85	0.01
47	R1	0.98	0.06	0.70	0.01	0.12	0.00
	R2	1.91	0.04	0.80	0.10	0.71	0.16

6.2.3.5 DOC removal

Table 6.3 represents the total DOC and detailed DOC fraction removal trend of SMABRs with two different residence times regarding PAC. On the first day, both reactors showed superior DOC removal efficiencies of 73% (R1) and 69 % (R2) with high hydrophilic DOC fractions removal of 94-97% (biopolymers), 71-76% (humics), 63-69% (building blocks), and 55-61% (LMW neutrals). After 6d of operation, DOC removal efficiency started falling to 51-56% (total DOC), and after 13d, it deteriorated to 39% (R1) and only 8% (R2). This increase is due to the presence of LMW organic compounds (neutrals and acids) in SMABR effluents. After 6d of operation, LMW acids concentrations were increased from 0.01 mg/L to 0.14 mg/L in effluents of both reactors. It signifies that microbes have started to act in both reactors, resulting in the generation of lower molecular organics from decomposition of high molecular organics such as biopolymers and humics absorbed onto PAC. A long-term result shown in **Table 6.3** indicated a majority of biopolymers and humics (87(±9) % and 61(±22) %) were removed by R1.

After 13d adaptation in SMABR, organic removals in R1 (60-64 % of total DOC removals) were stabilized with high LMW organics removal (up to 86% removal at 47d). On the other hand, R2 still indicated poor quality of effluent with only 17-22% of total DOC removal efficiency. This again shows the need for PAC replacement. This again shows the need for PAC replacement. The biological activity is discussed in detail in **section 6.2.3.7** below.

6.2.3.6 Biopolymers removal

Table 6.4 represents the biopolymers concentration of SW and effluents from both SMABRs (R1 and R2).

Table 6.4 Biopolymers concentration of seawater (SW) and effluents of each reactor (R1: PAC 66d and R2: PAC ∞d) during the operation time.

Days	Sample	Bio-polymers (μg-C/L)	TEP (μg-C/L)	Protein (μg/L)
	SW	332	124	38
1	R1	9	1	N.D.*
	R2	17	2	N.D.*
	SW	249	92	36
6	R1	16	1	N.D.*
	R2	87	9	2
	SW	416	156	55
13	R1	77	9	3
	R2	298	36	15
	SW	234	88	32
21	R1	18	2	N.D.*
	R2	103	24	10
	SW	252	96	28
47	R1	56	4	N.D.*
	R2	49	16	9

*N.D.: Not detectable.

Biopolymers concentration of SW was 296.6 (±79.6) μg-C/L. TEP and protein concentration of SW was 112.2 (±28.8) μg-C/L and 37.8 (±10.4) μg/L, respectively, during the entire operation time. TEP comprised around a third of biopolymers in SW.

TEP is known as a severe biofoulant in seawater organic matter. R1 (with 66d of PAC residence time) removed more than 97% of TEP from start to finish.

On the other hand the TEP removal of SMABR without PAC replacement (R2) did decline after 13d of operation time. Similarly, as shown in **Table 6.4**, R1 demonstrated relatively superior protein removal regardless of PAC residence time. The protein removal of R2 worsened after 13 d of operation time. It showed optimal replacement of PAC (R1) was made almost complete removal of biopolymers from seawater, thus indicating a reduction in biofouling potential.

6.2.3.7 Bioactivity in SMABR

Bioactivity in both SMABRs was measured in terms of cell number counts (CFU; colony forming unit) and ATP (as live biomass concentration). Cell number counts were performed for mixed liquors of SMABR. Thus cell number was smaller in quantity than expected. Nevertheless it can be used as an indicator of biomass growth in the reactor. As explained in **section 6.2.3.4**, R1 operated well with a stable and gradual increase of biomass (from 4.0 (±1.0) x 10^3 to 12.0 (±1.0) x 10^3 CFU/mL). ATP results also supported this finding. During the SMABR's entire operation, ATP in R1 was increased gradually from 1.17 to 6.30 pg of ATP/L and it had a higher ATP concentration than R2 which indicates the numbers of active biomass increasing over the time. In other words, PAC control helped to the growth of active biomass and total cell. This biological activity shows the same trend as organic removal.

The dominance of adsorption over biological activity is roughly controlled by the retention time of activated carbon (or the age of the activated carbon) within the reactor. In the SMABR one can expect that both adsorption and biodegradation play a role in the overall process. When the operation commences, adsorption can be dominant, and this

effective organic adsorption by the PAC helps in the growth of microorganisms and biodegradation process undertaken by the microbes. They rapidly dominate and lead to more effective organic matter removal.

6.2.3.8 Biofouling potential reduction

Biofouling potential reduction can be determined using measurement of cell number counting and AOC concentration in effluents (or feed water to RO unit).The variation in AOC concentration of raw SW (feed water) and SMABR effluents (R1 and R2) during the operation time is represented in **Figure 6.11**. The cell number counting can be a direct indicator of microbes being transferred to the poor treatment of RO in seawater desalination. Raw seawater had 2.73 (±1.57) x 10^5 cells/mL. On the first day of operation, both SMABRs (R1 and R2) producing effluent had a similar number of cells with 1.65 (±0.07) x 10^2 cells/mL. During the entire operation, R1 showed relatively stable quality of effluents while R2 increased gradually the number of cell in effluents to 2.00 (±0.23) x 10^4 cells/mL at 47days of operation. However, both SMABRs (R1 and R2) limited most of the microorganisms entering from seawater and they showed 99.7 (±0.3) % and 95.8 (±5.6) % cell number removal efficiency, respectively.

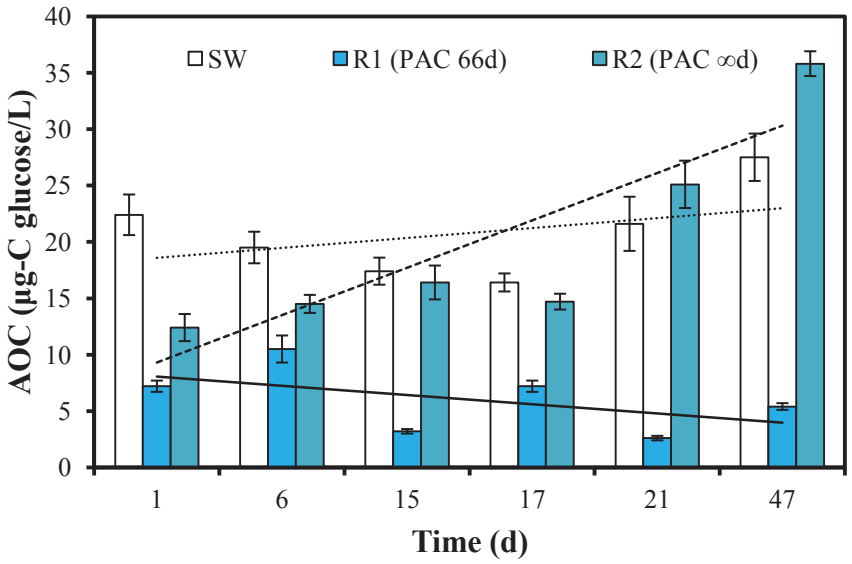


Figure 6.11 Changes of AOC concentrations of SW and effluents.

The AOC measurement can be used to indicate the biological growth potential of the water (or biofouling potential) and serve as a suitable parameter for predicting fouling potential. AOC refers to a fraction of labile DOC that is readily assimilated and utilized by microorganisms resulting in an increase of biomass. AOC can influence biological fouling (biofouling) in water treatment systems and distribution processes. Thus, a high value of AOC is directly linked to rapid biofilm formation and loss of performance in membrane processes (Hambsch and Werner, 1996; Chien et al., 2007). In this study, AOC concentration of raw seawater (SW) was 20.8 (±4.0) µg-C glucose equivalents/L. On average, the AOC was removed by R1 (66d) significantly which is 6.0 (±2.9) µg-C glucose/L indicating 71.0 % (as a mean value with less than 5% of standard deviation) of AOC removal efficiency. On the other hand, R2 effluents showed slightly higher AOC concentration (14-23%) than seawater after 21d. This may be due to the LMW organics (generated and remained, but they could not be removed, **Table 6.3**) which can be easily utilized by microorganisms. Meyer et al. (1987) found that bacterial growth was greatest in the low molecular weight fraction (Mw<1000g/mol) of water. Thus the presence of low molecular weight fraction measured to high concentration in AOC.

During most of the operation periods, AOC in R1 effluents was less than 10 μg-C glucose/L. It has been reported that at AOC levels of <10μg/L can limit the growth/regrowth of some heterotrophic plate counts and coliform bacteria (Van der Kooij and Veenendaal, 1994). Thus, SMABR could reduce the biofouling potential by removing of AOC compounds and biomass.

6.2.3.9 Effect of PAC residence time on microbial community

To investigate the specific microbial species in the SMABRs, water samples were collected during the operation time. In the culture-dependent study, 8 isolates taken from the sub-cultured samples were sequenced with 16S rRNA gene. There was not much difference in microbial community at initial operation time in SMABRs operated at two different conditions. SMABRs operated at different conditions indicated that γ-Proteobacteria such as *Pseudomonas otitidis* strain MCC10330 and *Pseudomonas aeruginosa* strain DSM 50071 (with 99% similarity) was the dominant species throughout the duration of the experiment. Species of Pseudomonas have been known to play an important role in the biodegradation of marine dissolved organic matter (Arnosti et al., 1998). However, microbial communities in the SMABR after 15days showed a dynamic shift in the dominant bacterial species (to halophlic) such as *Marinobacter excellens* strain KMM 3809 and *Marinobacter hydrocarbonoclasticus* strain ATCC 49840 (77%). At the same time γ-Proteobacteria such as *Pseudomonas mendocina* strain NCIB 10541, *Pseudomonas asplenii* strain ATCC 23835, *Pseudomonas putida* strain IAM 1236, *Nereida ignava* strain =2SM4 including *Pseudomonas aeruginosa* strain DSM 50071, *Pseudomonas otitidis* strain MCC10330 were also presented in SMABR samples (23%). They would be grown at various NaCl concentrations (of 0.08 to 3.5 M) and used various hydrocarbons in aerobic conditions as the sole source of carbon and energy. These groups of microorganisms contain a large number of aerobic heterotrophs

that are able to biodegrade organic carbon matter from saline water (Lay et al., 2010). As discussed earlier (Lefebvre and Moletta, 2006), the feasibility of biological treatment at high salt concentrations was proved with the adaptation of the biomass or using halophilic microorganisms.

This abundance of microbial community in SMABR (66d of PAC residence time), which indicates appropriate replacement of PAC, may be attributed to high organic removal. These communities rely on extracellular enzymes to hydrolyze high-molecular-weight organic matter to sizes sufficiently small for cellular uptake. They, then, respire fraction of the organic carbon and excrete transformation products as DOC that may in turn be used by other members of the microbial community. The dominance of adsorption over biological activity has been reported as being roughly controlled by the residence time of the activated carbon within the carbon contactor (i.e. the age of the activated carbon) (Gai and Kim, 2008). To conclude, SMABR is a sustainable and environmentally friendly (using biological activity without the biocides and chemicals) pretreatment strategy for reducing biofouling potential. Even the amount of PAC used is minimal. The amount of PAC necessary is only 2.14 g/m^3 under the operation conditions used (flux = 20LMH; initial amount of PAC of 1.5 g/L of reactor volume; PAC replacement rate = 1.5 %).

6.2.4 SUMMARIZING THE SMABR

SMABR emerged as a suitable biological pretreatment strategy for RO with minimum biofouling. PAC replenishment was optimized in terms of DOC removal and stable biomass increase. PAC retention time of 66d was found to be the optimum. A small amount of PAC (approximately 2.13g/m^3 of seawater treated) in SMABR was sufficient to obtain an effluent with low biofouling potential. High rates of removal of DOC were maintained with a marginal increase of TMP and low fouling potential with a residence time of PAC of 66d. High removal rates of biopolymers including protein and TEP were also achieved with a residence time of PAC of 66d. Low fouling potential permeates with low AOC concentration of 6.0 (±2.9) μg-C glucose equivalents/L (PAC age of 66d) were also achieved.

CHAPTER 7

University of Technology Sydney

Faculty of Engineering& Information Technology

APPLICATION OF CONTACT FLOCCULATION FILTRATION (CFF) AS PRETREATMENT TO SWRO

This chapter is divided into two parts. The first part discusses the effect of operating parameters of contact flocculation filtration (CFF) such as filtration velocity, flocculant dose and contact time through a short-term experimental study (**Section 7.1**). The second part presents the results of long-term CFF experimental study to investigate its biological activity. This is important in reducing the biofouling of RO membrane (**Section 7.2**).

<Publications related to this chapter>

– Jeong, S., T.V. Nguyen, H.K. Shon, S. Vigneswaran. (2012) The performance of contact flocculation–filtration as pretreatment of seawater reverse osmosis. Desalination and Water Treatment 43(1-3): 246-252.

– Jeong, S. and S. Vigneswaran. (2013) Contact flocculation filtration as a pretreatment in seawater desalination: Assessment of biological activity (*Preparation*).

7.1 CONTACT FLOCCULATION FILTRATION (CFF)

7.1.1 INTRODUCTION

Deep bed filtration has been used as a common pretreatment method in water treatment as well as seawater desalination for removing suspended solids or particulates (Jegatheesan and Vigneswaran, 1997; Stephan and Chase, 2001). This filtration process is normally used for the clarification of dilute suspensions of less than 500 mg/L. Particles mainly adhere to the surfaces and introduce the filtration layer themselves. With continuing filtration, deposits accumulate within the filter pores and lead to a change in pore geometry and hydrodynamic conditions. Removal of deposits can take place throughout the whole filter (Ison and Ives, 1969). However, conventional deep bed filtration cannot remove dissolved organic matter which is mainly responsible for reverse osmosis (RO) fouling.

The application of contact flocculation–filtration (CFF) based on deep bed filtration is a promising pretreatment solution due to its simplicity and relatively cheaper operating and maintenance costs. In CFF, flocculation of particles and the separation of flocs and particles occur simultaneously within the filter bed itself. Flocculation takes place through raw water contacting the flocculant. This is followed by floc formation through the velocity gradient created by the flow water with particles and coagulant in the filter bed. To date, CFF studies have focused on the particle removal mechanism in the filter bed (Johir et al., 2009). However, not much information is available on the optimization of CFF, especially in terms of organic removal. Biological activity in the filter in the long-term led to organic removal by biodegradation (Chinu et al., 2010).

This paper presents the experimental results for the influence of operational conditions (filtration velocity, contact time of flocculant and flocculant dose) on CFF performance

with seawater using Chowder Bay, New South Wales, Australia. Here, the performance of CFF was evaluated in terms of organic removal efficiency and ultrafilter-modified fouling index (UF-MFI) reduction. Detailed organic fractionations were also done in this study. The CFF performance results were compared with that of in-line flocculation microfiltration (MF) system.

7.1.2 MATERIALS AND METHODS

7.1.2.1 Materials

7.1.2.1.1 Seawater

In this study, seawater was collected from Chowder Bay, Sydney, Australia. The average turbidity, pH and dissolved organic carbon (DOC) values of seawater used in experiments were 0.92 NTU, 7.8, and 1.12mg/L, respectively. Average UF-MFI value was 12,795 s/L^2 and total suspended solid (TSS) was 3.6 mg/L.

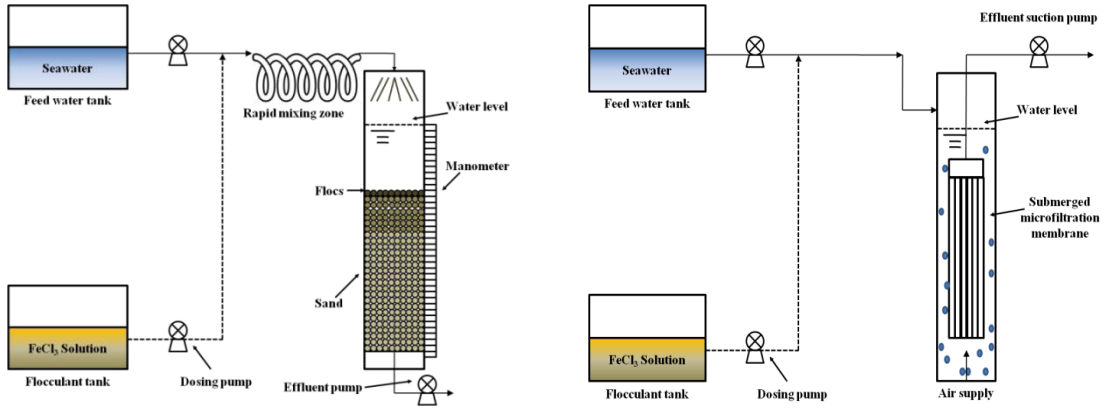
7.1.2.1.2 Filter medium

The deep bed filter was packed with sand (as medium). Sand provided from Riversands P/L, Australia was used as the medium in this study and its properties are summarized in **Table 7.1**.

Table 7.1 Physical properties of sand.

Parameter	Sand
Effective Size (mm)	0.55-0.65
Uniformity Coefficient	< 1.5
Acid Solubility	< 2%
Specific Gravity	2.65
Bulk Density (kg/m^3)	1500

7.1.2.2 Experimental methods



(a) CFF **(b) SMCHS**

Figure 7.1 Schematic diagram of (a) contact flocculation-filtration (CFF) and (b) submerged microfiltration coagulation hybrid system (SMCHS).

7.1.2.2.1 Contact flocculation–filtration (CFF)

Short-term filtration experiments were carried out with in-line flocculant added into the filtration column packed with sand. The experimental run was kept short at 6 h. The experimental set-up is shown in **Figure 7.1(a)**. The internal diameter of the filtration column was 2.0 cm. It was packed with sand to a depth of 60 cm from the bottom. The filtration velocities and flocculant doses applied varied from 5.0 to 10.0m/h and 0.5 to 3.0 mg/L, respectively. The rapid mixing was performed in a spiral coagulator unit which contained a PVC tube. The length of the spiral tube used as the rapid mixing zone was retained at 50 cm but the tube diameter was changed from 0.40 to 0.16cm so that the velocity gradient and retention time for rapid mixing also changed. Mixing times were calculated based on length, diameter of a tube, and flow rate of feed water. Flocculant was added using a dosing pump to the rapid mixing unit for contact with feed water. Using gravity the solution (destabilized water) was then sent through the packed filter column. To maintain a constant filtration rate in the system, an effluent

pump was used in the outlet. The filtered samples (filtrates) were collected at the bottom of the column for further analysis.

A few submerged microfiltration coagulation hybrid system (SMCHS) experiments were also conducted to compare its performance with that of CFF. MF membrane of 0.1 μm pore size was submerged in a 6 L reactor (**Figure 7.1 (b)**).

An effective mixing of flocculant with water was achieved by rapid mixing. This is vital for an effective coagulator. An appropriate range of velocity gradient is necessary for proper flocculation. If the G value is too high, the flocs may be sheared but if it is too low, sedimentation may occur within the coagulator (Mhaisalkar et al., 1986). G value in the rapid mixing unit was determined by measuring the head loss across the given length of the spiral tube. The relationship between the head loss and the G value is expressed by Eq. (7.1).

$$G = \sqrt{\left(\frac{g}{v}\right)\left(\frac{Q}{V}\right)\Delta H} \tag{7.1}$$

Where G = velocity gradient (/s), Q = flow rate (cm^3/s), V = volume of the coagulator (cm^3), H = head loss through the coagulator (cm H_2O), g = gravitational acceleration (cm/s^2), v = linear flow rate (cm/s) and d = internal diameter of the tube (cm). In tube type rapid mixing unit, G value was varied by the flow rate and calculated by the empirical relationship (Eq. (7.2)) established by previous research (Vigneswaran and Setiadi, 1986).

$$G = 6.02\left(\frac{v}{d}\right)^{1.15} \tag{7.2}$$

The operation parameters used in this study are given in **Table 7.2**.

Table 7.2 Operating conditions used in CFF experiment.

Filtration rate		Rapid mixing tube length	Tube diameter	Mixing time	velocity gradient (G)	Flocculant dose
(m/h)	(mL/min)	(cm)	(cm)	(s)	(/s)	(mg Fe^{3+}/L)
5.0	26.2	50	0.40	14.4	72	3.0
						1.0
7.5	39.3		0.40	10.8	101	3.0
						1.0
			0.16	1.7	2,418	1.0
						0.5
10.0	52.4		0.40	7.2	160	3.0
						1.0

7.1.3 RESULTS AND DISCUSSION

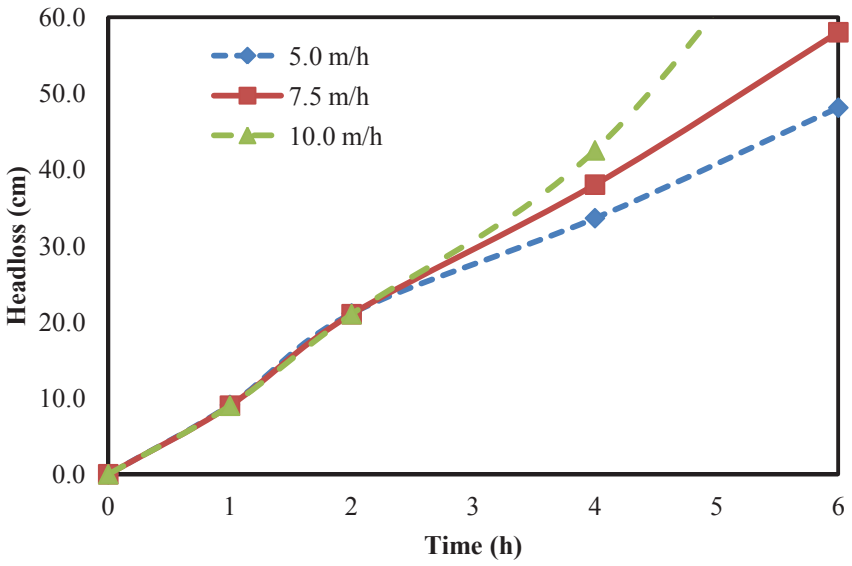
7.1.3.1 Effect of filtration rate

Previous study of the author with Chowder Bay seawater indicated that ferric concentration of 3.0 mg/L was the optimum dose for removing organic matter (**section 4.1**) and this dose was selected for evaluating the effect of filtration rate (5.0, 7.5, and 10.0 m/h) on CFF performance. In this study, there were no differences concerning headloss in the first 2 h operation among different filtration rates. The increase in the filtration rate only resulted in higher headloss after 2 h of operation (**Figure 7.2(a)**).This phenomenon can be explained by the increase of solid loading rate at a higher flow rate and after 2 h of operation, the accumulation of particles in the pores of the filter at different flow rates was high enough to increase the headloss rate. Furthermore the filtration rate increase encouraged particles to infiltrate deeper into the filter bed. Some small particles may have escaped from the filter. As a result the turbidity in the effluent at filtration rate of 10.0 m/h was remarkably higher than that of filtration rate of 7.5 m/h and 5.0 m/h. The flocculation efficiency in CFF is affected by rapid mixing provided with different velocity gradient (G) and mixing time values. Here the rapid mixing times and G values varied from 14.4 to 7.2 s and 72 to 160 /s when the filtration rates increased from 5.0 to 10.0 m/h respectively (**Table 7.2**). As can be seen from **Figure 7.2(b)**, turbidities of flocculated seawater after rapid mixing through spiral tube decreased from 6.4 to 5.2 NTU.

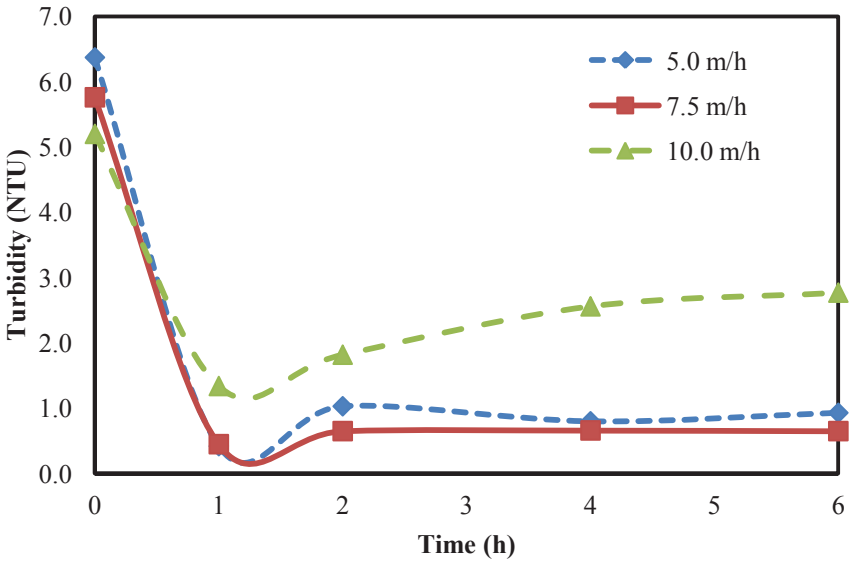
The results of experiments show that at lower filtration rates of 5.0 and 7.5 m/h, the UF-MFI reduction did improve with time but at high filtration rate of 10m/h, the UF-MFI value increased after 2 h operation (**Figure 7.2(c)**). The increase in UF-MFI could be the result of the increase of turbidity in the effluent. Filtration rate also affected the

DOC removal efficiency, which was at its best when the filtration rate stood at 7.5 m/h (**Figure 7.2(d)**).

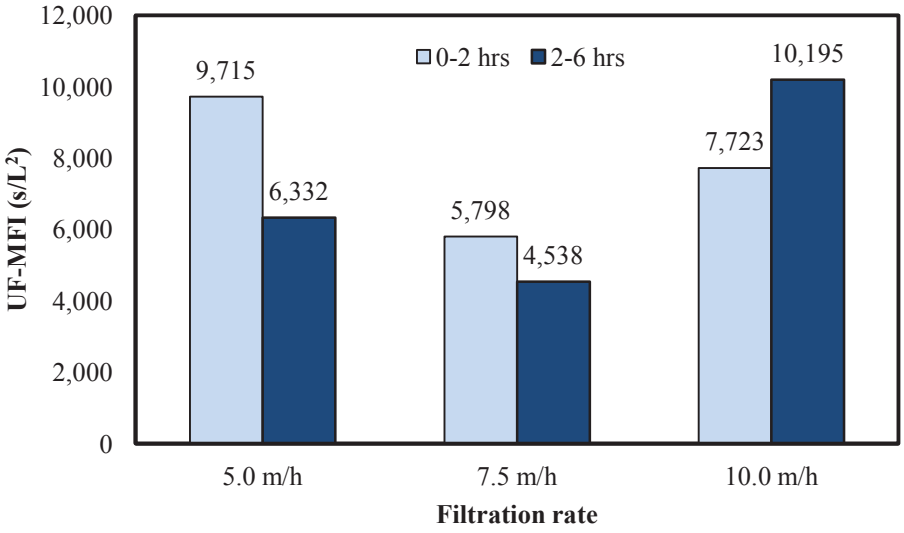
From these results, filtration rate of 7.5 m/h was proved to be the most suitable velocity in terms of the removal of turbidity, DOC, and UF-MFI. Therefore, this filtration rate was used in the subsequent experiments.



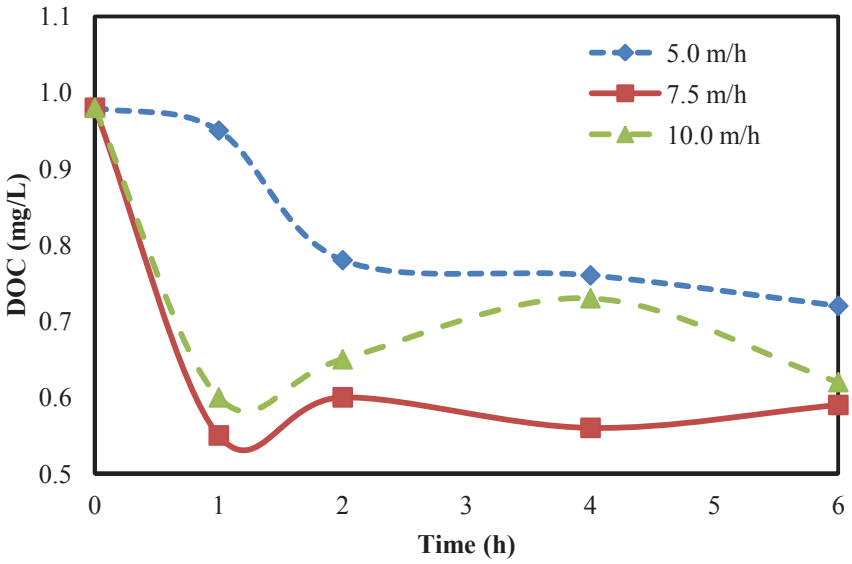
(a) Headloss



(b) Turbidity (Seawater: 0.92 NTU)



(c) UF-MFI (Seawater: 12,795 s/L^2)

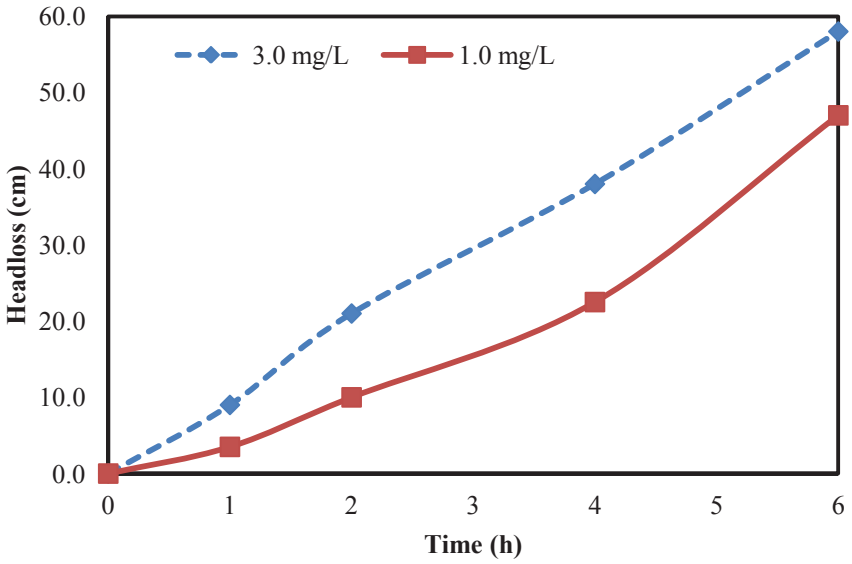


(d) DOC (Seawater: 1.12 mg/L)

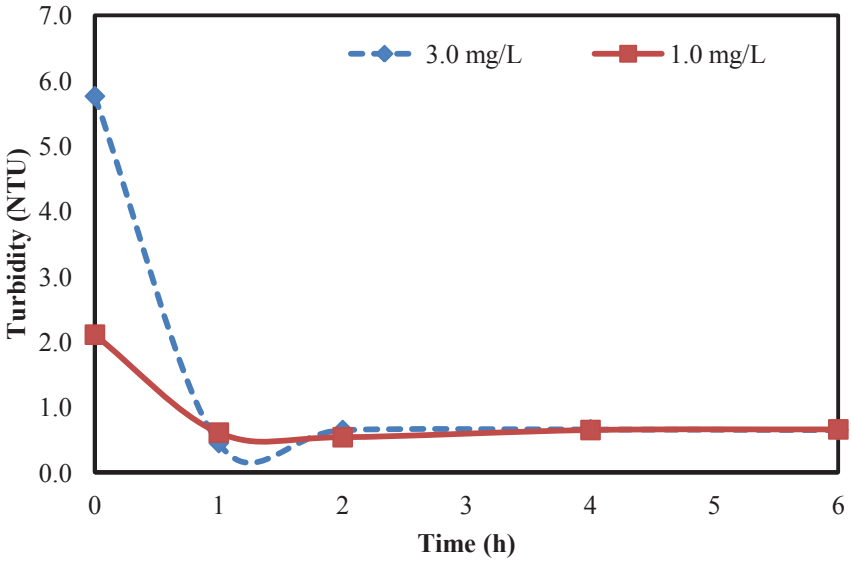
Figure 7.2 Effect of filtration velocity on the performance of CFF (3.0 mg of Fe^{3+}/L).

7.1.3.2 Effect of flocculant dose

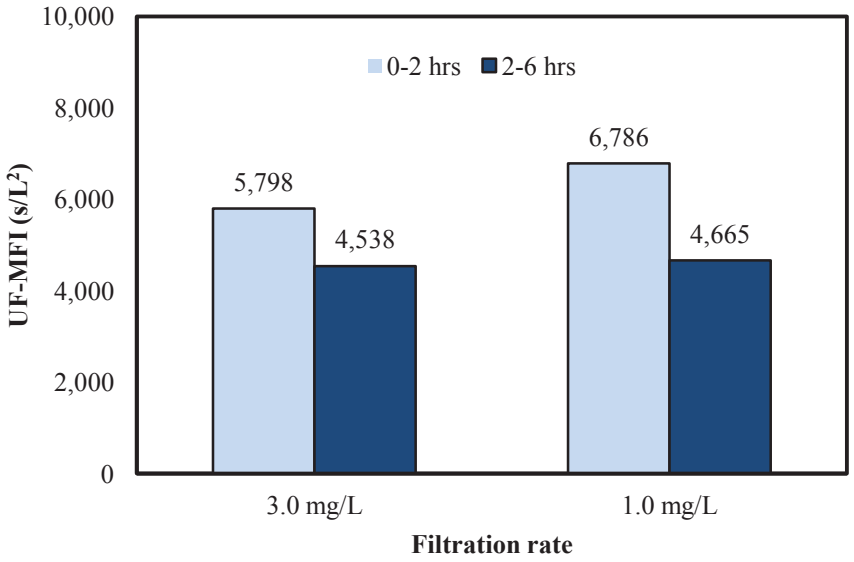
Figure 7.3 shows the effect of flocculant dose at filtration rate of 7.5 m/h and rapid mixing with a velocity gradient (G) value of 101 /s. In this experiment, flocculant dose was decreased from 3.0 mg of Fe^{3+}/L to 1.0 mg of Fe^{3+}/L. The lower concentration of ferric led to lower headloss. After a contact with 1.0 mg/L of flocculant through spiral rapid mixing unit, the turbidity was less than that of contact with 3.0 mg/L of flocculant (**Figure 7.3(b)**). The results also show that the turbidity after filtration was constant (approximately 0.65 NTU) with both concentrations of flocculant. Furthermore there was not much difference in UF-MFI value when a low concentration of ferric was used. However, the DOC removal was very low (less than 27%) when a low concentration of ferric was applied.



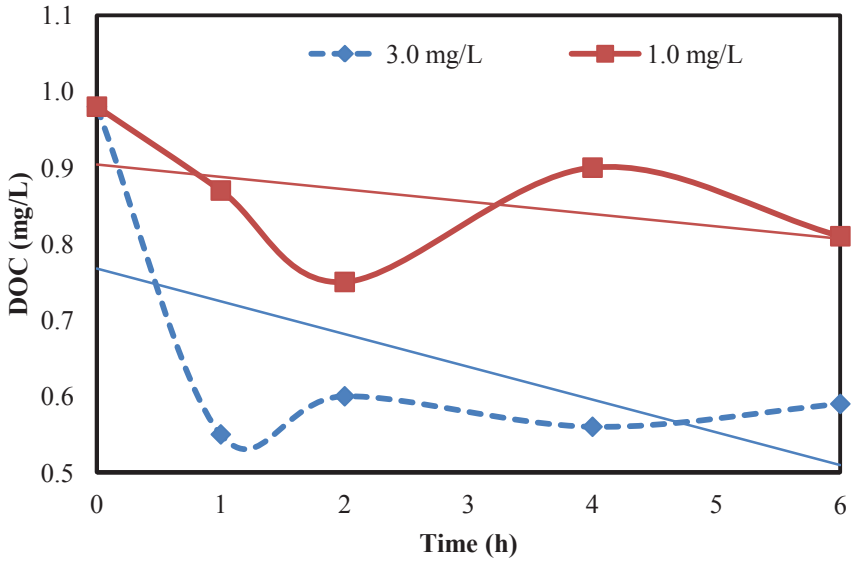
(a) Headloss



(b) Turbidity (Seawater: 0.92 NTU)



(c) UF-MFI (Seawater: 12,795 s/L^2)



(d) DOC (Seawater: 1.12 mg/L)

Figure 7.3 Effect of flocculant dose (filtration velocity: 7.5 m/h; velocity gradient of rapid mixer G: 101 /s; contact time in the rapid mixing unit: 10.8 s).

7.1.3.3 Effect of velocity gradient

G value of rapid mixing unit changes with the change in tube diameter. It is inversely proportional to tube diameter. The linear velocity through tube is increased in small diameter tube at a given filtration rate. In this study the tube's internal tube diameter (*d*) used as a rapid mixing device fell from 0.40 cm to 0.16 cm. As tube diameter decreased to 0.16 cm, G value increased to approximately 24 times from 101 /s to 2,418 /s. Due to the increase of velocity gradient, DOC removal efficiency improved significantly from approximately 26% to 44% although the rapid mixing time was as low as 1.7 s. In addition, when G value was increased to 2,418 /s, the turbidity in effluent was superior: less than 0.4 NTU. This also led to a lower pressure drop during operation time of 6 h (**Table 7.3**).

Table 7.3 Effect of velocity gradient of rapid mixing device on CFF performance (filtration rate: 7.5 m/h; flocculant dose: 1.0 mg of Fe^{3+}/L).

G value (/s)	101			2,418		
Filtration time (h)	Head loss (cm)	Filtrate turbidity (NTU)	Filtrate DOC (mg/L)	Head loss (cm)	Filtrate turbidity (NTU)	Filtrate DOC (mg/L)
0	0	2.11	1.12	0	3.45	1.12
1	3.5	0.61	0.87	4.0	0.59	0.62
2	10.0	0.54	0.75	8.5	0.43	0.75
5	22.5	0.65	0.90	18.5	0.35	0.60
6	47.0	0.66	0.81	32.0	0.37	0.76

Table 7.4 Detailed organic fractions by CFF at optimum condition compared with SMCHS.

Sample	DOC			Hydrophilic DOC			
	Total	Hydro-Phobic	Hydro-Philic	Bio-polymer	Humics	Building blocks	LMW Neutrals
Seawater (mg/L)[a]	1.12	0.23	0.89	0.12	0.47	0.22	0.08
Treatment by CFF*(mg/L)[a]	0.47	0.08	0.39	0.11	0.12	0.11	0.05
Removal efficiency by CFF (%)[b]	58.0	65.2	56.2	8.3	74.5	50.0	37.5
Seawater (mg/L)[a]	1.29	0.46	0.83	0.13	0.43	0.18	0.09
Treatment by SMCHS**(mg/L) [a]	0.57	0.02	0.55	0.05	0.25	0.14	0.04
Removal efficiency by SMCHS (%)[b]	55.8	95.7	33.7	61.5	41.9	22.2	55.6

[a] Concentrations of the different organic fractions in seawater

[b] Removal efficiencies of different organic fractions in seawater after treatment

* CFF (contact flocculation filtration) at 7.5 m/h (39.3 mL/min), G= 2418/s, Fe^{+3}: 0.5 mg/L

** SMCHS (submerged membrane coagulation hybrid system) at 20 L/m^2.h (33.3 mL/min), Fe^{+3}: 0.5 mg/L

7.1.3.4 Organic fractionation

Low pressure membrane systems such as microfiltration (MF) system have been widely used as pretreatment to RO because they can: firstly, remove macromolecules, bacteria and discrete particles from feed water; and secondly, help to reduce RO membrane fouling. CFF is more cost-effective than MF and can be considered an alternative

pretreatment for RO. In this study, the performance of CFF was compared to submerged microfiltration coagulation hybrid system (SMCHS) in terms of the detailed organic fractions. Previous jar test with the same seawater showed that there was no effective flocculation at a low concentration of 0.5 mg of Fe^{3+}/L (**section 4.1** of **Chapter 4**). At this concentration, flocs size was less than 2μm and flocs could not be observed by the naked eye. In the experiment with CFF the flocculation performance improved by incorporating the rapid mixing through the use of spiral coagulator. The CFF performance was compared with the result we obtained previously with submerged microfiltration coagulation hybrid system (SMCHS) (**section 4.1** of **Chapter 4**). The total DOC removal efficiency by CFF compare to the SMCHS was nearly the same. Although the hydrophobic compound removal by CFF was less, CFF could remove a significant portion of hydrophilic compounds (**Table 7.4**). In particular the removal efficiency of humic substances using CFF reached up to 74.5 %. This outcome needs to be investigated further so that a concrete conclusion can be obtained.

7.1.4 SUMMARIZING THE CFF SHORT-TERM TEST

The performance of contact flocculation - filtration (CFF) was evaluated at different operation conditions. As filtration rate increased from 5.0 to 10.0 m/h, the pressure drop (head loss) increased and removals in terms of turbidity and DOC declined. The incorporation of rapid mixing device prior to CFF had a positive effect on the improvement of filtration quality. At low velocity gradient (101 /s) of rapid mixing unit, the reduction in flocculation dose led to inferior DOC removal efficiency. However, in the same operation conditions, increasing velocity gradient (to 2,418 /s) enhanced the in-line flocculation performance, and in particular, the turbidity and DOC removal efficiencies were improved. At low concentration of 0.5 mg of Fe^{3+}/L, CFF could remove both hydrophobic and hydrophilic compounds. The organic removal of CFF was comparable to that of SMCHS.

7.2 ASSESSMENT OF BIOLOGICAL ACTIVITY IN CFF

7.2.1 INTRODUCTION

Contact flocculation-filtration (CFF), which is DBF coupled with in-line flocculation, is initially used in water treatment as well as in pretreatment for RO desalination. In CFF, flocculation of particles and the filtration of flocs occur within the filter bed itself. In the previous short-term CFF study (**section 7.1**); it was found out that CFF could remove both hydrophobic and hydrophilic organic compounds with low $FeCl_3$ concentration of 0.5mg of Fe^{3+}/L. However in the previous study, only short-term experiments lasting 6-h were conducted to study the removal of particulate and organic matters. On the other hand, this study concentrates on a long-term on-site filtration experiment where the main emphasis is to examine in detail biological activity in the deep bed filter.

When relatively slow flow rates are used, DBF functions as a biofiltration. Here, biofilm is developed on the medium and it helps in decomposing biodegradable organic material (Hu et al., 2005). Following the adsorption of organic matters onto the filter media, the initial degradation is accomplished by extracellular enzymatic hydrolysis of macromolecules to smaller substrates, which can then be transported into the biofilm. Further degradation takes place by a diverse microbial biofilm community developed in the filter media (Larsen and Harremoes, 1994).

However, so far, only little is known about biological activity in the CFF systems used in seawater desalination as a pretreatment strategy. Due to the frequent backwashing and relatively rapid flow of water through these filters, the impact of biological activity in CFF is assumed to be minimal. However, our study showed that there is a significant biological activity in CFF. The specific aim of this paper is to investigate the biological activity in the CFF through a long-term experiment. Organic removal by flocculation and biological activity in filter media were investigated using two different commonly used filter media (sand and anthracite).

The water quality of CFF effluent is usually determined by parameters related to particulates fouling such as turbidity and headloss. However, this work highlighted the need for monitoring biological water quality characteristics such as dissolved organic carbon (DOC), biopolymers, especially transparent exopolymer particles (TEP) which affect significantly the RO biofouling (Drews et al., 2006; Villacorte et al., 2009).

Microbial activity on the CFF was measured in terms of: firstly, heterotrophic bacterial count (or colony forming unit, CFU); and secondly, adenosine tri-phosphate (ATP as an active biomass). During a 50d operation of CFF packed with Sand (S-CFF) and 90d operation of CFF packed with anthracite (A-CFF), the development of the microbial community on the media was also investigated using the 16S rRNA sequencing of cultural colonies. The biological activity of the CFF at different depths of filter media (top, middle and bottom layers) was also studied.

7.2.2 MATERIALS AND METHODS

7.2.2.1 Materials

7.2.2.1.1 Seawater

The filtration experiments were conducted at Sydney Institute of Marine Science (SIMS), Chowder Bay, Australia. The seawater pumped from 1 m below seawater surface level was first filtered through a 140 μm pore filtration system (to remove the large particles). During the experiment of 90d duration, the average pH, dissolved oxygen (DO), turbidity and DOC values of seawater used in experiments were 7.97 (±0.15), 4.9 (±0.3) mg/L, 0.61 (±0.24) NTU and 2.33 (±0.51) mg/L, respectively.

7.2.2.1.2 $FeCl_3$

$FeCl_3$ was selected as a flocculant in this study. A stock solution (Fe^{3+} = 10 mg/L) was prepared and injected into a rapid mixing unit of the CFF with seawater at a ratio of 1:20 (ferric chloride:seawater) using a dosing pump (Cole Parmer Masterflex Pump). The dose was calculated as 0.5 mg of Fe^{3+}/L to DBF.

7.2.2.1.3 Filter media

Long-term filtration experiments were carried out with in-line flocculant addition in the filtration columns packed with two different media; sand and anthracite. Sand and anthracite were washed with 1N-HCl, 1N-NaOH and Milli-Q water several times prior to their use. The physical properties of sand and anthracite used in this study are shown in **Table 7.5**.

Table 7.5 Physical properties of filter media.

Parameter	Sand (S) Estimated value	Anthracite (A) Estimated value
Effective size (mm)	0.6	1.0 ~ 1.1
Bulk density (kg/m^3)	1,500	660-720
Uniformity coefficient	<1.50	1.30
Specific gravity	2.65	1.45

7.2.2.2 CFF set-up

The CFF experimental set-up is shown in **Figure 7.4**. The internal diameter of the filtration column was 3.8 cm. It was packed with sand (S-CFF) and anthracite (A-CFF) to a depth of 60 cm from the bottom. Thus, the packing volume was 680 cm^3. The filtration velocity and flocculant ($FeCl_3$) dose were set at 7.5 m/h and 0.5 mg of Fe^{3+}/L respectively. These values were determined as constituting the optimal condition in the study of **section 7.1**. The rapid mixing was done in a spiral coagulator unit containing a PVC tube. The length of spiral tube used as the rapid mixing zone was 50 cm and its diameter was 0.16 cm. Rapid mixing time was calculated from the tube's length and diameter, as well as flow rate of the feed water. The rapid mixing time and velocity gradient (G value) were 0.2 s and 1.2 x 10^4 /s, respectively. This calculation was based on an empirical equation established for the spiral coagulator and the details are given in **section 7.1**. The flocculant solution was channeled through a dosing pump to the rapid mixing unit for contact with feed water. The solution (water with destabilized suspension) was then sent through the filter column under gravity. To maintain a constant filtration rate within the system during the entire duration of the operation, an

effluent pump was used. The filtered samples (filtrate) were collected at the bottom of the column for further analysis. Additionally, to investigate the effect of depth of packing media, sampling (media and water) was also carried out at three ports located on 15cm, 35cm and 55 cm from the bottom of the filter column.

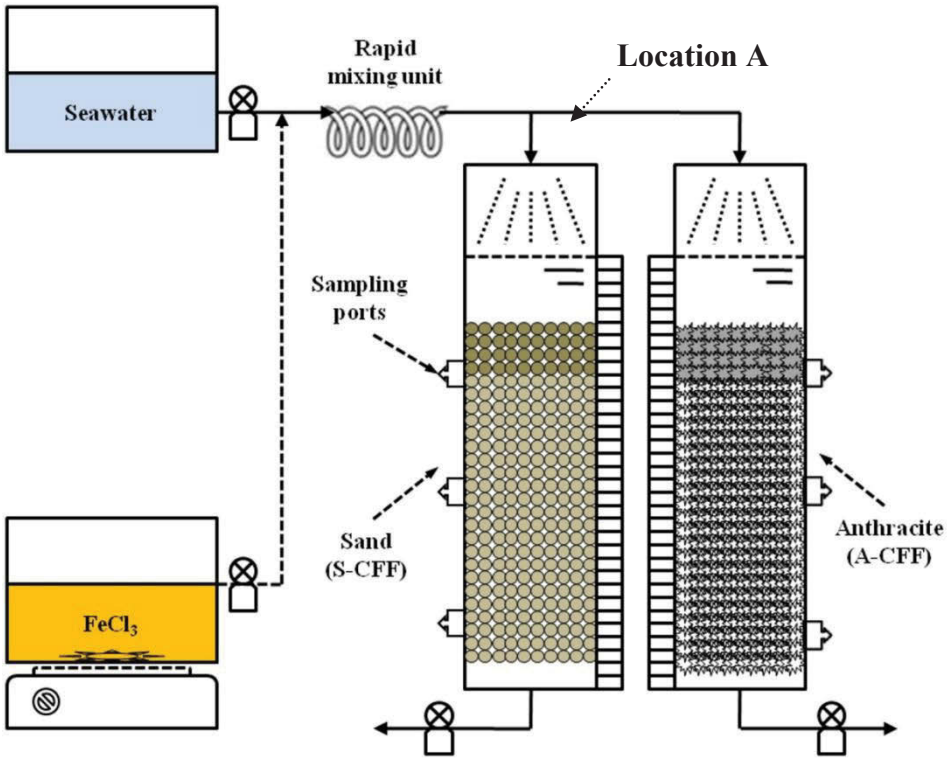


Figure 7.4 Experimental set-up of contact flocculation-filtration (S-CFF: CFF packed with sand; A-CFF: CFF packed with anthracite).

7.2.2.3 Biological activity

The filter media (sand and anthracite) were collected on-site at different times of filtration and were washed with Milli-Q water gently. The washed media placed in test tubes were extracted with phosphorus buffer solution (PBS) on shaker at 200 rpm for 1 h. It was sonicated for 30 sec and the water with detached particles from the media finally was collected for microbial assay.

In this study, biological activity in filtration media was determined in terms of cell number and Adenosine tri-phosphate (ATP) concentration. Cell numbers in the biofilter present in the media and CFF effluent were measured using plate count on marine agar. ATP was used as a direct indicative parameter of active biomass in this study since it is the energy currency of all living cells (Hammes et al., 2010). Thus, the higher value of ATP concentration represents the higher biological activity of microbes present on the filter media of CFF. ATP was measured using Microbial Cell Viability Assay kit according to the manufacturer's instructions (BacTiter-Glo™, Promega). To produce luminescence, prepared samples were mixed with ATP reagent at room temperature. A 96-well luminometer Wallac 1420 VICTOR2™ plate reader (PerkinElmer Inc., USA) was used to measure the luminescence.

7.2.2.4 Microbial community

In this study, the changes of dominant species were investigated at different depths of filter bed at different filtration times. Media samples were collected at different depths occasionally. Extracts of from the biofilm on the filter media was spread on the marine agar plate and incubated for 24 h at room temperature. From this plate, several marine strains (8) were isolated and they were suspended into nutrient buffer solution for DNA extraction. Extracted DNA was amplified using polymerase chain reactions (PCR) with

forward 27F (5’ to 3’ AGAGTTTGATCATGGCTCAG) and reverse 1492R (5’ to 3’ GGTTACCTTGTTACGACTT) primers for 16S-rRNA. The PCR conditions were employed as follows: 95°C for 5 min followed by 30 cycles of 94°C for 0.5 min, 57°C for 0.5 min, 72°C for 0.5 min, followed by 72°C for 5 min. The amplified 16S rRNA gene was purified using a resin spin column and 1 μg of each amplified DNA extract was mixed and subjected to sequencing and alignment. Sequence reading was manually annotated 16S rRNA gene information (served with BLAST queries) of cultured type strains.

7.2.3 RESULTS AND DISCUSSION

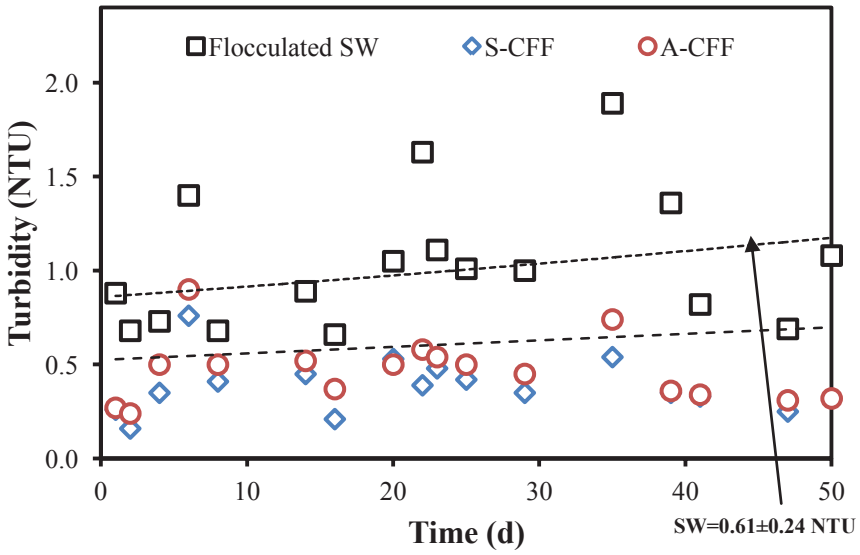
S-CFF and A-CFF were operated at a filtration rate of 7.5 m/h with an empty bed contact time (EBCT) of 4.8 min. The run time of S-CFF and A-CFF were 50d and 90 d, respectively. S-CFF achieved the biological activity more quickly than A-CFF. Both CFFs were planned to be operated for 50 d. However, due to the slower stabilization time (in terms of biological activity) of the A-CFF column, its operation was continued up to 90 d.

7.2.3.1 Removal of particulate and colloidal fouling

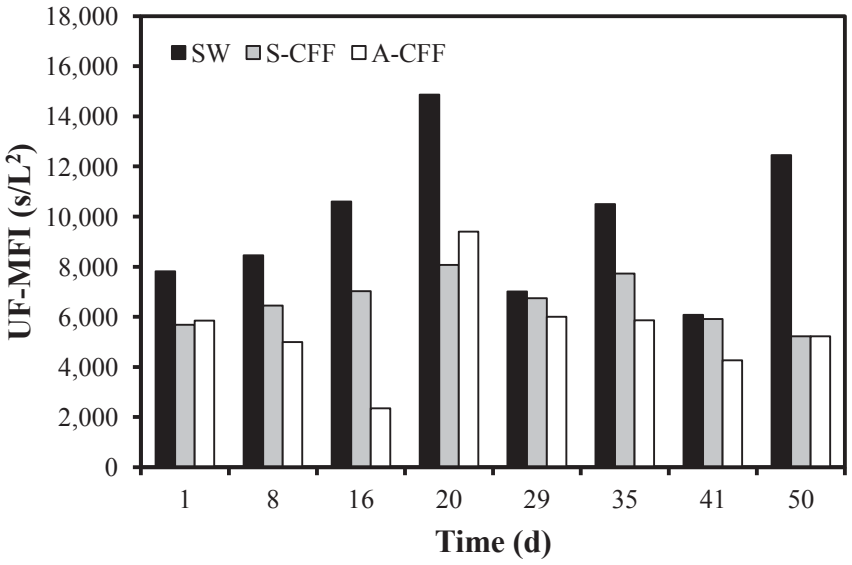
Turbidity and UF-MFI were determined to assess the particulate and colloidal fouling potential of CFF effluents. Turbidity of seawater was 0.61±0.24 NTU but after the rapid mixing with the coagulant (location A in **Figure 7.4**), it was increased to 1.11±0.36 NTU. This is due to the destabilized particles, particulates associated with organics and also the color of $FeCl_3$. However, the turbidity due to particles could be removed by both the CFFs (**Figure 7.5(a)**). More than 54% of turbidity removal efficiency was achieved by S-CFF (0.39±0.15 NTU) and A-CFF (0.51±0.19 NTU). As expected, S-CFF led to a better particle removal due to the sand's smaller size. However, this caused higher headloss development in S-CFF.

The UF-MFI of raw seawater was 10,026±3,276 s/L^2 during the experimental period. The UF-MFI value decreased to more than half after the filtration through A-CFF (after 50 d of operation) while UF-MFI of S-CFF was only decreased by a third throughout the filtration period (**Figure 7.5(b)**). This result suggested that A-CFF was able to decrease colloidal and part of the organic fouling potential once it reached a steady period (after 29 d of filter run). In previous studies, UF-MFI was used to examine the organic fouling potential. Some correlation was observed between DOC and UF-MFI

value. Higher DOC led to a higher UF-MFI value (Boerlage et al., 2000). Organic removal by two CFFs is discussed in detail in the following **sections 7.2.3.4** to **7.2.3.6**.



(a) Turbidity



(b) UF-MFI

Figure 7.5 Turbidity and UF-MFI values: (a) Turbidity, (b) UF-MFI values.

7.2.3.2 Headloss on different filter media of CFFs

Figure 7.7 presents the headloss development in both CFFs. Backwashing was carried out daily with seawater at a rate of 15 m/h (twice as filtration rate) in up-flow direction for 1 min. Relatively lower backwashing rates and very short backwashing duration were used to reduce the loss of biofilm layer that may have formed. Filters retained aggregates of particles, flocculants and organics associated with particles which cause clogging and headloss development. This increased local velocities in the filter with a potentially negative impact on filtrate turbidity and filter run time (Cleasby, 1990). In CFF, headloss development results from deposition of flocculated flocs which are formed in the filter bed. The flocculation (aggregation) of particles occurs during the passage of destabilized particles and small flocs through the filter medium. The headloss development of A-CFF was only 7 cm for 90 d run while that of S-CFF was 15 cm after 50 d of filter operation (**Figure 7.6**). Most of the headloss that developed in CFF was recoverable through daily backwashing. Relatively higher headloss development in S-CFF was due to the filter medium's smaller size (**Table 7.5**).

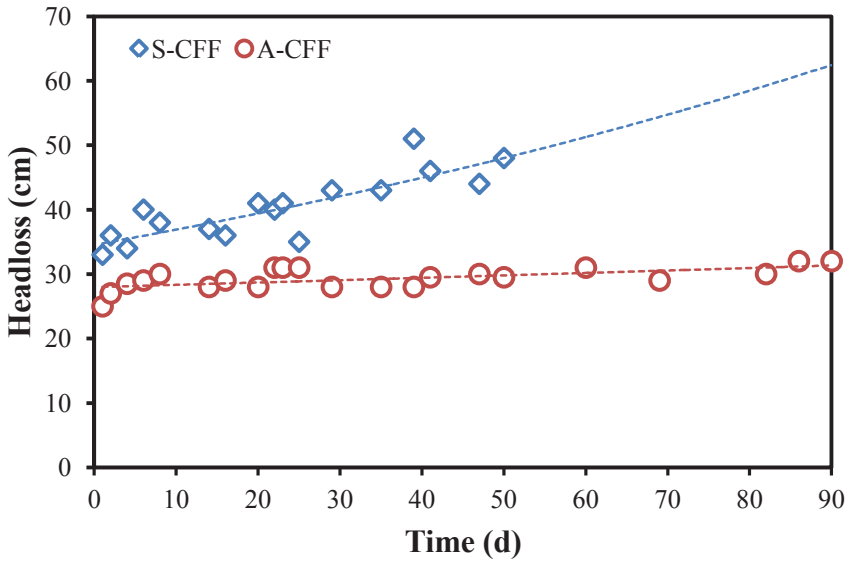


Figure 7.6 Headloss development in the filters (filter depth: 60 cm; filtration velocity: 7.5 m/h; flocculant: 0.5 mg of Fe^{+3}/L of $FeCl_3$).

7.2.3.3 DO and pH

Most living organisms require oxygen for their basic metabolic processes. The greater decline in DO concentration in biofilter represents the higher density of microbes and bioactivity. Microorganisms change the pH of their substrate by producing by-products during growth. They can change conditions such that the environment can no longer support their growth. Thus, DO and pH can be used as indicators of the bioactivity (Hambrick et al., 1989).

After 29 d of filter operation, DO in packed bed of S-CFF dramatically declined (especially in the top layer of column). In the case of A-CFF, significant DO decline was recorded after 50 d of operation period. After 41 d of filter operation, DO of seawater declined from 5.4 mg/L to 2.6 mg/L at the top layer followed by 2.8 mg/L at the middle layer and 3.9 mg/L at the bottom layer of S-CFF. It indicated that most microbial growth occurred at the top layer of S-CFF. However, DO decline trend along the filter depth of A-CFF was different from that of S-CFF. In A-CFF, DO gradually

decline from the top layer to bottom layer, indicating that microbes' consumption of DO, was evenly distributed throughout the bed. This shows that anthracite is a more suitable medium than sand to inhabit the microbes. Other studies (LeChevalier et al., 1992; Shin and O'Melia, 2006) also suggested that anthracite can be a more effective biofiltration medium in some situations. The advantage of anthracite is due to its irregular surface providing a better attachment surface for bacteria. It also has the capacity to slowly adsorb biodegradable compounds which may then be degraded by the bacteria.

The pH of a biofilter is influenced by microbial activities that generate inorganic acids and CO_2. The pH values started to decline after 29 d of operation for S-CFF and 50 d of operation for A-CFF. This was similar to the DO concentration trend.

From these observations, biological stabilization time of S-CFF and A-CFF was set at 29d and 50d respectively. The subsequent discussion divides the CFF duration into two periods - before and after the bio-stabilization times.

7.2.3.4 Dissolved organic carbon

Figure 7.7 shows the total DOC removal profiles by CFFs. DOC concentration of seawater was 2.33±0.51 mg/L during entire filtration time. On average, slightly higher DOC removal efficiency was achieved by A-CFF (1.47±0.44 mg/L; 37.3±14.7% removal efficiency) than S-CFF (1.66±0.19 mg/L; 31.9±6.9% removal efficiency). However, an increase in DOC removal was observed before and after bio-stabilization time in both the CFFs. Up to 29 d of filter operation, S-CFF reduced the DOC to only 27.6±4.2% while this removal efficiency was increased to 39.2±1.7% after bio-stabilization (29d~). In the case of A-CFF, after bio-stabilization time DOC removal was increased appreciably to 29.6±9.6% to 55.3±1.8% than before bio-stabilization.

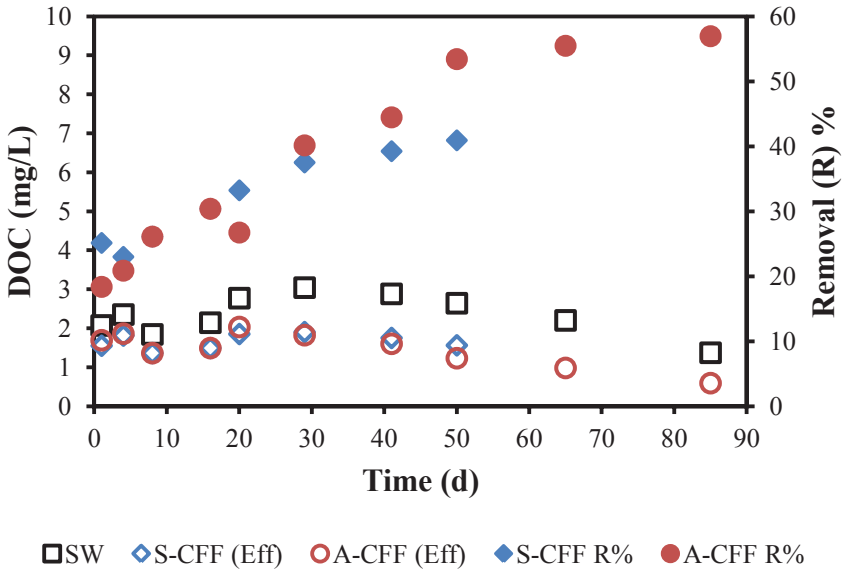
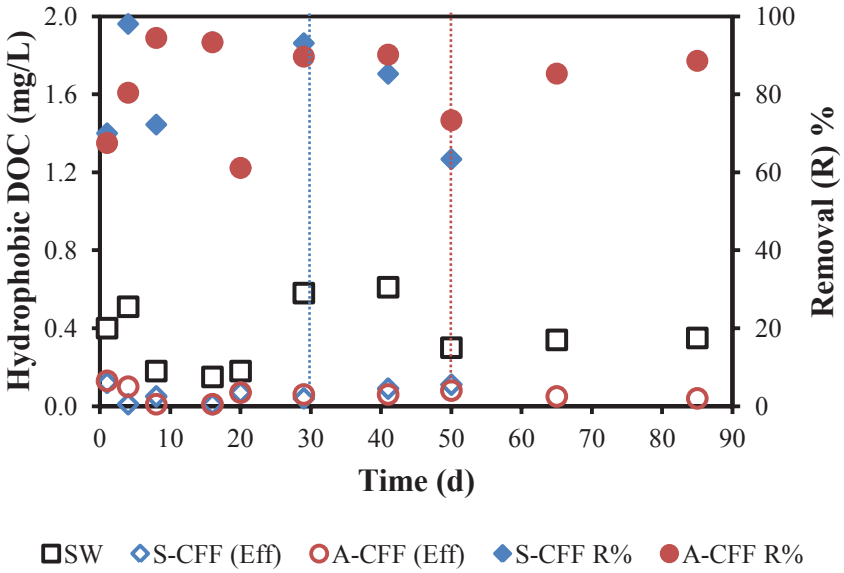


Figure 7.7 Removal of dissolved organic carbon concentration.

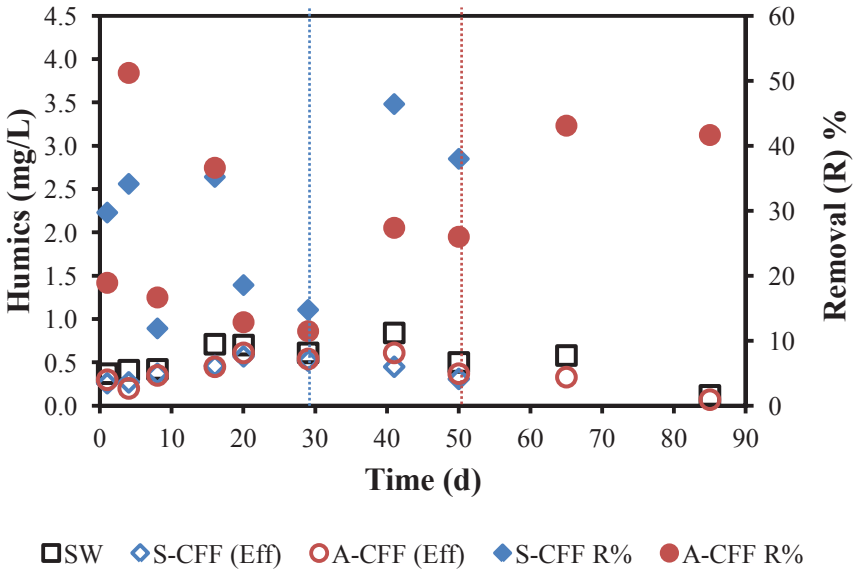
7.2.3.5 Hydrophobic DOC and Humics

In this study, DOC in seawater (obtained by LC-OCD) was divided into two kinds of compounds: firstly, sorbable DOC (hydrophobic DOC and humics which can be removed by flocculation) and secondly, bio-related DOC (TEP produced by microbes and LMW neutrals obtained from the decomposition by microbes).

Hydrophobic DOC and humic substances can be usually removed using the flocculation process. Thus the removal efficiencies of these two fractions of DOC compounds were stable throughout the CFF filtration periods. More than 80% of hydrophobic DOC was removed by both the CFFs. Both CFF effluents had only a negligible amount of hydrophobic DOC (0.06±0.04 mg/L) (**Figure 7.8**). As expected hydrophobic removal efficiency was not improved after bio-stabilization time (but remained same).



(a) Hydrophobic DOC



(b) Humic substances (Humics)

Figure 7.8 Removal of hydrophobic DOC and humics concentration.

Humic substances represent compounds with molecular weights approximately 1,000 g/mol in raw seawater. The concentration of humic substances in raw seawater was 0.53±0.21 mg/L. The C-CFF and A-CFF were able to remove almost similar amounts of these humic substances (28.6±13.9%). Bio-stabilization contributed to only a slight increase (an additional 10%) in the removal of humics. A previous study (Wang et al.,

1995) had also suggested that humic substances that seemed to be more refractory to biodegradation had a low removal effect with biofilter. The amount of humic substances removed (adsorbed onto metal hydroxides by coagulation) depends on the concentration of the associated form of humic and fulvic acids in seawater. Negatively charged humics can be removed by reaction with positively charged Fe while fulvic was difficult to removed using Fe-coagulation since it has a positive charge (Edzwald and Haarhoff, 2011). The amount of fulvic acid-like compounds is generally more than humic acid-like in seawater (Penru et al., 2001).

7.2.3.6 Bio-related DOC compounds

Table 7.6 presents the removal of TEP and LMW neutrals concentration by both the CFFs. TEP, being a very sticky substance, may act like "natural glue" that can entrap or bind organic and inorganic colloids from the feed stream onto the membrane surface. Thus, TEP leads not only to biological or organic fouling but also enhances colloidal/particulate fouling as well. Villacorte et al. (2009) discovered evidence of accumulation of TEP-like substances on RO membranes through membrane autopsies. Some of these substances may have even been produced locally by biofilm bacteria and not from the feedwater.

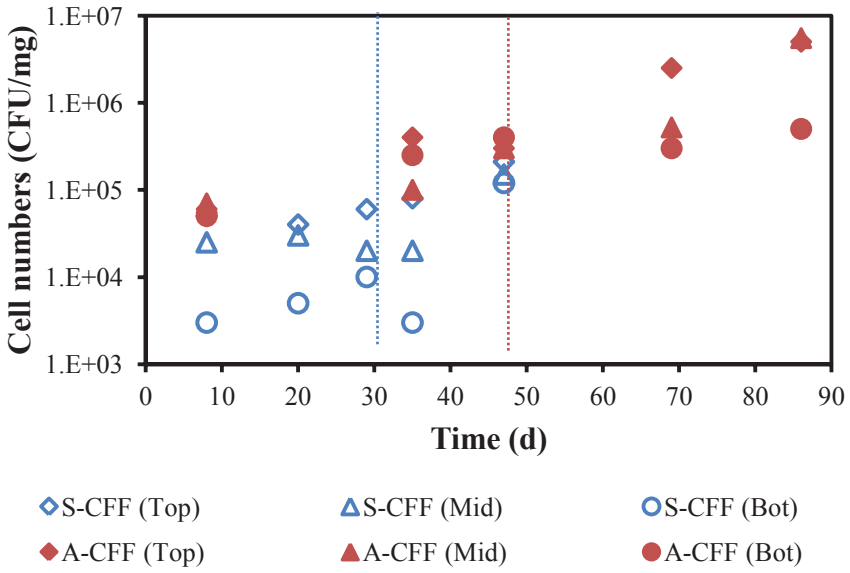
The TEP concentration in seawater was estimated to be 27.20±15.35 µg-C/L. In this study, TEP was estimated using LC-OCD-OND. On average a 65.19±20.44% of removal efficiency was achieved with A-CFF (7.30±2.26 µg-C/L in A-CFF effluent). S-CFF achieved a slightly lower TEP removal (57.13±21.75% removal with 8.88±1.25 µg-C/L in S-CFF effluent) (**Table 7.6**).

Table 7.6 Organic fractions related to biological activity.

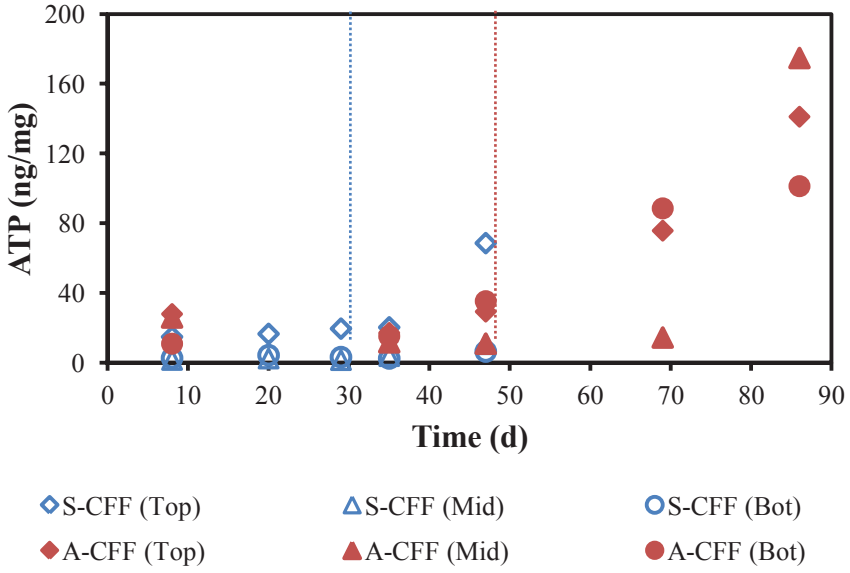
Parameter	SW (μg-C/L)		S-CFF Effluent (μg-C/L)	Removal Efficiency (%)		A-CFF Effluent (μg-C/L)	Removal Efficiency (%)
	27.20 (±15.35)	(Average)	8.88 (±1.25)	57.13 (±21.75)	(Average)	7.30 (±2.26)	65.19 (±20.44)
TEP		~ 29		54.03 (±25.25)	~ 50		62.17 (±23.29)
		29 ~ 50		62.29 (±17.79)	50 ~ 90		72.22 (±7.51)
	1,160 (±270)	(Average)	770 (±300)	37.18 (±25.15)	(Average)	645 (±270)	40.99 (±29.92)
LMW Organics		~ 29		23.73 (±20.25)	~ 50		23.86 (±14.18)
		29 ~ 50		59.59 (±13.68)	50 ~ 90		80.93 (±0.80)

LMW organic matter in the feed water causes bacterial growth and re-growth on the RO membrane (Croue et al., 1999). Thus LMW removal has been considered significantly important to the biofouling problem. It can be easily utilized by microorganisms (Hammes et al., 2006). S-CFF reduced LMW neutrals by around 60% from seawater during the bio-stabilization period. On the other hand, more than 80% of LMW neutrals removal was achieved by the bio-stabilized A-CFF.

7.2.3.7 Biological activities



(a) Cell number



(b) ATP concentrations

Figure 7.9 Cell numbers and ATP concentrations in filter media: (a) Cell number (CFU) and (b) ATP.

Cell number counts and ATP concentration measurements are direct indicators of a bioactivity in biofilter (compared to DOC removal trend). As can be seen from **Figure 7.9**, A-CFF had a larger population of heterotrophic bacteria in the filter bed than S-CFF. The number of cells increased remarkably after around 50 d in the case of A-CFF. A-CFF showed a similar number of cells throughout the entire depth of the column. On the other hand, the bioactivity was dominant on the top layer in the S-CFF. The cell number in S-CFF decreased from top to bottom of the bed. This result was further supported by ATP measurement. In A-CFF, the ATP concentration reached to 174.81 ng/mg of anthracite at the middle layer of A-CFF. Thus, A-CFF is a more effective biofilter, maintaining a highly active biomass population.

To investigate the specific microbial species on the CFF, media were collected at different depths of column over time. In the culture-dependent study, 8 isolates (which then underwent 16S rDNA gene sequencing) were taken from the samples collected at different filter depth and filtration run time. There was not much difference in microbial community at different filter depths. This may be due to the frequent filter backwashing (daily) and relatively short operation time (50~90d). Both CFFs indicated that γ-Proteobacteria such as *Pseudomonas otitidis* strain MCC10330 and *Pseudomonas aeruginosa* strain DSM 50071 (with 99% of similarity) was the dominant species throughout the duration of the experiment (**Table 7.7**). Species of *Pseudomonas* have been known to play an important role in the biodegradation and a broad affinity for hydrocarbon. They can degrade alkanes, alycyclics, thiophenes, aromatics, etc. (Abalos et al., 2004; Mohammad et al., 2007). However, microbial communities in the A-CFF after 50 d changed in that they demonstrated a dynamic shift in the dominant bacterial species (to halophlic) such as *Marinobacter guineae* strain LMG 24048 and *Marinobacter hydrocarbonoclasticus* strain ATCC 49840. This change of microbial

community in A-CFF may be attributed to high organic removal during the bio-stabilization period (Gauthier et al., 1992).

Table 7.7 Dominant species in filter media of CFF.

Origin	Strains	Type strain	Query coverage	Max ident
S-CFF and A-CFF	*Pseudomonas otitidis* strain MCC[a]10330	ATCC[b] BAA-1130^T	99%	98~99%
	Pseudomonas aeruginosa strain DSM[c] 50071	ATCC 10145^T	99%	98%
A-CFF	*Marinobacter guineae* strain LMG[d] 24048	M3B^T	98-100%	97%
	Marinobacter hydrocarbonoclasticus strain ATCC 49840	ATCC 49840^T	98~99%	94~95%

[a]MCC, Mycobacterial Cell Wall-DNA complex

[b]ATCC, American Type Culture Collection

[c]DSM, DSMZ-Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH

[d]LMG, BCCM/LMG Bacteria Collection

Table 7.8 Summary of two different CFFs.

	Sand CFF (S-CFF)		Anthracite CFF (A-CFF)
Head loss	15 cm for 50 d	>	7cm for 90d
Particle removal (%)			
Turbidity	65%	>	54%
UF-MFI	32%	<	47%
DOC removal (%)	32%	<	37%
Hydrophobic DOC / Humics	80% / 29%	≈	82% / 29%
TEP / LMW neutrals	57% / 37%	<	65% / 41%
Bioactivity		<	
Effect of depth	Top >> Mid > Bot		Top ≥ Mid ≈ Bot
Stabilization time	29 d	<	50 d

7.2.4 SUMMARIZING THE BIOACTIVITY OF CFF

CFFs with two different media (sand; S-CFF and anthracite; A-CFF) were investigated for their biological activity during long-term filtration. Particulate and organic removal efficiencies were measured. The cell number counts, ATP and microbial community were also determined to gauge the biological activity and its influence on organics removal. The results are summarized in **Table 7.8**.

(1) S-CFF showed higher particulate than A-CFF, however, headloss development was higher for S-CFF.

(2) After around 29 d, S-CFF showed evidence of biological activity while A-CFF did so after approximately 50 d.

(3) Bioactivity in both CFFs helped in removing DOC compounds in seawater, especially, bio-related DOC compounds such as TEP and LMW neutrals.

(4) Total cell number and active biomass increased in the CFF column over time. Biological activity was dominant at the top layer of the S-CFF while it was relatively uniform at all depths of the A-CFF.

(5) In both CFFs *Pseudomonas* sp. was dominant, but after 50 d of operation, halophilic species (which can biodegrade the organics) were found in A-CFF.

(6) Both CFFs can be used as a biofilter after bio-stabilization. A-CFF emerged as having more effective biofiltration potential than S-CFF.

CHAPTER 8

University of Technology Sydney

Faculty of Engineering& Information Technology

CONCLUSIONS AND RECOMMENDATIONS

Seawater reverse osmosis (SWRO) desalination constitutes a promising (non-conventional) technology. However, SWRO has suffered from the problem of microbial and organic adhesion to the membrane surface which causes biofouling and organic fouling. In turn this deteriorates membrane performance and increases overall operational costs. For this reason pretreatment is essential to remove or reduce undesirable materials such as organic matters and biofouling in raw seawater to acceptable levels. In most cases, organic foulants can lead to biological growth. In order to control fouling in an efficient manner, organic matters (especially, biodegradable organics) must be removed with microbial inactivation. However, the control of organic fouling and biological fouling is difficult as it requires advanced pretreatment.

Membrane hybrid system (MHS) as pretreatment

A recent trend in the development of membrane filtration for water treatment is integrating different pretreatment strategies to improve the performance of low pressure membranes. An integrated submerged low pressure membrane system with physico-chemical treatment such as coagulation/flocculation or adsorption, namely, "submerged membrane hybrid system (SMHS)" was studied in detail in this thesis.

Firstly, the commonly used ferric chloride ($FeCl_3$) was selected as coagulant for removing organic compounds from seawater. In-line coagulation coupled with micro-filtration process (submerged membrane coagulation hybrid system; SMCHS) was investigated as a pretreatment strategy for RO. Ferric chloride removed 57% of DOC from seawater. The removal efficiency of hydrophobic compounds by coagulation was much higher than that of hydrophilic compounds; 95% of hydrophobic compounds and 37% of hydrophilic compounds could be removed at a Fe^{3+} dosage of 3.0 mg/L. The coagulation improved membrane filtration performance in SMCHS.

In order to model the DOC removal by $FeCl_3$ coagulation, coagulation test was carried out with different doses of coagulant and pHs. The removal of DOC (hydrophobic; HB and hydrophilic; HF) in seawater by coagulation improved marginally as pH was increased from pH 5 to 9. Measured HB and HF DOC were fitted successfully with the proposed model. Maximum error in prediction was 0.053 mg/L for HB and 0.002 mg/L for HF. The DOC removal model is helpful in the design the $FeCl_3$ coagulation as pretreatment in seawater desalination.

The performance of modified poly ferric silicate (PFSi-δ) as a new flocculant was compared with $FeCl_3$. Both PFSi-δ and $FeCl_3$ were effective in removing dissolved organic compounds in seawater. Higher removal efficiencies of turbidity and DOC were obtained at lower doses of PFSi-δ (1.2 mg/L as Fe^{3+}) in comparison with $FeCl_3$ (3 mg/L as Fe^{3+}). In particular, hydrophilic compounds were removed more effectively by PFSi-δ (about 55% with PFSi-δ 1.2 mg Fe^{3+}/L). However, in SMCHS, the smaller size and larger amount of flocs generated with PFSi-δ lowered critical flux and increased fouling potential on the MF membrane.

$TiCl_4$, which is another alternative coagulant, was investigated in terms of organic removal. TiO_2 recovered from flocculated $TiCl_4$ sludge of seawater was characterised in terms of particle structure and atomic composition so that its application for different uses could be evaluated. The removal of hydrophilic compounds of seawater by $TiCl_4$ flocculation was higher than that of $FeCl_3$ flocculation. Biopolymers were removed completely during $TiCl_4$ flocculation. Higher humics removal of 63.6% was observed with $TiCl_4$ flocculation. $TiCl_4$ could remove high LMW neutrals even at low doses. LMW neutral is a significant compound causing organic fouling and biofouling of membranes. The recovered TiO_2 nanoparticles from $TiCl_4$ flocculated sludge had a Si-doped anatase structure according to XRD and SEM/EDX analyses.

Brief comparison of performance and rough cost estimation at optimal dose of different coagulants and absorbent are made in **Table 8.1**.

Table 8.1 Comparison of performance and cost estimation at optimal dose.

	$FeCl_3$	**PFSi**	**$TiCl_4$**	**PAC**
Optimum dose (mg/L)	3.0	1.2	3.8	2.14[a]
DOC removal %	57	68	79	77
HPO removal %	95	88	76	81
HPI removal %	35	55	80	70
UF-MF I (s/L^2)	3,025	4,292	7,990	3,852
Critical flux (LMH) at SMHS	55	30	N.A.	40-50
Sludge production (mg/L)	20	13.9	28.2	N.A.
Comparison of cost estimated based on 10,000 ton/d treated water				
Chemical (US$/d)[b]	29	35	294	21
Sludge treatment (US$/d)[c]	7	5	12[e]	4[d]
By-products (US$/d)	-	-	282[e]	-
Total Cost (US$/d)	36	40	24	25

[a] PAC amount was calculated based on the SMABR experiment (2.14 g of PAC/m^3 of water treated **section 6.2** of **Chapter 6**).

[b] Chemical cost ($FeCl_3 \cdot 6H_2O$-200US$/ton; PFSi-580US$/ton;$TiCl_4$-1950$/ton; and PAC-1000US$/ton).

[c] Sludge treatment cost is 37US$/ton.

[d] Seawater is usually cosists of 10mg/L of suspended solids. Thus it produces 0.1ton/d of sludge based on 10,000 m^3/d treatment of seawater.

[e] A 5% (recovery rate) of valuable by-product (such as TiO_2) can be recovered from $TiCl_4$ coagulated sludge through incineration (it costs 44US$/ton). TiO_2 costs US$20/kg. Thus it covers the high price of $TiCl_4$.

Organic and biofouling reduction using MHS as pretreatment

The effect of SMAHS on the removal of organic compounds in seawater was studied in detail. The mitigation of initial biofouling potential was studied through short-term RO experiments. In addition the SMCAHS (addition of coagulation into SMAHS) was evaluated in view of reducing the PAC dose and further reducing the biofouling. SMAHS and SMCAHS could significantly reduce organic matter in seawater, especially the biopolymer and humics in the hydrophilic fraction of organic compounds. This led to a smaller permeate flux decline in RO operation. Moreover, after the pretreatment of SMHSs, bacteria cell number and cell viability declined significantly. Active biomass (as microbial ATP concentration) on fouled RO membrane was also deactivated with SMCHS and SMCAHS to a certain extent. Therefore, SMHSs as a pre-treatment can be effective in reducing the biofouling potential.

Application of membrane fouling model for MHS as pretreatment

Three different configurations of SMHS - SMCHS, SMAHS and SMCAHS (as explained before) - were evaluated according to: trans-membrane pressure (TMP) development; critical flux; ultrafilter modified fouling index (UF-MFI); and DOC removal efficiency and detailed organic fractions. Filtration fouling models were used to study the fouling behavior of SMHSs. In this study, when $FeCl_3$ coagulation and PAC adsorption were combined (SMCAHS), both hydrophobic and hydrophilic compounds could be removed at low doses of flocculant and adsorbent. The suitable doses of $FeCl_3$ and PAC were found to be 0.5 mg of Fe^{3+}/L and 0.5 g/L, respectively. More than 72% of DOC was removed with a pretreatment of SMCAHS and particularly a majority of biopolymer and humics were removed even at low chemical doses. Among the three filtration models, cake formation emerged as the dominant fouling mechanism on

SMHS. A very high critical flux was observed for SMHS through TMP experiments and it was predicted by the model developed in this study.

Organic characterization of MHS effluent

Before and after pretreatment by SMHSs, seawater organic matter (SWOM) was characterized though advanced analytical techniques. In this study, different fractions and molecular weight distribution (MWD) of SWOM were measured using XAD resin, fluorescence spectroscopy and size exclusion methods. After proper SWOM isolation from salt, the structure of SWOM was studied using ^{1}H NMR, LC/MS-IT-TOF and Py-GC/MS. The results obtained from the characterization by different advanced analysis techniques provided additional useful information and helped in selecting suitable SMHS pretreatment methods. SMHSs could remove effectively organic compounds of larger MW of more than 900Da representing biopolymers and humics. The EEM fluorescence showed the removal of humic-like materials by SMHSs. After the SMHSs pretreatment, a ratio of humic-like to protein-like compounds was significantly reduced from 12.7 to 1.41-2.31 but the aromaticity of humics increased. NMR analysis showed that peaks corresponding to carbohydrate and amino acid or peptide structural bonds changed slightly. The changes of SWOM element composition by the pretreatment used were observed through the liquid chromatographic technology. The pretreatment of SMCAHS removed the protein-like SWOM. Overall, detailed SWOM characteristics, which had an impact on the SMHSs pretreatment, were attempted from the bulk analysis to the structural study. These analyses procedures led to a better understanding of the SMHSs pretreatment.

Foulant characterization

The RO membrane fouling reduction was analysed with the pretreated seawater. SMHS, SMCHS and SMCAHS were used as pretreatment. Detailed investigations on organic and biological foulant were made using representative analytical methods. The pretreatment by SMHSs helped to reduce the organic foulant on RO. Less biopolymers and humics (high molecular weight organic content) in the RO feed by SMHS pretreatment led to a reduction in the flux decline of the RO membrane (from 31.5 LMH with raw SW to 36.0 LMH with SMCHS and 45.4 LMH with SMCAHS). SMHSs also resulted in less deposition of low molecular weight organic matter on the RO membrane. This caused a lower initial biomass accumulation (from $4.10E^{+08}$cells/cm^2 with raw SW to $1.77E^{+08}$cells/cm^2 with SMCHS and $2.75E^{+08}$cells/cm^2 with SMCAHS) and cell viability (from 0.5 with raw SW to 0.3 with pre-treated seawater by both SMHSs). Pretreatment led to a reduction of hydrophilic organic foulants which helped to preserve the RO membrane surface during the initial fouling stage.

Representative method for assimilable organic carbon (AOC)

In this study, the assimilable organic carbon (AOC) assay was considered as an effective indicator of the biological growth potential of the water (or biofouling potential). However, there is only limited information available on AOC test for seawater. Additionally, previous AOC tests proved to be time-consuming and laborious to do. Thus, developing of a rapid and easily usable AOC test method is required.

In our AOC study, *Vibrio fischeri* MJ-1 (bioluminescence AOC method) was used. Direct bioluminescence measurement was used as an instantaneous indicator of cell number as well as AOC concentration. This was feasible because bioluminescence was consequently correlated to the AOC in seawater samples. In order to verify this method,

pretreated seawater samples by bio-filtration was tested. Compared to the previously developed methods, new AOC assay was more accurate and could be measured in less time. This method was rapid (within 1 h), and sensitive (R^2 = 0.978) for seawater. Reproducibility (<10% of standard deviation) of the method was evaluated through the biofiltration seawater sample.

Detection of rapid biofouling potential

Biofouling results in an additional energy cost. Usage of chemical cleaning (and waste disposal) is also increased and it would involve additional manpower and down time, and decreased membrane life. These scenarios will in turn increase operational costs. If regular monitoring is not done, fouling cannot be observed until after it has reached an advanced stage. Early biofouling detection enables preventive measures to be implemented such as optimising of pretreatment. Therefore, early biofouling detection can postpone membrane replacement and reduce chemical costs (**Figure 8.1**).

A rapid AOC test for seawater developed through this study significantly shortens the measurement time together with increased accuracy. In desalination plants, it can be utilized effectively to screen the pretreatment to meet the need of suitable feedwater quality. It can be used to warn the biofouling potential of the influent prior to RO.

It is thus important to test this new AOC method in a desalination plant (over a long period).

Figure 8.1 Expected effect of early detection of biofouling potential.

Membrane bioreactor as pretreatment

As discussed previously the removal of biodegradable organics as well as microbial inactivation is required to effectively control biofouling. Submerged membrane adsorption bio-reactor (SMABR) was investigated as a new pretreatment to control biofouling.

Prior to a SMABR experiment, PAC replenishment was optimized to maintain stable bioactivity and produce high quality permeate in terms of organic removal and consistent increase of biomass. PAC retention time of 66d was found to be optimum. The effect of PAC residence time in SMABR to treat seawater was evaluated by comparing optimal PAC replenishment with maximum biological mode (PAC retention time of ∞d or no PAC replacement). The measurement of biofouling potential was carried out in terms of assimilable organic carbon (AOC). The results showed that a small amount of PAC (approximately 2.13g/m^3 of seawater treated) was sufficient to maintain low biofouling potential in SMABR. High removal of DOC was maintained with marginal increase of TMP and low fouling potential in SMABR with a residence time of PAC of 66d. Low fouling potential permeates with low AOC concentration of 6.0 (±2.9) µg-C glucose/L (PAC age of 66d) were also achieved.

A pilot-scale study on SMABR with on-line AOC and fouling indices measurements is useful.

Deep bed filtration as pretreatment to reduce biofouling

Conventionally used deep bed filter (DBF) in seawater pretreatment can also function as a biofiltration. Here, biofilm developed on the filter medium can help decomposing the biodegradable organic material. Following the adsorption of organic matters onto the

filter media, the initial degradation is accomplished by extracellular enzymatic hydrolysis of macromolecules to smaller substrates. Further degradation can take place by a diverse microbial biofilm community that has developed.

A detailed study conducted on CFF highlighted the need for monitoring biological water quality characteristics such as DOC, biopolymers, especially transparent exopolymer particles (TEP) which significantly affect the RO biofouling. Microbial activity on the CFF was measured in terms of heterotrophic bacterial count (or colony forming unit, CFU) and ATP (as an active biomass). During a 50d operation of CFF packed with sand (S-CFF) and 90d operation of CFF packed with anthracite (A-CFF), the development of microbial communities on the media was also investigated using the 16S rRNA sequencing of cultural colonies.

The biological activity of the CFF at different depths of filter media (top, middle and bottom layers) was also studied. S-CFF showed higher particulate removal than A-CFF. However headloss development was higher for S-CFF. S-CFF showed evidence of biological activity after around 29 d of filtration time, while A-CFF did so after approximately 50 d. Bioactivity in both CFFs helped in removing DOC from seawater, especially, bio-related DOC compounds such as TEP and LMW neutrals. Total cell number and active biomass increased in a CFF column over the time. Biological activity was dominant at the top layer of the S-CFF while it was relatively uniform throughout the depth in A-CFF. In both CFFs, *Pseudomonas sp.* was dominant but after 50 d of operation, halophilic species (which can biodegrade the organics) were found in the A-CFF. Therefore both CFFs can be used as a biofilter after bio-stabilization time. A-CFF is found to have more effective biofiltration potential than S-CFF.

A detailed pilot-scale study on deep bed filter in existing desalination plant will be useful to optimize the backwash condition and frequency, and filtration velocity to enhance the biological activity in the deep bed filter, thus to reduce biofouling.

A detailed organic characterization is also important at different times of the filtration cycle to extend the filter run time.

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