Seawater Pre-treatment for Reverse Osmosis System

By

Anil Kumar Shrestha

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CERTIFICATE OF ORIGINAL AUTHORSHIP

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

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

Anil Kumar Shrestha

Date: 31/07/2017

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ABSTRACT

Membrane based desalination technology such as reverse osmosis (RO) has rapidly become a viable alternative to conventional treatment for drinking water production from seawater. However, membrane fouling is a major concern in reverse osmosis (RO) based seawater desalination. The fouling on RO membrane deteriorates the performance of RO membranes and increases the energy consumption and even requires more frequent replacement of the membranes. The objective of the study was to assess the different pre-treatment systems to reduce membrane fouling reduction, and remove organic matter in terms of dissolved organic carbon in RO desalination projects. Silt density index (SDI), modified fouling index (MF/UF-MFI) and cross-flow sampler modified fouling index (CFMF-MFI) were used to study the pre-treatment efficiency of different process such as flocculation, deep bed filtration, microfiltration, ultrafiltration and biofiltration.

A long term on site biofilter experiment was investigated in terms of removal of particulate matter, different fouling indices and dissolved organic carbon (DOC) from sea water by the use of biofiltration. In this study, three biofilter columns were operated packed with granular activated carbon (GAC), anthracite and sand as a filter media. The experimental results indicated that biofiltration pre-treatment systems reduced organic matter and particulate matter. It was expected that biofilter can lower fouling to a subsequent RO process in desalination plant. In terms of DOC removal efficiency, GAC biofilter showed higher and stable removal efficiency (41-88%), than sand biofilter (7-76%) and anthracite

biofilter (3-71%). All biofilters used in this study removed most of hydrophobic organic compounds (around 94%). On the other hand, hydrophilic organic removal varied depending on the media filter. GAC biofilter removed more organic bio-polymers (51%), humic substances (75%) and building blocks (50%) compared with sand and anthracite biofilters. Thus GAC filter was the best medium to provide the lowest fouling potential as it showed the highest removal efficiency of DOC, including hydrophilic, humic, building blocks and biopolymer. The fouling potential of treated seawater (filtrate) was evaluated using three different fouling MF-MFI, UF-MFI, and CFMF-MFI. GAC biofilter had lower fouling potential compared to sand and anthracite biofilters.

The in-line flocculation and spiral-flocculation followed by media filtration (sand or anthracite) have been investigated as a pre-treatment of seawater to reverse osmosis (SWRO). In the case of in-line flocculation filtration system, the seawater was passed through the media filter just after rapid mixing of raw seawater with flocculants for 10 seconds. In the case of spiral-flocculation filtration, after the rapid mixing of seawater with flocculants, it was then passed through the spiral-flocculation. Both filtrations showed good turbidity removal efficiency (up to 71%). In-line flocculation filtration showed 2-3 times higher headloss than the spiral-flocculation filtration. The UF-MFI reduction was 63-70% for sand as medium in the presence of the flocculant whereas it was 65-76% for anthracite. Both filtration systems in the presence of flocculant (3 mg/L Fe^{3+}) led to 50-65% removal of hydrophobic organics. The hydrophilic organic removal was around 30-38%. The predominant portion of hydrophilic was humic substances which had a poor removal. In general sand filter gave a higher removal than anthracite filter.

The performance of $TiCl_4$ and $Ti(SO_4)_2$ was compared to $FeCl_3$ at different coagulant concentrations (1-30 mg/l) of Ti salts and $FeCl_3$ and at different pH of 5 to 9. Coagulation was conducted using conventional jar test. For each jar test, six 1 litre beakers were filled with raw seawater. The pH was adjusted with 0.1 N solution of hydrochloride acid and sodium hydroxide prior to coagulant addition. The solution was subjected to rapid mixing (100 rpm) for 2 min followed by slow mixing (20 rpm) for 30 min. It was then stopped to allow the aggregated flocs to settle down for 30 min. The supernatant samples were drawn for the measurements of turbidity, UV-254 absorbance and DOC, zeta potential and particle size distribution. The results showed that at pH of 8.0 (similar to seawater pH), $TiCl_4$ had advantages over $FeCl_3$ and $Ti(SO_4)_2$ at the same coagulant dose of 20 mg/L. Under this condition, $TiCl_4$ achieved ~70% DOC and UV-254 removal. This was approximately two times higher than $FeCl_3$ and $Ti(SO_4)_2$. Nevertheless, $FeCl_3$ and $Ti(SO_4)_2$ showed better turbidity removal. At higher coagulant dose (30 mg/L), the turbidity removal of $TiCl_4$, was especially compromised. The differences in the performance of the coagulants were associated with the coagulant mechanisms based on the floc zeta potential evaluation. The coagulant mechanisms of Ti-salts could be associated to charge neutralization while $FeCl_3$was inclined towards adsorption mechanism.

The study found that biofiltration, in-line flocculation and spiral-flocculation followed by media filtration, coagulation and flocculation are appropriate pre-treatment before RO. In particular, Biofilter showed to a consistent removal of organic matter over a long period of time.

ACKNOWLEDGEMENT

This thesis could not be completed without the assistance, understanding and counseling of several people throughout the research work. First and foremost, I would like to express my foremost and deepest thanks to my supervisors, Associate Professor Jaya Kandasamy, Professor Vigneswaran for all their guidance and support during my PhD study in UTS. Your unconditional support from start to finish, your encouragement and your exceptional guidance along this exciting research project has been a constant source of motivation.They provided me precious knowledge and skills in the field of my research. They encouraged and supported me both in academic study and daily life. Apart from the academic supervision, inspiring suggestions for work-family life balance and future career development from my supervisors were the important factors for successful completion of my thesis.

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LIST OF PUBLICATIONS BASED ON THIS RESEARCH

Journal Articles

1. Shrestha, A., Johir, M.A.H., Vigneswaran, S., &Kandasamy, J. (2014), “A comparative study on in-line flocculation and spiral flocculation followed by media filtration as a pre-treatment of seawater”, Desalination and Water Treatment, Vol. 55, Iss. 4, 2015.

2. Shrestha, A., Jeong, S., Vigneswaran, S., Kandasamy, J. (2013), "Seawater biofiltration pre-treatment system: comparison of filter media performance", Desalination and Water Treatment, in press, Vol. 52 , Iss. 34-36,2014.

3. Shrestha, A., Naidu, G. Johir, M.A.H., Vigneswaran, S., &Kandasamy, J. (2017) Performance Of Titanium Salts Compared To Conventional $Fecl_3$ For Seawater Reverse Osmosis Pre-Treatment, Desalination and Water Treatment, submitted for publication.

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RO = Reverse osmosis

SWRO = Seawater reverse osmosis

SDI = Silt density index

MFI = Modified fouling index

MF/UF-MFI = Micro filtration / Ultra filtration modified fouling index

CFS-MFI = Cross-flow sampler modified fouling index

GAC = Granular activated carbon

DOC = Dissolved organic carbon

MF-MFI = Micro filter - modified fouling index

CFMF-MFI = Cross flow micro filter -modified fouling index

UF-MFI = Ultra filter - modified fouling index

NF-MFI = Nano filter - modified fouling index

UNEP = United Nations Environment Program

IWMI = International Water Management Institute

CSIRO = Commonwealth Scientific and Industrial Research Organisation

NOM = Natural organic matter

MF = Microfiltration

UF = Ultrafiltration

NF = Nanofiltration

LC-OCD = Liquid chromatography-organic carbon detection

DOM = Dissolved organic matter

Da = Dalton

Ppm = Parts per million

EPS = Extracellular polymeric substances

NTU = Nephelometric Turbidity Unit

TOC = Total organic carbon

COD = Chemical oxygen demand

BOD = Biochemical oxygen demand

EfOM = Effluent organic matter

BTSE = Biologically treated secondary effluent

IE = Ion exchangers

ZVI = Zero-valent iron

TDS = Total dissolved solid

PAC = Powdered activated carbon

DMF = Dual media filters

DAF = Dissolved air flotation

TSS = Total suspended solids

ASTM = American standard testing and method

UV = Ultra violet

t_i = Initial filtration time (to filter a fixed volume)

t_f = Final filtration time (to filter the same fixed volume)

T_f = Elapsed time

Spb = Pore blocking slope by critical time – pore blocking index (1/L)

V = Total permeate volume (l)

R_m = Membrane resistance (m^{-1})

t = Filtration time (s)

ΔP = Applied trans-membrane pressure (Pa)

η = Water viscosity at 20°C (N s/m^2)

α = The specific resistance of the cake deposited

C_b = The concentration of particles in a feed water (mg/l)

A = The membrane surface area (m^2).

SAC = Spectral absorption coefficient

SEC = Size exclusion chromatography

BDOC = Biodegradable organic carbon

AOC = Assimilable organic carbon

G = Velocity gradient, 1/s

g = Gravitional acceleration, cm^2/s

υ = Kinematic viscosity,cm^2/s

Q = Flow rate, cm^3/s

V = Volume of the flocculator (in this case, tube volume), cm^3

ΔH = Headloss through the flocculator, cm

LMW = Low molecular weight

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CHAPTER 1

BACKGROUND AND INTRODUCTION

1. INTRODUCTION

1.1 Background

Water is essential for human life. Every day human beings perform a remarkable variety of activities which directly or indirectly involve the use of water, often in very large quantities. Given increasing regional fresh water scarcity and that almost half of the world's population lives within 100 km of an ocean, seawater represents a virtually infinite water resource (Amy et al., 2017). Water is needed in all industrial activities, in agriculture and for domestic purposes. The earth surface is covered by a vast amount of water of nearly 1.4 billion km^3(Miller, 2003).Of this total amount of water, 97.5% is seawater (about 1.365 billion km^3) and 2.5% is fresh water (about 0.035 billion km^3). Out of freshwater available, a majority of water is frozen in ice caps and in glaciers (about 2.4 million km^3) (Figure 1.1) and is inaccessible to people. Only 0.77% (about 1.1 million km^3) of all the earth's water is held as groundwater, surface water such as in lakes, swamps, rivers, etc. and in plants and the atmosphere(Shiklomanov, 1993). Of the 2.5% of fresh water available 20% of the fresh water is in remote place and only 0.08% earth water is assessable to people.

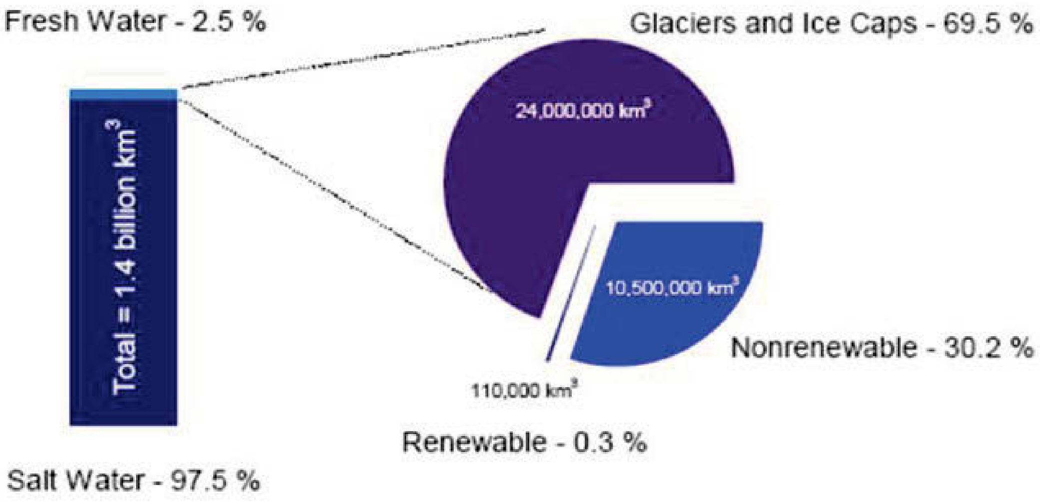

Figure 1.1 Distribution of the world's water. (Shiklomanov, 1993)

Water scarcity is becoming a major problem in the world. Many countries in the world suffer from a shortage of natural fresh water. A rapidly increasing population is placing pressure on existing water resources. As a result of rise in population rates and enhanced living standards, together with the expansion of industrial and agriculture activities, increasing amounts of fresh water will be needed in the future. The number of people affected by severe water shortages is expected to increase fourfold in the next 25 years (Engelman et al., 2000).In addition to the development of the industrial and commercial activities around the world that result in the pollution of the available water resources, the waste of natural sources, deforestation and climatic alteration due to global warming play a significant role in the reduction of average rainfall and runoff (North et al., 1995). Available fresh water resources from rivers and groundwater are presently limited and are being increasing depleted at an alarming rate in many places. Limited sources of water cause a threat to the availability of fresh water for human beings. The United Nations

Environment Program (UNEP) in 1999 identified water shortage as one of the two most worrying problems in the new millennium. Water demand is expected to increase by about 40% over the next decade. According to the United Nation's "World Water Development Report" more than 50 percent of the nations in the world will face water crises by 2025. By 2050 about 75 percent of the world population will have a significant possibility of facing water shortages (Danoun, 2007).

However, water is not only a problem for developing countries but also for many developed countries. Australia is one of them. In one of its report, the International Water Management Institute states that Australia is one of the high water stress regions ((IWMI), 2006). Pressure on the availability of Australian freshwater resources is increasing considerably due to emerging climate change and population growth(Dismitriadis, 2005). Moreover, Australia is the world's driest continent. By 2010, most of the eastern part of the Australian continent had almost 5 years of continued lower-than-average rainfall across. Many Australian cities and towns faced drought conditions with some water supply reservoirs recording their lowest levels (Willis et al., 2010). An Australian National Climate Centre report showed the decreasing trend of annual rainfall by up to 50 mm per year over the southern half of the continent (CSIRO, 2007). Most of Australia's large urban populations are currently suffering water shortage problems. Australians use more than 980 cubic meters of fresh water annually per person for different purposes. According to NSW Government (2006), Sydney is the worst affected in terms of water storage. With limited water supplies in urban cities coupled with increasing urban population, providing safe, reliable and sustainable water services for Australian cities is a major challenge for the 21st century. Sustainable urban water consumption has thus become a critical issue in Australia.

Inadequate clean water for potable and non-potable use has become a major problem worldwide due to the increasing demand and shortage of water resources (Shanmuganathan et al., 2017). Reusing and recycling alternative water supplies is a key part of reducing the pressure on water resources and the environment. Water recycling is becoming a favoured solution for the community water management. More than 50% of water is used for toilets, gardens and laundry, where recycle water quality is adequate. However, at present, potable-quality water is supplied for all household purposes. There are some places that recycle water is used. Table 1.1 indicates the total amount of wastewater and grey water produced by an average household.

Table 1.1Water use by an average household in NSW (Adapted from enviro-friendly, http://www.enviro-friendly.com/greywater-systems-australia.shtml, online accessed 9th April2011)

Wastewater source	**Total wastewater**		**Total greywater**	
	% Total	**Litres/day**	**% Total**	**Litres/day**
Toilet	32	186	-	-
Hand basin	5	28	8	28
Bath/shower	33	193	54	193
Kitchen	7	44	-	-
Laundry	23	135	38	135
Total	100	586	100	356

Australia over the last 20 years has been very effective in reducing water use, but further savings through water demand management is hard to achieve. The use of recycled water in industry as well as in residential areas has grown considerably over the past decade. The continued growth of cities calls for the development of alternative sources. Desalinated seawater is an alternative solution as a source of fresh water.

Membrane based desalination technology such as reverse osmosis (RO) has rapidly become a good alternative to conventional treatment for drinking water production from seawater. However, membrane fouling is a major concern in reverse osmosis (RO) based seawater desalination. The fouling on RO membrane deteriorates the performance of RO membranes and increases the energy consumption and even requires more frequent replacement of the membranes. Thus, membrane fouling is a major concern in RO based seawater desalination. The main fouling mechanisms of RO membranes include (i) particulate and/or colloidal fouling resulting from accumulation of suspended solids and some metal based hydroxide which can accumulate on the surface of the membrane over time and form cake fouling, (ii) biofouling due to the formation of biofilms caused by the attachment and metabolism of biological matter which includes micro-organism and macro-organism such as bacteria, fungus or algae which may also accelerate the chemical decomposition of RO membranes posing serious threats to the operation of RO plants, (iii) inorganic fouling including scaling caused by exceeding the solubility of soluble salts such as $CaSO_4$, $BaSO_4$ and $MgSO_4$ which is considered less problematic and can be controlled by adjusting the pH and adding anti-scalant, and (iv) organic fouling resulting from the deposition of organic matter such as humic and fulvic acids, polysaccharides, and aromatic compounds on to membrane surface (Chua et al., 2003, Pontié et al., 2005).

On the other hand, the organic matters are also an energy source for microorganism leading to biofouling. Seawater Reverse Osmosis(SWRO) foulants consist of biofouling (48%), inorganic colloids (18%), organic compounds (15%), silicites/silicates (13%), mineral deposits (6%) and coagulants (5%) (Shon et al., 2008).

Thus, it is necessary to have an effective pre-treatment to prevent fouling of RO membranes. The main objective of a pre-treatment system is to remove particulate, colloidal, organic, mineral and microbiological contaminants contained in the raw seawater and to protect the membranes from fouling in the downstream SWRO.

Pre-treatment such as bio-filtration, coagulation, adsorption, in-line flocculation, filtration and ozonation have been used to remove the natural organic matter (NOM) and to alleviate fouling (Park et al., 2002, Tomaszewska and Mozia, 2002, Chinu et al., 2009, Johir et al., 2009). Flocculation, coagulation and sedimentation have become important unit processes because of their low cost and easy application in the treatment of water and wastewater in conjunction with convectional mechanical, biological and physio-chemical plants.

1.2 Research Objectives

The objective of the study is to assess the different pre-treatment system to reduce membrane fouling in RO desalination projects. Optimisation and comparison of different pre-treatment systems will be conducted to remove organic matter, reduce the fouling potential and particulate matter of sea water by using different pre-treatment methods. The research work involved extensive experiments both in laboratory and in the field to verify the validity of pre-treatment reduced membrane fouling. Detailed objectives of the project can be summarised as follows:

- Evaluate performance of anthracite, sand and GAC as a filter media in the terms of biofiltration pre-treatment system.
- Comparative study of in-line flocculation and spiral-flocculation followed by media filtration as a cost-effective pre-treatment of seawater.
- Compare two Ti-based coagulants with commonly used ferric chloride ($FeCl_3$) coagulant in desalination plants.
- Evaluate the performance of titanium tetrachloride ($TiCl_4$) and titanium sulphate ($Ti(SO_4)_2$) in actual seawater in terms of turbidity, DOC,UV-254 and zeta potential at different coagulant doses and solution pH.
- Study and evaluate different pre-treatments such as MF, UF, in-line flocculation and spiral-flocculation in terms of fouling reduction.
- Study of the behaviour of the fouling tendency of Reverse Osmosis (RO) after different pre-treatment.

1.3 Scope

The study is divided into three parts:

Part 1: Evaluate performance of Anthracite, Sand and GAC as a filter media in the terms of biofiltration pre-treatment system. The results are reported in chapter 4.

Part 2: Comparative study on in-line flocculation and spiral-flocculation followed by media filtration as a pre-treatment of seawater. The results are reported in chapter 5.

Part 3: Evaluate performance of titanium salts compared to conventional $FeCl_3$ for seawater reverse osmosis pre-treatment. The results are reported in chapter 6.

The results of this thesis was published in the following publications

1. Shrestha, A., Johir, M.A.H., Vigneswaran, S., & Kandasamy, J. (2014), “A comparative study on in-line flocculation and spiral flocculation followed by media filtration as a pre-treatment of seawater”, Desalination and Water Treatment, Vol. 55, Iss. 4, 2015.
2. Shrestha, A., Jeong, S., Vigneswaran, S., & Kandasamy, J. (2013), "Seawater biofiltration pre-treatment system: comparison of filter media performance", Desalination and Water Treatment, in press, Vol. 52, Iss. 34-36,2014.
3. Shrestha, A., Naidu, G. Johir, M.A.H., Vigneswaran, S., &Kandasamy, J. (2017) Performance Of Titanium Salts Compared To Conventional $Fecl_3$ For Seawater Reverse Osmosis Pre-Treatment, Desalination and Water Treatment, submitted for publication.

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CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 Desalination in Australia

Water management and water reclamation is not the only solution to ensure an adequate water source. To meet the water demand it is necessary to create and find alternative source of fresh water. Presently, seawater reverse osmosis (SWRO) dominates the global desalination market based on installed capacity, having surpassed thermal technologies multi-stage flash distillation (MSF) and multi-stage distillation (MED) that are common in the Gulf Cooperation Council (GCC) and Middle East-North Africa (MENA) regions (Amy et al., 2017). Given an increase in regional freshwater scarcity, interest in, and the practice of, seawater desalination are rapidly increasing. Desalinated seawater is an alternative solution as a source of fresh water. The oceans represent the earth's major water reservoir. However, seawater is unsuitable for human consumption and for industrial and agricultural uses. By removing salt from the virtually unlimited supply of seawater, desalination has emerged as an important source of fresh water (Khawaji et al., 2008). Therefore, creating a new source of potable water has been a significant issue worldwide and as consequence desalination plants are one of the most vital and valuable alternative resource in many countries around the world. According to International Desalination Association, in June 2015 there are approximately 18426 desalination plants operated worldwide with a combined capacity of over 86.8 million cubic meters per day, providing water for 300 million people. About 54% of these plants are located in the Middle East (Figure 2.1) equivalent to 60% of the worldwide capacity.

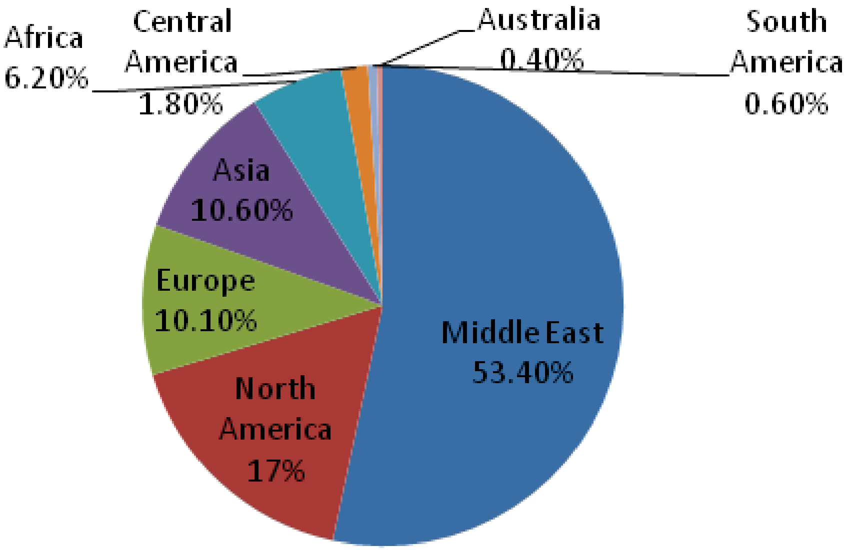


Figure 2.1 Presents the existing desalination facilities worldwide by region. (Danoun, 2007)

Australia is facing a major issue in the demand for clean water as in most other countries around the world. Australia is not only the driest inhabited continent in the world, but also the greatest consumer of water per capita. Australians use more than 980 cubic meters of fresh water annually per person for various purposes such as agriculture, households, water supply, sewerage and drainage services, electricity and gas, manufacturing, and mining. Desalination is an important component of securing water supplies in Australia; it can provide water all year round, regardless of rainfall. To meet clean water demand, major desalination plants have been constructed or are proposed for a number of urban centres in Australia to supplement existing infrastructure (Figure 2.2&2.3).

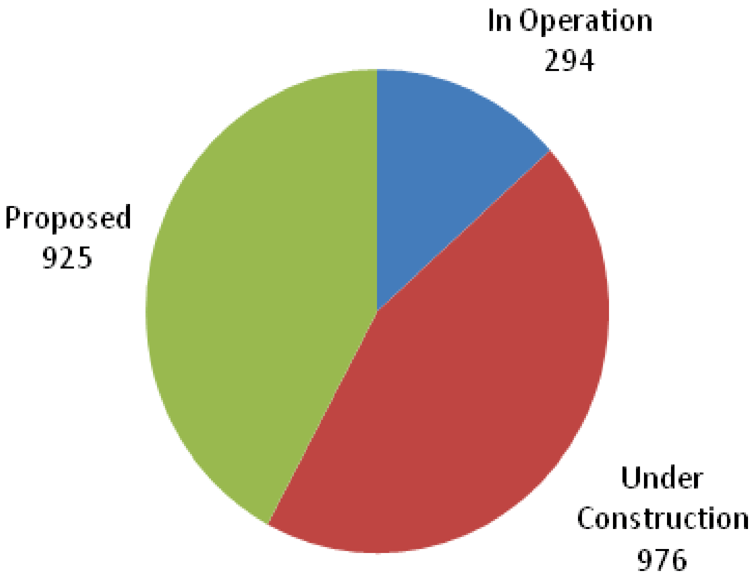


Figure 2.2 Present and proposed desalination plant (to 2013) status and design capacity (ML/day) (Manh Hoang et al., 2009)

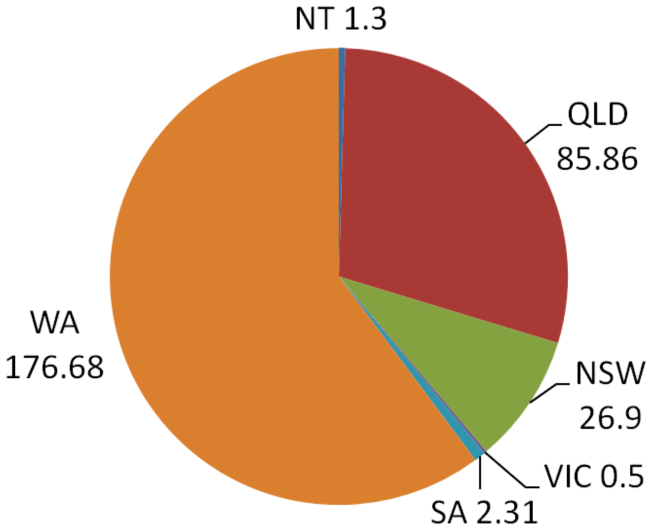


Figure 2.3 Desalination capacity in the different States in operation, in ML/day in 2008 (Manh Hoang et al., 2009)

Table 2. 1 Water supply capacity and desalination status for some Australian big cities

(Source: http://www.ceem.unsw.edu.au/content/userDocs/OzWaterpaperIMRP_000.pdf)

Urban Centre	Population	Desalination
Sydney & Wollongong	4.41 million	Construction of a desalination plant of 500 ML/d capacity
Melbourne & Geelong	3.6 million	150GL/annum desalination plant approved, to supply Melbourne, Geelong, Westernport and Wonthaggi.
Brisbane and Gold Coast	2.77 million	Approval granted for a 120 ML/d plant at Tugun t to be connected to the SEQ grid
Perth	1.46 million	A 130 ML/d desalination plant at Kwinana, is operational since November 2006. Second 130 ML/d desalination plant proposed as alternative supply option for future growth.
Adelaide	1.12 million	Desalination proposed at Port Augusta, in conjunction with BHP.
Central Coast	0.3 million	Approval being sought for the use of temporary desalination plants with capacity of up to 10 ML/d

The above information gives a clear picture of water demand and water reuse and desalination will be a key solution for this problem. It should be noted that desalination technology alone is not the only solution and we should consider wastewater and stormwater as an alternative source of water to fulfill the water demand as it is economical and environmentally viable. Recently, seawater desalination by reverse osmosis method has been getting popular as an alternative source of clean water produced from seawater.

2.2 Reverse Osmosis

Desalination offers the potential of an unlimited source of freshwater purified from seawater. Reverse osmosis (RO) has achieved great advances in recent years among the many desalination technologies. Desalination allows a widening in utilisation of available water resources by producing freshwater from saline or brackish natural water sources. Over the past decade conventional water production costs have been rising in many parts of the world and costs for desalination have been declining, consequently desalination has become more economically attractive and competitive (Burn et al., 2015).

As water scarcity in many regions of the world is becoming an undeniable fact, efforts have been made to develop technologies for alternative water resources. Thermal desalination processes have been a great option, yet require high capital and operating costs due to installation, maintenance, and energy used. Toward minimizing the overall desalination cost, reverse osmosis membrane filtration (RO) has been widely used and is recently becoming an important alternative source of clean water. There are more than 15,000 desalination plants around the world providing fresh water from saline water through which this number will continue to rise as researchers work to improve the process, both in terms of cost effectiveness and energy efficiency (Jamaly et al., 2014).

Seawater desalination is the most used solution to address water shortage especially for portable water applications (Figure 2.4 & 2.5).Living without drinking water or in areas where it is difficult to obtain is a reality that many people face. Technology can help to improve this situation. One such technology is reverse osmosis, which is a process that uses membranes to separate salt from seawater (Qureshi and Zubair, 2016). Among the desalination technologies, seawater reverse osmosis (SWRO) is widely used in desalination plants, attributed to capabilities such as ease of operation and cost-effective drinking water production (Greenlee et al., 2009). Nevertheless, a key challenge of SWRO technology is membrane fouling, specifically, organic, colloidal and bio-fouling (Jeong et al., 2016). In RO process, seawater diffuses through a membrane under high pressure, removing salts and impurities and results in pure water production. RO is the most popular technology among seawater desalination. It was commercialized in the 1970s for desalination applications. Desalination plants are being used in more than 120 countries and produce more than 13 million m^3/day of potable water (Voutchkov, 2005). The process is used for desalinating brackish water, and seawater. Hundreds of reverse osmosis desalination plants have been built worldwide during the last two decades and each year the plant sizes and cost-effectiveness have increased. Reverse osmosis has achieved growing acceptance as an economical and viable alternative to multistage flash distillation (MSF) process for desalting seawater in recent years (Jamal et al., 2004).

Most of the desalination plants are in Middle East and North Africa. Some of the largest new desalination plants under construction and in operation including Ashkelon in Isarel and Tuas in Singapore now use RO membrane. The growth in membrane applications for desalination has been exponential over the last decade. Ashkelon, the largest desalination plant in the world produces 395 ML of water per day (Prihasto et al., 2009). With the recent advances in membrane technology and its broad application, RO systems now represent the fastest growing segment of the desalination market with more than 50% of the world's desalination capacity. However, due to membrane fouling under challenging water quality conditions the operation of membrane-based desalination plants still remains complex.

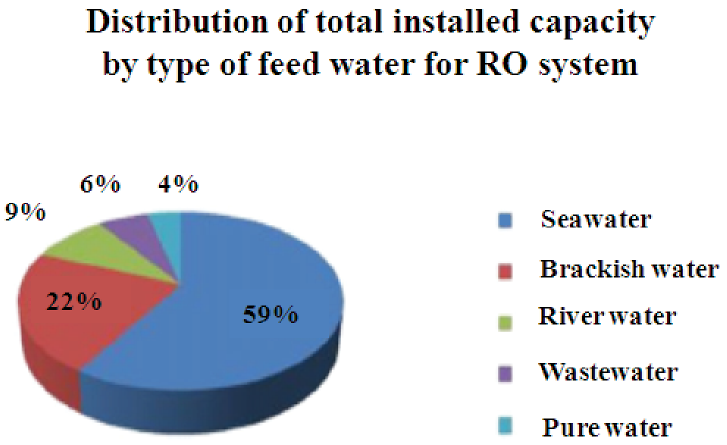


Figure 2.4Distribution of total world installed capacity by type of feed water for RO system(Pankratz, 2013)

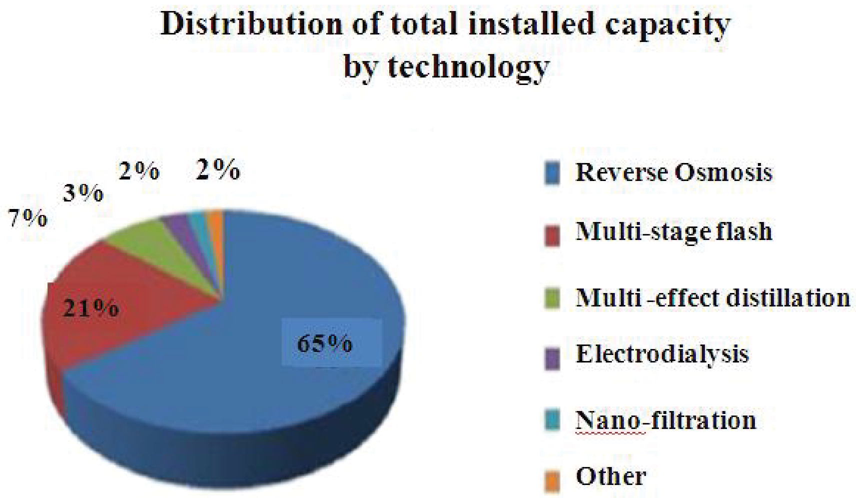


Figure 2.5 Distribution of total world installed capacity by technology (Pankratz, 2013)

2.3 Seawater as Source

Seawater consists of 96.5% water, 2.5 % salts, and other substances such as dissolved organic and inorganic materials, particulates, and a few atmospheric gases in smaller amounts. Nearly all natural elements exist in seawater, but the concentration of four major constituents; sodium, magnesium, chloride and sulphate comprise more than 95% of the dissolves solids. The five major cations are Na^+, Mg^{2+}, K^+, Ca^{2+} and Sr^{2+} and four major anions are Cl-,SO_4^{2-}, Br^- and F^-. These ions make up about 99 percent of sea salts by weight. The various cations, anions, particulate matter, and living organisms present in seawater makes up seawater impurities. These impurities are the main fouling agents to the membrane process equipment. Inorganic compounds are the major constituents of seawater at about 40000-50000 ppm and organic compounds are about 2-4 ppm (Dalvi et al., 2000). Though organic compounds are present in small amount compared to the inorganic compounds, it causes more serious problem in the seawater reverse osmosis (SWRO) desalination process.

2.3.1 Seawater Organic Matter

Dissolved organic matter (DOM) in the sea is one of the largest reservoir of organic matter on the earth's surface holding approximately as much as carbon available in atmospheric carbon dioxide (Ogawa and Tanoue, 2003). Organics are negligible in concentration (2-4 ppm) as compared to inorganic constituents. However, they create severe fouling problems to reverse osmosis desalination process. SWOM varies with the season and location. Humic substances are major organic compounds in seawater which mainly consists of acid rich aliphatic polymers with molecular weight of 500-1000 (Da) that bear little resemblance to any known biochemical or humic substances in soil (Hedges, 1987). Some of other dissolved organic substances in seawater are carbohydrates and amino acids, and organic-rich particulates. These materials originate primarily in the upper 100 m of the ocean, where dissolved inorganic carbon is photo-synthetically transformed into organic matter.(Shon et al., 2008) found the molecular weight composition for the seawater organic compounds as 1200Da (biopolymers), 950 Da (fulvic acids), 650 Da (hydrolysates of humic substances), 250 Da (low MW acids) and 90 Da (low MW neutrals and amphiphilics).

2.3.2 Seawater Inorganic Matter

Inorganic constituents present in seawater that are most likely to cause fouling are chloride (Cl^-), sodium (Na^+), sulfate (SO_4^{2-}), magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^+). Calcium carbonate ($CaCO_3$), calcium sulphate ($CaSO_4$), silica and barium sulphate ($BaSO_4$) are major inorganic that may deposit in a membrane surface if the solubility limits are exceeded. The amount of calcium ions is in the range of 400 to 600 ppm; HCO_3^- approximately 150 ppm; sulphate ions approximately 3000 ppm. Calcium sulphate and calcium carbonate are the most common inorganic foulants in seawater RO andcalcium carbonate is the most likely inorganic scale to be deposited.

2.4 Fouling Mechanisms on SWRO

Fouling is the loss of membrane permeability due to the deposition of undesirable material on a membrane surface and/or into its pores causing serious flux decline and increased salt passage and it is one of main disadvantages in membrane filtration processes.

To establish a strategy for controlling membrane fouling, an understanding of fouling mechanisms, including the detailed characteristics of the constituents causing membrane fouling (foulants) is essential (Miyoshi et al., 2016). For a seawater RO (SWRO) membrane, both organic and inorganic matter could cause membrane fouling depending on feed water characteristics (Khan et al., 2013). Among them, the management of membrane fouling caused by inorganic matter is relatively easy by applying suitable operating conditions including appropriate recovery selection, addition of antiscalants and pH adjustment (Kumar et al., 2006,Ning, 1999). Controlling membrane fouling caused by organic matter, including microorganisms, is generally more challenging (Ning, 1999).

The main fouling mechanisms of RO membranes are particulate/colloidal fouling, biofouling, inorganic fouling (including scaling) and organic fouling (Pontié et al., 2005). The SWRO foulants consist of biofouling (48%), inorganic colloids (18%), organic compounds (15%), silicites/silicates (13%), mineral deposits (6%) and coagulants (5%) (Shon et al., 2008). The preferential order of essential foulants on RO membranes is silica colloids > adsorbed organic compounds > particulate matter (iron and aluminium colloids) > microorganisms > metallic oxides (Shon et al., 2008). The complex foulants consists of particulate matter, colloids(Si-Al-Fe), hydrophobic organics and microorganisms (Shon et al., 2008). Scaling is caused when the solubility of a salt is exceeded which has less effect on the membrane surface and it can be controlled adding antiscalants and adjusting pH. Therefore, information on the detailed characteristics of organic matter causing membrane fouling of an SWRO membrane is important for stable operation of the SWRO membrane filtration process. However, it is very difficult to prevent fouling from colloidal, organic and biological matters.

2.5 Types of membrane fouling

Membrane fouling is an extremely complex phenomenon which occurs by the formation of undesirable deposition of particulate/colloidal or organic matter to the membrane surfaces(Al-Amoudi and Lovitt, 2007).

RO fouling can be classified on the basis of fouling material into three types

1. inorganic fouling due to deposition on membrane surface of inorganic scales (mainly $BaSO_4$, $CaSO_4$ $CaCO_3$) ,
2. organic fouling due to organic material (OM) found in the process stream (humic acids, protein and carbohydrate), and ;
3. biofouling due to microbial attachment to membrane surface followed thereafter by their growth and multiplication in presence of adequate supply of nutrients in the pre-treated feed or nutrients that deposit on membrane surfaces.

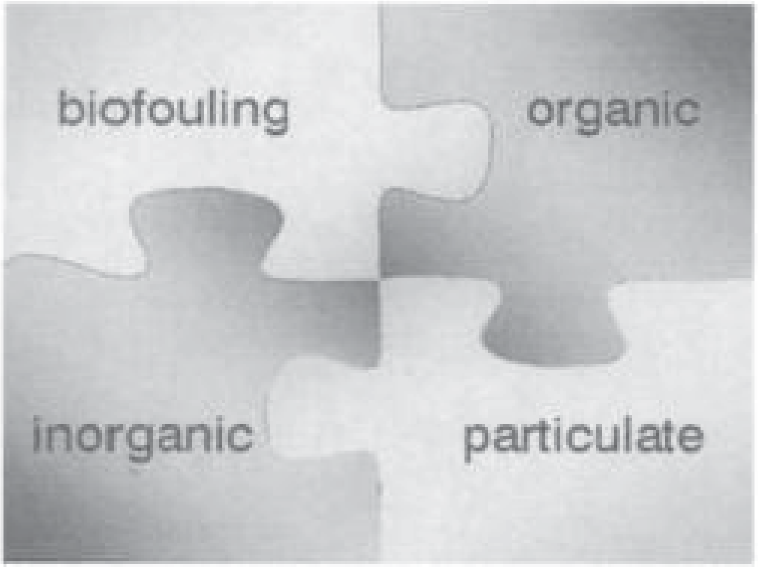


Figure 2.6 Complete picture of fouling (Vrouwenvelder et al., 2003)

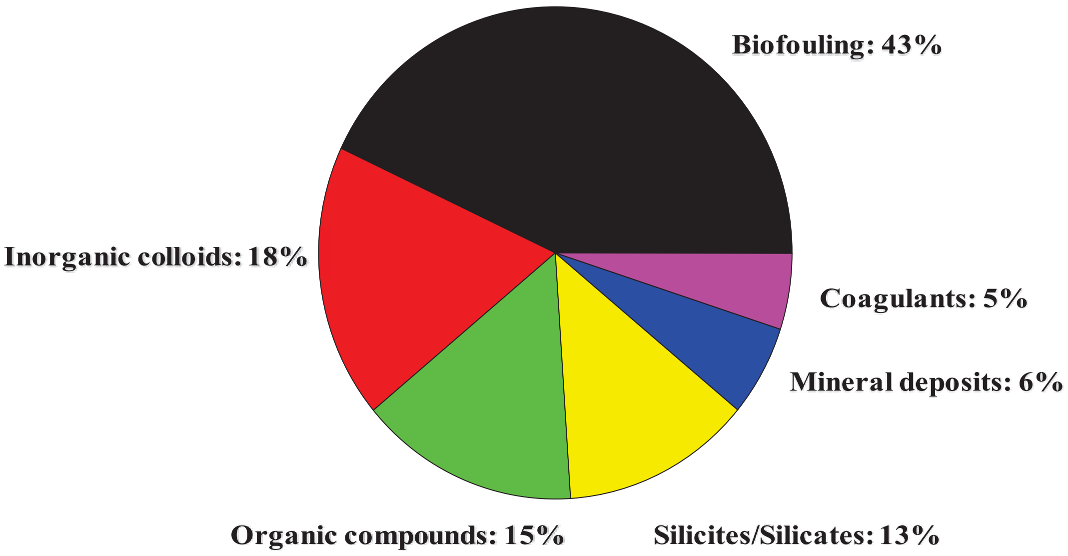


Figure 2.7 Types of membrane foulant in reverse osmosis membrane (Khedr, 2000)

2.5.1 Inorganic fouling (including scaling)

Inorganic fouling or scale formation is serious problem which occurs from the increased concentration of inorganic matter present in the seawater beyond their solubility limits and their ultimate precipitation onto the membranes (Wiesner, 1992). Inorganic fouling is caused by metal hydroxides and carbonates which precipitate on and in the membranes due to changes in water chemistry (Pontié et al., 2005). Scaling is caused by the exceeding solubility of soluble salt such as $CaCO_3$, $CaSO_4 \cdot xH_2O$, silica, and calcium phosphate along with $BaSO_4$, $SrSO_4$, $Ca(PO_4)_2$, ferric and aluminium hydroxides. The physical and chemical parameters, those are responsible for crystallization process are temperature, pH, flow velocity, permeation rate, types of pretreatment, salt concentration and concentration polarization, membrane type, materials and metal ions and natural organic matter (NOM) (Al-Amoudi et al., 2007). The major effects of scaling are listed below (Baran, 1990).

- Decrease in salt rejection in end stages
- Decrease in normalized permeate flow
- Scale formation on membrane surface
- Increase in pressure drop in end stages
- Formation of salt bridge facilitating protein adsorption
- High concentration at membrane surface can cause denaturation of proteins which then are more of a fouling problem

2.5.2 Particles/colloids fouling

Colloids or particulate matters dominate the membrane fouling (Potts et al., 1981). Particulate matters in the size range of nanometres to micrometer are defined as colloids. Inorganic (clays, silica salt, metal oxides), organic (aggregated natural and synthetic organic) and biological (bacteria, microorganism) are the examples of common colloidal foulants. Champlin, (2000) reported that removal of the particles size of down to 1 µm may not be sufficient to avoid fouling in many cases. MF/UF pre-treatment sometimes fail to remove colloids below the size of few hundred nm in diameter and conventional processes used to pre-treat NF/RO feed water fail to remove sub-micron colloids (Schafer et al., 2005). The high concentration of the rejected ions in the membrane surface could promote the aggregation of dissolved matter in to colloidal sized particles. Moreover, the influence of salt retention and concentration polarization in the membrane surface area electrostatic particle-membrane and particle-particle interaction allow colloids to foul the membrane.

Particulate fouling occurs when the suspended solids or colloids in the feed water get accumulated onto the surface of the membrane. Particulate matter in natural waters and waste waters can be classified as settleable solids (>100 µm), supra-colloidal solids (1 - 100 µm), colloidal solids (0.001 - 1 µm) and dissolved solids (<0.001 µm) (Yiantsios et al., 2005). The colloidal matter that usually present in water and seawater are given below (Yiantsios et al., 2005).

- Microorganisms
- Biological debris (plant and animal)
- Polysaccharides (gums, slime, plankton, fibrils)
- Lipoproteins (secretions)
- Clay (hydrous aluminum and iron silicates)
- Silt
- Oils
- Kerogen (aged polysaccharides, marine snow)
- Humic acids, lignins, tannins
- Iron and manganese oxides
- Calcium carbonate

- Sulfur and sulfides

Particulate fouling resulting in formation of gel layer on membrane surface, decrease in normalized permeate flow and decrease in salt rejection (Baran, 1990).

2.5.3 Organic fouling

Organic fouling is very common with surface waters containing natural organic matters (NOM.). Organic compounds consist of humic acid, fulvic acid, polysaccharides, and aromatic compounds in addition to lower molecular weight compounds such as phenols, pesticides, trihalomethanes (THM) and a variety of toxic chemicals (Potts et al., 1981). These are also energy source for microorganism. It may cause irreversible or reversible flux decline (Al-Amoudi and Lovitt, 2007). The effects of organic fouling are formation of H bonds on contact with membrane, partial diffusion through membrane - dependent on degree of branching (Baran, 1990). The driven factors of natural organic matter are ionic strength concentration, pH, divalent cations, NOM fraction (hydrophobic/hydrophilic), molecule or membrane charge, concentration polarization, surface morphology, permeate flux and pressure (Al-Amoudi and Lovitt, 2007). Among these factors, most of them increase the fouling rate. Only the hydrophilic NOM fraction decreases fouling rate.

2.5.4 Biofouling

Biological fouling occurs on RO membranes when bacteria and nutrients are present in conditions that are conducive to growth and proliferation of the bacteria. Controlling microbial growth on the membranes is typically limited to biocide application (i.e., disinfectants) in seawater RO plants. Biofouling is the inhibition of effective membrane desalination caused by the formation of a biofilm from the growth of microorganisms on the membrane surface. Biofouling impacts SWRO treatment by decreasing permeate flux, increasing pressure drops in the RO modules, increasing salt passage, and causing irreversible damage to the RO membrane (Weinrich et al., 2016).

Biological fouling occurs from the formation of a biofilm. This results from the attachment and metabolism of biological matter which includes microorganism and macroorganism such as bacteria, virus, algae, fungi etc. Biofilm is defined as a surface accumulation, which is not necessarily uniform in time or space that comprises cells immobilized at a substratum and frequently embedded in an organic polymer matrix of microbial origin (Characklis W. G. et al., 1990).

Lappin-Scott and Costerton, (1989) reported that biofouling is the fouling where biologically active organisms are involved. Membrane biofouling is caused by bacteria, fungi and other eukaryote microorganisms (Flemming et al., 1997). Biofouling is a dynamic process of microbial colonization and growth, which results in the formation of microbial biofilms. Biofilm formation consistently precedes biofouling, which becomes an issue only when biofilms reach thickness and surface coverage that may cause problems such as declined normalized flux and/or increase in normalized pressure drops during RO operation (Vrouwenvelder et al., 1998, Ridgway and Flemming, 1996).

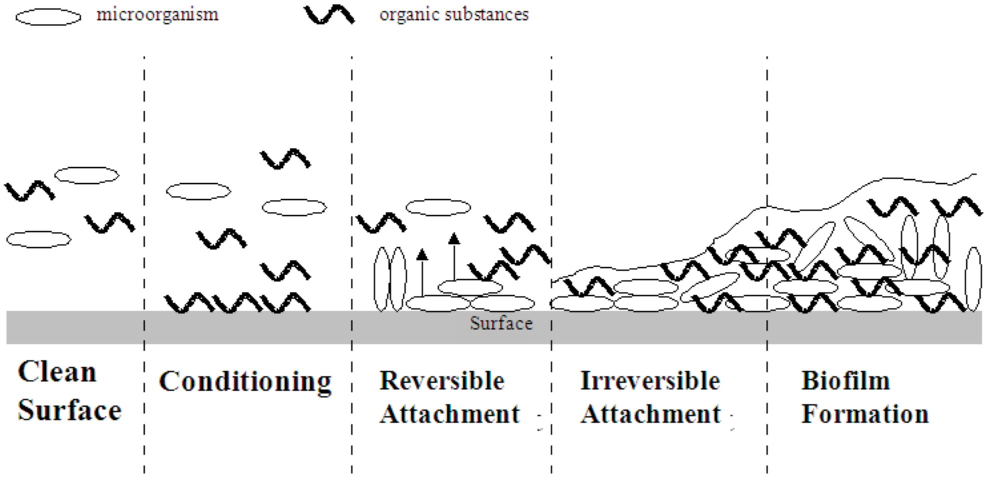


Figure 2.8Formation of biofilm (Sheikholeslami, 2007)

Once bacteria attaches to the membrane, they multiply and produce extracellular polymeric substances (EPS), which develops into a viscous slimy gel. The biofouling process may be divided into five stages: the formation of conditioning film, bacteria transport, reversible and irreversible adhesion, biofilm development and accumulation, bio-film detachment (Characklis W. G. et al., 1990). The adverse effects of biofouling are listed below (Baran, 1990)

- Decrease in normalized permeate flow
- Initial increase in salt rejection
- Increase in pressure drop

- Accumulation of byproducts of metabolism
- Eventual deterioration of the membrane resulting in a decrease in rejection
- Decrease in flow at membrane surface can exacerbate concentration polarization phenomena

2.6 SWRO Pre-treatment Systems

Seawater pre-treatment is a major component of desalination plants (Voutchkov, 2010a). The main objective of pre-treatment system is to remove particulate, colloidal, organic, mineral and microbiological contaminants contained in the source seawater and to protect the membranes from fouling on the downstream seawater reverse osmosis (SWRO). Pre-treatment systems can remove most, but not all, suspended solids contained in source seawater and SWRO are prone to fouling by the suspended solids, particulates and silt that remain after pre-treatment. Therefore, the selection of a pre-treatment method is very important. It influences the overall performance of a desalination plant and determines the success or failure of the plant. Typically, two types of pre-treatment systems are used to protect the SWRO membranes from fouling; 1) Conventional granular media filtration and 2) Non-conventional pre-treatment system (Membrane filtration). The conventional pre-treatment usually used in water treatment includes coagulation, flocculation and filtration supported by an extensive chemical treatment, including biofouling control (chlorination, dechlorination), and scaling prevention (dosing of acids or antiscalant additives). Pressure driven membrane processes, such as microfiltration (MF) and ultrafiltration (UF), are excellent techniques for the removal of suspended solids and thus lowering fouling. Micro and ultrafiltration have wider spectrum particle removal capabilities than conventional media filtration. Further, adsorption and flocculation (alone or together with MF/UF in hybrid configuration) can remove most of the dissolved organic foulants.

2.6.1 Coagulation and Flocculation Followed by Filtration

The conventional technologies (coagulation–flocculation, disinfection, pH adjustment, scale inhibition, and filtration with granular media) can be applied as pretreatment technologies to RO membrane systems. Coagulation has been shown to be a successful method for improving the water quality not only in conventional pretreatment technologies, but also in low pressure membrane pretreatment technologies (Jamaly et al., 2014).

Conventional (granular media) filtration is the most widely used seawater pre-treatment technology. This process includes source seawater conditioning by coagulation and flocculation followed by filtration through one or more layers of granular media (e.g., anthracite coal, silica sand, and garnet). Pre-treatment such as bio-filtration, coagulation, adsorption, in-line flocculation, filtration and ozonation have been used to remove the natural organic matter (NOM) and to alleviate fouling (Park et al., 2002, Tomaszewska and Mozia, 2002, Chinu et al., 2009, Johir et al., 2009). Flocculation, coagulation and sedimentation have become important unit processes because of their low cost and easy application in the treatment of water and wastewater in conjunction with convectional mechanical, biological and physio-chemical plants. In-line flocculation filtration is a commonly used pre-treatment system in RO desalination (Tenzer et al., 1999, Johir et al., 2009) showed that coagulation followed by media filtration produced a good quality feedwater to RO.

Coagulation and flocculation processes are usually applied to remove small particles and Disinfection Byproduct (DBP) precursors from water. Organic particles with the size less than 10mm cannot settle down by themselves but when they react with coagulant agents, they can form larger aggregates which can be steadily separated from water by settlement, floating and filtration processes. While coagulation refers to initial coalescing of colloidal particles, especially hydrophobic colloids, flocculation is the long term process of forming large particles and can be useful in removing hydrophilic colloids. In practice, aluminium and iron salts such as aluminium sulphate, sodium aluminate, ferrous sulphate, ferric chloride and ferric sulphate are usually used as coagulants (Percival et al., 2000).

Coagulation can reduce trihalomethanes formation up to 50% and organic carbon by 40-70% (Freese et al., 2001). (Abdessemed et al., 2000) achieved a high removal of COD (86%) and turbidity (from 18 to 3.5 NTU) when they combined flocculation and powder activated carbon (PAC) adsorption. Flocculation when combined with sedimentation can effectively remove organism up to 99.9% of poliovirus and 99.7% of bacteriophage (Percival et al., 2000). The performance of coagulation processes strongly depends on pH and coagulants dosage. Therefore pH adjustment and coagulant dosage can increase TOC removal and DBP precursor removal. Enhanced coagulation is less economical in large scale treatment plants because of expenses for removing coagulants and reducing organics content in water, but in small water works, it can be cost effective (Freese et al., 2001).

Colloidal particles that are present in water range from 10 nm to 10 μm. Colloidal particles consist of hydrophilic colloidal such as humic acid, fulvic acid, protein, soap, wallpaper paste, etc., and hydrophobic colloidal such as clay particle, non-hydrated metal oxides, etc.,(Binnie et al., 2002). Since colloidal particles is one of the major foulant, it is important to remove colloidal particles from water before membrane application. The objectives of coagulation and flocculation consist of producing aggregates of large size that can be separated through sedimentation, filtration, centrifugation or other separation methods (which are important processes in water and wastewater treatment). Coagulation is the process by which destabilization and initial combining of colloidal and very fine particles present in water and wastewater occurs by physical and chemical procedure. Flocculation results in the formation of larger settleable particles by aggregation due to particle-particle bridging. During flocculation three main processes arise (Binnie et al., 2002) i) a Brownian motion which provide some degree of small particle transport resulting in particle-particle collisions ii) stirring which encourage particle to collide as particle increase in size and iii) differential settling.

The coagulants and flocculants used in water treatment are mainly the aluminium and iron coagulants such as aluminum sulfate or alum, ferric sulfate, ferric chloride, polyaluminium chloride, polyaluminium silica sulfate, polymerized ferric sulfate. In addition, some polyelectrolyte such as polyacrylamides or polyamines are used which are cationic, anionic or non-ionic in nature. They are used as a coagulant aid to strengthen weak flocs and to improve the settleability of floc particles (Binnie et al., 2002). The use of proper coagulants or flocculants depends on the water characteristics, the efficiency of coagulants and overall cost and benefit of chemical pretreatment as coagulants and flocculants are influenced by organic matter concentration, pH, temperature and fluid-mixing conditions (Crittenden et al., 2005). In case of aluminum coagulant, at a pH value less than 6 the positive charge Al remains in solution to interact with particulates causing destabilization by charge neutralization. For ferric ion this happens at a pH of about 4 (Montgomery, 1985). A study conducted by (Fabris et al., 2002)found that natural organic matter (NOM) removal efficiency was high at optimum pH and this was dependent on the sources and characteristics of the raw water. Other studies found a TOC removal efficiency of 60-70%, COD removal efficiency of 77-99.3%, total suspended solids of 80-90% and bacteria removal efficiency of 80-90% when alum and ferric chloride were used as the coagulant (Shon et al., 2004, Shon et al., 2005, Al-Malack et al., 1996, Abdessemed and Nezzal, 2003, Tchobanoglous and Burton, 1991, Guida et al., 2007).

Flocculation is becoming an attractive pre-treatment before the application of membrane filtration. Many studies found that flocculation and membrane (microfilter, MF; ultrafilter, UF) filtrations could efficiently remove the NOM from typical water (Shon et al., 2004, Shon et al., 2005, Qin et al., 2006, Leiknes, 2009). An investigation on the implication of the flocculation step showed that in-line flocculation was found to have similar removal efficiencies at significantly shorter hydraulic retention times compared to conventional flocculation (two stage and one stage paddle flocculation) (Leiknes, 2009). A study conducted by Choi and Dempsey (2004) reported that in line coagulation at under dose condition (with respect to conventional treatment)was also effective for removal of NOM by UF. Finally, to obtain superior result by flocculation it is vital to perform sufficient jar tests, bench scale experiments or pilot test with different coagulants/flocculants to obtain the best possible coagulation/flocculation condition as each of these coagulants/flocculants have numerous adverse effects such as scale formation.

2.6.2 Membrane Filtration /Non-Conventional pre-treatment

Membrane technology is currently growing at a great rate due to its excellent ability to remove contaminants and smaller footprint requiring less space compared to conventional treatment technologies. Of the different types of membrane filtration, reverse osmosis (RO) is widely used in water reuse applications due to its greater efficiency in removing contaminants including organic micropollutants (Shanmuganathan et al., 2017).

One of the limitations of the RO membrane desalination is to treat effluents with a very low concentration of suspended solids to minimize the problems associated with membrane fouling. As a result, the efficiency of the desalination process is reduced as increasing the osmotic pressure may increase the overall energy consumption. Therefore, the need for an appropriate pretreatment method becomes inevitable to ensure the feasibility and efficiency of RO systems. Several research investigations revealed that pretreatment technologies ahead of the RO membrane desalination could have positive effects on the overall operational performance such as minimizing membrane fouling, increasing the removal of suspended solids and dissolved organic matters from sea waters. These pretreatment technologies may be conventional such as coagulation, flocculation and scale inhibition or non-conventional such as ultrafiltration (UF), microfiltration (MF) and nanofiltration (NF) (Jamaly et al., 2014).

Membrane hybrid systems are becoming increasingly important as cost effective solutions in seawater treatment and reuse. Advanced membrane technology such as microfiltration (MF) and ultrafiltration (UF) has been widely applied in water, seawater and wastewater treatment due to their high efficiency, ease of operation and small footprint (Qin et al., 2006).

Microfiltration (MF) and ultrafiltration (UF) are pressure driven membrane processes which are excellent techniques for the removal of suspended solids and for lowering fouling. Energy consumption in MF is relatively low, less than one half of matching conventional pre-treatment (Van der Bruggen and Vandecasteele, 2002, Ebrahim et al., 2001). MF generally provides good quality feedwater for RO, with slightly lower COD/BOD, and silt density index (SDI) compared to untreated seawater. Further improvements can be obtained by using UF, where microorganisms, macromolecules and colloids can also be removed. Because of higher applied pressure, UF cost is higher than that for MF, but is still competitive with conventional pre-treatment. On the other hand, the

UF permeate used as RO feed is significantly improved. Despite the above advantages of MF and UF, organic fouling remains a problem both for the pre-treatment (MF/UF) and also the downstream process (RO) due to the existence of small organic molecules which pass even through UF membranes. Detailed studies have been carried out to characterize Natural Organic Matter (NOM) which is present in surface waters, and effluent organic matter (EFOM) in biologically treated secondary effluent (BTSE) (Shon et al., 2004). Furthermore, recent studies proved that hybrid membrane processes (coupling flocculation and/or adsorption and/or ion exchange resins with membranes) are efficient in simultaneously reducing membrane fouling and improving water quality (Shon et al., 2004, Guo et al., 2004). However, such results are not available for sea and brackish waters and are of paramount importance for the rational design of pre-treatment.

Past studies focused on cross-flow MF/UF which is an energy intensive process. Low-pressure immersed (submerged) MF/UF is energy efficient and is presently used successfully from small-scale (0.1 ML/d) to large-scale (375 ML/d) in surface water and wastewater treatment plants.

MF generally have a pore size of 0.1-0.2 μm, although there are exceptions, as MF membranes with pores sizes of up to 10 μm are available. For UF, pore sizes generally range from 0.01 – 0.05 μm or less (Allgeier et al., 2005). In addition, in terms of a pore size, the lower cutoff for a UF membrane is approximately 0.005 μm. Basic comparisons between MF and UF membrane are given on Table 2.2.

Table 2. 2 Comparing MF and UF Membrane Processes (Wagner, 2001)

	MF	**UF**
Membrane	Symmetrical Asymmetrical	Asymmetrical
Thickness (µm)	10-150	150-250
Thin film (µm)		1
Pore size (µm)	4-0.2	0.2-0.02
Rejection of	Particles, clay, bacteria	Macro molecules, proteins, polysaccharides, virus
Membrane materials	Polysulfone (PSO), Polyvinylidenedifluoride (PVDF), Polypropylene (PP)	Polysulfone (PSO), Cellulose acetate (CA), Polyvinylidenedifluoride (PVDF), polypropylene (PP)
Membrane module	Tubular, hollow fiber	Tubular, hollow fiber, spiral wound, plate-and-frame
Operating pressure (kPa)	100-1000	<200

The pathogen removal ability from water of each type of membrane (MF/UF) is presented in Figure 2.9.

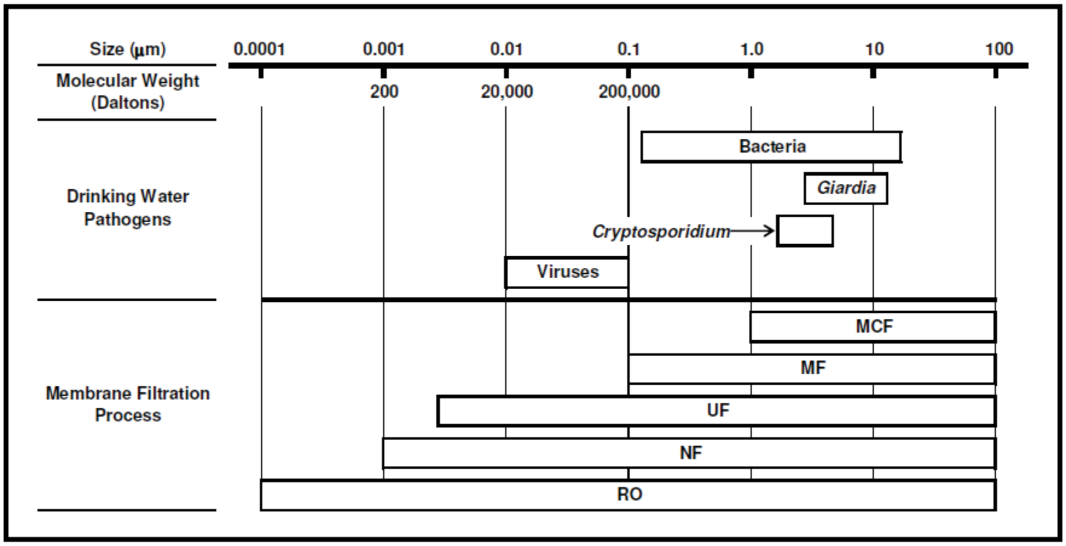


Figure 2.9 Pathogen removal ability of membrane filtration (Adapted from (Allgeier et al., 2005)

Past study on MF/UF has shown that MF and UF are capable of consistently reducing turbidities to below 0.1 NTU, removing total coliform, bacteria, Giardia and Cryptosporidium. UF is also very effective in removing viruses (Ebrahim et al., 1997). So, UF has advantages over MF to provide a better disinfection barrier in removing pathogen since UF excludes viruses. MF generally provides good quality feed water for RO, with slightly lower COD, BOD and silt density index (SDI) in comparison to the untreated seawater (Ebrahim et al., 1995) while the UF effluent typically has a 15-min silt density index (SDI_{15}) of less than 2 and provides excellent feed water to the RO enabling stable performance of the RO system (Vedavyasan, 2007). From a previous study, a comparison between conventional pre-treatment (coagulation-flocculation-media filtration) and MF/UF showed that the SDI values of the filtrate from the conventional treatment was unsteady and they vary between 2.5-4%, while the MF system provided acceptable SDI values throughout the operation period and it varied between 0.24 and 3% and the average SDI value was 2.02%. The SDI of the seawater feed was over 6% (Bou-Hamad et al., 1997) whereas, UF reduced SDI from 13-25 to less than 0.8(Brehant et al., 2002). These processes provided other advantages such as the limited use of chemical and low space requirement(Glucina et al., 1998). Basic comparisons between conventional and MF/UF pretreatment are given in Table 2.3.

Table 2. 3 Comparison of conventional and MF/UF pre-treatment (Vedavyasan, 2007)

	Conventional	MF/UF	Benefits of MF/UF
Capital costs	Cost slightly lower than MF/UF	Higher than conventional as MF/UF requires pumping of water through the membrane	Capital costs of MF/UF could be 0–25% higher, whereas life cycle costs using either of the treatment schemes are comparable
Foot print	Calls for larger footprint	Significantly smaller footprint	Foot print of MF/UF could be 30-50 % of conventional filters.
Energy requirements	Less than MF/UF as it could be gravity flow	Higher than conventional MF/UF requires pumping of water through the membranes	This can vary depending on the type of membrane and water quality

	Conventional	MF/UF	Benefits of MF/UF
Chemical costs	High due to coagulant and process chemicals needed for optimization	Chemical use is low, dependent on raw water quality	Less chemicals
RO capital cost	Higher than MF/UF since RO operates at lower flux	Higher flux is logically possible resulting in lower capital cost	Due to lower SDI values, RO can be operated at 20% higher flux if feasible, reducing RO capital costs
RO operating costs	Higher costs as fouling potential of RO feed water is high resulting in higher operating pressure. One experiences frequent cleaning of RO membranes.	Lower RO operating costs are expected due to less fouling potential and longer membrane life	The net driving pressure is likely to be lower if the feed water is pretreated by MF/UF. Membrane cleaning frequency is reduced by 10–100%, reducing system downtime and prolonged element life.

Membrane separation process can be operated in both dead-end and cross-flow filtration modes. Both of these processes have some advantages and disadvantages. For example energy consumption in cross-flow mode is higher than dead-end mode (Glucina et al., 1998) while, solid removal efficiency in cross-flow mode is higher than dead-end mode

(Tansel et al., 2005). So, low-pressure submerged MF/UF systems are presently used successfully from small-scale (0.1 ML/d) to large-scale (375 ML/d) installations. Submerged membrane reactor will have an additional advantage of lower energy requirement. The key features of submerged membranes are the removal of the permeate by suction (to avoid pressurising the membrane reactor) and the use of air bubbling as a primary fluid mechanical method to control deposition and fouling (Fane et al., 2002). The membranes with the submerged systems are aligned either vertically or horizontally. A long-term study with immersed membrane/adsorption hybrid system conducted by (Guo et al., 2004) showed a consistent and superior organic removal with practically no membrane fouling. MF and UF membranes can be formulated in either flat sheet or hollow fibre configurations. Hollow fibre membranes have some advantages over flat sheet membrane. An experiment conducted with flat sheet and hollow fibre MF and UF by (Howe et al., 2007)found that flat sheet membranes fouled more rapidly than hollow fibre membranes. Although MF and UF pre-treatment provide excellent pathogen removal ability from water, organic fouling remains a problem both for the pre-treatment (MF/UF) and also the downstream process (RO) due to the existence of small organic molecules which pass even through UF membranes.

2.6.3 Biofiltration

Biological filtration or biofiltration is one water treatment process that can effectively remove organic matter from water and biologically treated sewage effluent that is not able to be removed in conventional sewage treatment (Carlson et al., 1996). Biological filter works mainly rely on the activities of the community of micro-organisms that are attached onto filter media. The activities of microbes determine the performance of biological filtration. Microbes oxidize organic matters in water to produce energy therefore available nutrients sources in feed water is essential for their development. In addition, the parameters such as hydraulic loading rate, back washing techniques, temperature and pH etc. can affect the growth of biomass onto GAC in the biofilter. Moreover, biological filtration is economical and safe for environment. Therefore, biofiltration is more suitable than other treatment methods in terms of removing organic matter.

The biological filtration using granular activated carbon (GAC) is an efficient process in water treatment. Many studies showed that GAC biological filter has a great potential in removing disinfectant by-products, biodegradable organic matter and synthetic substances (Mckay, 1996). The removal of organic matters in water impairs the regrowth of microbes in the distribution system, thus improving the quality of water in term of colour, odour and organic precursors. Minear and Amy(1995) proposed enhanced coagulation and GAC as the best available technologies for precursors control.

Even though it has high adsorption capacity, GAC can only maintain its adsorption for a short time of biofilter operation and then its adsorption capacity becomes exhausted, thus leading to lower treatment efficiency. To recover its capacity, GAC can be regenerated by different methods such as thermal, hydrothermal, chemical and ultrasonic regeneration. However, regeneration usually reduces GAC adsorption capacity and requires high energy expense. Another way to extend GAC life is using exhausted GAC as support filter media for biological filtration. GAC provides its huge surface area for microorganism growth and development in the biofilter. In this case, both adsorption and biological degradation take part in treatment processes. Adsorption is more dominant in the first stage or acclimatized stage when GAC is in full adsorption capacity and microbes start to attach to surface of filter media and grow up. The latter stage or pseudo-steady state was controlled by microbiological activity (Dussert and Tramposch, 1996). In this stage, biological degradation plays the major role in a biofilter; therefore maintaining sufficient biomass is very important. Applying backwash is an effective method to avoid the accumulation of excess biomass that can cause biofilter clogging. It is also useful in maintaining the balance of microbiological community in a biofilter by removing dead cells and end products that may poison the microbiological environment and create free sites for new organisms.

It is found in many studies that biofilter can remove the greater part of organic matters from water and wastewater (Thi To Loan Hoang. et al., 2008, Mckay, 1996). Visvanathan et al.(2003) observed that, in continuous experiments, MBR gave better DOC removal efficiency than control membrane reactor. (Hu et al., 2005) studied biofiltration (activated clay, zeolite) and found out that the biofilter can reduce biofouling for RO. The following are the advantages of biofilter used in water and wastewater treatment:

- Widely applied for removing biodegradable organic matter (BOM) from water
- Biofilter can effectively eliminate organic substances through the biodegradation process utilizing activities of microorganisms fixed on filter media

- GAC (granular activated carbon) provides a high surface area for micro-organism growth
- Adsorption and biological degradation take place in treatment processes

The use of GAC and anthracite as biofilter media has several advantages. GAC possesses an extremely large and irregular surface of the order of several hundred m^2/g of carbon that provides a large number of available sites for the adsorption of organic substrates and microorganisms (Mckay, 1996). During the biofilter operation the GAC structure can protect microbes from shear loss. On the other hand anthracite as medium is cheaper and provides similar advantages like GAC.

2.6.4 Deep bed filtration

Deep bed filtration often referred to as media filtration or rapid filtration has been widely used for water treatment as a final clarification unit to remove particles. Deep bed filtration is an effective method in removing particles of various nature and sizes that are present in water and wastewater. Rapid filtration finds its greatest application in the clarification of dilute suspensions (less than 500 mg/l) of particles ranging in size from about 0.1 to about 50 μm (Vigneswaran et al., 1990). Deep bed filtration is the most common pre-treatment technology used for seawater reverse osmosis (SWRO). Deep bed filter is usually used single medium, dual media or mixed media operating as pressure or gravity filters (Wilf and Klinko, 1994). The filtration velocity of deep bed filter is usually 5-20 m/h. As water passes through the filter media, particles are captured by the filter media and reduce the filtration rate resulting in a pressure drop. The available pressure for the gravity filter and pressure filter are 50 kpa and 200-400 kPa respectively. When the pressure difference between the inlet and the outlet increased to 14.5-24.5 kpa for gravity filter and 30-60 kPa for pressure filters, the filter need to be backwashed. Backwash is generally carried out using water at a velocity of 10-40 m/h or using air at a flow rate of 60-90 $m^3/h/m^2$. For reverse osmosis (RO) applications, filtrate quality is determined through the measurement of turbidity and Silt density index (SDI) (Wilf et al., 2007). Although there is no defined and consistent correlation between turbidity and SDI, field experience shows that to achieve an SDI below 3, the filtrate turbidity has to be below 0.1 NTU, preferably below 0.05 NTU (Wilf et al., 2007). Except for relatively clean surface water sources, such low filtrate turbidity is difficult to achieve in a single stage filtration. Additional treatment steps may include clarification or diffused air flotation, prior to filtration to enhance filter performance. (Bonnelye et al., 2004)showed that coagulation followed by dual media filtration produced good quality feed water to RO. In-line filtration is commonly used as a pretreatment system in RO desalination (Tenzer et al., 1999). The use of in-line flocculation has some advantages prior to conventional coagulation and sedimentation. This process produces smaller flocs that can be intercepted by the filter media. There is no need of preliminary sediment. Further, it is simple, easy to operate and cheap. The ideal filter medium size should be chosen in such a way that will provide a satisfactory effluent, retain a maximum quantity of solids and minimum head loss. Generally single medium, dual media and mixed media filter are widely used in water treatment. According to the Water Desalination Technical Manual, Department of Army, USA (1986), the following suggestions have been put forward for single media, dual media and mixed media filtration:

- Single media: Single media filter generally consists of one medium of sand, anthracite, GAC, etc. Some of the desalination pretreatment systems also used green sand to remove iron and manganese compounds.
- Dual media: Dual media filter consists of two media with different specific gravity such as sand and anthracite. Usually, less dense media are placed on the top of filter and dense media at the bottom. The use of dual media filters provides larger quantity of filtered water and less headloss during operation.
- Mixed media: Consists of more than two media such as silica sand, garnet and anthracite. Mixed media filter provides a better coarse to fine filtration arrangement and creates a media flow pattern to achieve a very low SDI.

The design of rapid filter depends on the quality of water to be treated. General filter characteristics according to the Water Desalination Technical Manual, Department of Army, USA (1986) is given Table 2.4.

Table 2. 4 Characteristics of rapid filters:

Characteristics	Sand filter	Anthracite filter
Filtration rate, m/h	10-20	10-20
Depth of bed, cm	80	80
Particle size, mm	0.35-0.5	0.7-0.8
Max headloss (gravity filter), m	5	5
Max headloss (pressure filter), kPa	200-400	200-400
Backwash rate, m/h	40-50	40-50

2.6.5 Fibre filtration

A high rate fibre filter was developed by (Lee et al., 2006) and its high efficiency for the tertiary treatment of wastewater was proved in terms of high filtration velocity and good removal of particulate matter. In place of the sand, fibre media consisting of bundles of U-shaped fine polyamide fibers may be used. Compared with the conventional rapid sand filter, the filtration velocity of a fibre filter is more than 5-20 times and the specific surface is more than twice (Lee et al., 2006, Lee et al., 2007). Possible in-line additions of powdered absorbents, flocculants, ion exchangers (IE), zero-valent iron (ZVI), could remove both dissolved organics and trace metals. In-line additions of these are feasible due to the large pore area in the fiber filter. The fibre packing combines the two advantages of a large specific surface area and very large porosity (more than 90%) which results in high removal efficiency and low pressure drop despite the high filtration velocity (Lee et al., 2006). Several wastewater treatment plants (more than 2 millions m^3/day capacity) in Korea now apply fibre filters for obtaining treated water of high quality. The turbidity was reduced to less than 2 NTU and COD to less than 10 ppm (BenAim et al., 2004).The fibre filter was also studied for the possible application in drinking water treatment process(Lee et al., 2006, Lee et al., 2008). The fibre filter was used for seawater pretreatment at optimal operating conditions using a combination of coagulant and reagents and was evaluated on the basis of headloss, particle count, turbidity and SDI_3(Jeanmaire et al., 2007).In this study the fibre filter was operated at extremely high filtration velocities ranging between 50-200 m/hr. It is resulted in a headloss of about 10-13 kPa and a high turbidity removal. The effluent turbidity was below 0.1 NTU. The effluent contained about 300 particles larger than 1 μm/mL, less than 15 particles larger than 5μm/mL and achieved a removal efficiency of 98% for particles sized above 5 μm. However, the fibre filter did not decrease the value of SDI_3.

2.7 Media filtration as a pre-treatment of SWRO

Deep bed (media) filtrations have been widely used for pretreatment of seawater. Some of the examples are tabulated below:

Table 2. 5 Jeddah SWRO Plant (Al-Sheikh, 1997)

Characteristics of seawater	Pre-treatment	Coagulant	Post - treatment	Problems during operation	Solution
Red Sea surface water with the mixture of sodium hypochlorite TDS: 43,300 mg/L SDI_{15} of 5.5 - 6	Dual media filter (DMF) (anthracite and sand)	Ferric chloride before DMF	10 µm cartridge filters	Membrane degradation due to oxidation caused by chlorine reaction Control of SDI limit during seasonal variation	Cationic poly-electrolyte at a rate of 0.1 ppm with 0.3 ppm of ferric chloride. This helps to improve the decrease of the feed SDI

Table 2. 6 Doha Research Plant, Kuwait (Ebrahim et al., 1995)

Characteristics of seawater	Pre-treatment	Coagulant	Problems during operation
Surface seawater in Doha TDS: 47,000 mg/L SDI_{15}> 6.5 (average)	Flocculation and media filtration (silica sand (0.7-1.2 mm, 1 m) and anthracite (1.4-2.5 mm, 0.7 m)	$FeClSO_4$(ferric chloride sulfate)	Clogging of dual media filters, Effect of pH, Dosing rate of $FeClSO_4$ Dosing rate of polyelectrolyte, Energy input, and Climatic conditions (such as temperature, dust storm and wind).

Table 2. 7 Persian Gulf (Bonnelye et al., 2004)

Characteristics of seawater	Pre-treatment	Coagulant	Problems during operation
High turbid water, possibility of algal bloom and/or hydrocarbon pollution, SDI_{15} (10- 45%/min)	Dissolved air flotation (DAF) and DAF with double direct filtration and two coagulants injection	$FeCl_3$ and flocculant aid	SDI_{15} in the range of 1.8- 2.9% min UV absorbance removal was in the range of 20-30%

Table 2. 8 French Institute of Marine Research (Bonnelye et al., 2004)

Characteristics of seawater	Pre-treatment	Results
Turbidity 4-5 NTU SDI15: 6.1-6.4	Coagulation followed by sand filtration (10 µm)	For conventional, permeate SDI was between 5.8 and 5.9 while the RO membrane had lost 28% of its permeability within 30 days.
Conductivity level 50-57.3 mS/cm, pH- 8, SS: 10-20 mg/L, Temperature variation 9-25 ^{0}C	Pilot trial of UF; PAC polysulfone hollow fiber membrane in dead-end mode, MWCO 100 kDa and pore size of 0.01 µm.	UF membrane pilot trial showed a constant TMP under the condition that the flux was lower than 50 LMH with backwash water containing chlorine. The SDI of the UF permeate was between 1 and 2, turbidity was < 0.1 NTU, and SS was < 0.01 mg/L.

Table 2. 9 ONDEO Services, Gibraltar (Brehant et al., 2002)

Characteristics of seawater	Pre-treatment	Coagulant	Problems during operation
The seawater of Gibraltar is considered as difficult water because it is subject to algal bloom Conductivity of 48.7 mS/cm at 20°C SDI_{15} between 13 and 15.	Three dual media filters (DMF), a 10 µm cartridge filtration and then followed by a RO pilot.	Coagulation with Organic coagulant RO Floc 10	DMF filtrate SDI remained between 2.7 and 3.4 DMF filtrate turbidity fluctuated.

Table 2. 10 Singapore SWRO (Chua et al., 2003)

Characteristics of seawater	Pre-treatment	Coagulant	Problems during operation
SDI: 6.1-6.5, Turbidity 1.5-3.0 NTU, TSS - 6 mg/L	Gravity-driven single-medium sand filters and a three-stage (10-5-1µm) polishing cartridge filtration	Coagulant is dosed prior to sand filter	After sand filter SDI_{15} 4.0±0.5.

Table 2. 11 Ashdod, Mediterranean Sea (Glueckstern et al., 2002)

Characteristics of seawater	Pre-treatment	Coagulant	Problems during operation
Surface seawater turbidity in the range of 1 – 10 NTU TDS -40,500 ppm, SDI_{15} was consistently 6.5 SS: 2 – 14 ppm.	Coagulation followed by media filtration (velocity of the sand filters was 6.5 – 7.2 m/h. Backwash with air scouring was applied every 100 h. Chlorination in the level of 1.2 ppm)	Ferric salt with dosing rate of 0.3 – 0.7 ppm	The turbidity was in the range of 0.1–0.2 and SDI_{15} was reduced to 2.6 – 3.8 for conventional filtration In regards to the flux stability of the RO units, the feed water from both conventional and UF membrane pre-treatment gave similar performance.

2.8 Fouling Indices

To assess the membrane fouling, a rapid, reliable and suitable parameter to represent the fouling potential is needed. Silt density index (SDI) is the standardized method used by American Standard Testing and Method (ASTM) D4189-95 to predict the fouling potential. SDI was first introduced by DuPont Company (Permasep Products) at the request of U.S.A. Bureau of Reclamation on 1970s. This method evaluates the quantity of matter in water, based on fouling variation of a 0.45-μm membrane during a filtration. SDI cannot predict the fouling rates and does not linearly vary with the concentration of the feed foulants (Brauns et al., 2002, Yiantsios and Karabelas, 2003). As SDI fails to predict true fouling of membrane some of these shortcomings were taken into account in the development of the Modified Fouling Index (MFI) and the Mini-Plugging Factor Index. The Modified fouling index (MFI) is an extension of the SDI and was developed by (Schippers and Verdouw, 1980, Schippers et al., 1985). The MFI can be used to predict the fouling potential of the feed in membrane systems and assumes that the particulate fouling of membranes is dominated by cake filtration. However, both of these fouling indexes (SDI and MF-MFI) cannot predict the fouling of colloidal and dissolved matter. Consequently a new modified fouling index using ultra-filtration namely UF-MFI was recommended by (Boerlage et al., 2002) which considered the effect of colloidal and dissolved matter in water. (Khirani et al., 2006) developed a new method using nanofiltration (NF) membranes (NF-MFI) which is applicable to most waters, including the ones which have high fraction of small MW (molecular weight) matter. Their method is practical, as it requires only about one hour to complete the measurement. However the choice of a standard NF membrane with high organic rejection and low salt rejection remains unresolved. According to (Mosset et al.,

2008) some additional parameters need to be taken into consideration (Table 2.12) in order to evaluate the fouling tendency of water.

Table 2. 12 Parameters to be checked in the evaluation of the fouling tendency of water (Mosset et al., 2008)

Parameter	Comment
pH, conductivity, specific salts	According to the precipitation risk on reverse-osmosis (mainly on brackish water)
Turbidity, SDI, particles	SDI to a larger extent than just particles
TOC, UV absorbance	To evaluate the organic matter concentration
Redox, chlorine	If prechlorination (chock) is in operation, to prevent from membrane oxidation
Residual coagulant	Mainly iron or aluminium
Algae counts, chlorophyll	Generally performed on raw water for pre-treatment adjustment

2.8.1 Silt Density Index (SDI)

The most successful test is the silt density index (also known as fouling index), followed by the silting index. SDI is a simple correlation of increase in filtration time of a known volume of the feed after a certain period of filtration time (usually 15 minutes). SDI is typically applied on low fouling potential water such as pre-treated water feeding reverse osmosis (SDI_{15} min < 5).

It is usually applied to water that are to be processed by reverse osmosis (RO). A simplified mathematical hypothesis that shows the relationship between the measured SDI value and the corresponding amount of foulants deposited on the test filter disc was studied by (Kremen and Tanner, 1998). Increase in SDI values corresponds to the geometric increase in the amount of foulants deposited. Such a hypothesis may not be applied to different feeds especially feeds containing different particle sizes and dissolved organic matter. However, the relationship between fouling of a microporous 0.45 µm MF membranes (used in the test method) and a non-porous RO membrane is different and not clear (Schippers and Verdouw, 1980, Kremen and Tanner, 1998, Brauns et al., 2002). The SDI is a sensitive parameter and precaution is required during the measurement of SDI(Mosset et al., 2008). Some of the main precautions for measuring SDI are given below:

- Equipment flushing
- Air purge (to avoid air going at the surface of the membrane)
- Membrane wetting (for a 100% grip of membrane to the holder)
- Avoiding contact between membrane/hands, especially outside of the joint's place

However, this method is not fully capable of addressing the fouling of RO membrane as dead end filtration mode is applied to predict SDI, whereas RO filtration mode is a cross flow. So, SDI has many shortcomings and limitations, the most important being the use of a MF membrane, the characteristics of which are not precisely specified in the standard (Schippers and Verdouw, 1980). These tests generally do not have a good theoretical basis so that their value is limited. This applies to the silt density index even though it has proved to be of great practical use. The situation as outlined has led to the development of an index which has a theoretical basis and which is of practical use. The silt density index has been taken as the basis, and the principle of the silting index has also been taken into consideration.

The SDI value cannot address the relationship between index value and foulant concentration in seawater. It depends on the amount of particles but also representative of other fouling compounds (Mosset et al., 2008) (Figure 2.10).

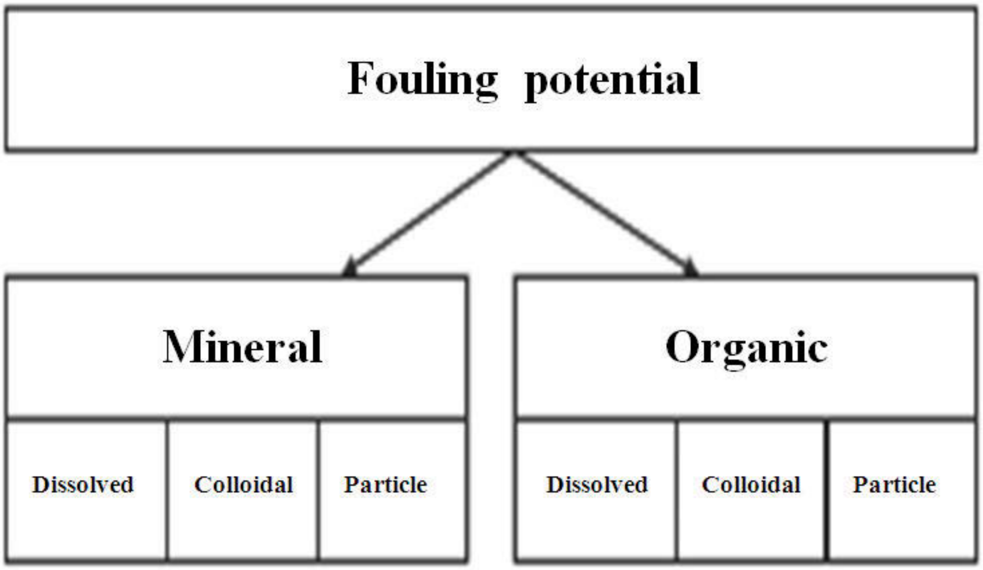


Figure 2.10Classification of fouling compounds. (Mosset et al., 2008)

The SDI is calculated from the following equation

$$SDI_{15} = \frac{1-(t_i/t_f)}{T_t} \times 100$$ Equation 1

Where

t_i = Initial filtration time (to filter a fixed volume)

t_f = Final filtration time (to filter the same fixed volume)

T_f =Elapsed time

2.8.2 Modified Fouling Index (MFI):

The Modified fouling index (MFI) is an extension of the SDI and was developed by Schippers in 1980. The MFI can be used to predict the fouling potential of the feed in membrane systems and assumes that the particulate fouling of membranes is dominated by cake filtration. The MFI is determined from the gradient of the general cake filtration equation for constant pressure in a plot of t/V versus V (Boerlage et al., 1998).

$$\frac{t}{V} = \frac{\eta R_m}{\Delta P A} + \underset{\text{Slope (MFI)}}{\underleftrightarrow{\frac{\eta \alpha C_b}{2 \Delta P A^2}}} V \qquad \text{Equation} \quad 2$$

Where,

V = total permeate volume (l)

R_m = membrane resistance (m^{-1})

t = filtration time (s)

ΔP = applied trans-membrane pressure (Pa)

η = water viscosity at 20^{o}C (N s/m^2)

α = the specific resistance of the cake deposited

C_b = the concentration of particles in a feed water (mg/l)

A = the membrane surface area (m^2).

The t/V versus V plot typically shows three regions in a MFI test using the 0.45 μm membranes. These regions correspond to (i) blocking filtration, (ii) cake filtration without compression and (iii) cake plugging and/or cake compression. The first sharp increase in slope is attributed to membrane pore blocking followed by cake filtration, which is the linear region of the curve. The MFI is defined as the gradient of the linear region of the t/V vs. V plot normalized to standard reference values of 2 bar (207±3 kPa) transmembrane pressure, a feed water viscosity of 20^{o}C and the surface area of the 47 mm diameter of 0.45μm. Alternatively, the MFI index can be determined from a plot of MFI over time where cake filtration is observed as a minimum or stable MFI value depending on the length of cake filtration.

2.8.3 UF-MFI

To describe fouling behaviour more precisely, the UF-MFI was developed to include smaller colloidal particles not measured in the existing Silt Density Index (SDI) and $MFI_{0.45}$ fouling indices by (Boerlage et al., 2003). This research investigates the application of the UF-MFI to measure and predict the particulate fouling potential of reverse osmosis (RO) feedwater and also to assess pre-treatment efficiency. Moreover, it was shown that cake resistance increased with ionic strength in UF-MFI tap water experiments and therefore, a correction of the UF-MFI index is required for salinity effects in RO concentrate (Boerlage et al., 2003).

2.8.4 NF-MFI

Based on recent studies, it seems that fouling of RO membranes is better represented by the value of the specific resistance of the cake formed by the fouling components on a NF membrane during a standard filtration test. Khirani et al.(2006) developed a new method using nanofiltration (NF) membranes (NF-MFI) which is applicable to most waters, including the ones which have a high fraction of small MW (dissolved) matter. Their method is practical, as it requires only about one hour to complete the measurement. However the choice of a standard NF membrane with high organic rejection and low salt rejection remains unresolved.

2.9 Liquid Chromatography with Organic Carbon Detector (LC-OCD)

LC-OCD was developed to categorize the classes of organic compounds in natural water. It gives qualitative results regarding molecular size distribution of organic impurities as well as quantitative information on natural organic matter (NOM). Quantification is done on the basis of carbon mass determination, similar to total organic carbon (TOC) analysis which is performed with a special organic carbon detector (Dr.Huber, 2004).The qualitative analysis is based on size exclusion chromatography (SEC) and it separates organic matter according to their molecular size. Water samples are injected into a column filled with a chromatographic gel material. Substances having small molecular sizes can access more of the internal pore volume than those having larger molecular sizes (Pelekani et al., 1999). Therefore, large molecules elute first followed by the smaller compounds. In addition to the organic carbon detector, LC-OCD uses UV detection and determination of the spectral absorption coefficient (SAC) at 254 nm to complete the information about the analysed water samples. In this study, DOC analysis was done before and after pre-treatment of seawater twice a week for the first week and afterwards it was analysed once a week during the remaining experimental period. All samples were filtered through a 0.45 micron filter before being analysed in LC-OCD machine.

2.10 Conclusion

Presently, little information is available for detailed particulates and organic matter removal using a long-term biofiltration with different media. Therefore, this detailed knowledge on the filtration performance would significantly contribute to a more efficient application of biofilter for seawater pre-treatment.

Flocculation, coagulation and sedimentation have becoming important unit processes because of their low cost and easy application in the treatment of water and wastewater in conjunction with convectional mechanical, biological and physio-chemical plants. Jar test has been used as an effective method to determine the suitability for different types and amount of flocculants on coagulation/flocculation and sedimentation process for raw water. However, the jar test is not standardized and as a result there are difficulties in making comparisons. Full scale plants are flow through units; therefore the results obtained from the jar test, which are batch tests, may not correspond with the results obtained from full scale plants. Spiral flocculator is more rapid and uses a smaller volume of water than jar tests in providing information on optimum chemical dosage. From previous studies it is also found that in-line flocculation filtration effectively reduced membrane fouling by removing particulate matters as well as colloidal and dissolved organic matters. Therefore, in-line flocculation and spiral-flocculation followed by media filtration (sand or anthracite) will be highly important in the field of seawater membrane desalination pretreatment.

Previous studies used $TiCl_4$ as a coagulant and the Ti-salt flocculated sludge was recovered to produce valuable by-product namely TiO_2.All these experiments confirmed the flocculation ability of titanium salts. However, the effective pH environment of titanium flocculation was not clearly defined. Furthermore, there has not been a comparative study on the performance of Ti-salt coagulant and the other most-widely used coagulants such as $Al_2(SO4)_3$, PACl, $FeCl_3$ and PFS. In this regard, only a few studies have evaluated the suitability of Ti–salt flocculation for SWRO pre-treatment application. The suitable conditions for Ti-salts performance in seawater in terms of coagulant mechanism and the influence of dose and pH have not been evaluated in detail.

The study on flocculation performance of Ti-salt ($Ti(SO_4)_2$ and $TiCl_4$) and $FeCl_3$ coagulants in seawater will provide valuable information in this regards in desalination process.

University of Technology, Sydney

CHAPTER 3

EXPERIMENTAL INVESTIGATION

3. EXPERIMENTAL INVESTIGATION

3.1 Introduction

An experimental study was conducted to determine the effect of different pre-treatment methods on reverse osmosis desalination. Experiments were conducted both laboratory and also in the field. The water characteristics, experimental and analytical procedures are described in this chapter.

3.2 Experimental Materials

3.2.1 Seawater (Chowder bay)

Laboratory scale experiment was conducted in Sydney Institute of Marine Science (SIMS), Chowder Bay, Mosman, Sydney, Australia. Seawater was pumped from 1 m below the sea surface level and filtered using a centrifuge filtration system to remove large particles. The filtered seawater had the following characteristics presented in Table 3.1.

Table 3. 1Seawater characteristics

Specification	Estimated value
pH	8.01-8.10
MF-MFI (s/L^2)	4.2-9.7

Specification	Estimated value
UF-MFI (s/L^2)	9500-11589
CFMF-MFI (s/L^2)	49.6-56.7
Turbidity (NTU)	0.40-065
DOC (mg/L)	0.55-2.79

3.2.2 Seawater (Cabarita)

Seawater was collected from Cabarita, Sydney. The seawater characteristics are presented in Table 3.2.Laboratory scale experiment was conducted with seawater collected from Cabarita, Sydney, Australia.

Table 3. 2Seawater characteristics

Specification	Estimated value
UV_{254} (cm^{-1})	0.0288 – 0.0515
Turbidity (NTU)	6.1 – 6.7
DOC (mg/l)	1.7 – 2.9
pH	7.8 – 8.0
Zeta (mV)	-1.86

3.2.3 Physical properties of Granular activated carbon (GAC),Anthracite and Sand

The physical properties of GAC, anthracite and sand used are presented in Table 3.3. GAC and anthracite used were manufactured from Australian coal seam by James Cumming and Sons P/L, Australia. It has a relatively small nominal size of 0.3 mm with a bulk density of 748 kg/m^3. The most important characteristic of GAC is the extremely large surface area (more than 1,000 m^2/ g GAC). This ability makes GAC suitable for adsorbing of substances and micro-organisms present in seawater. Sand used in this study was sourced from Riversands P/L Australia. GAC, sand and anthracite were washed with distilled water, then dried at 103°C and desiccated prior to use.

Table 3. 3 Physical properties of Granular activated carbon (GAC), Anthracite and Sand

Parameter	Anthracite	GAC	Sand
Specification	Estimated value	Estimated value	Estimated value
Effective size (mm)	1.05	0.3	0.6
Bulk density (kg/m^3)	660-720	748	1,500
Uniformity coefficient	1.3	1.3	<1.5
Specific surface area (m^2/gm)	N.A.	1,000	N.A.

N.A – not available and these values are very small as compared to that of GAC.

3.3 Experimental Methods

3.3.1 Long term biofiltration

In this study, biofiltration experiments were conducted using transparent acrylic filter columns (Figure 3.1).

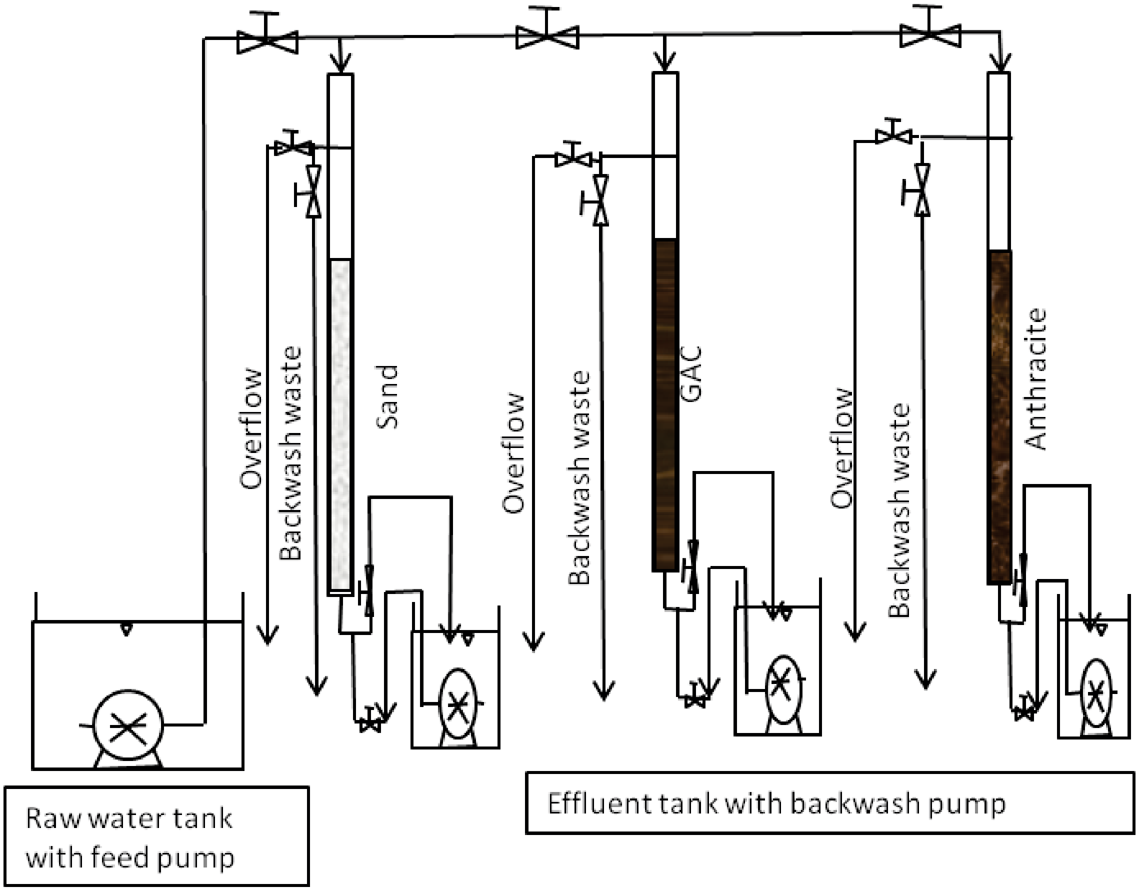


Figure 3.1Schematic diagram of biofiltration column

Biofiltration experiment was conducted using transparent acrylic filter columns which have a length of 150 cm and a diameter of 9.5 cm as shown in Figure 3.1. These columns have sampling ports along the length as well as at the bottom of the column. Prepared filter media (GAC, anthracite and sand) were packed up to a depth of 80 cm from the bottom of the columns and biofilters were connected in parallel. Seawater was pumped from the feeding tank to the top of the columns and then passed through the filter bed at filtration velocity of 0.12 m/h. An overflow outlet was placed above the filter bed in the column to maintain a constant velocity. Backwashing was applied to remove particles and excess biomass in the filter bed that cause biofilter clogging during experiments. Backwashing was conducted with tap water in the up-flow direction from the bottom of the column and the filter bed expanded up to 30% during a backwash of 2 minutes. The entire filtration period was 120 days. Effluent samples (filtrates) were collected from the bottom of the column for further analyses.

3.3.2 In-line flocculation filtration and spiral-flocculation filtration systems

In this study transparent acrylic filter columns were used. The spiral-flocculation was made by winding a tube of 25 m length, and 6 mm in diameter, around a cylindrical column of 9 cm in diameter (Figure 3.2).

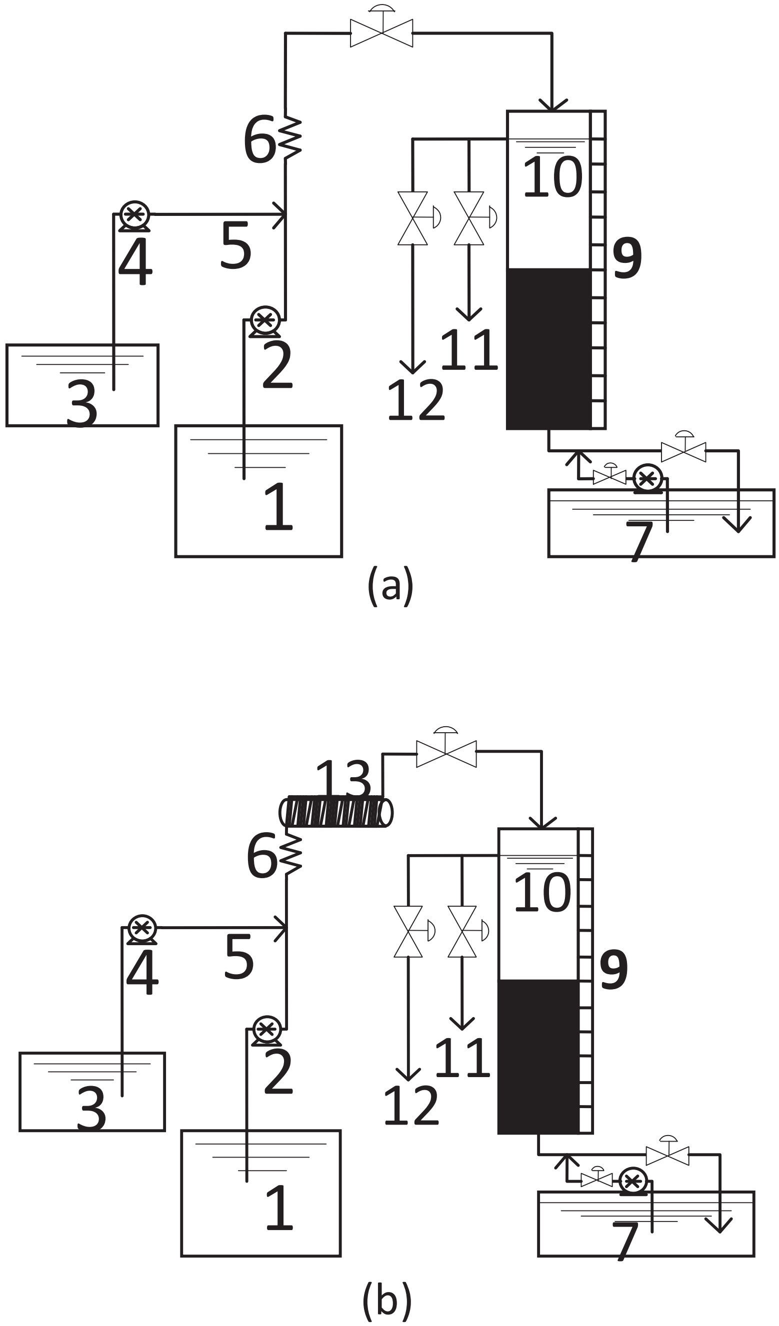


Figure 3.2Schematic diagram of (a) in-line flocculation filtration and (b) spiral-flocculation filtration system (1-feed tank, 2-feed pump, 3-coagulant tank, 4-dosing pump, 5-cogulant addition, 6-rapid mixing device, 7-effluent tank with backwash pump, 8-filter media, 9-manometer, 10-static head, 11-backwash water, 12-verflow, 13-spiral flocculator (slow mixing device)

Short term in-line flocculation filtration and spiral-flocculation filtration was conducted (Figure 3.2 a and b). The filter columns were made of transparent acrylic filter columns which have a length of 135 cm and internal diameter of 1.8 cm. These columns have sampling ports along its length and at the bottom. Prepared filter media (anthracite or sand) were packed up to a depth of 90 cm in these columns. Seawater was pumped from a feeding tank and coagulant was added using a dosing pump.

The flocculants used was $Fe_2(SO_4)_3$ and it was fed at a dose of 1-5 mg-Fe^{3+}/L. The rapid mixing device was a 20 cm tube, 3 mm in diameter, wound around a tube of 5 cm. It was used for uniform mixing of seawater with coagulant for 10 seconds.

In the case of in-line flocculation filtration system, the seawater was passed through the media filter just after rapid mixing of raw seawater with flocculants for 10 seconds. The flocculation and solid liquid separation occur in the filter.

In the case of spiral-flocculation filtration, after the rapid mixing of seawater with flocculants, it was then passed through the spiral-flocculation. The spiral-flocculation was made by winding a tube of 25 m length, and 6 mm in diameter, around a cylindrical column of 9 cm in diameter. The headloss and thus the velocity gradient was measured using the piezometric arrangement across the two ends of the spiral-flocculation. Seawater after the flocculation through the spiral-flocculation was passed through a filter bed with down flow filtration at velocities of 5 m/h and 10 m/h. The effluent samples were collected on a regular basis from the bottom of the filter column for analysis. An overflow chamber was in place at the top of the filter bed to maintain a constant head. The headloss was measured every hour using a piezometer.

3.3.3 Coagulation and Flocculation

Coagulation was conducted using conventional jar test at different coagulant concentrations (1-30 mg/l) of Ti salts and $FeCl_3$ at different pH of 5 to 9. $FeCl_3$ stock solution (i.e. 10 g/L) was prepared by dissolving $FeCl_3$ powder in deionized (DI) water. $TiCl_4$ and $Ti(SO_4)_2$ stock solution was made by adding drop by drop of concentrated solution (>99% purity, Sigma Aldrich, Australia) to frozen cubes of deionized water to obtain a final concentration of 1% w/w. For each jar test, six 1 litre beakers were filled with raw seawater. The pH was adjusted with 0.1 N solution of hydrochloride acid and sodium hydroxide prior to coagulant addition. The solution was subjected to rapid mixing (100 rpm) for 2 min followed by slow mixing (20 rpm) for 30 min. It was then stopped to allow the aggregated flocs to settle down for 30 min. After settling, the supernatant samples were drawn from ~5 cm below water surface without disturbing the aggregated flocs sediment in the sample for the measurements of turbidity, UV-254 absorbance and DOC, zeta potential and particle size distribution.

3.4Analytical methods

3.4.1 Turbidity, Floc Size and Zeta Potential

The turbidity of the influent and effluent was measured in terms of NTU (Nephelometric

Turbidity Units) using a 2100P turbidity meter, HACH, USA. The influent and effluent turbidity was measured thrice for each sample and the mean value was recorded with the range.

Zeta potential and particle size were measured with a Zetasizer 3000HSa (Malvern Instruments UK). After 2 min of stabilisation, the data were recorded automatically. For each sample, the instrument automatically made triplicate measurements, and a mean value was recorded. Measurements for zeta potential and particle size were undertaken twice for each sample and a mean value of the two measurements were taken as a result. The initial and final pH values of the solution for each experiment were also recorded with HACH pH meter.

3.4.2 UF-MFI and MF-UFI

Fouling indices are used to measure and predict the fouling potential of the feed water to membrane filtration systems. In industry, the Silt Density Index (SDI) is the only standard method presently used despite having many shortcomings that often fail to reflect the true fouling strength of the seawater or pre-treated seawater. In this study the reduction of the fouling potential of raw sea water arising from biofilters with different media was studied.

Modified fouling index (MFI) was measured using dead-end cell unit with a 0.45 μm micro-filter (MF-MFI) and a 17.5 KDa (molecular weight cut-off; MWCO) ultra-filter (UF-MFI). The fouling index experimental set-up of MF-MFI and UF-MFI is shown in Figure

3.3. Seawater before and after pre-treatment were pressurized using N_2 gas through a flat sheet membrane module (a diameter of 47 mm) at a feed water temperature of $20^{\circ}C$. The operating trans-membrane pressure was controlled at 207±3 kPa by means of a pressure regulating valve. In each experiment, new membranes were used to avoid the effect of residual fouling and to allow a comparison of results obtained under different conditions.

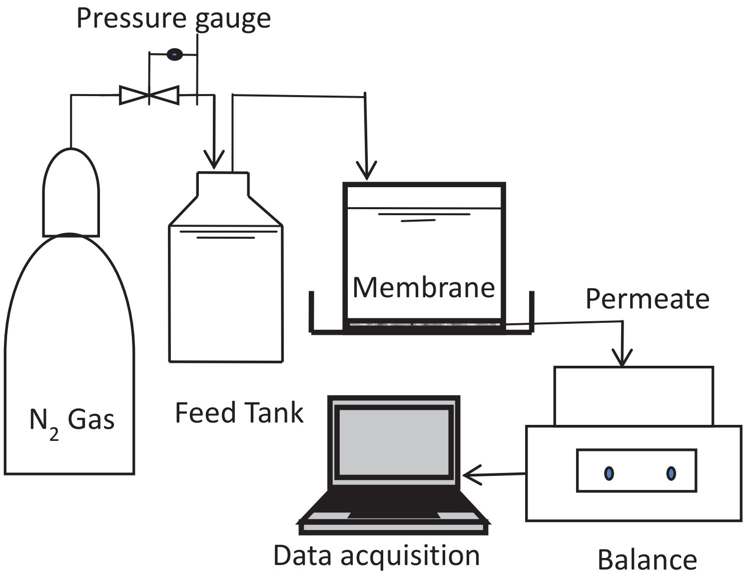


Figure 3.3UF-MFI or MF-MFI experiment setup

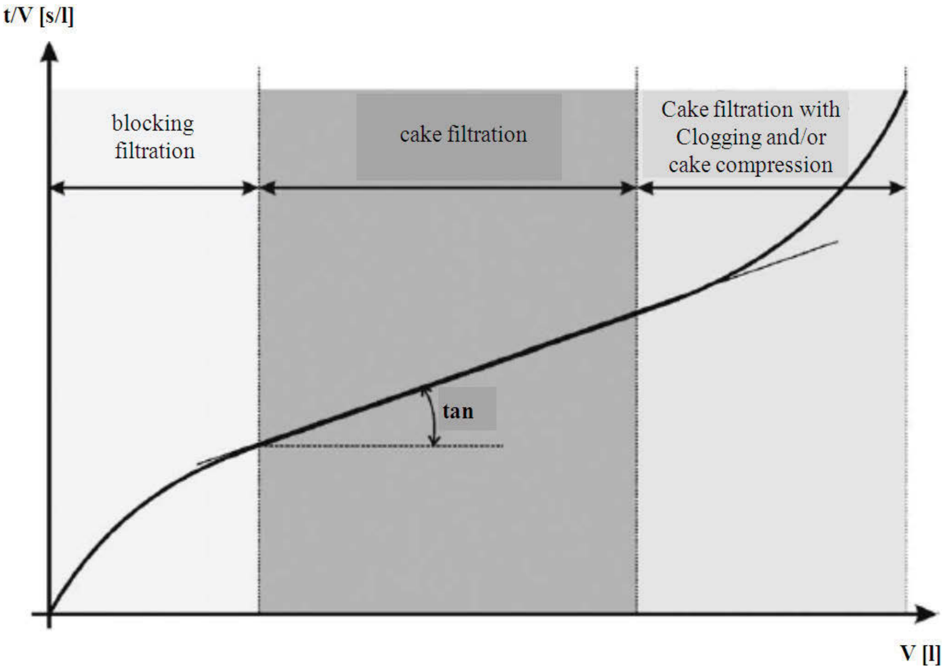


Figure 3.4 Cake filtration curve (Boerlage et al., 1997)

MFI was calculated according to the method by (Schippers and Verdouw, 1980). The MFI is determined from the gradient of the general cake filtration equation at constant pressure by plotting t/V versus V using the equation 1 as shown in figure 3.4.

$$\frac{t}{V}=\frac{\eta R_m}{\Delta PA}+\underset{\text{MFI}}{\underleftrightarrow{\frac{\eta\alpha C_b}{2\Delta PA^2}}}V$$

Equation 1

Where,

a) V = total permeate volume (L)

b) R_m = membrane resistance (1/m)

c) t = filtration time (s)

d) ΔP = applied trans-membrane pressure (Pa)

e) η = water viscosity at 20°C ($N.s/m^2$)

f) α = the specific resistance of the cake deposited

g) C_b = the concentration of particles in a feed water (mg/L)

h) A = the membrane surface area (m^2)

In addition to MF-MFI, UF-MFI was conducted to study the fouling potential in this study. This was because in many cases MF-MFI does not provide a good representation of organic fouling due to the relatively large pore size of MF membrane compared to a UF membrane (Boerlage et al., 2003). Thus, the use of UF-MFI could give better information on some of the larger molecular weight organics than MF-MFI. Thus, UF-MFI was conducted for only a few samples as a representative result during an operational period of 92 to 120 days.

3.4.3 Pore blocking index

The pore blocking slope was determined from the gradient of the general filtration equation at constant pressure using a plot of t/V versus t.

$$\frac{t}{v} = S_{pb}t + b \qquad \text{Equation} \quad 2$$

where,

v = total permeate volume (L)

t = filtration time (s)

Spb = pore blocking slope by critical time – pore blocking index (1/L)

b =constant

Here, vc and tc are defined as the critical values below which we could obtain a linear relation between t/v and t.

Spb was obtained with the slope of the straight line between t/v and t (from t = 0 to the critical point) (Figure 3.5).

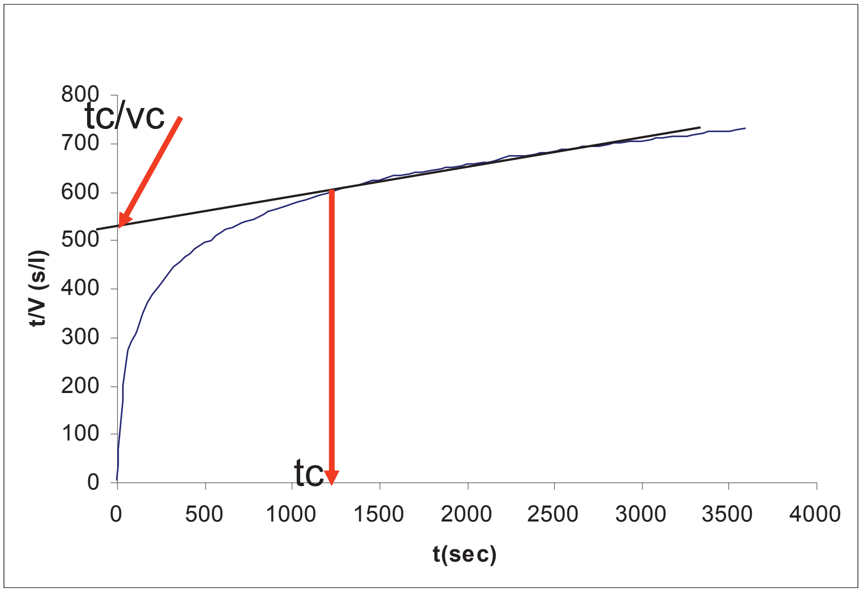


Figure 3.5 t (time)/ v (permeate volume) vs. t for feed water

3.4.4 CFMF-MFI

A cross flow sample cell was employed to study the flux decline. The fouling index experimental set-up of CFMF-MFI is shown in Figure 3.6. The raw and pre-treated seawater were pressurized at 10 kPa through a 0.45 μm MF membrane at a cross-flow velocity of 4.3 m/h. A temperature controller was used to maintain the temperature at 29˚C. The cross-flow velocity and trans-membrane pressures were controlled by bypass and regulating valves.

In dead-end filtration used in measuring MF-MFI and UF-MFI, foulants in the feed are deposited on or pass through the membrane surface, whereas in cross-flow filtration, foulants are fractioned by selective deposition. The hydrodynamics effects of cross-flow filtration, which were not simulated in SDI and MFI tests, can be considered in a cross-flow sampler unit. It is critical since the crossflow velocity in the crossflow sampler unit influences the particle concentration and the particle size distribution in its permeate(Sim et al., 2010). Thus, modified fouling index using a cross-flow unit with MF membrane (CFMF-MFI) was conducted to closely simulate the hydrodynamic conditions of a crossflow RO unit Figure 3.6. A few samples were tested on CFMF-MFI to obtain a representative result during the operational period of between 21-50 days.

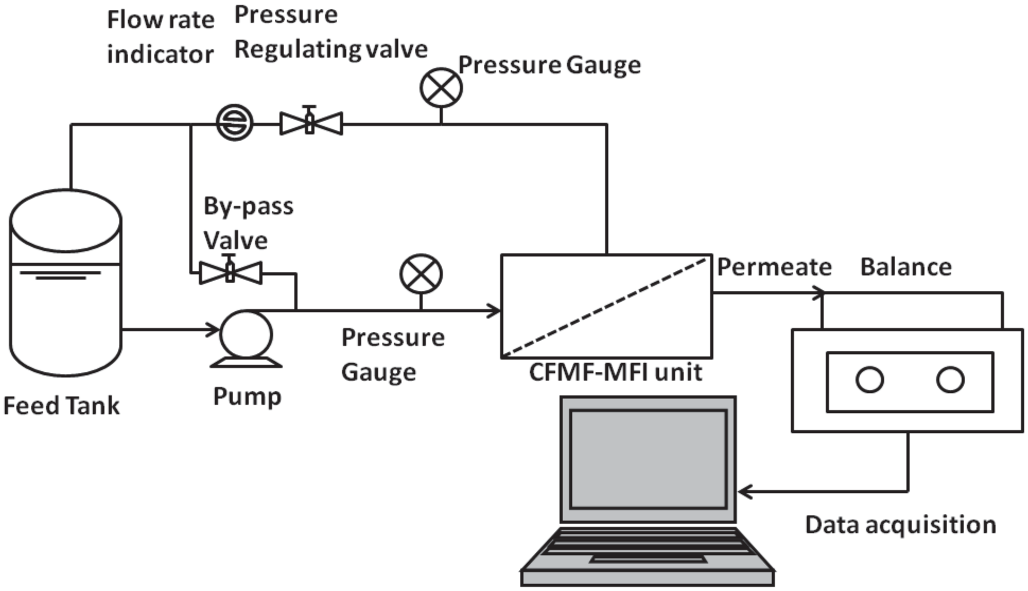


Figure 3.6 Fouling Index experimental setup: CFMF-MFI

3.4.5 Liquid chromatography-organic carbon detection (LC-OCD)

Liquid chromatography-organic carbon detection (LC-OCD) categorizes and fractionates the classes of organic compounds in water(Huber et al., 2011). It gives qualitative results regarding molecular size distribution of organic matter as well as quantitative information on natural organic matter (NOM). Quantification is done on the basis of carbon mass determination, similar to total organic carbon (TOC) analysis which is performed with a special organic carbon detector. The qualitative analysis is based on size exclusion chromatography (SEC) and it separates organic matter according to their molecular size. Water samples are injected into a column filled with a chromatographic gel material. Substances having small molecular sizes can access more of the internal pore volume than those having larger molecular sizes (Pelekani et al., 1999). Therefore, large molecules elute first followed by the smaller compounds. In addition to the organic carbon detector, LC-OCD uses UV detection and determination of the spectral absorption coefficient (SAC) at 254 nm to complete the information about the water samples. In this study, DOC analysis was conducted on the samples collected before and after biofiltration (pre-treatment) of seawater twice a week for first week and afterwards samples were analysed once a week for the reminder of the experimental period. All samples were filtered through a 0.45 µm micro-filter prior to the LC-OCD. The measurements of turbidity and the DOC were made in duplicate for at least 30% of the samples. The deviation was less than 5%.

University of Technology, Sydney

CHAPTER 4

SEAWATER BIOFILTRATION PRE - TREATMENT SYSTEM – COMPARISON ON FILTER MEDIA PERFORMANCE

4. SEAWATER BIOFILTRATION PRE-TREATMENT SYSTEM – COMPARISON ON FILTER MEDIA PERFORMANCE

4.1 Introduction

Seawater pre-treatment is a major component of a desalination plant (Voutchkov, 2010b). The main objective of pre-treatment system is to remove particulate, colloidal, organic, mineral and microbiological contaminants contained in raw seawater and to protect the downstream seawater reverse osmosis (SWRO) membranes from fouling. The selection of a pre-treatment method is very significant since it can influence the overall performance and determine the success or failure of the plant. In traditional pre-treatment, suspended materials are removed by deep bed filtration coupled with flocculation or extensive use of chemical treatment (Chinu et al., 2009). Even though conventional pre-treatment methods can remove a small portion of dissolved organic matter it is not sufficient to overcome the organic fouling in RO. Previous research by Clark and Boutin (2001), Mckay (1996), Hoang et al.(2008) showed that biofilter can remove a majority of organic matter from water and wastewater, resulting in less operation and maintenance requirements. It can effectively remove organic substances by utilizing activities of micro-organisms attached on the filter media through a biodegradation process. Both aerobic and anaerobic microbes in suspended or attached forms can be used in the biological processes. The microbes convert biodegradable organic substances present in the influent into biomass and inorganic carbon through their metabolisms. In addition to this, it can also remove small fractions of organic matter which cannot be removed by other conventional treatment processes.

Moreover, biological filtration is economical and safe to the environment in comparison to other physical and chemical treatment methods.

In this study, three deep bed filters were operated at a slow filtration velocity using three different media: GAC, anthracite and sand respectively. The performance of biofilter with different media was compared to evaluate the effectiveness of the pre-treatment to reverse osmosis (RO). GAC possesses an extremely large and irregular surface of the order of several hundred m^2/g of carbon and offer a large number of available sites for the adsorption of organic substrates and micro-organisms (Mckay, 1996). Further, Naidu et al. (2013) showed the reduction of biofouling potential with stable microbial activity in the GAC filter bed. During biofilter operation, the GAC structure also protects microbes from shear loss. On the other hand, anthracite and sand are cheaper compared to GAC. Thus sand and anthracite were used single or dual as a conventional granular media in water industry (Bae et al., 2011).

In this study, a slow filtration velocity is used to mimic the natural infiltration like a beach well system. In certain cases it may be constrained by shorter depths and residence times. By contrast, beach wells (a technology similar to river bank filtration) can provide longer travel times and distances (> 10 days and > 10 m), and can be used as a biofiltration. The beach well constitutes a natural biological filter and achieves effective removal of biodegradable organic carbon (BDOC) and assimilable organic carbon (AOC). It also reduces bio- and organic-fouling, and colloidal fouling. It has the advantage of providing a seawater intake system (Bonnelye et al., 2004). It eliminates the need for complex intake structures that protrude into the sea and the problem of organism impingement/entrainment at intakes. This system appeals to large desalination plants which use open sea intake.

Presently, little information is available for detailed particulates and organic matter removal using a long-term biofiltration with different media. Therefore, this detailed knowledge on the filtration performance would significantly contribute to a more efficient application of biofilter for seawater pre-treatment. The aim is to develop a cost effective biofilter with a high potential to remove the dissolved organic matter to prevent fouling of reverse osmosis membranes.

4.2 Seawater and Filter media

Biofiltration experiment was conducted on-site at Sydney Institute of Marine Science (SIMS), Chowder Bay, Sydney, Australia. Seawater was collected from 1 m below the sea surface level and continuously fed into biofilter. The characteristics of seawater were monitored regularly during the biofiltration experiments. The average pH, turbidity, dissolved organic carbon (DOC), and UF-MFI, MF-MFI, CFMF-MFI values of raw seawater were 8.10, 0.40-065 NTU, 0.55-1.82 mg/L 9500-10900 s/L^2, 4.2-9.7 s/L^2, 49.6-56.7 s/L^2 respectively.

Biofilter packed with different media; GAC, anthracite and sand was operated in parallel. GAC and anthracite used were manufactured from Australian coal seam by James

Cumming and Sons P/L, Australia. It has a relatively small nominal size of 0.3 mm with a bulk density of 748 kg/m^3. The most important characteristic of GAC is the extremely large surface area (more than 1,000 m^2/ g GAC). This ability makes GAC suitable for adsorbing of substances and micro-organisms presented in seawater. Sand used in this study was sourced by Riversands P/L Australia. The physical properties of GAC, anthracite and sand used are presented in Table 3.3. GAC, sand and anthracite were washed with distilled water, then dried at 103°C and desiccated prior to use.

4.3Efficiency in terms of turbidity and pH removal

Biofilters were operated on-site at Chowder bay, Sydney, for duration of 120 days. The variation of seawater temperature and turbidity was monitored during the entire operation. The turbidity of raw seawater was relatively consistent in the range of 0.40-0.65 NTU (Figure 4.1). The turbidity increased slightly up to 0.78 NTU during the rainy period. The turbidity of filtrates (effluents) from the GAC, sand and anthracite biofilters were found to be 0.16-0.41 NTU, 0.16-0.40 NTU and 0.19-0.43 NTU, respectively. The temperature of seawater was fairly uniform at around 20˚C during the experimental period. There was no significant change in pH over the entire duration of the experiment. Except for the first 10 days, the pH was relatively stable between 7.75-8.50 until the end of experiment for both seawaters before and after filtration (Figure 4.2). Seawater pre-treated with GAC biofilter showed slightly lower pH in comparison with seawaters followed by sand and anthracite biofilters. Tabular data is presented in Appendix A.1. The rainfall pattern is presented in Appendix A.2.

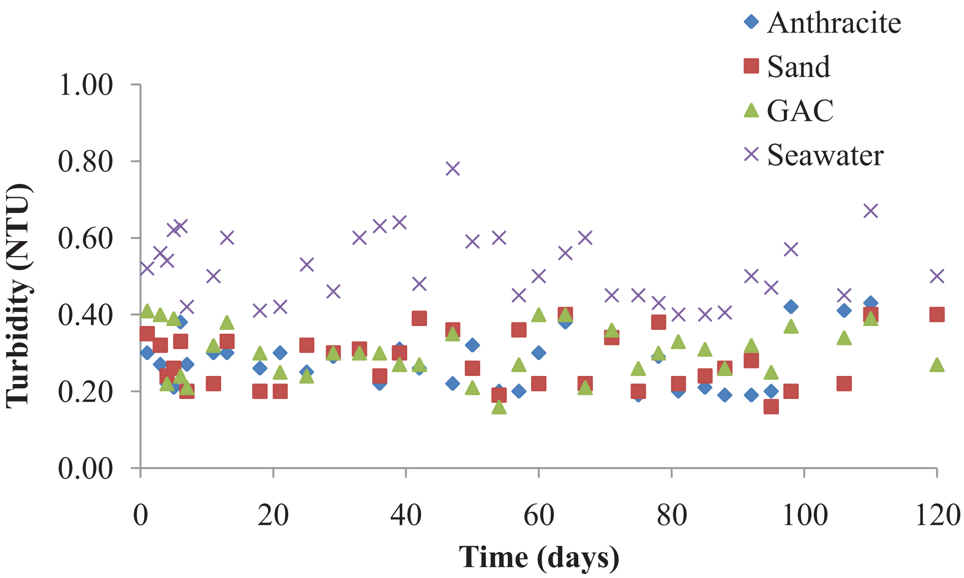


Figure 4.1Turbidity removals with biofilters

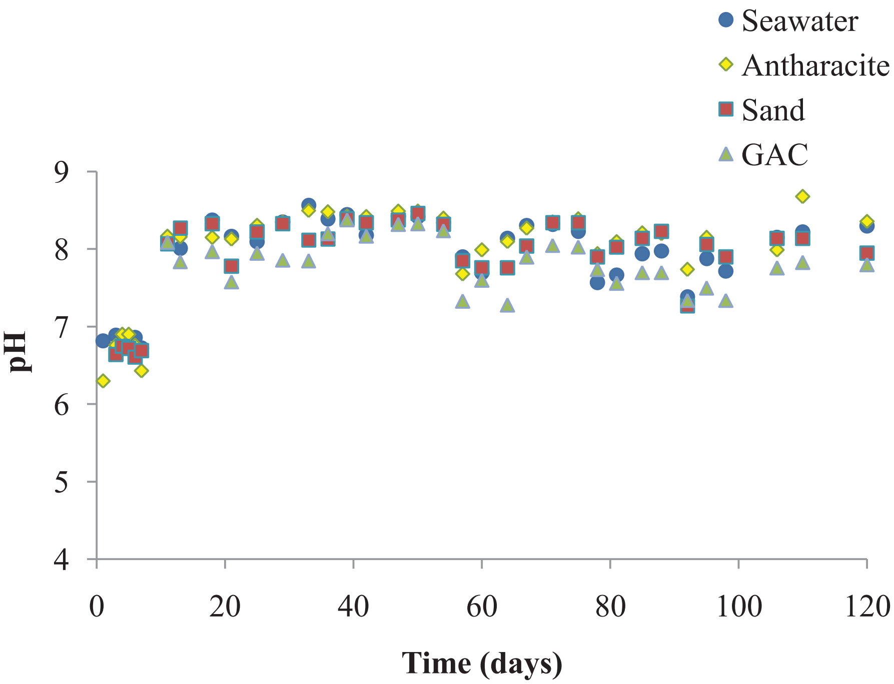


Figure 4.2Variation of pH during experimental period

4.4 Efficiency in terms of MF – MFI

The effectiveness of biofilter filtration on fouling propensity of the feed was studied using raw seawater. MF-MFI was conducted in terms of the fouling removal in addition to UF-MFI and CFMF-MFI. The measurement of fouling potential using MF-MFI showed that raw seawater varied in the range of 4.2-9.7 s/L^2. MF-MFI was mainly carried out to determine the fouling reduction by colloidal particles. After filtration through GAC, sand and anthracite biofilters, MF-MFI value decreased to 1.2-3.7 s/L^2, 1.9-5.9 s/L^2 and 2.1-8.2 s/L^2, respectively, (Figure 4.3). This indicated that the GAC biofilter could reduce a majority of fouling potential during the experimental period of 120 days compared to sand and anthracite biofilters. In the case of sand and anthracite biofilters, the MF-MFI value decreased gradually after the beginning of experiment (13 to 30 days of operation) till the period between 33 to 64 days of operation. After 64 days of operation, the MF-MFI values (in the case of sand and anthracite biofilters) fluctuated between 2.0-8.2 s/L^2, even though during this period, the MF-MFI value of raw seawater fluctuated between 4.4-9.7 s/L^2. This could be due to the unsteady removal of colloidal and particulate organic matters by sand and anthracite biofilters. Tabular data is presented in Appendix A.3. MF_ MFI sample data for seawater is presented in Appendix 8.

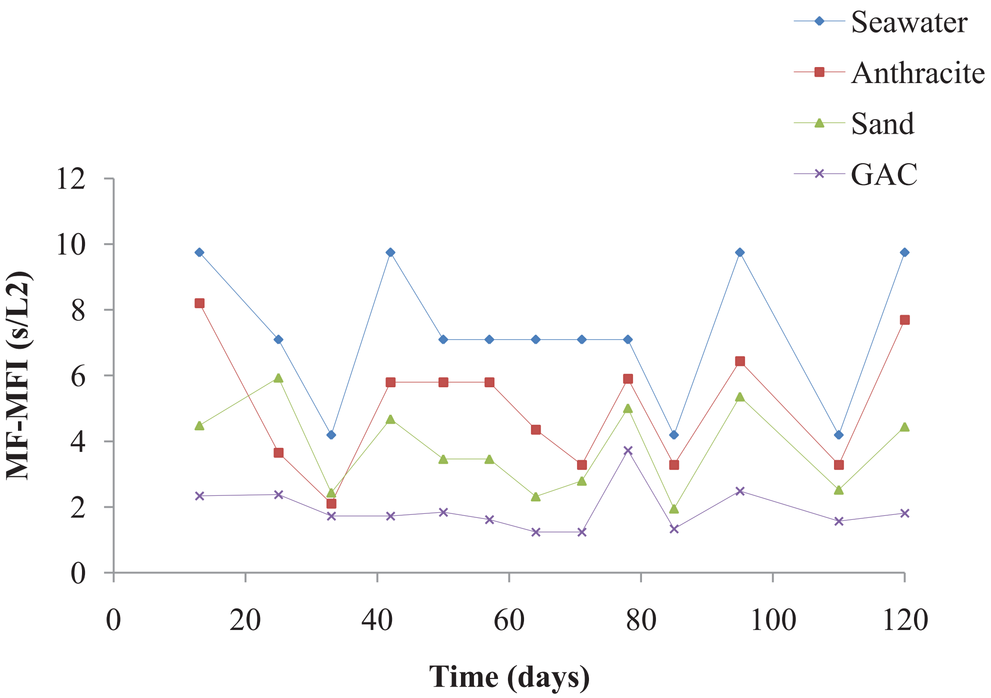


Figure 4.3The MFI values of seawater and effluents through biofilters: MF-MFI

4.5 Efficiency in terms of UF – MFI

The UF-MFI was measured mainly to see the fouling reduction by larger organic matter (such proteins, polysaccharides and humics) in addition to the colloidal particles. This is vital in seawater pre-treatment. It was found from the UF-MFI result that the all biofilters showed superior reduction in fouling potential. The UF-MFI of raw seawater was between 9,500-10,900 s/L^2. The UF-MFI values of filtrate seawater treated with GAC, sand and anthracite biofilters varied between 1500-4800 s/L^2, 2200-6600 s/L^2, and 1500-8000 s/L^2, respectively (Figure 4.4). GAC biofilter showed a better reduction in the UF-MFI compared to sand and anthracite biofilters. In a similar result to the MF-MFI, the GAC biofilter showed an almost steady reduction of UF-MFI values till the end of experimental period of

120 days. This is due to better removal of organic matters with GAC biofilter. The DOC value of GAC biofilter effluent was relatively stable and lower than that of sand and anthracite biofilter effluent (Figure 4.4).Tabular data is presented in Appendix A.4.

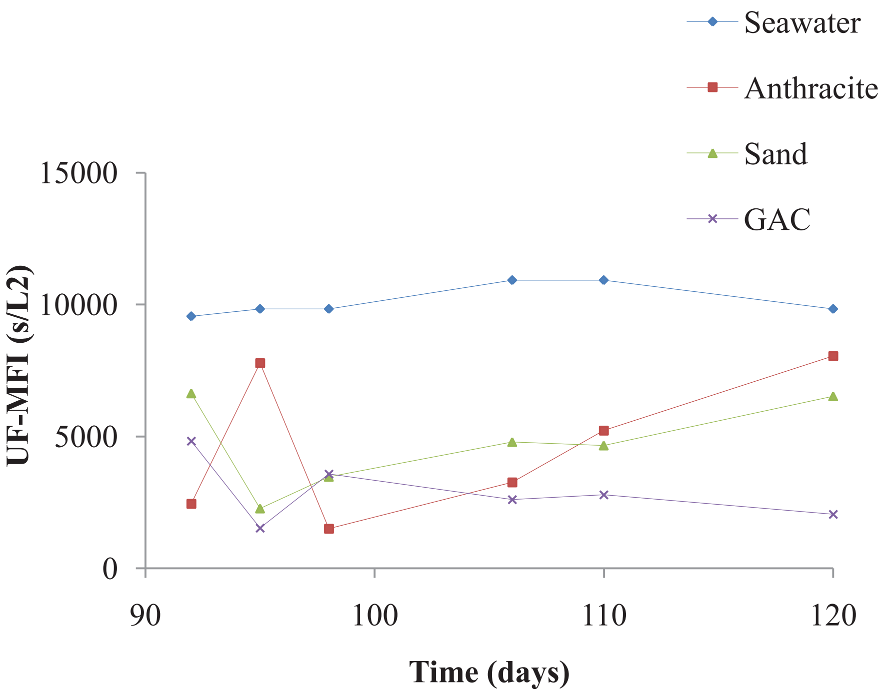


Figure 4.4The MFI values of seawater and effluents through biofilters: UF-MFI

4.6 Efficiency in terms of CFMF – MFI

The CFMF-MFI value for raw seawater varied between 49.6-56.7 s/L^2 (Figure 4.5).The CFMF-MFI values for effluent filtered through GAC, sand and anthracite biofilters varied between 4.2-12.0 s/L^2, 7.5-15.0 s/L^2, and 4.4-20.0 s/L^2, respectively. GAC biofiltershowed a better reduction in the CFMF-MFI in comparison with sand and anthracite biofilters. In results similar to MF-MFI and UF-MFI, the GAC biofilter showed an almost steady reduction during a period between 21-50 days. This suggests that it is possible to decrease the fouling potential (particulates, organic matter and foulant deposit by crossflow) to the RO membrane using the biofilters studied in this study. Tabular data is presented in Appendix A.5.

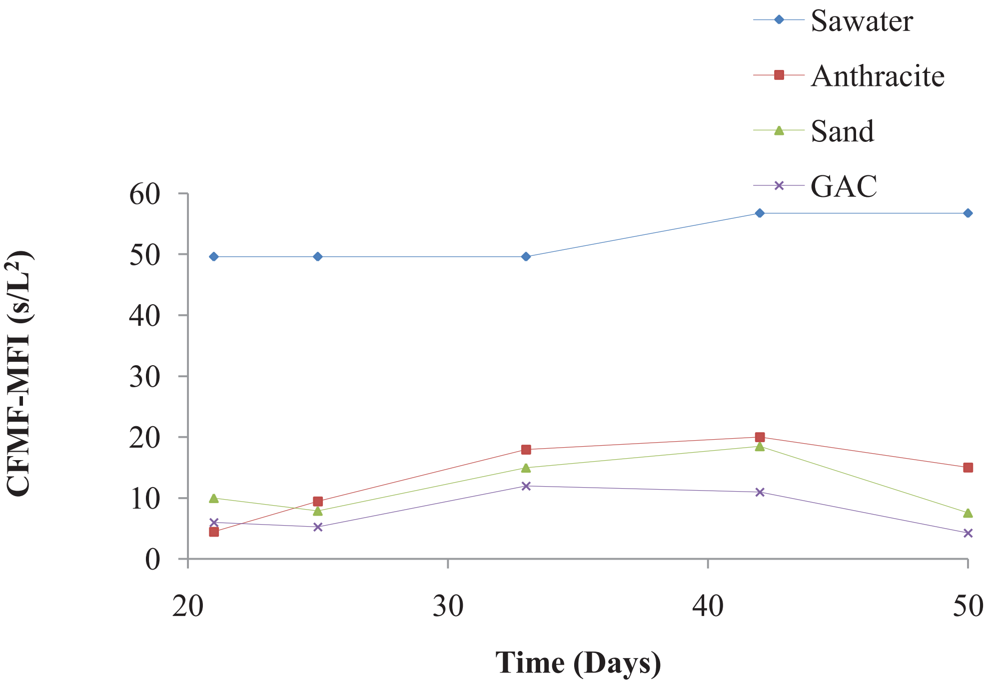


Figure 4.5The MFI values of seawater and effluents through biofilters: CF-MFI

4.7Efficiency in terms of DOC removal

Figure 4.6 presents the reduction of DOC after filtration with GAC, sand and anthracite biofilters. This shows a significant amount of dissolved organic matter was removed by biofilter pre-treatment. GAC biofilter had a better removal efficiency of between 41-88%, whereas the DOC removal efficiency of sand and anthracite biofiltersin seawater was lower (7-76% and 3-71%, respectively). As discussed above, GAC produced a steady and superior quality of effluent.LC-OCD chromatograms of seawater and effluents through three different media biofilters are shown in Figure 4.7 and their detailed organic fractions are given in Table 4.2. The seawater used in this study comprised of more hydrophilic compounds (79%) causing severe organic fouling on the RO membrane. The removal efficiency of DOC in seawater by GAC biofilter was superior at more than 69%. As can be seen from Table 4.2, all biofilters tested in this study removed most (94%) of the hydrophobic organic compounds. On the other hand, hydrophilic organic removals varied depending on the different media filters. GAC biofilter removed more organic bio-polymers (51%) than sand and anthracite biofilter. Also, a higher amount of building blocks (as humic substances-hydrolysates with molecular weights between 300-450 g/mol) were removed by the GAC biofilter (50.0%). In particular, the removal efficiency of humic substances by GAC biofilter was 74.5% whereas both anthracite biofilter and sand biofilter could not remove as much. This shows that GAC biofiltration is effective pre-treatment to reduce organic fouling. Tabular data is presented in Appendix A.6. and A.7.

Table 4. 1 Removal of different organic fractions by different media biofilters

Sample	DOC	Hydro-phobic	Hydro-philic	Bio-polymer	Humics	Building blocks	LMW Neutrals
Seawater (mg/L)[a]	1.65	0.34	1.31	0.35	0.47	0.14	0.35
Effluent through GAC Biofilter(mg/L)[a]	0.51	0.02	0.49	0.17	0.12	0.07	0.13
Removal efficiency (%)[b]	69.1	94.1	62.6	51.4	74.5	50.0	62.9
Effluent through Sand Biofilter (mg/L)[a]	0.90	0.02	0.88	0.19	0.46	0.10	0.13
Removal efficiency (%)[b]	45.5	94.1	32.8	45.7	2.1	28.6	62.9
Effluent through Anthracite Biofilter (mg/L)[a]	1.06	0.02	1.04	0.26	0.46	0.12	0.20
Removal efficiency (%)[b]	35.8	94.1	20.6	25.7	2.1	14.3	42.9

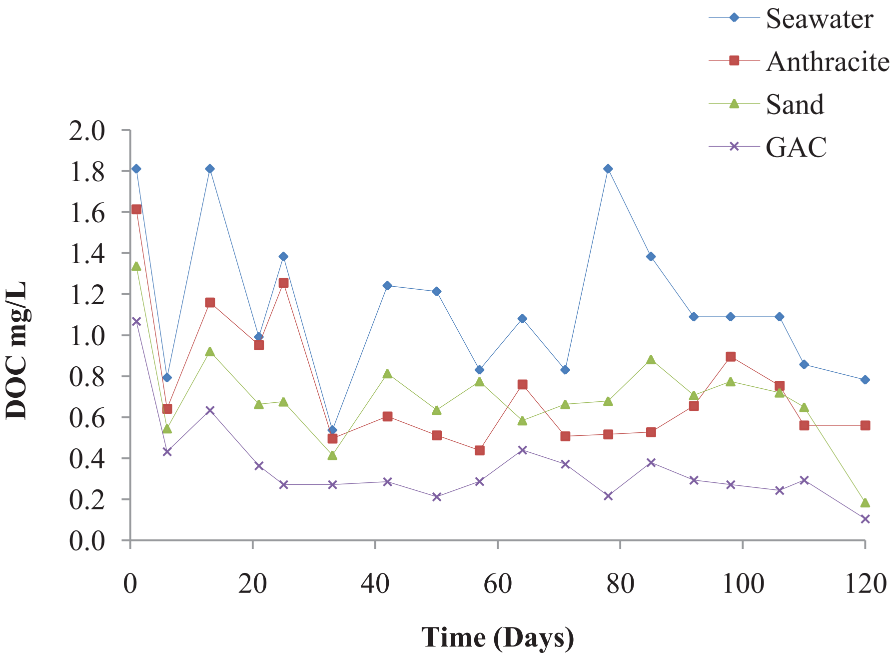


Figure 4.6Variation of DOC concentration of seawater and effluents through biofilters during the experimental period

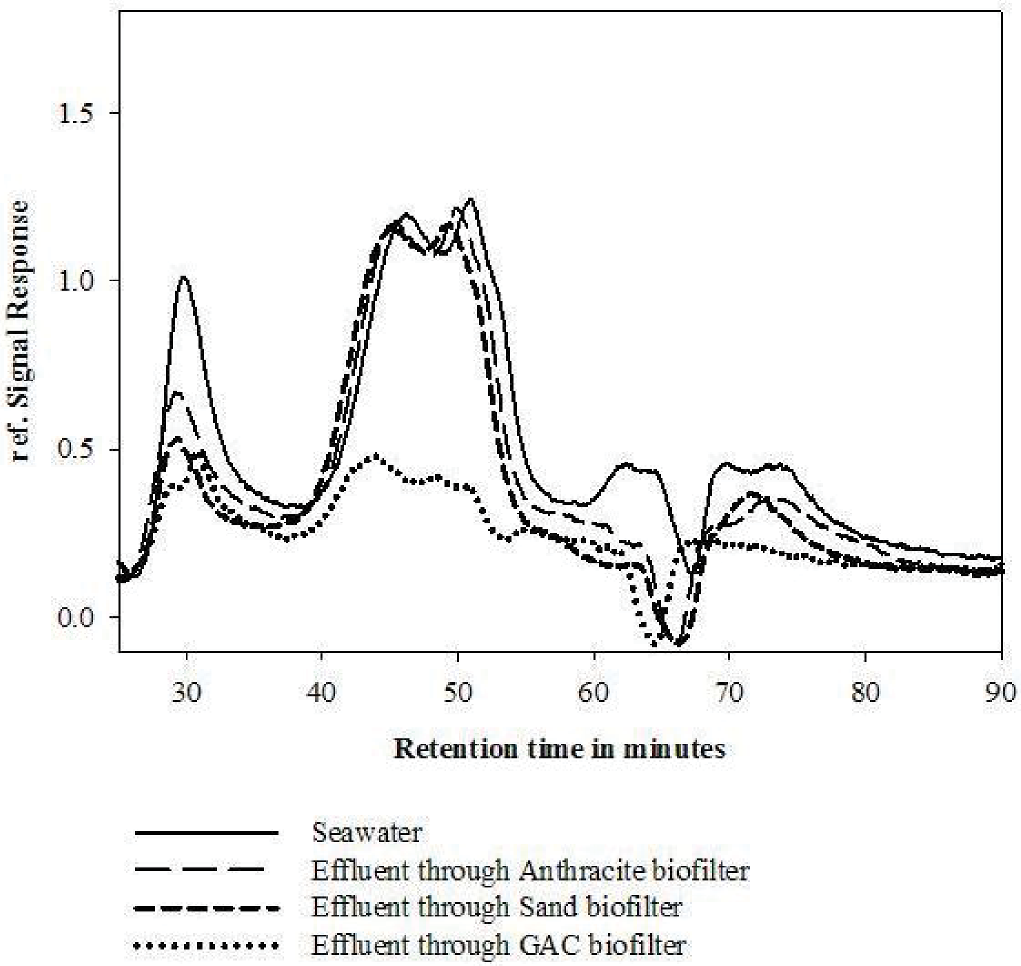


Figure 4.7LC-OCD chromatogram of seawater and effluents through biofilters

4.8 Conclusion

The experimental results indicate that biofiltration pre-treatment systems reduced organic matter and particulate matter. It is expected that biofilter can lower fouling to a subsequent RO process in desalination plant. The biofiltration performance of GAC biofilter was significantly better than that of conventional media such as sand and anthracite. All the biofilters had almost similar turbidity removal efficiency. The results measured by various fouling indices showed that the filtrate (effluent) from the GAC biofilter had lower fouling potential compared to sand and anthracite biofilters. In terms of DOC removal efficiency, GAC biofilter had better and consistent removal efficiency compared to sand and anthracite. All biofilters tested in this study removed most of the hydrophobic organic compounds. On the other hand, removal of hydrophilic organic varied depending on the different media filters. GAC removed more organic bio-polymer and building blocks than sand and anthracite biofilters. In particular, the removal efficiency of humic substances by the GAC biofilter was 74.5% whereas both sand and anthracite biofilter could not remove as much. Thus the GAC filter was the best medium to provide the lowest fouling potential as it showed the highest removal efficiency of DOC, including hydrophilic, humic, building blocks and biopolymer. The lowest efficiency was found for anthracite medium.

University of Technology, Sydney

CHAPTER 5

A COMPARATIVE STUDY ON IN-LINE FLOCCULATION AND SPIRAL-FLOCCULATION FOLLOWED BY MEDIA FILTRATION AS A PRE-TREATMENT OF SEAWATER

5. A COMPARATIVE STUDY ON IN-LINE FLOCCULATION AND SPIRAL-FLOCCULATION FOLLOWED BY MEDIA FILTRATION AS A PRE-TREATMENT OF SEAWATER

5.1 Introduction

Membrane based desalination technology such as reverse osmosis (RO) has rapidly becoming an efficient alternative to conventional treatment for drinking water production from seawater. However, membrane fouling is a major concern in reverse osmosis (RO) based seawater desalination. The fouling on RO membrane deteriorates the performance of RO membranes and increases the energy consumption and even requires more frequent replacement of the membranes. The main fouling mechanisms of RO membranes include (i) particulate and/or colloidal fouling resulting from accumulation of suspended solids and some metal based hydroxide which can accumulate on the surface of the membrane over time and form cake fouling, (ii) biofouling due to the formation of biofilms caused by the attachment and metabolism of biological matter which includes micro-organism and macro-organism such as bacteria, fungus or algae which may also accelerate the chemical decomposition of RO membranes posing serious threats to the operation of RO plants (iii) inorganic fouling including scaling caused by exceeding the solubility of soluble salts such as $CaSO_4$, $BaSO_4$ and $MgSO_4$ which is considered less problematic and can be controlled by adjusting the pH and adding antiscalant and (iv) organic fouling resulting from the deposition of organic matter such as humic and fulvic acids, polysaccharides, and aromatic compounds on to membrane surface (Chua et al., 2003, Pontié et al., 2005).

Pre-treatment such as bio-filtration, coagulation, adsorption, in-line flocculation, filtration and ozonation have been used to remove the natural organic matter (NOM) and to alleviate fouling (Park et al., 2002, Tomaszewska and Mozia, 2002, Chinu et al., 2009, Johir et al., 2009). Flocculation, coagulation and sedimentation have becoming important unit processes because of their low cost and easy application in the treatment of water and wastewater in conjunction with convectional mechanical, biological and physio-chemical plants. Pre-treatment steps widely employed in SWRO plants include disinfection, coagulation– flocculation, filtration and anti-scalant dosing. Conventional pre-treatment includes acid addition, coagulation-flocculation, disinfection and media filtration (Isaias, 2001, Bonnelye et al., 2004, Naidu et al., 2013, Chinu et al., 2010).

Jar test has been used for since a long time and it is an effective method to determine the suitability for different types and amount of flocculants on coagulation/flocculation and sedimentation process for raw water. Despite its popularity, the jar test has a number of disadvantages. The jar test is not standardized and as result there are difficulties in making comparisons. Full scale plants are flow through units; therefore the results obtained from the jar test, which are batch tests, may not correspond with the results obtained from full scale plants. Spiral flocculator is more rapid and uses a smaller volume of water than jar tests in providing information on optimum chemical dosage. It provides results which are more closely related to flocculation performance in an actual flocculation plant (Vigneswaran and Setiadi, 1986). From previous studies it is also found that in-line flocculation filtration effectively reduced membrane fouling. For example Johir et al.(2009) found lower membrane fouling of RO after an inline-flocculation-dual media filtration than without pre-treatment. Another study by Chinu et al.(2010) showed that the flux decline of MF without any pre-treatment of seawater was 45%, was about 42% after pre-treatment of $FeCl_3$ flocculation, 24% after pre-treatment of sand filtration with in-line coagulation and 22% after pre-treatment of dual media filtration (sand and anthracite), respectively. Similarly Lee et al.(2010) found 50% lower fouling of membrane filtration when in-line flocculation fibre media filtration was used. All of these studies revealed that the in-line flocculation filtration can effectively reduce membrane fouling by removing particulate matters as well as colloidal and dissolved organic matters.

In this study in-line flocculation and spiral-flocculation followed by media filtration (sand or anthracite) was investigated as a pre-treatment to sea water RO. In our subsequent discussion, we refer to rapid mixing followed by media filtration (sand or anthracite) as in-line flocculation filtration; and rapid mixing with spiral-flocculation and then by media filtration as spiral-flocculation filtration. A comparison of filter performances was made between sand and anthracite medium filters. Short term (6 h) experiments were carried out with in-line flocculation filtration and spiral-flocculation filtration at a velocity of 5 m/h and 10 m/hand a flocculent dose of 0-5 mg-Fe^{3+}/L. The efficiencies of these pre-treatments were carried out in terms of ultra-filtration–modified fouling index (UF-MFI), head loss development and turbidity and organic matter removal.

5.2Seawater and Filter media

Seawater used in this study was collected from Chowder Bay, Mosman, Sydney. The average pH, turbidity, dissolved organic carbon (DOC), and UF-MFI values of seawater were 8.01, 0.42-0.44 NTU, 2.07-2.79 mg /L and11589 s/L^{2}respectively.

The physical properties of anthracite and sand used in this study are given in Table 5.1. The anthracite and sand were obtained from James Cumming and Sons P/L and Riversands P/L respectively. Sand and anthracite were washed with distilled water then dried at 103°C and desiccated prior to their use.

Table 5.1 Physical properties of Anthracite and Sand

Parameter	Anthracite	Sand
Specification	Estimated value	Estimated value
Effective size (mm)	1.0-1.1	0.5-0.6
Bulk density (kg/m^3)	660-720	1,500
Uniformity coefficient	1.3	<1.5
Acid solubility	1%	<2%

5.3 Calculation of velocity gradient for spiral-flocculation system

First of all, the velocity gradient of a spiral-flocculation during the passage of suspension was determined by measuring the headloss across the length of spiral tube. The relationship between headloss and the velocity gradient is given by equation 2.

$$G = \sqrt{\left(\frac{g}{\nu}\right)\left(\frac{Q}{V}\right)\Delta H} \qquad \text{(Eq. 2)}$$

Where

G = velocity gradient, 1/s

g = gravitional acceleration, cm^2/s

ν = kinematic viscosity, cm^2/s

Q = flow rate, cm^3/s

V = volume of the flocculator (in this case, tube volume), cm^3

ΔH= headloss through the flocculator, cm

Based on the experimental conditions, the velocity gradients were found to be 13.6/s and 27.2/s respectively when the filtration velocity was 5 m/h and 10 m/h. The higher the velocity gradient, the smaller will be the floc size (Vigneswaran and Setiadi, 1986)however this difference in floc size could be significant after the growth phase.

5.4Turbidity removal

The removal of turbidity by in-line flocculation filtration (sand or anthracite filtration) is presented in Table 5.2. The filters were operated at two filtration velocities of 5 and 10 m/h with and without the addition of coagulant dose of 0-5 mg-Fe^{3+}/L. The average turbidity of raw seawater was 0.42-0.44 NTU. From Table 5.2, it is found that the removal of turbidity without the addition of coagulant was in the ranges of 40-50%. The lower removal of turbidity without the addition of coagulant is due to the fact that colloidal suspended particle could easily get through the filter media. Thus, it is important to use the flocculation or coagulation prior to the filtration system which will help to aggregate the colloidal as well as organic matter and will improve turbidity removal efficiency. Therefore, the remaining sets of experiments were conducted with the addition of coagulant to investigate the effect of coagulation on turbidity removal.

From the results present in Table 5.2, it is found that the addition of coagulant helped to reduce the turbidly of the filtrate water resulting in more removal of turbidity by up to 70% at higher flocculant doses of 3 and 5 mg-Fe^{3+}/L. The increase in removal of turbidity with the addition of coagulant is due to the aggregation of colloidal particle by the coagulant which was then captured by the media filter.

In the case of the effect of filtration velocity, a lower filtration velocity of 5 m/h showed higher turbidity removal efficiency of upto 71% compared with a higher filtration velocity of 10 m/h where the removal was slightly lower (up to 66%) (Table 5.2). In addition, among the two different filter media namely sand and anthracite, the removal efficiency of turbidity by sand filter was slightly higher than that of the anthracite filter (Table 5.2). The slightly higher removal of turbidity by sand filter was due the smaller particle size of sand used in this study. This could be due to the change in physical properties of these two filter media used in this study. From the physical characteristics of sand and anthracite (presented in Table 5.1) the effectively size of the anthracite filter media (1.05 mm) is almost 1.5 times larger than the sand filter (0.6 mm). This can be validated from the previous study which showed higher removal (%) with finer filter (Johir et al., 2009). In addition, the turbidity removal by spiral-flocculation filtration systems was also investigated. In all cases, it was found that the spiral-flocculation filtration also showed almost similar removal efficiency of turbidity (Table 5.2). Hence, it can be concluded that both of the filtration systems showed good removal of turbidity thus both types of filtration produced almost same quality of water in terms of turbidity reduction.Tabular data is presented in Appendix B.1 and B4.

Table 5.2 Performance summary of in-line flocculation filtration and spiral-flocculation filtration

(depth of filter media = 90 cm; seawater turbidity = 0.42-0.44 NTU; Seawater UF-MFI= 11589 s/L2)

Filter Media	Flocculant dose ($mg\text{-}Fe^{3+}/L$)	Velocity (m/h)	Turbidity removal (%)	Final headloss development (cm)	UF-MFI reduction (%)
			In-line flocculation filtration		
Sand	0	5	47.6±8.1	3.5	46.5±1.3
	1	5	51.7±6.3	23.0	60.2±2.8
	3	5	67.4±6.9	38.5	69.3±1.7
	5	5	71.4±4.7	151.5	63.2±5.5
	3	10	64.4±3.3	228.5	67.2±9.6
Anthracite	0	5	39.5±6.9	1.5	50.8±3.1
	1	5	48.2±5.4	30.0	70.4±2.8
	3	5	63.9±8.1	52.0	65.6±2.0
	5	5	64.2±7.1	58.0	76.5±8.9
	3	10	58.8±4.4	105.5	65.0±7.4

Filter Media	Flocculant dose (mg-Fe^{3+}/L)	Velocity (m/h)	Turbidity removal (%)	Final headloss development (cm)	UF-MFI reduction (%)
		Spiral-flocculation filtration			
Sand	3	5	71.9±9.5	17.5	60.2±10
		10	69.5±7.1	52.0	61.0±5.3
Anthracite		5	67.1±4.2	2.5	65.4±9.2
		10	60.0±6.2	16.0	62.4±2.5

5.5 Headloss development

The total headloss development of in-line flocculation filtration system after a filter operation of 6h is presented in Table 5.2. From Table 5.2 it is found that the application of coagulant increased the headloss development. The headloss development without the addition of coagulant was only 3.5 cm (for sand filter) and 1.5 (for anthracite filter). However, in both cases (sand and anthracite) when inline coagulation was applied, the headloss development increased significantly (84-97%). The higher headloss development with the application of coagulant is because of the creation of flocs particle resulting from the aggregation of colloidal and organic matter. These floc particles are then captured by the filter media which led to a faster blocking of the filter media resulting in higher head loss development.

In terms of filtration velocity and filter media, higher filtration velocity (10 m/h) and finer filter medium (sand) resulted in higher headloss compared with a lower filtration velocity of 5 m/h and a coarser filter medium (anthracite) at the same coagulant dose (Table 5.2).

The higher headloss development with finer filter media of sand could be due to the smaller particle size of sand than anthracite used in this study. Thus the void space between sand filter (smaller particle size) was clogged more by the flocculated particle or colloidal particle than by particles of larger size (here anthracite filter). Similarly, at a higher filtration velocity (10 m/h) the higher headloss was likely due to the faster rate of deposition of floc/colloidal particle inside the pores of the filter bed.

In addition, the total headloss development of spiral-flocculation filtration system is also presented in Table 5.2. A comparison between the two different filtration systems, shows that the in-line flocculation filtration system had almost 2-3 times higher headloss development than the spiral-flocculation filtration system (Table 5.2) when operated at the same filtration velocity and coagulant dose.

For the in-line flocculation filtration system, the coagulant was mixed with seawater for only 10 second. This resulted in destabilisation of particles and formation of very small flocs which then passed through the filter and was trapped within the media filter. The small flocs could easily penetrate through the filter medium and quickly clogged the filter media. Further there will be additional flocculation of destabilised particles during the passage of the particles through the filter. On the other hand, in the case spiral-flocculation filtration after rapid mixing of 10 seconds, the mixed flocculated seawater was passed through spiral-flocculation for slow mixing (i.e. flocculation) for 16.6 to 33.33 min. Thus, the spiral-flocculation provided additional contact time for the aggregation of colloidal and organic matter with the coagulant which produced relative larger floc than the in-line flocculation filtration system before the suspension passes through the filter. Thus the relatively larger flocs entering the system caused decrease in headloss development.

In summary, based on the turbidity removal both the filtration systems had almost similar performances, but the result of headloss development showed that the spiral-flocculation filtration system had a lower tendency to clog compared to in-line flocculation filtration system. This shows the benefit of using of short term spiral flocculation, in addition to rapid mixing and in-line flocculation filtration. Tabular data is presented in Appendix B.1 and B4.

5.6 Fouling reduction

The fouling potential was also measured in terms of UF-MFI for the raw seawater and for the effluent from both filters operated at a filtration velocity of 5 and 10 m/h with a coagulant doses of 0-5 mg-Fe^{3+}/L (Table 5.2). The UF-MFI value for raw seawater was 11589 s/L^2. The fouling potential in terms of UF-MFI index showed that both filtration systems reduced the UF fouling. The UF-MFI of the filter effluent without the addition of coagulant reduced by 40-50% whereas with the addition of coagulant, the UF fouling reduced by 60-70%. The fouling of UF membrane could be due to the deposition of colloidal matter and to some extent the deposition of organic matter. Thus the higher reduction of UF-MFI with the addition of coagulant is due to the removal of both colloidal and organic matter by the coagulant. The filtration velocity and filter media type (or size) had almost no effect on the UF-MFI fouling reduction. Both the filtration systems (in-line flocculation filtration and spiral-flocculation filtration) showed almost the same reduction in fouling potential. Tabular data is presented in Appendix B.2 and B.5.

5.7Organic removal and characterisation of organic matter

The removal of dissolved organic carbon (DOC) by in-line flocculation filtration and spiral-flocculation filtration is presented in Tables 5.3 and 5.4. DOC was measured for filters operated at a filtration velocity of 5 m/h and 10 m/h with and without the addition of coagulant. From Table 5.3 it is found that the removal of DOC without the addition of coagulant was low (13-21%). The addition of coagulant increased the DOC removal efficiency (35-47%). The DOC removal efficiency increased with increase larger doses of coagulant from 1 to 5 mg-Fe^{3+}/L for both in-line flocculation filtration and spiral-flocculation filtration (sand or anthracite filter). From literature it is also found that the removal of organic by Fe^{3+} is due to the complexation of Fe (Shon et al., 2005)(here $Fe_2 (SO_4)_3$ as source of Fe^{3+}). Both the in-line flocculation filtration and spiral-flocculation filtration showed almost same performance in terms of DOC removal (Table 5.3 and 5.4)

A detailed organic characterisation of raw seawater and filtrate seawater was also done using LC-OCD which provides detailed quantitative as well as qualitative data of different organic matter removed. The LC-OCD results of raw seawater and filtrate are presented in Table 5.3 and 5.4. The results show that the seawater used in this study had a DOC concentration of 2.07-2.79 mg/L among which more hydrophilic compounds (1.69-1.82 mg/L; 65.2-81.4 %) were present than hydrophobic compounds (0.38-0.98 mg/L; 18.6-34.8%). This is responsible for organic fouling on the membrane. The hydrophilic compounds contains of biopolymers, humic substances, building block, low molecular weight (LMW) neutrals and LMW acids. The concentration of biopolymers present in raw seawater was 0.11-0.21 mg/L (3.9-10.1% of total DOC), whereas the portion of humic substances, building block, LMW neutrals and LMW acids present in seawater was 14.4-24.0, 6.6-8.2, 40.7-46.9% of the DOC respectively. Their concentrations were 0.44-0.5, 0.08-0.14, 0.76-1.19 mg/L respectively.

From Tables 5.3 and 5.4, it can be seen that the filtration system used in this study could help to remove majority of hydrophobic type of substances. In the case of in-line flocculation filtration (sand or anthracite filter), the removal of hydrophobic compound (45-76%) was higher than that of hydrophilic compounds (18-37%). Among of the hydrophilic compound the removal of biopolymers was higher than that of humic and building blocks which showed very low removal (less than 10%). In all cases, the removal of LMW neutrals and acids were 31-62%.

Spiral-flocculation filtration (sand or anthracite) also showed almost similar trend of hydrophobic and hydrophilic organic removal to that of in-line flocculation filtration system. In spiral-flocculation filtration system, the concentration of biopolymers after filtration was reduced to 0.05-0.09 mg/L (from 0.21 mg/L) which is around 2.7 to 5.8 % of total DOC of filtrate water. The removal of humic substances was less than 10 % and the amount of humic substances present in filtrate water was 22-36% of DOC present in filtrate water (around 0.38-0.60 mg/L). After filtration, the concentration of building block type substances reduced from 0.14 mg/L (in raw seawater) to 0.05 to 0.09 mg/L (3.8 to 6.3 % of DOC). After filtration, the concentration of LMW neutrals reduced from 0.84 to 0.38-0.56 mg/L (23-47% reduction). It could be concluded that both the tested filtration systems can remove 30-40% of the hydrophilic compounds which comprises of biopolymer, building blocks, LMW neutrals and acids. However, both filters removed more hydrophobic compounds as expected. The removal of hydrophilic substances may be by complexation mechanism (Shon et al., 2005).Tabular data is presented in Appendix B.3 and B.6.

Table 5. 3 DOC removal and fractionation of organic matter presented in seawater and effluent from different in-line flocculation filtration

Filter Media	Velocity (m/h)	Flocculant dose (mg-Fe^{3+}/L	DOC (mg/L)	HOC (mg/L)	CDOC (mg/L)	Bio-polymers (mg/L)	Humic substances (mg/L)	Building blocks (mg/L)	LMW neutrals and acids (mg/L)
Raw sea water			2.79	0.98	1.82	0.11	0.44	0.08	1.19
Sand	**5**	**0**	2.41±0.29 (13.75±10.3)	0.78±0.02 (20.58±1.92)	1.63±0.31 (10.07±16.9)	0.07±0.01 (36.07±7.4)	0.44±0.02 (0.51±5.04)	0.08±0.03 (7.22±30.9)	1.05±0.30 (11.5±25.2)
		1	2.07±0.07 (25.76±2.51)	0.51±0.04 (47.33±4.09)	1.56±0.03 (14.16±1.67)	0.11±0.04 (3.42±35.04)	0.48±0.04 (-)	0.17±0.02 (-)	0.81±0.03) (31.90±2.83)
		3	1.45±0.14 (47.96±5.08)	0.34±0.02 (65.55±2.44)	1.12±0.12 (38.50±6.50)	0.07±0.01 (35.73±7.28)	0.37±0.00 (16.51±0.69)	0.10±0.02 (-)	0.58±0.11 (51.18±9.05)
		5	1.55±0.02 (44.45±0.60)	0.41±0.01 (58.17±1.33)	1.14±0.00 (37.08±0.21)	0.07±0.01 (40.31±7.73)	0.54±0.04 (-)	0.09±0.01 (-)	0.45±0.04 (62.34±3.31)
	10	**3**	1.80±0.06 (35.38±2.12)	0.32±0.05 (67.10±5.36)	1.48±0.01 (18.32±0.38)	0.04±0.01 (63.62±9.09)	0.56±0.03 (-)	0.09±0.02 (-)	0.76±0.04 (36.37±2.95)

Filter Media	Velocity (m/h)	Flocculant dose (mg-Fe^{3+}/L	DOC (mg/L)	HOC (mg/L)	CDOC (mg/L)	Bio-polymers (mg/L)	Humic substances (mg/L)	Building blocks (mg/L)	LMW neutrals and acids (mg/L)
Anthracite	**5**	**0**	2.19±0.03 (21.6±1.14)	0.68±0.01 (30.84±1.54)	1.51±0.02 (16.64±0.92)	0.09±0.01 (22.7±4.55)	0.40±0.01 (8.68±2.28)	0.08±0.01 (1.04±12.07)	0.96±0.01 (15.51±0.42)
		1	1.78±0.13 (36.35±4.58)	0.53±0.15 (45.87±15.49)	1.25±0.02 (31.23±1.29)	0.07±0.01 (37.58±7.92)	0.38±0.00 (12.72±1.00)	0.14±0.01 (-)	0.66±0.03 (44.26±2.18)
		3	1.68±0.08 (39.74±2.98)	0.47±0.11 (51.74±11.37)	1.21±0.03 (33.29±1.53)	0.06±0.00 (48.91±1.77)	0.41±0.06 (6.15±14.06)	0.12±0.01 (-)	0.62±0.09 (47.56±7.93)
		5	1.62±0.01 (42.10±0.47)	0.38±0.16 (61.06±16.43)	1.24±0.15 (31.90±8.12)	0.07±0.00 (34.45±3.31)	0.50±0.05 (-)	0.12±0.00 (-)	0.55±0.10 (54.03±8.53)
	10	**3**	1.59±0.17 (42.89±6.17)	0.23±0.01 (76.93±1.37)	1.37±0.16 (24.59±8.76)	0.06±0.00 (45.31±0.08)	0.55±0.05 (-)	0.08±0.01 (2.41±9.40)	0.68±0.12 (42.70±9.95)

Note: % removal is in bracket (); HOC: Hydrophobic organic carbon; CDOC: Hydrophilic organic carbon.

Table 5. 4 DOC removal and fractionation of organic matter presented in seawater and effluent from different spiral-flocculation filtration

Filter Media	Velocity (m/h)	Flocculant dose (mg-Fe^{3+}/L	DOC (mg/L)	HOC (mg/L)	CDOC (mg/L)	Bio-polymers (mg/L)	Humic substances (mg/L)	Building blocks (mg/L)	LMW neutrals and acids (mg/L)
Raw sea water			2.07	0.38	1.69	0.21	0.58	0.14	0.76
Sand	**5**	**3**	1.33±0.04 (35.73±1.98)	0.08±0.02 (80.47±3.98)	1.26±0.06 (25.52±3.34)	0.07±0.01 (67.81±3.41)	0.52±0.00 (10.40±0.18)	0.11±0.00 (18.69±0.19)	0.56±0.05 (26.59±6.35)
	10		1.26±0.13 (39.08±6.40)	0.10±0.01 (73.39±3.69)	1.16±0.12 (31.12±7.02)	0.07±0.01 (64.75±3.73)	0.51±0.02 (11.86±3.41)	0.07±0.01 (48.93±10.87)	0.51±0.08 (33.27±9.97)
Anthracite	**5**	**3**	1.22±0.04 (41.29±1.77)	0.11±0.01 (72.17±1.74)	1.11±0.03 (34.25±1.78)	0.06±0.01 (73.11±3.55)	0.50±0.03 (14.22±5.06)	0.05±0.00 (60.30±3.21)	0.51±0.00 (33.40±0.36)
	10		1.12±0.06 (45.67±2.94)	0.09±0.01 (76.88±2.68)	1.04±0.05 (38.55±3.00)	0.04±0.00 (81.13±2.35)	0.45±0.03 (21.64±5.47)	0.07±0.00 (50.97±3.16)	0.48±0.08 (37.42±10.87)

Note: % removal is in bracket (); HOC: Hydrophobic organic carbon; CDOC: Hydrophilic organic carbon

5.8Conclusion

In this study the performance of in-line flocculation and spiral-flocculation with single media filters (sand or anthracite) were investigated as pre-treatment to seawater reverse osmosis (SWRO). The efficiency was studied in terms of turbidity removal, head loss development, ultra filter modified fouling index (UF-MFI) and organic matter removal. From this study the following conclusion could be derived:

- Both in-line flocculation filtration and spiral-flocculation filtration showed good removal efficiency of solids in terms of turbidity (up to 71%).
- In-line flocculation filtration showed relatively higher headloss development than that of spiral-flocculation filtration system which was 2-3 times lower than the former. Moreover, the finer media of sand filter showed higher headloss development than coarser anthracite filter media. Thus the spiral-flocculation filtration is better in terms of lower headloss development.
- Both the filtration systems reduced the fouling propensity by 70%. The UF-MFI reduction was 63-70% for sand as medium in the presence of the flocculent whereas it was 65-76% for anthracite. In terms of fouling propensity (UF-MFI) both media behaved in a similar manner.
- Both filtration systems helped to removed more hydrophobic substance than hydrophilic substances. Both media in the presence of flocculant (3 mg/L Fe^{3+}) led to 50-65% removal of hydrophobic organics. The hydrophilic organic removal was around 30-38%. The predominant portion of hydrophilic was humic

substances which had a poor removal. In general sand filter gave a higher removal than anthracite filter.

In conclusion, the spiral-flocculation filtration process was better than the in-line flocculation filtration system in terms of on headloss development which can be an attractive pre-treatment for seawater desalination.

University of Technology, Sydney

CHAPTER 6

PERFORMANCE OF TITANIUM SALTS COMPARED TO CONVENTIONAL $FECL_3$ FOR SEAWATER REVERSE OSMOSIS PRE-TREATMENT

6. PERFORMANCE OF TITANIUM SALTS COMPARED TO CONVENTIONAL $FECL_3$ FOR SEAWATER REVERSE OSMOSIS PRE-TREATMENT

6.1 Introduction

Seawater desalination offers the potential of meeting fresh water demands. Among the desalination technologies, seawater reverse osmosis (SWRO) is widely used in desalination plants, attributed to capabilities such as ease of operation and cost-effective drinking water production (Greenlee et al., 2009). However, membrane fouling is one of the major challenges in membrane filtration processes, which is the loss of membrane permeability due to the deposition of undesirable material on a membrane surface and/or into its pores causing serious flux decline and increased salt passage. Fouling will lead to higher operational cost: higher energy demand, increase of cleanings, and reduced life time of the membrane elements. Nevertheless, a key challenge of SWRO technology is membrane fouling, specifically, organic, colloidal and bio-fouling (Jeong et al., 2016).

During seawater reverse osmosis (SWRO) operation, membrane fouling has been a major obstacle for the last four decades. Colloidal impurities, inorganic precipitates, macromolecules, and biological contaminants are the main foulants that form on the high pressure side of the membrane. The SWRO foulants consist of (i) biofoulant (48%), (ii) inorganic colloids (18%), (iii) organic compounds (15%), (iv) silicates/silicates (13%), (v) mineral deposits (6%) and (vi) coagulants (5%) (Khedr, 2000).

Pre-treatment steps widely employed in SWRO plants include disinfection, coagulation–flocculation, filtration and anti-scalant dosing. Conventional pre-treatment includes acid addition, coagulation-flocculation, disinfection and media filtration (Isaias, 2001, Bonnelye et al., 2004, Naidu et al., 2013, Chinu et al., 2010) whereas microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) are recently used as advanced pre-treatment.

Coagulation–flocculation is a well-established SWRO pre-treatment method that can remove particles, colloids and organics in water and wastewater treatment (Isaias, 2001, Chinu et al., 2010).Coagulation and flocculation constitute the backbone processes in the most water and advanced wastewater pre-treatment process. Coagulation and flocculation processes are commonly used to remove Humic Acid and colloidal particles in drinking water, seawater and wastewater. Coagulation applies chemicals to assist water particulates to adhere together. Flocculation leads to formation of larger settleable particles in the water which can be removed using simple physical methods.

Coagulation and dual media filtration reduced bacterial number in the feed by 32–100% depending on initial chemical pre-treatment of raw seawater. In most of the cases coagulation and filtration effectively removed a large portion of total bacterial mass (82%) and particulate organic matter in the feed. Bacterial growth in the feed after media filtration was significantly affected by chemical treatment of raw seawater (Al-Tisan et al., 1995). The conventional pre-treatment usually used in water treatment includes coagulation, flocculation and filtration supported by an extensive chemical treatment, including biofouling control (chlorination, dechlorination), and scaling prevention (dosing of acids or antiscalant additives).

Aluminium sulphate ($Al_2(SO_4)_3$), ferric chloride ($FeCl_3$), polyferric sulphate (PFS) and polyaluminum chloride (PACl) are some examples of commonly used coagulants for water and wastewater treatment(J. DeWolfe et al., 2003). Al-salts are suspected of being harmful to human life and living organism(Cheng and Chi, 2002). Comparatively, $FeCl_3$ as Fe-salt flocculant is more widely applied due to its better DOC removal efficiency with no significant toxicity effect (Bell-Ajy et al., 2000, Edzwald and Tobiason, 1999). However, $FeCl_3$ flocculation produces a large amount of sludge (the settled floc) that needs to be disposed(Gabelich et al., 2002).

Among different coagulants, Ferric chloride flocculation is generally used to remove suspended and dissolved organic matter which causes severe membrane fouling. This has led to the increased use of iron (Fe) salts, which have better DOC removal efficiency than Al-salts (Bell-Ajy et al., 2000, Edzwald and Tobiason, 1999). However, $FeCl_3$ flocculation produces a large amount of sludge (the settled floc) that needs to be disposed to landfill. $FeCl_3$ flocculation greatly reduced colloidal fouling propensity; moreover, the corrosive nature of Fe (III) may attack un-cathodically protected metals leading to enhanced polyamide membrane oxidation in the presence of chloramines by liberated Fe (II) ions (Gabelich et al., 2002).

The quest for new coagulants in water treatment to meet increasingly stringent guidelines has led to a renewed interest in Ti-salt. Upton and Buswell(1937) first investigated the possibility of Titanium salts as a chemical for water treatment. They reported that coagulation could be effected dosing Titanium sulphate which can be flocculated easily at lower temperature and was more efficient for colour removal as compared with alum. The Ti-salt can be used in a wide range of pH for good floc formation and the titanium flocs settle down faster.Okour et al.(2009a), Okour et al.(2009b)used TiCl4 and titanium sulphate to treat a synthetic sewage. They reported greater reductions in turbidity, UV254 absorbance and DOC, as compared with the treatment using ferric chloride and aluminium sulphate $Al_2(SO4)_3$.

Subsequently, a number of studies evaluated the performance of Ti-salts such as $TiCl_4$ and $TiSO_4$ for wastewater treatment using synthetic solutions(Shon et al., 2007, Okour et al., 2009b). Similarly, Zhao et al.(2011)used reservoir water to compare the coagulation effect of $TiCl_4$ with PACl. These studies highlighted the superior ability of Ti-salt flocculation and the additional advantage to recover TiO_2 from the sludge.

Shon et al.(2009), Shon et al.(2007) also used $TiCl_4$ as a coagulant and the Ti-salt flocculated sludge was recovered to produce valuable by-product namely TiO_2. TiO_2 was the mostly used metal oxide for environmental applications as photo catalyst, cosmetics, paints, electronic paper and solar cells. Therefore, recycling of Ti-flocculated offers a novel solution to sludge disposal from water and wastewater treatment plants associated with production of TiO_2 with a wide range of environmental applications.

All these experiments confirmed the flocculation ability of titanium salts. However, the effective pH environment of titanium flocculation was not clearly defined. Furthermore, there has not been a comparative study on the performance of Ti-salt coagulant and the other most-widely used coagulants such as $Al_2(SO4)_3$, PACl, $FeCl_3$ and PFS.

In this regard, only a few studies have evaluated the suitability of Ti–salt flocculation for SWRO pre-treatment application. For instance, Okour et al.(2009a) analysed the capacity to produce TiO_2 from sludge after Ti-salt flocculation with seawater. Jeong et al.(2013a)studied the detail organics removal of $TiCl_4$ compared to $FeCl_3$ coagulants and highlighted the efficiency of Ti-salts to reduce low molecular weight (LWM) organics in seawater. LMW organics are associated to biofouling development in SWRO membranes (Naidu et al., 2013, Jeong et al., 2013b). Nevertheless, the suitable conditions for Ti-salts performance in seawater in terms of coagulant mechanism and the influence of dose and pH have not been evaluated in detail.

In this study, flocculation performance of Ti-salt ($Ti(SO_4)_2$ and $TiCl_4$) and $FeCl_3$ coagulants in seawater were investigated in terms of turbidity, organics removal (DOC and UV-254 absorbance) and zeta potential at varying coagulant doses (1 to 30 mg/L) and pH (5-9).

6.2 Seawater and Coagulant

Seawater was collected from Cabarita, Sydney. The average UV, Turbidity, DOC, pH and Zeta potential are 0.3029-0.0515 cm^{-1}, 6.1-6.7 NTU, 1.7-2.9 mg/l, 7.8-8.0 and -1.86 mV respectively.

In this study, different doses of coagulants (1 .0 to 30.0 mg/L) were used. $FeCl_3$ stock solution (i.e. 10 g/L) was prepared by dissolving $FeCl_3$ powder in deionized (DI) water. $TiCl_4$ and $Ti(SO_4)_2$ stock solution was made by adding drop by drop of concentrated solution (>99% purity, Sigma Aldrich, Australia) to frozen cubes of deionized water to obtain a final concentration of 1% w/w.

Coagulation was conducted using conventional jar test at different coagulant concentrations (1-30 mg/l) of Ti salts and $FeCl_3$ at different pH of 5 to 9. For each jar test, six 1 litre beakers were filled with raw seawater. The pH was adjusted with 0.1 N solution of hydrochloride acid and sodium hydroxide prior to coagulant addition. The solution was subjected to rapid mixing (100 rpm) for 2 min followed by slow mixing (20 rpm) for 30 min. It was then stopped to allow the aggregated flocs to settle down for 30 min. After settling, the supernatant samples were drawn from ~5 cm below water surface without disturbing the aggregated flocs sediment in the sample for the measurements of turbidity, UV-254 absorbance and DOC, zeta potential and particle size distribution.

6.3Performance of $TiCl_4$, Ti $(SO_4)_2$ and $FeCl_3$ flocculation with seawater

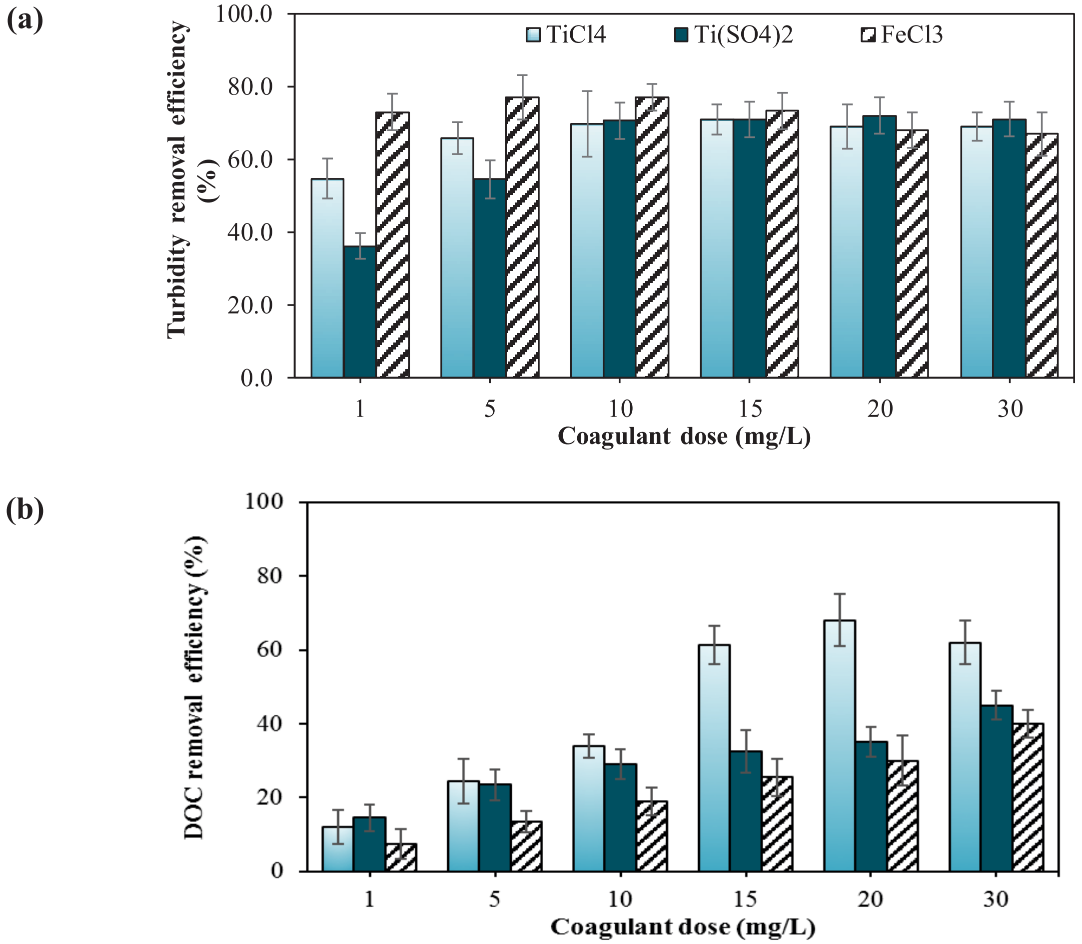
6.3.1Turbidity removal efficiency

A higher turbidity removal was observed in seawater (average pH = 8.0, turbidity = 6.67) as the coagulate dose was increased from 1 to 15 mg/L. At 15 mg/L dose, the highest turbidity removal of 71 to 73% was achieved for all the coagulated water (Figure 6.1a). At higher doses (20 to 30 mg/L), a slight reduction in turbidity removal was observed. This was especially apparent for $FeCl_3$ coagulated water. A similar pattern of increase of seawater turbidity at higher $FeCl_3$ dose was observed in other studies (Jeong et al., 2011, Chinu et al., 2010). This was attributed to the addition of $FeCl_3$ generating ferric hydroxide and ferric oxide which causes the increase in turbidity after coagulation. (Okour et al., 2009b)reported on the presence of micro-suspended flocs with Ti-salts and $FeCl_3$ in seawater, causing turbidity increment at higher doses and therefore used a hybrid flocculation followed by media filtration.Tabular data is presented at Appendix C.1 – C.3.

6.3.2 DOC and UV-254 removal efficiency

A pattern of higher DOC (Figure 6.1b) and UV-254 (Figure 6.1c) removal efficiency was observed in seawater (average pH = 8.0, DOC = 2.0 mg/L) as the coagulant doses were increased. $TiCl_4$ coagulant achieved better DOC and UV-254 removal efficiency than $Ti(SO_4)_2$ and $FeCl_3$. A 68% and 71% removal of DOC and UV-254 was obtained at 20 mg/L of $TiCl_4$ with a slight reduction (61to 65%) at 30 mg/L. Comparatively, only 34 to 40% removal of DOC and UV-254 was achieved at 30 mg/L of $FeCl_3$. In line with this

(Jeong et al., 2013a)reported on the superior removal of DOC by $TiCl_4$ compared to $FeCl_3$. The difference in DOC removal efficiency achieved by the coagulants could be attributed to the coagulant mechanism. This factor has not been reported in the context of flocculation with seawater. As such a further evaluation on the charge (zeta potential) was carried out in Section 6.4. The changes in floc zeta potential are generally utilized to analyse the coagulation mechanism in terms of charge neutralization(Ghernaout and Ghernaout, 2012).Tabular data is presented at Appendix C.1 – C.3.



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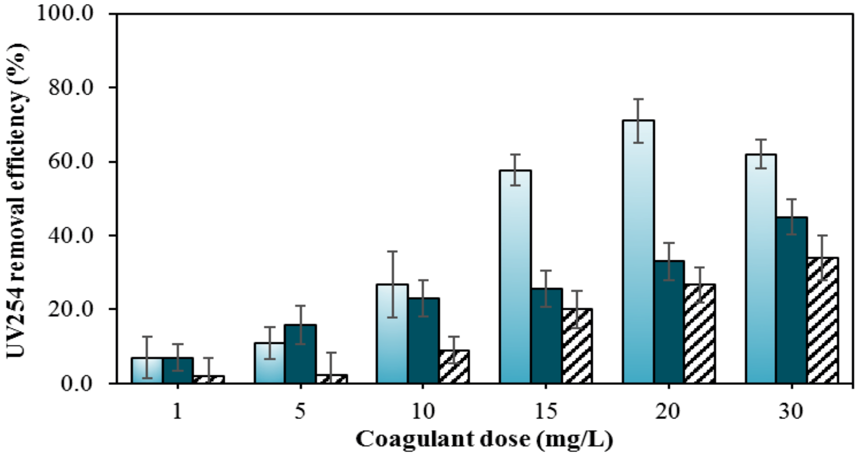

Figure 6.1 Performance of $TiCl_4$, $Ti(SO_4)_2$ and $FeCl_3$in terms of (a) turbidity, (b) UV-254 and (c) DOC removal efficiencies at different coagulant doses (seawater solution: average pH = 8.0; turbidity = 6.67 NTU; UV_{254} = 0.030 cm^{-1} and DOC = 2.1 mg/L).

6.4 Influence of charge (zeta potential)

All three coagulants showed a similar pattern of negative zeta potential values at low doses followed by a shift to positive zeta potential at high doses (Figure 6.2). However, $TiCl_4$ showed a significant shift to positive zeta potential values from 15 mg/L onwards (3.0 mV for $TiCl_4$ at 30 mg/L). Comparatively, $FeCl_3$ and $Ti(SO_4)_2$ showed relatively negative zeta potential values with a slight shift from -1.56 to -1.65 mV at 1 mg/L doses to -0.52 to -1.34 mV at 30 mg/L.

As the $TiCl_4$ coagulant dose was increased, the negative charge of colloidal particles decreased and an isoelectric point appeared at about 20 mg/L. In line with this, the highest DOC and UV-254 removal efficiencies (UV-254 of 71% and DOC of 68%) was achieved at 20 mg/L $TiCl_4$ dose. At this dose, the zeta potential was close to the isoelectric point. As the dose was further increased, a pattern of positive zeta charge became more dominant, which may have led to electrostatic repulsion between particles. This can likely explain the slightly lower DOC and UV-254 removal efficiencies at 30 mg/L (Figure 6.1b and c). This may have also caused a charge repulsion among the particles because of similar charges resulting in a lower turbidity removal efficiencies compared to $Ti(SO_4)_2$ and $FeCl_3$ (Figure 6.1a). Based on the zeta potential results, charge neutralization appears to play a major role during the flocculation process using $TiCl_4$ coagulant. Charge neutralization is a well-established coagulation mechanism(Ghernaout and Ghernaout, 2012, Sharp et al., 2006). Likewise, $Ti(SO_4)_2$ showed the same zeta potential pattern as $TiCl_4$, however with comparatively weaker charge value charges. This could be the reason for $Ti(SO_4)_2$ to display lower DOC and UV-254 removal capacity compared to $TiCl_4$.

Meanwhile, for $FeCl_3$, the low negative zeta potential values suggest that charge neutralization was rather weak for these coagulants. This may explain the lower DOC and UV-254 removal efficiency with $FeCl_3$ (34 to 40%). In this regard, previous studies of $FeCl_3$ have highlighted that charge neutralization was not the dominant coagulation mechanism of $FeCl_3$ due to its zeta potentials remaining negative. Rather precipitation entrapment as $Fe(OH)_3$ and adsorption mechanism play a more dominant role for humics removal by $FeCl_3$ at pH ranges of 7 to 9(Cheng and Chi, 2002, Ghernaout and Ghernaout, 2012). Therefore, the influence of initial solution pH on the different coagulant's removal mechanism is an important factor that must be evaluated, which is discussed in the subsequent Section 6.5. Tabular data is presented at Appendix C.1 – C.3.

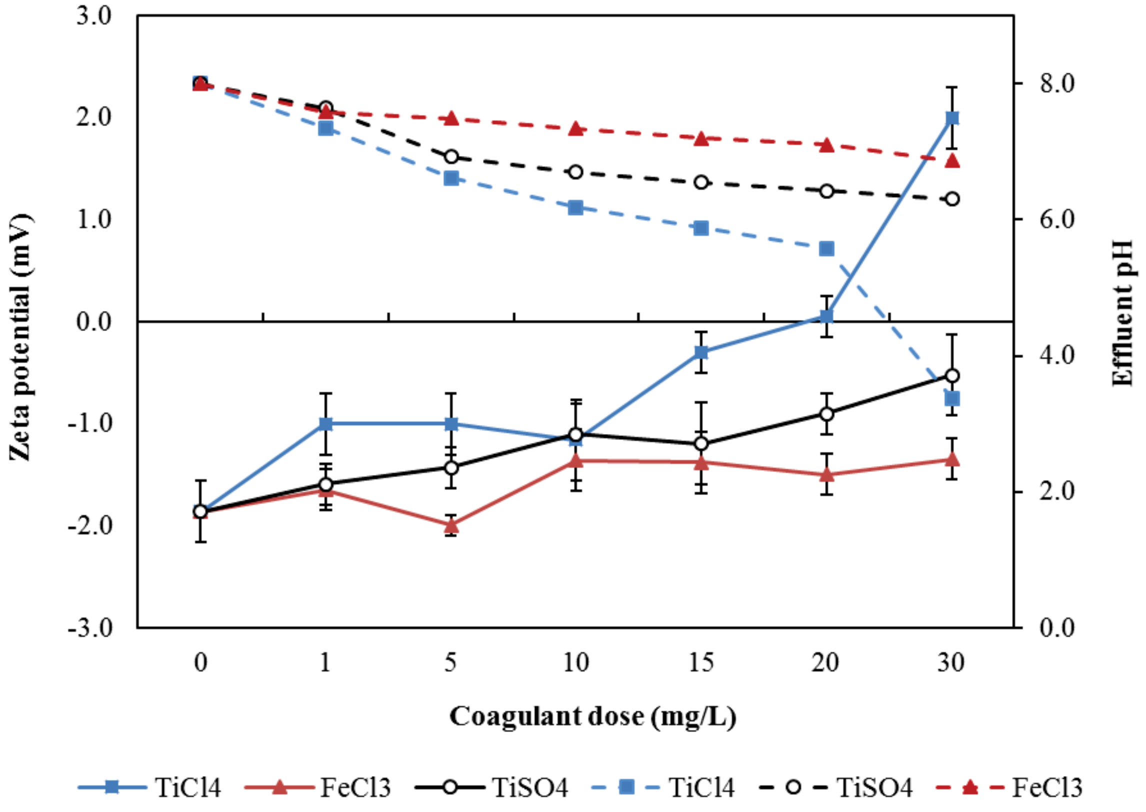

Figure 6.2 TiCl4, Ti(SO4)2 and FeCl3 zeta potential and effluent pH at different coagulant doses (seawater feed solution: average pH = 7.84 ± 0.02; zeta potential = -1.86 mV).

6.5 Influence of initial solution pH

6.5.1 Turbidity removal

Initial solution pH plays a significant role in influencing the turbidity removal pattern as shown in Figure 6.2. A pattern of increased turbidity removal with increase of pH from 5 to 7 was observed. Above pH 7, a slight decrease of turbidity was observed, which was especially apparent for $FeCl_3$. Overall, $FeCl_3$ coagulant displayed better turbidity removal to Ti-salts especially in acidic conditions. Generally, turbidity removal is associated to adsorption and physical entrapment of colloids, which appears to be the dominant coagulant mechanism of $FeCl_3$ as highlighted in Section 6.4. This could explain $FeCl_3$ coagulant's better turbidity removal capacity to Ti-salts. At higher pH (above pH 7), the decrease of turbidity removal with $FeCl_3$ might be attributed to the competition between hydroxyl ions and negatively charged colloidal particles.Tabular data is presented at Appendix C.1 – C.3.

6.5.2 DOC and UV-254removal

All coagulants showed a similar DOC and UV-254 removal pattern, by which $TiCl_4$ achieved the highest removal efficiencies at pH of 8. Meanwhile $FeCl_3$ and $Ti(SO_4)_2$ achieved the highest removal efficiencies at pH< 6 with a gradual reduction as the pH was increased. The variation of DOC and UV-254 removal performance between the coagulants indicated that pH play a significant role on the coagulant removal mechanisms. This could be related to coagulant hydrolysis as discussed in Section 6.5.3.Tabular data is presented at Appendix C.1 – C.3.

6.5.3 Zeta potential

The floc charge of $Ti(SO_4)_2$ and $FeCl_3$ showed a similar pattern, by which the zeta potential values decreased from positive to negative with increase of solution pH from 5 to 9

(Figure6.2). Meanwhile $TiCl_4$ floc charge showed an inverse pattern of increment from negative to positive zeta values from pH of 5 to 8, followed by a decrease of zeta potential value from pH 8 to 9.

Generally, at different pH ranges, floc zeta potential changes correlates with hydrolysis variation of the coagulant. Studies have shown that the hydrolysis of coagutants such as Ti-salts and $FeCl_3$ are inhibited at pH 5 resulting in dominant positive monomer hydrolysates (Zhang et al., 2008). This enables to neutralize negative charges of the particles and organic matters, and destabilize colloids. Nevertheless, when the positive charges were not enough for full charge neutralization, it would yield flocs with negative charges. This was especially apparent in the case of $TiCl_4$, by which the zeta potential remained significantly negative at pH 5 to 6. This may explain the reason for low DOC and UV-254 removal at pH 5 to 6 for $TiCl_4$ (Figure6.2). Comparatively, at these pH ranges, $Ti(SO_4)_2$ and $FeCl_3$ displayed positive zeta potential and likewise, both these coagulant achieved the highest DOC and UV-254 removal at pH 5.

For $TiCl_4$, when the pH was increased from 5 to 8, it is likely that polymeric hydrolysis with high positive charges and large surface area are formed (Zhang et al., 2008, Zhao et al., 2011a). The charge neutralization between the negative colloids and the positive coagulant resulted in high DOC and UV-254 removal (Figure6.2) and produced flocs with positive charges. At pH above 8, the dropped in zeta potential value suggest that bulk and rapid hydrolysis likely occurred, producing coagulant species with less positive charges such as $Ti(OH)_4^-$. In this condition, complete neutralization was not achieved, producing the flocs with negative charges. As a result, DOC and UV-254 removal reduced in this pH range. Similarly, for $TiSO_4$ and $FeCl_3$ at pH < 6, the reaction between the negatively charged pollutants and the positively charged coagulants generated flocs with positive charges. Above pH 6, the drop in zeta potential value suggest that bulk and rapid hydrolysis has likely occurred, producing coagulant species with less positive charges such as Fe $(OH)4^-$.Tabular data is presented at Appendix C.1 – C.3.

6.6 Conclusion

This study evaluated the performance of $TiCl_4$, $Ti(SO_4)_2$ and $FeCl_3$ coagulants with seawater. The results showed that at natural seawater solution pH of 8, $TiCl_4$ had advantages over $FeCl_3$ and $Ti(SO_4)_2$ at the same coagulant dose of 20 mg/L. $TiCl_4$ achieved higher removal of DOC and UV-254 removal. Nevertheless, $FeCl_3$ and $Ti(SO_4)_2$ showed slightly better turbidity removal. At higher coagulant dose (30 mg/L), the turbidity removal of $TiCl_4$, was especially compromised. The difference in the performance of the coagulants were associated with the coagulant mechanisms based on the floc zeta potential evaluation. The coagulant mechanisms of Ti-salts could be associated charge neutralization while $FeCl_3$ was inclined towards adsorption mechanism. A further study on the detail floc characteristics such as the dynamic variation of the floc size and breakage would be useful to establish the suitability of $TiCl_4$ as a coagulant for SWRO pre-treatment.

University of Technology, Sydney

CHAPTER 7

SUMMARY, CONCLUSION AND RECOMMENDATION

7. SUMMARY, CONCLUSION AND RECOMMENDATION

7.1 Introduction

Membrane based desalination technology such as reverse osmosis (RO) has rapidly becoming a viable and efficient alternative to conventional treatment for producing drinking water from seawater. However, membrane fouling is a major concern in reverse osmosis (RO) based seawater desalination. The fouling on RO membrane deteriorates the performance of RO membranes and increases the energy consumption and even requires more frequent replacement of the membranes. Thus, membrane fouling is a major concern in RO based seawater desalination. As a result, there is a necessity for a pre-treatment to prevent the membrane fouling, increase the life of RO membrane and to maintain a constant permeate flux. The main objective of pre-treatment system is to remove particulate, colloidal, organic, mineral and microbiological contaminants contained in raw seawater and to protect the downstream seawater reverse osmosis (SWRO) membranes from fouling. The selection of a pre-treatment method is very significant since it can influence the overall performance and determine the success or failure of the plant.

7.2 Seawater Biofiltration Pre-treatment System - Comparison of Filter Media Performance

In this part of the study, a slow filtration velocity was used to mimic the natural infiltration like a beach well system. In certain cases it may be constrained by shorter depths and residence times. By contrast, beach wells (a technology similar to river bank filtration) can provide longer travel times and distances (> 10 days and > 10 m), and can be used as a biofiltration. The beach well constitutes a natural biological filter and achieves effective removal of biodegradable organic carbon (BDOC) and assimilable organic carbon (AOC). It also reduces bio- and organic-fouling, and colloidal fouling. It has the advantage of providing a seawater intake system. It eliminates the need for complex intake structures that protrude into the sea and the problem of organism impingement/entrainment at intakes. This system appeals to large desalination plants which use open sea intake.

Presently, there is little information available for detailed particulates and organic matter removal using a long-term biofiltration with different media. Therefore, this detailed knowledge on the filtration performance would significantly contribute to a more efficient application of biofilter for seawater pre-treatment. The aim is to develop a cost effective biofilter with a high potential to remove the dissolved organic matter to prevent fouling of reverse osmosis membranes.

The laboratory based test was conducted using three deep bed filters at a slow filtration velocity using three different media: GAC, anthracite and sand respectively. Biofiltration experiment was conducted using transparent acrylic filter columns. Backwashing was applied to remove particles and excess biomass in the filter bed that cause biofilter clogging during experiments. The biofilters were run for 120 days at a slow filtration velocity of 0.12 m/hr. Biofiltration performances were evaluated in terms of turbidity, different fouling indices, and dissolved organic carbon (DOC). The performance of biofilter with different media was compared to evaluate the effectiveness of the pre-treatment to reverse osmosis (RO).

The experimental results indicated that biofiltration pre-treatment systems reduced organic matter and particulate matter. It was expected that biofilter can lower fouling to a subsequent RO process in desalination plant. In terms of DOC removal efficiency, the GAC biofilter showed higher and stable removal efficiency (41-88%), than sand biofilter (7-76%) and anthracite biofilter (3-71%). All biofilters used in this study removed most of hydrophobic organic compounds (around 94%). On the other hand, hydrophilic organic removal varied depending on the media filter. GAC biofilter removed more organic bio-polymers (51%), humic substances (75%) and building blocks (50%) compared with sand and anthracite biofilters. In terms of DOC removal efficiency, GAC biofilter had better and consistent removal efficiency compared to sand and anthracite. The biofiltration performance of GAC biofilter was significantly better than that of conventional media such as sand and anthracite. Thus the GAC filter was the best medium to provide the lowest fouling potential as it showed the highest removal efficiency of DOC, including hydrophilic, humic, building blocks and biopolymer. The lowest efficiency was found for anthracite medium. The removal efficiencies of turbidity by the three biofilters were similar with low headloss development. The fouling potential of treated seawater (filtrate) was evaluated using three different fouling indices such as microfiltration (MF-MFI), ultrafiltration (UF-MFI) and microfiltration at a cross flow (CFMF-MFI).The analyses of three different fouling indices showed that the reduction of fouling potential was in following order GAC>sand>anthracite. All the biofilters had almost similar turbidity removal efficiency. The results measured by various fouling indices showed that the filtrate (effluent) from the GAC biofilter had lower fouling potential compared to sand and anthracite biofilters. Thus the GAC filter was the best medium to provide the lowest fouling potential as it showed the highest removal efficiency of DOC, including hydrophilic, humic, building blocks and biopolymer. The lowest efficiency was found for anthracite medium.

7.3 A comparative study on in-line flocculation and spiral-flocculation followed by media filtration as a pre-treatment of seawater

Pre-treatment such as bio-filtration, coagulation, adsorption, in-line flocculation, filtration and ozonation have been used to remove the natural organic matter (NOM) and to alleviate fouling. Flocculation, coagulation and sedimentation have becoming important unit processes because of their low cost and easy application in the treatment of water and wastewater in conjunction with convectional mechanical, biological and physio-chemical plants.

Jar test has been used for since a long time and it is an effective method to determine the suitability for different types and amount of flocculants on coagulation/flocculation and sedimentation process for raw water. Despite its popularity, the jar test has a number of disadvantages. The jar test is not standardized and as result there are difficulties in making comparisons. Full scale plants are flow through units; therefore the results obtained from the jar test, which are batch tests, may not correspond with the results obtained from full scale plants. Spiral flocculator is more rapid and uses a smaller volume of water than jar tests in providing information on optimum chemical dosage. It provides results which are more closely related to flocculation performance in an actual flocculation plant. Previous studies it is also found that in-line flocculation filtration effectively reduced membrane fouling.

In this study in-line flocculation and spiral-flocculation followed by media filtration (sand or anthracite) was investigated as a pre-treatment to sea water RO. Here we refer to rapid mixing followed by media filtration (sand or anthracite) as in-line flocculation filtration; and rapid mixing with spiral-flocculation and then by media filtration as spiral-flocculation filtration. A comparison of filter performances was made between sand and anthracite medium filters.

Short term in-line flocculation filtration and spiral-flocculation filtration was conducted. The filter columns were made of transparent acrylic filter columns and prepared filter media (anthracite or sand) were packed in the columns. Seawater was pumped through and coagulant was added using a dosing pump. The flocculants used was $Fe_2(SO_4)_3$ and was used for uniform mixing of seawater with coagulant for 10 seconds.

In the case of in-line flocculation filtration system, the seawater was passed through the media filter just after rapid mixing of raw seawater with flocculants for 10 seconds. The flocculation and solid liquid separation occur in the filter. In the case of spiral-flocculation filtration, after the rapid mixing of seawater with flocculants, it was then passed through the spiral-flocculation. Seawater after the flocculation through the spiral-flocculation was passed through a filter bed with down flow filtration. The efficiencies of these pre-treatments were carried out in terms of ultra-filtration–modified fouling index (UF-MFI), head loss development and turbidity and organic matter removal.

The experimental results indicated that both in-line flocculation filtration and spiral-flocculation filtration showed good removal efficiency of solids in terms of turbidity (up to 71%). In-line flocculation filtration showed relatively higher headloss development than that of spiral-flocculation filtration system which was 2-3 times lower than the spiral-flocculation filtration. Moreover, the finer media of sand filter showed higher headloss development than coarser anthracite filter media. Thus the spiral-flocculation filtration is better in terms of lower headloss development. Both the filtration systems reduced the fouling propensity by 70%. The UF-MFI reduction was 63-70% for sand as medium in the presence of the flocculent whereas it was 65-76% for anthracite. In terms of fouling propensity (UF-MFI), both media behaved in a similar manner. These filtration systems helped to reduce dissolved organic carbon (DOC) about 30-45%. Both filtration systems helped to remove more hydrophobic substance than hydrophilic substances. Both media in the presence of flocculent (3 mg/L Fe^{3+}) led to 50-65% removal of hydrophobic organics. The hydrophilic organic removal was around 30-38%. Among the hydrophilic compounds, the removal of biopolymer and lower molecular weight neutrals and acid were higher than humic substances and building blocks. The predominant portion of hydrophilic was humic substances which had a poor removal. In general sand filter gave a higher removal than anthracite filter. In conclusion, the spiral-flocculation filtration process was better than the in-line flocculation filtration system in terms of on headloss development which can be an attractive pre-treatment for seawater desalination.

7.4 Performance of titanium salts compared to conventional $FeCl_3$ for seawater reverse osmosis pre-treatment

Coagulation–flocculation is a well-established SWRO pre-treatment method that can remove particles, colloids and organics in water and wastewater treatment. Coagulation and flocculation processes are commonly used to remove Humic Acid and colloidal particles in drinking water, seawater and wastewater. The conventional pre-treatment usually used in water treatment includes coagulation, flocculation and filtration supported by an extensive chemical treatment, including biofouling control (chlorination, dechlorination), and scaling prevention (dosing of acids or antiscalant additives).

The quest for new coagulants in water treatment to meet increasingly stringent guidelines has led to a renewed interest in Ti-salt. Past studies reported that coagulation could be effected dosing Titanium sulphate which can be flocculated easily at lower temperature and was more efficient for colour removal as compared with alum. The Ti-salt can be used in a wide range of pH for good floc formation and the titanium flocs settle down faster. Previous studies used TiCl4 and titanium sulphate to treat a synthetic sewage. They reported greater reductions in turbidity, UV254 absorbance and DOC, as compared with the treatment using ferric chloride and aluminium sulphate $Al_2(SO4)_3$.

All these experiments confirmed the flocculation ability of titanium salts. However, the effective pH environment of titanium flocculation was not clearly defined. Furthermore, there has not been a comparative study on the performance of Ti-salt coagulant and the other most-widely used coagulants such as $Al_2(SO4)_3$, PACl, $FeCl_3$ and PFS. In this regard, only a few studies have evaluated the suitability of Ti–salt flocculation for SWRO pre-treatment application. The suitable conditions for Ti-salts performance in seawater in terms of coagulant mechanism and the influence of dose and pH have not been evaluated in detail.

In this part of the study, flocculation performance of Ti-salt ($Ti(SO_4)_2$ and $TiCl_4$) and $FeCl_3$ coagulants in seawater were investigated in terms of turbidity, organics removal (DOC and UV-254 absorbance) and zeta potential at varying coagulant doses (1 to 30 mg/L) and pH (5-9).

Coagulation was conducted using conventional jar test at different coagulant concentrations (1-30 mg/l) of Ti salts and $FeCl_3$ at different pH of 5 to 9. For each jar test, six 1 litre beakers were filled with raw seawater. The pH was adjusted with 0.1 N solution of hydrochloride acid and sodium hydroxide prior to coagulant addition. The solution was subjected to rapid mixing (100 rpm) for 2 min followed by slow mixing (20 rpm) for 30 min. It was then stopped to allow the aggregated flocs to settle down for 30 min. After settling, the supernatant samples were drawn from ~5 cm below water surface without disturbing the aggregated flocs sediment in the sample for the measurements of turbidity, UV-254 absorbance and DOC, zeta potential and particle size distribution.

The two Ti based coagulants were compared with commonly used ferric chloride ($FeCl_3$) coagulant in desalination plants. The results showed that at pH of 8.0 (similar to seawater pH), $TiCl_4$ had advantages over $FeCl_3$ and $Ti(SO_4)_2$ at the same coagulant dose of 20 mg/L. Under this condition, $TiCl_4$ achieved ~70% DOC and UV-254 removal. This was approximately two times higher than $FeCl_3$ and $Ti(SO_4)_2$. Nevertheless, $FeCl_3$ and $Ti(SO_4)_2$ showed better turbidity removal. At higher coagulant dose (30 mg/L), the turbidity removal of $TiCl_4$, was especially compromised. The differences in the performance of the coagulants were associated with the coagulant mechanisms based on the floc zeta potential evaluation. The coagulant mechanisms of Ti-salts could be associated to charge neutralization while $FeCl_3$was inclined towards adsorption mechanism.

Based on the experiments, it was found that biofiltration, line flocculation and spiral-flocculation followed by media filtration, coagulation and flocculation are appropriate pre-treatment before RO. In particular, Biofilter showed to a consistent removal of organic matter over a long period of time.

7.5 Recommendation of future research

The main objective of the study was to assess the different pre-treatment system to reduce membrane fouling in RO desalination projects. Optimisation and comparison of different pre-treatment systems was conducted to remove organic matter, reduce the fouling potential and particulate matter of sea water by using different pre-treatment methods. The research work involved extensive experiments both in laboratory and in the field to verify the validity of pre-treatment reduced membrane fouling .Based on the findings of this study, the following recommendations are made for further study on pre - treatment of seawater

- Pilot scale experiments to test the effectiveness of spiral flocculation followed by media filtration at desalination plants.
- Study on the detail floc characteristics such as the dynamic variation of the floc size and breakage would be useful to establish the suitability of $TiCl_4$ as a coagulant for SWRO pre-treatment.

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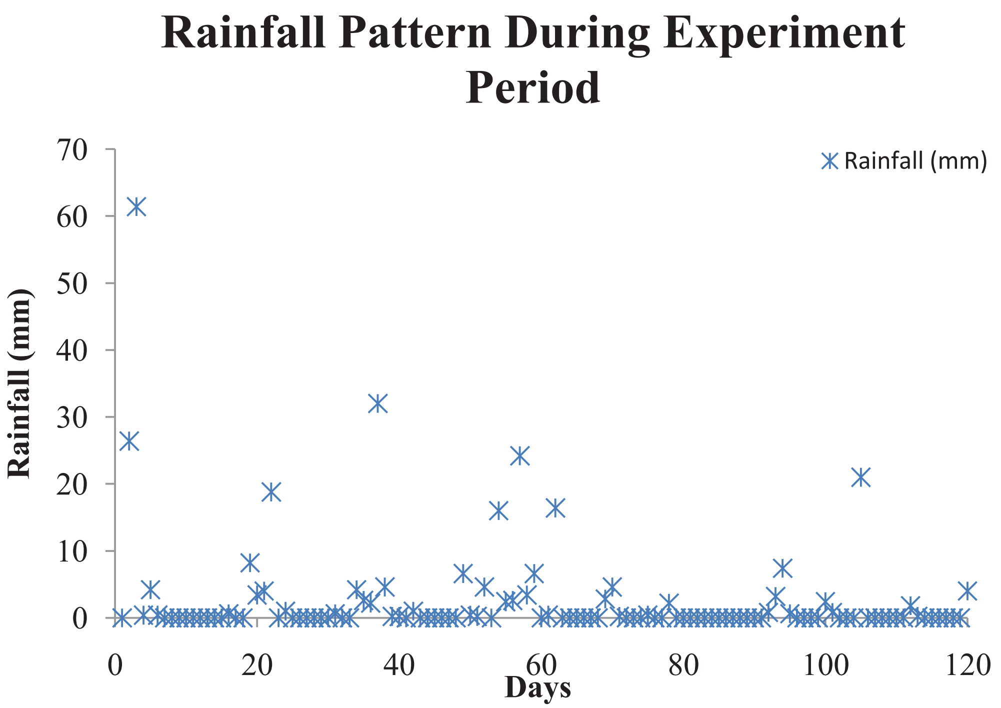
APPENDIX – A: SEAWATER BIOFILTRATION PRE – TREATMENT SYSTEM – COMPARISON ON FILTER MEDIA PERFORMANCE

A.1 Efficiency in terms of turbidity and pH removal

No of	Turbidity				pH			
Day	Anthracite	Sand	GAC	Seawater	Anthracite	Sand	GAC	Seawater
1	0.30	0.35	0.41	0.52	6.30	6.28	5.98	6.82
3	0.27	0.32	0.40	0.56	6.76	6.64	5.95	6.89
4	0.22	0.24	0.22	0.54	6.90	6.75	6.05	6.85
5	0.21	0.26	0.39	0.62	6.90	6.72	6.22	6.81
6	0.38	0.33	0.24	0.63	6.76	6.61	6.04	6.86
7	0.27	0.20	0.21	0.42	6.43	6.69	6.31	6.73
11	0.30	0.22	0.32	0.50	8.17	8.07	8.09	8.11
13	0.30	0.33	0.38	0.60	8.16	8.27	7.84	8.01
18	0.26	0.20	0.30	0.41	8.15	8.33	7.97	8.38
21	0.30	0.20	0.25	0.42	8.13	7.78	7.58	8.17
25	0.25	0.32	0.24	0.53	8.31	8.22	7.95	8.10
29	0.29	0.30	0.30	0.46	8.35	8.33	7.86	8.35
33	0.30	0.31	0.30	0.60	8.50	8.12	7.85	8.57
36	0.22	0.24	0.30	0.63	8.48	8.13	8.20	8.39
39	0.31	0.30	0.27	0.64	8.43	8.39	8.38	8.45
42	0.26	0.39	0.27	0.48	8.42	8.34	8.17	8.18
47	0.22	0.36	0.35	0.78	8.49	8.38	8.32	8.43
50	0.32	0.26	0.21	0.59	8.49	8.46	8.33	8.42
54	0.20	0.19	0.16	0.60	8.40	8.32	8.24	8.34
57	0.20	0.36	0.27	0.45	7.68	7.85	7.33	7.90
60	0.30	0.22	0.40	0.50	7.99	7.76	7.60	7.70
64	0.38	0.40	0.40	0.56	8.10	7.76	7.28	8.14
67	0.21	0.22	0.21	0.60	8.27	8.04	7.90	8.31
71	0.34	0.34	0.36	0.45	8.35	8.34	8.05	8.32
75	0.19	0.20	0.26	0.45	8.39	8.34	8.03	8.23
78	0.29	0.38	0.30	0.43	7.94	7.90	7.74	7.57
81	0.20	0.22	0.33	0.40	8.10	8.03	7.56	7.67
85	0.21	0.24	0.31	0.40	8.21	8.14	7.70	7.94

No of Day	Turbidity				pH			
	Anthracite	Sand	GAC	Seawater	Anthracite	Sand	GAC	Seawater
88	0.19	0.26	0.26	0.41	8.20	8.23	7.70	7.98
92	0.19	0.28	0.32	0.50	7.74	7.27	7.34	7.39
95	0.20	0.16	0.25	0.47	8.15	8.06	7.50	7.88
98	0.42	0.20	0.37	0.57	7.90	7.90	7.34	7.72
106	0.41	0.22	0.34	0.45	7.99	8.14	7.76	8.15
110	0.43	0.40	0.39	0.67	8.68	8.14	7.83	8.22
120	0.40	0.40	0.27	0.50	8.36	7.95	7.80	8.30

A.2 Rainfall Pattern During Experiment



A.3 Efficiency in terms of MF-MFI removal

	MF-MFI s/L^2			
Day	**Anthracite**	**Sand**	**GAC**	**Seawater**
13	8.203	4.48	2.34	9.74
25	3.66	5.93	2.37	7.09
33	2.11	2.43	1.72	4.18
42	5.80	4.68	1.72	9.74
50	5.80	3.46	1.84	7.09
57	5.80	3.46	1.62	7.09
64	4.36	2.32	1.24	7.09
71	3.29	2.79	1.24	7.09
78	5.91	5.00	3.72	7.09
85	3.28	1.95	1.34	4.18
95	6.44	5.36	2.49	9.74
110	3.28	2.52	1.57	4.18
120	7.70	4.45	1.81	9.74

A.4 Efficiency in terms of UF-MFI removal

	UF-MFI s/L^2			
Day	**Anthracite**	**Sand**	**GAC**	**Seawater**
2	2452	6634	4825	9553
95	7782	2266	1531	9838
98	1504	3465	3582	9838
106	3263	4787	2611	10928
110	5226	4660	2794	10928
120	8055	6522	2056	9838

A.5 Efficiency in terms of CFMF-MFI removal

	CFMF-MFI s/L^2			
Day	**Anthracite**	**Sand**	**GAC**	**Seawater**
21	4.49	10.00	6.00	49.60
25	9.47	7.89	5.26	49.60
33	17.96	14.99	12.00	49.60
42	20.00	18.5	11.00	56.77
50	15.00	7.561	4.27	56.77

A.6 Efficiency in terms of DOC removal

	DOC mg/l				DOC Removal (%)		
Day	Anthracite	Sand	GAC	Seawater	Anthracite	Sand	GAC
1	1.62	1.34	1.07	1.81	10.82	26.12	41.03
6	0.64	0.55	0.43	0.79	19.04	31.27	45.52
13	1.16	0.92	0.63	1.81	35.93	49.09	64.99
21	0.95	0.66	0.36	0.99	3.94	33.00	63.27
25	1.26	0.68	0.27	1.38	9.26	51.12	80.40
33	0.50	0.42	0.27	0.54	7.45	22.72	49.53
42	0.60	0.81	0.29	1.24	51.37	34.54	77.05
50	0.51	0.64	0.21	1.21	57.79	47.57	82.44
57	0.44	0.78	0.29	0.83	47.29	6.74	65.46
64	0.76	0.58	0.44	1.08	29.54	45.90	59.17
71	0.51	0.66	0.37	0.83	38.99	20.10	55.35
78	0.52	0.68	0.22	1.81	71.45	62.51	88.02
85	0.53	0.88	0.38	1.38	61.82	36.23	72.52
92	0.66	0.71	0.29	1.09	39.82	35.05	73.12
98	0.90	0.77	0.27	1.09	17.80	28.99	75.14
106	0.75	0.72	0.24	1.09	30.83	33.94	77.63
110	0.56	0.65	0.29	0.86	34.59	24.28	65.80
120	0.56	0.18	0.10	0.78	28.22	76.43	86.68

A.7 Removal of different organic fractions by different media biofilters

Days	Sample	DOC Dissolved mg/l,%DOC	HOC Hydrophobic mg/l,%DOC	CDOC Hydrophilic mg/l,%DOC	Biopolymers mg/l,%DOC	Humic substance mg/l,%DOC	Building blocks mg/l,%DOC	LMW neutrals mg/l,%DOC	LMW acids mg/l,%DOC
1	Seawater	1.811	0.105	1.706	n.q.	0.164	1.521	n.q.	0.021
		100%	5.8%	94.2%	--	9.0%	84.0%	--	1.2%
	Anthracite	1.615	1.045	0.570	0.005	0.190	0.375	n.q.	n.q.
		100.0%	64.7%	35.3%	0.3%	11.8%	23.2%	--	
	Sand	1.338	0.465	0.872	0.043	0.640	0.189	n.q.	n.q.
		100%	34.8%	65.2%	3.2%	47.9%	14.1%	--	
	GAC	1.068	0.861	0.207	0.132	0.042	0.025	n.q.	0.008
		100%	80.6%	19.4%	1230.0%	390.0%	2.4%	--	0.7%
6	Seawater	0.793	0.340	0.454	0.017	0.354	0.083	n.q.	n.q.
		100%	42.8%	57.2%	2.2%	44.6%	10.4%	--	--
	Anthracite	0.642	0.199	0.442	0.009	0.292	0.142	n.q.	n.q.
		100%	31.1%	68.9%	1.3%	45.5%	22.1%	--	--
	Sand	0.545	0.015	0.529	0.009	0.302	0.218	n.q.	n.q.
		100%	2.8%	97.2%	1.7%	55.5%	40.0%	--	--
	GAC	0.432	0.319	0.113	0.009	0.012	n.q.	n.q.	0.004
		100%	73.8%	26.2%	22.8%	2.7%	--	--	0.9%

Days	Sample	DOC Dissolved mg/l,%DOC	HOC Hydrophobic mg/l,%DOC	CDOC Hydrophilic mg/l,%DOC	Biopolymers mg/l,%DOC	Humic substance mg/l,%DOC	Building blocks mg/l,%DOC	LMW neutrals mg/l,%DOC	LMW acids mg/l,%DOC
13	Seawater	1.811	0.105	1.706	n.q.	0.164	1.521	n.q.	0.021
		100%	5.8%	94.2%	--	9.0%	84.0%	--	1.2%
	Anthracite	1.160	0.395	0.765	0.347	0.292	0.066	n.q.	0.060
		100%	34.1%	65.9%	29.9%	25.2%	5.7%	--	5.1%
	Sand	0.922	0.381	0.541	0.109	0.330	0.098	n.q.	0.003
		100%	41.3%	58.7%	11.9%	35.8%	10.7%	--	0.3%
	GAC	0.634	0.442	0.192	0.167	0.025	n.q.	n.q.	0.003
		100%	69.7%	30.3%	26.4%	3.9%	--	--	0.5%
21	Seawater	0.991	0.258	0.733	0.275	0.350	0.096	n.q.	0.011
		100%	26.0%	74.0%	27.8%	35.3%	9.7%	--	1.1%
	Anthracite	0.952	0.291	0.661	0.213	0.325	0.122	n.q.	0.001
		100%	30.6%	69.4%	22.4%	34.1%	12.8%	--	0.1%
	Sand	0.664	0.263	0.401	0.007	0.259	0.135	n.q.	n.q.
		100%	39.6%	60.4%	1.1%	39.0%	20.3%	--	--
	GAC	0.364	0.316	0.048	0.017	0.029	0.002	n.q.	n.q.
		100%	86.9%	13.1%	4.6%	8.0%	0.5%	--	--

Days	Sample	DOC Dissolved mg/l,%DOC	HOC Hydrophobic mg/l,%DOC	CDOC Hydrophilic mg/l,%DOC	Biopolymers mg/l,%DOC	Humic substance mg/l,%DOC	Building blocks mg/l,%DOC	LMW neutrals mg/l,%DOC	LMW acids mg/l,%DOC
25	Seawater	1.383	0.914	0.469	n.q.	0.281	0.181	n.q.	0.006
		100%	66.1%	33.9%	--	20.3%	13.1%	--	0.5%
	Anthracite	1.255	0.384	0.872	0.029	0.512	0.330	n.q.	n.q.
		100%	30.6%	69.4%	2.3%	40.8%	26.3%	--	--
	Sand	0.676	0.245	0.431	0.012	0.298	0.117	n.q.	0.004
		100%	36.3%	63.7%	1.8%	44.0%	17.3%	--	0.6%
	GAC	0.271	0.209	0.062	0.012	0.038	0.005	n.q.	0.006
		100%	77.3%	22.7%	4.5%	14.1%	2.0%	--	2.2%
33	Seawater	0.54	0.08	0.45	0.01	0.30	0.14	n.q.	n.q.
		100%	15.4%	84.6%	1.6%	56.6%	26.4%	--	--
	Anthracite	0.497	0.082	0.415	0.004	0.244	0.162	n.q.	0.006
		100%	16.4%	83.6%	0.8%	49.0%	32.6%	--	1.2%
	Sand	0.415	0.037	0.377	n.q.	0.012	0.317	0.031	0.017
		100%	9.0%	91.0%	--	2.9%	76.4%	7.5%	4.1%
	GAC	0.271	0.209	0.062	0.012	0.038	0.005	n.q.	0.006
		100%	77.3%	22.7%	4.5%	14.1%	2.0%	--	2.2%

Days	Sample	DOC Dissolved mg/l,%DOC	HOC Hydrophobic mg/l,%DOC	CDOC Hydrophilic mg/l,%DOC	Biopolymers mg/l,%DOC	Humic substance mg/l,%DOC	Building blocks mg/l,%DOC	LMW neutrals mg/l,%DOC	LMW acids mg/l,%DOC
42	Seawater	1.242	0.384	0.858	0.026	0.316	n.q.	n.q.	0.874
		100%	30.9%	69.1%	2.1%	25.4%	--	--	70.3%
	Anthracite	0.604	0.128	0.476	0.013	0.390	0.073	n.q.	n.q.
		100%	21.3%	78.7%	2.1%	64.5%	12.1%	--	--
	Sand	0.813	0.306	0.508	0.043	0.381	0.084	n.q.	n.q.
		100%	37.6%	62.4%	5.3%	46.8%	10.3%	--	--
	GAC	0.285	0.198	0.087	0.013	0.049	0.024	n.q.	n.q.
		100%	69.3%	30.7%	4.6%	17.3%	8.5%	--	--
50	Seawater	1.213	0.849	0.364	n.q.	0.281	0.083	n.q.	n.q.
		100%	70.0%	30.0%	--	23.1%	6.8%	--	--
	Anthracite	0.512	0.034	0.478	n.q.	0.410	0.068	n.q.	n.q.
		100%	6.6%	93.4%	--	80.1%	13.3%	--	--
	Sand	0.636	0.201	0.434	0.001	0.195	0.229	n.q.	n.q.
		100%	31.7%	68.3%	1.6%	30.7%	36.0%	--	--
	GAC	0.213	0.138	0.076	0.004	0.040	0.031	n.q.	n.q.
		100%	64.5%	35.5%	2.1%	18.9%	14.4%	--	--

Days	Sample	DOC Dissolved mg/l,%DOC	HOC Hydrophobic mg/l,%DOC	CDOC Hydrophilic mg/l,%DOC	Biopolymers mg/l,%DOC	Humic substance mg/l,%DOC	Building blocks mg/l,%DOC	LMW neutrals mg/l,%DOC	LMW acids mg/l,%DOC
57	Seawater	0.831	0.314	0.517	0.136	0.287	0.088	n.q.	0.006
		100%	37.8%	62.2%	16.3%	34.5%	10.6%	--	0.7%
	Anthracite	0.438	0.024	0.414	n.q.	0.276	0.138	n.q.	n.q.
		100%	5.5%	94.5%	--	63.0%	31.5%	--	--
	Sand	0.775	0.261	0.515	0.108	0.299	0.108	n.q.	n.q.
		100%	33.6%	66.4%	13.9%	38.6%	13.9%	--	--
	GAC	0.287	0.232	0.055	0.004	0.045	0.004	n.q.	0.002
		100%	80.8%	19.2%	1.6%	15.7%	1.4%	--	0.5%
64	Seawater	1.08	0.575	0.505	0.089	0.223	0.192	n.q.	n.q.
		100%	53.26%	46.74%	8.26%	20.63%	18%	--	--
	Anthracite	0.761	0.212	0.549	0.065	0.320	0.164	n.q.	n.q.
		100%	27.9%	72.1%	8.6%	42.0%	21.5%	--	--
	Sand	0.584	0.057	0.527	0.036	0.366	0.088	n.q.	0.038
		100%	9.8%	90.2%	6.2%	62.6%	15.0%	--	6.4%
	GAC	0.441	0.217	0.224	0.073	0.097	0.052	0.002	n.q.
		100%	49.1%	50.9%	16.6%	22.0%	11.7%	0.4%	--

Days	Sample	DOC Dissolved mg/l,%DOC	HOC Hydrophobic mg/l,%DOC	CDOC Hydrophilic mg/l,%DOC	Biopolymers mg/l,%DOC	Humic substance mg/l,%DOC	Building blocks mg/l,%DOC	LMW neutrals mg/l,%DOC	LMW acids mg/l,%DOC
71	Seawater	0.831	0.314	0.517	0.136	0.287	0.088	n.q.	0.006
		100%	37.8%	62.2%	16.3%	34.5%	10.6%	--	0.7%
	Anthracite	0.507	0.028	0.479	0.003	0.395	0.081	n.q.	n.q.
		100%	5.5%	94.5%	0.6%	77.9%	16.0%	--	--
	Sand	0.664	0.144	0.519	0.031	0.381	0.107	n.q.	n.q.
		100%	21.8%	78.2%	4.7%	57.4%	16.0%	--	--
	GAC	0.371	0.207	0.164	0.057	0.090	0.016	n.q.	0.001
		100%	55.8%	44.2%	15.3%	24.2%	4.4%	--	0.3%
78	Seawater	1.811	0.105	1.706	n.q.	0.164	1.521	n.q.	0.021
		100%	5.8%	94.2%	--	9.0%	84.0%	--	1.2%
	Anthracite	0.517	0.018	0.500	n.q.	0.426	0.072	n.q.	0.001
		100%	3.4%	96.6%	--	82.4%	13.9%	--	0.2%
	Sand	0.679	0.154	0.525	0.024	0.393	0.108	n.q.	n.q.
		100%	22.7%	77.3%	3.5%	57.9%	15.9%	--	--
	GAC	0.217	0.120	0.098	n.q.	0.090	0.006	n.q.	0.006
		100%	55.0%	45.0%	--	41.3%	2.9%	--	0.5%

Days	Sample	DOC Dissolved mg/l,%DOC	HOC Hydrophobic mg/l,%DOC	CDOC Hydrophilic mg/l,%DOC	Biopolymers mg/l,%DOC	Humic substance mg/l,%DOC	Building blocks mg/l,%DOC	LMW neutrals mg/l,%DOC	LMW acids mg/l,%DOC
85	Seawater	1.383	0.914	0.469	n.q.	0.281	0.181	n.q.	0.006
		100%	66.1%	33.9%	--	20.3%	13.1%	--	0.5%
	Anthracite	0.528	0.046	0.482	n.q.	0.414	0.067	n.q.	n.q.
		100%	8.8%	91.2%	--	78.4%	12.7%	--	--
	Sand	0.882	0.356	0.526	0.027	0.379	0.118	n.q.	0.001
		100%	40.4%	59.6%	3.1%	42.9%	13.4%	--	0.1%
	GAC	0.380	0.229	0.151	0.045	0.086	0.018	n.q.	0.002
		100%	60.3%	39.7%	11.9%	22.7%	4.6%	--	0.5%
92	Seawater	1.090	0.548	0.542	n.q.	0.311	0.231	n.q.	n.q.
		100%	50.3%	49.7%	--	28.5%	21.2%	--	--
	Anthracite	0.656	0.130	0.527	0.002	0.428	0.096	n.q.	n.q.
		100%	19.8%	80.2%	0.3%	65.2%	14.7%	--	--
	Sand	0.708	0.165	0.544	0.059	0.365	0.120	n.q.	n.q.
		100%	23.2%	76.8%	8.3%	51.5%	16.9%	--	--
	GAC	0.293	0.16	0.13	0.03	0.08	0.02	n.q.	0.00
		100%	55.7%	44.3%	8.6%	27.4%	7.5%	--	0.8%

Days	**Sample**	**DOC** **Dissolved** **mg/l,%DOC**	**HOC** **Hydrophobic** **mg/l,%DOC**	**CDOC** **Hydrophilic** **mg/l,%DOC**	**Biopolymers** **mg/l,%DOC**	**Humic substance** **mg/l,%DOC**	**Building blocks** **mg/l,%DOC**	**LMW neutrals** **mg/l,%DOC**	**LMW acids** **mg/l,%DOC**
98	Seawater	1.090	0.548	0.542	n.q.	0.311	0.231	n.q.	n.q.
		100%	50.3%	49.7%	--	28.5%	21.2%	--	--
	Anthracite	0.896	0.357	0.539	0.027	0.356	0.152	n.q.	0.003
		100%	39.9%	60.1%	3.1%	39.8%	17.0%	--	0.3%
	Sand	0.774	0.251	0.522	0.037	0.418	0.067	n.q.	n.q.
		100%	32.5%	67.5%	4.8%	54.0%	8.7%	--	--
	GAC	0.271	0.128	0.144	0.028	0.086	0.028	n.q.	0.001
		100%	47.1%	52.9%	10.3%	31.7%	10.5%	--	0.4%
106	Seawater	1.090	0.548	0.542	n.q.	0.311	0.231	n.q.	n.q.
		100%	50.3%	49.7%	--	28.5%	21.2%	--	--
	Anthracite	0.754	0.187	0.567	0.013	0.383	0.171	n.q.	n.q.
		100%	24.8%	75.2%	1.8%	50.8%	22.7%	--	--
	Sand	0.720	0.170	0.550	0.048	0.329	0.172	n.q.	n.q.
		100%	23.6%	76.4%	6.7%	45.6%	23.9%	--	--
	GAC	0.244	0.053	0.191	0.070	0.110	0.007	n.q.	0.003
		100%	21.9%	78.1%	28.7%	45.0%	3.1%	--	1.4%

Days	Sample	DOC Dissolved mg/l,%DOC	HOC Hydrophobic mg/l,%DOC	CDOC Hydrophilic mg/l,%DOC	Biopolymers mg/l,%DOC	Humic substance mg/l,%DOC	Building blocks mg/l,%DOC	LMW neutrals mg/l,%DOC	LMW acids mg/l,%DOC
110	Seawater	0.858	0.226	0.631	0.072	0.314	0.177	0.039	0.029
		100%	26.4%	73.6%	8.4%	36.5%	20.6%	4.6%	3.4%
	Anthracite	0.561	0.048	0.513	0.037	0.328	0.132	n.q.	0.016
		100%	8.6%	91.4%	6.6%	58.5%	23.5%	--	2.8%
	Sand	0.650	0.135	0.515	0.078	0.263	0.145	0.012	0.017
		100%	20.8%	79.2%	11.9%	40.5%	22.4%	1.8%	2.6%
	GAC	0.293	0.068	0.225	0.067	0.131	0.021	n.q.	0.007
		100%	23.2%	76.8%	22.7%	44.7%	7.0%	--	2.3%
120	Seawater	0.782	0.189	0.593	0.034	0.345	0.189	0.013	0.011
		100%	24.2%	75.8%	4.4%	44.1%	24.2%	1.7%	1.4%
	Anthracite	0.561	0.048	0.513	0.037	0.328	0.132	n.q.	0.016
		100%	8.6%	91.4%	6.6%	58.5%	23.5%	--	2.8%
	Sand	0.184	0.053	0.131	n.q.	0.118	0.012	n.q.	n.q.
		100%	29.0%	71.0%	--	64.1%	6.7%	--	--
	GAC	0.104	0.062	0.042	n.q.	0.038	n.q.	n.q.	0.008
		100%	60.0%	40.0%	--	36.6%	--	--	7.2%

A.8 MF-MFI sample data for Seawater

time t (sec)	volume (ml)	volume v (ltr)	t/v
0	0		
2	23.4	0.0234	85.470085
4	62.4	0.0624	64.102564
6	101.3	0.1013	59.23001
8	139.9	0.1399	57.183703
10	178.2	0.1782	56.116723
12	216.2	0.2162	55.504163
14	253.8	0.2538	55.161545
16	291.2	0.2912	54.945055
18	328.4	0.3284	54.811206
20	365.4	0.3654	54.734537
22	402.2	0.4022	54.699155
24	438.7	0.4387	54.707089
26	475	0.475	54.736842
28	511.1	0.5111	54.7838
30	547	0.547	54.844607
32	582.6	0.5826	54.926193
34	618.1	0.6181	55.00728
36	653.4	0.6534	55.096419
38	688.4	0.6884	55.200465
40	723.3	0.7233	55.302088
42	758	0.758	55.408971
44	792.6	0.7926	55.5135
46	827.1	0.8271	55.616008
48	861.3	0.8613	55.729711
50	895.3	0.8953	55.847202
52	929.3	0.9293	55.956096
54	962.8	0.9628	56.086415
56	996.6	0.9966	56.19105
58	1029.8	1.0298	56.321616
60	1063.2	1.0632	56.433409
62	1096.4	1.0964	56.548705
64	1129.2	1.1292	56.677294
66	1162	1.162	56.798623
68	1194.9	1.1949	56.908528

time t (sec)	volume (ml)	volume v (ltr)	t/v
70	1227.3	1.2273	57.03577
72	1259.7	1.2597	57.156466
74	1291.8	1.2918	57.284409
76	1324	1.324	57.401813
78	1355.6	1.3556	57.539097
80	1388.1	1.3881	57.632735
82	1419.1	1.4191	57.783102
84	1450.9	1.4509	57.8951
86	1481.8	1.4818	58.037522
88	1513.2	1.5132	58.154904
90	1544.2	1.5442	58.282606
92	1575.4	1.5754	58.397867
94	1606	1.606	58.530511
96	1636.8	1.6368	58.651026
98	1667.6	1.6676	58.76709
100	1697.9	1.6979	58.896284
102	1728	1.728	59.027778
104	1758.7	1.7587	59.134588
106	1788.3	1.7883	59.274171
108	1818.7	1.8187	59.383076
110	1848.1	1.8481	59.520589
112	1877.9	1.8779	59.641088
114	1906.8	1.9068	59.786029
116	1936.9	1.9369	59.889514
118	1965.8	1.9658	60.026452
120	1994.4	1.9944	60.168472
122	2023.8	2.0238	60.282637
124	2052.9	2.0529	60.402358
126	2081	2.081	60.547814
128	2110.1	2.1101	60.660632
130	2138.7	2.1387	60.784589
132	2166.9	2.1669	60.916517
134	2194.8	2.1948	61.053399
136	2223.4	2.2234	61.167581
138	2251.3	2.2513	61.297917
140	2279.6	2.2796	61.414283
142	2307.7	2.3077	61.533128
144	2335	2.335	61.670236
146	2362.4	2.3624	61.801558

time t (sec)	volume (ml)	volume v (ltr)	t/v
148	2389.9	2.3899	61.927277
150	2417.2	2.4172	62.055271
152	2444.8	2.4448	62.172775
154	2471.5	2.4715	62.310338
156	2498.7	2.4987	62.432465
158	2525.7	2.5257	62.556915
160	2552.8	2.5528	62.676277
162	2579.3	2.5793	62.807739
164	2605.7	2.6057	62.938942
166	2632.4	2.6324	63.060325
168	2658.7	2.6587	63.188776
170	2684.9	2.6849	63.31707
172	2711.1	2.7111	63.442883
174	2737.3	2.7373	63.566288
176	2763.2	2.7632	63.694268
178	2788.9	2.7889	63.824447
180	2814.7	2.8147	63.949977
182	2840.4	2.8404	64.075482
184	2866	2.866	64.200977
186	2891.7	2.8917	64.322025
188	2917	2.917	64.449777
190	2941.7	2.9417	64.588503
192	2967	2.967	64.71183
194	2992.2	2.9922	64.835238
196	3017.3	3.0173	64.958738
198	3042	3.042	65.088757
200	3066.6	3.0666	65.218809
202	3091.4	3.0914	65.342563
204	3116.3	3.1163	65.462247
206	3140.3	3.1403	65.598828
208	3164.7	3.1647	65.725029
210	3189.2	3.1892	65.847234
212	3212.9	3.2129	65.984002
214	3237.3	3.2373	66.10447
216	3261.4	3.2614	66.229227
218	3285.5	3.2855	66.352153
220	3308.9	3.3089	66.487352
222	3332.6	3.3326	66.614655
224	3356.3	3.3563	66.74016

time t (sec)	volume (ml)	volume v (ltr)	t/v
226	3379.6	3.3796	66.871819
228	3403.5	3.4035	66.989863
230	3426.7	3.4267	67.11997
232	3450	3.45	67.246377
234	3473.1	3.4731	67.374968
236	3496.3	3.4963	67.499928
238	3518.9	3.5189	67.634772
240	3542.2	3.5422	67.754503
242	3564.7	3.5647	67.887901
244	3587.6	3.5876	68.012041
246	3610.3	3.6103	68.138382
248	3632.4	3.6324	68.274419
250	3655.3	3.6553	68.393839
252	3677.6	3.6776	68.52295
254	3700.2	3.7002	68.644938
256	3721.8	3.7218	68.783922
258	3744.4	3.7444	68.902895
260	3766.3	3.7663	69.033269
262	3788.3	3.7883	69.160309
264	3810.4	3.8104	69.284065
266	3831.9	3.8319	69.41726
268	3853.9	3.8539	69.539947
270	3875.6	3.8756	69.666632
272	3896.7	3.8967	69.802654
274	3918.2	3.9182	69.93007
276	3939.8	3.9398	70.054317
278	3961	3.961	70.184297
280	3982.2	3.9822	70.312892
282	4003.5	4.0035	70.438366
284	4024.3	4.0243	70.571279
286	4045.5	4.0455	70.695835
288	4066.3	4.0663	70.826058
290	4086.9	4.0869	70.958428
292	4108.1	4.1081	71.079088
294	4128.6	4.1286	71.21058
296	4149.1	4.1491	71.340773
298	4169.5	4.1695	71.471399
300	4189.9	4.1899	71.600754
302	4210.4	4.2104	71.727152

time t (sec)	volume (ml)	volume v (ltr)	t/v
304	4230.5	4.2305	71.859118
306	4250.9	4.2509	71.984756
308	4271	4.271	72.114259
310	4291.1	4.2911	72.242549
312	4310.9	4.3109	72.374678
314	4330.9	4.3309	72.502251
316	4350.7	4.3507	72.63199
318	4370.3	4.3703	72.763883
320	4390.3	4.3903	72.887958
322	4409.5	4.4095	73.024152
324	4429.2	4.4292	73.150908
326	4448.8	4.4488	73.278187
328	4468.1	4.4681	73.409279
330	4487.2	4.4872	73.542521
332	4506.6	4.5066	73.669729
334	4525.6	4.5256	73.802369
336	4544.8	4.5448	73.930646
338	4563.8	4.5638	74.061089
340	4582.8	4.5828	74.190451
342	4601.8	4.6018	74.318745
344	4620.4	4.6204	74.452428
346	4639.2	4.6392	74.581824
348	4657.9	4.6579	74.71178
350	4676.7	4.6767	74.839096
352	4695	4.695	74.973376
354	4713.6	4.7136	75.101833
356	4731.9	4.7319	75.23405
358	4750.4	4.7504	75.362075
360	4768.5	4.7685	75.495439
362	4786.8	4.7868	75.624634
364	4804.9	4.8049	75.755999
366	4823	4.823	75.886378
368	4840.8	4.8408	76.020492
370	4858.8	4.8588	76.15049
372	4876.8	4.8768	76.279528
374	4894.6	4.8946	76.410738
376	4912.3	4.9123	76.542556
378	4929.8	4.9298	76.676539
380	4947.6	4.9476	76.804916

time t (sec)	volume (ml)	volume v (ltr)	t/v
382	4965	4.965	76.93857
384	4982.6	4.9826	77.068197
386	5000	5	77.2
388	5017.2	5.0172	77.333971
390	5034.7	5.0347	77.462411
392	5051.7	5.0517	77.59764
394	5068.9	5.0689	77.728896
396	5086.3	5.0863	77.856202
398	5103	5.103	77.993337
400	5120.3	5.1203	78.120423
402	5137.1	5.1371	78.254268
404	5153.9	5.1539	78.387241
406	5170.6	5.1706	78.520868
408	5187.5	5.1875	78.650602
410	5204.2	5.2042	78.782522
412	5220.8	5.2208	78.915109
414	5237.3	5.2373	79.048365
416	5253.7	5.2537	79.182291
418	5270.1	5.2701	79.315383
420	5286.7	5.2867	79.444644
422	5303.1	5.3031	79.576097
424	5319.3	5.3193	79.709736
426	5335.4	5.3354	79.84406
428	5351.7	5.3517	79.974588
430	5367.6	5.3676	80.110291
432	5383.7	5.3837	80.242213
434	5399.8	5.3998	80.373347
436	5415.8	5.4158	80.505189
438	5431.5	5.4315	80.640707
440	5447.2	5.4472	80.775444
442	5463	5.463	80.907926
444	5478.8	5.4788	81.039644
446	5494.4	5.4944	81.173559
448	5510	5.51	81.306715
450	5525.5	5.5255	81.440594
452	5540.9	5.5409	81.575195
454	5556.5	5.5565	81.70611
456	5571.7	5.5717	81.842167
458	5586.9	5.5869	81.977483

time t (sec)	volume (ml)	volume v (ltr)	t/v
460	5602.3	5.6023	82.109134
462	5617.6	5.6176	82.241527
464	5632.7	5.6327	82.376125
466	5647.6	5.6476	82.512926
468	5662.8	5.6628	82.644628
470	5677.9	5.6779	82.777083
472	5692.8	5.6928	82.911748
474	5707.7	5.7077	83.04571
476	5722.6	5.7226	83.178975
478	5737.2	5.7372	83.315903
480	5752.2	5.7522	83.446334
482	5766.7	5.7667	83.583332
484	5781.4	5.7814	83.716747
486	5796	5.796	83.850932
488	5810.4	5.8104	83.987333
490	5824.9	5.8249	84.121616
492	5839.4	5.8394	84.255232
494	5853.8	5.8538	84.389627
496	5868.1	5.8681	84.524804
498	5882.5	5.8825	84.657884
500	5896.6	5.8966	84.794627
502	5910.8	5.9108	84.929282
504	5924.9	5.9249	85.064727
506	5939	5.939	85.199529
508	5953.1	5.9531	85.333692
510	5967	5.967	85.470085
512	5981	5.981	85.604414
514	5995	5.995	85.738115
516	6008.8	6.0088	85.874051
518	6022.6	6.0226	86.009365
520	6036.4	6.0364	86.144059
522	6050	6.05	86.280992
524	6063.7	6.0637	86.415885
526	6077.3	6.0773	86.551594
528	6090.9	6.0909	86.686697
530	6104.4	6.1044	86.82262
532	6117.9	6.1179	86.957943
534	6131.3	6.1313	87.094091
536	6144.8	6.1448	87.228225

time t (sec)	volume (ml)	volume v (ltr)	t/v
538	6158	6.158	87.366028
540	6171.2	6.1712	87.503241
542	6184.6	6.1846	87.637034
544	6197.8	6.1978	87.773081
546	6211	6.211	87.908549
548	6224.2	6.2242	88.043443
550	6237.3	6.2373	88.17918
552	6250.2	6.2502	88.317174
554	6263.2	6.2632	88.453187
556	6276.2	6.2762	88.588636
558	6289.1	6.2891	88.724937
560	6301.9	6.3019	88.862089
562	6314.8	6.3148	88.997276
564	6327.5	6.3275	89.134729
566	6340.3	6.3403	89.270224
568	6353	6.353	89.40658
570	6365.7	6.3657	89.542391
572	6378.3	6.3783	89.679068
574	6390.9	6.3909	89.815206
576	6403.4	6.4034	89.952213
578	6415.9	6.4159	90.088686
580	6428.2	6.4282	90.227435
582	6443.2	6.4432	90.327787
584	6453.1	6.4531	90.49914
586	6465.5	6.4655	90.634908
588	6480.3	6.4803	90.73654
590	6490.2	6.4902	90.906289
592	6502.5	6.5025	91.041907
594	6514.8	6.5148	91.177012
596	6527	6.527	91.313008
598	6539.2	6.5392	91.448495
600	6551.4	6.5514	91.583478
602	6563.5	6.5635	91.719357
604	6575.5	6.5755	91.856133
606	6587.5	6.5875	91.99241
608	6599.6	6.5996	92.126796
610	6611.5	6.6115	92.26348
612	6623.4	6.6234	92.399674
614	6635.2	6.6352	92.536774

time t (sec)	volume (ml)	volume v (ltr)	t/v
616	6647.1	6.6471	92.671992
618	6658.8	6.6588	92.809515
620	6670.5	6.6705	92.946556
622	6682.3	6.6823	93.081723
624	6694	6.694	93.217807
626	6705.6	6.7056	93.354808
628	6717.1	6.7171	93.492728
630	6728.6	6.7286	93.630176
632	6740.1	6.7401	93.767155
634	6751.5	6.7515	93.905058
636	6763	6.763	94.041106
638	6774.3	6.7743	94.179472
640	6785.7	6.7857	94.315988
642	6797	6.797	94.453435
644	6808.2	6.8082	94.591816
646	6819.4	6.8194	94.729742
648	6832.8	6.8328	94.83667
650	6844	6.844	94.9737
652	6855.1	6.8551	95.111669
654	6866.2	6.8662	95.249192
656	6877.3	6.8773	95.386271
658	6888.3	6.8883	95.524295
660	6899.2	6.8992	95.663265
662	6910.2	6.9102	95.800411
664	6921	6.921	95.939893
666	6931.9	6.9319	96.077554
668	6942.7	6.9427	96.21617
670	6953.5	6.9535	96.354354
672	6964.3	6.9643	96.49211
674	6975	6.975	96.630824
676	6985.8	6.9858	96.767729
678	6996.4	6.9964	96.906981
680	7007	7.007	97.045811
682	7017.6	7.0176	97.184223
684	7028.2	7.0282	97.322216
686	7038.7	7.0387	97.461179
688	7049.2	7.0492	97.599728
690	7059.7	7.0597	97.737864
692	7070.1	7.0701	97.876975

time t (sec)	volume (ml)	volume v (ltr)	t/v
694	7080.5	7.0805	98.015677
696	7090.9	7.0909	98.153972
698	7101.2	7.1012	98.293246
700	7111.5	7.1115	98.432117
702	7121.7	7.1217	98.57197
704	7132.1	7.1321	98.708655
706	7142.2	7.1422	98.849094
708	7152.4	7.1524	98.987752
710	7162.6	7.1626	99.126016
712	7172.7	7.1727	99.26527
714	7182.7	7.1827	99.405516
716	7192.9	7.1929	99.542605
718	7202.9	7.2029	99.682072
720	7212.9	7.2129	99.821154
722	7222.8	7.2228	99.961234
724	7232.7	7.2327	100.10093
726	7242.6	7.2426	100.24025
728	7252.5	7.2525	100.37918
730	7262.3	7.2623	100.51912
732	7270.2	7.2702	100.68499
734	7282	7.282	100.79648
736	7291.7	7.2917	100.93668
738	7301.4	7.3014	101.07651
740	7311.1	7.3111	101.21596
742	7320.7	7.3207	101.35643
744	7330.4	7.3304	101.49514
746	7340	7.34	101.63488
748	7349.6	7.3496	101.77425
750	7359.1	7.3591	101.91464
752	7368.6	7.3686	102.05466
754	7378.1	7.3781	102.19433
756	7387.6	7.3876	102.33364
758	7397.1	7.3971	102.47259
760	7406.5	7.4065	102.61257
762	7415.8	7.4158	102.75358
764	7425.1	7.4251	102.89424
766	7434.5	7.4345	103.03316
768	7443.8	7.4438	103.17311
770	7453.1	7.4531	103.31272

time t (sec)	volume (ml)	volume v (ltr)	t/v
772	7462.3	7.4623	103.45336
774	7471.5	7.4715	103.59366
776	7480.7	7.4807	103.73361
778	7489.8	7.4898	103.8746
780	7499	7.499	104.01387
782	7508.1	7.5081	104.15418
784	7517.3	7.5173	104.29276
786	7526.3	7.5263	104.43379
788	7535.3	7.5353	104.57447
790	7544.3	7.5443	104.71482
792	7553.3	7.5533	104.85483
794	7562.2	7.5622	104.9959
796	7571.2	7.5712	105.13525
798	7580.1	7.5801	105.27566
800	7589	7.589	105.41573
802	7597.9	7.5979	105.55548
804	7606.7	7.6067	105.69629
806	7615.5	7.6155	105.83678
808	7624.3	7.6243	105.97694
810	7633	7.633	106.11817
812	7641.7	7.6417	106.25908
814	7650.5	7.6505	106.39827
816	7659.1	7.6591	106.53993
818	7667.8	7.6678	106.67988
820	7676.4	7.6764	106.82091
822	7685	7.685	106.96161
824	7693.5	7.6935	107.1034
826	7702.2	7.7022	107.24209
828	7710.6	7.7106	107.38464
830	7719.2	7.7192	107.5241

A.9 MF-MFI sample data for Anthracite

time t (sec)	volume (ml)	volume v (ltr)	t/v
0	0		
2	35	0.035	57.142857
4	70	0.07	57.142857
6	105	0.105	57.142857
8	140	0.14	57.142857
10	175	0.175	57.142857
12	210	0.21	57.142857
14	245.6	0.2456	57.003257
16	282.8	0.2828	56.577086
18	319.7	0.3197	56.302784
20	356.6	0.3566	56.08525
22	394.1	0.3941	55.823395
24	432.7	0.4327	55.465681
26	470.6	0.4706	55.248619
28	508.1	0.5081	55.107262
30	545.2	0.5452	55.025679
32	582.1	0.5821	54.973372
34	619	0.619	54.927302
36	655.4	0.6554	54.928288
38	691.7	0.6917	54.937111
40	727.7	0.7277	54.967706
42	763.7	0.7637	54.995417
44	799.5	0.7995	55.034396
46	834.9	0.8349	55.096419
48	870.5	0.8705	55.140724
50	905.7	0.9057	55.205918
52	940.7	0.9407	55.277984
54	975.7	0.9757	55.344881
56	1010.5	1.0105	55.41811
58	1045.3	1.0453	55.486463
60	1079.8	1.0798	55.565846
62	1114.3	1.1143	55.640312
64	1148.6	1.1486	55.720007
66	1182.7	1.1827	55.804515
68	1216.8	1.2168	55.884287

time t (sec)	volume (ml)	volume v (ltr)	t/v
70	1250.9	1.2509	55.959709
72	1284.7	1.2847	56.044213
74	1318.4	1.3184	56.128641
76	1351.9	1.3519	56.217176
78	1385.5	1.3855	56.297366
80	1418.5	1.4185	56.397603
82	1452.2	1.4522	56.466052
84	1485	1.485	56.565657
86	1518	1.518	56.653491
88	1550.9	1.5509	56.741247
90	1584	1.584	56.818182
92	1616.7	1.6167	56.906043
94	1648.8	1.6488	57.01116
96	1681.3	1.6813	57.098674
98	1713.7	1.7137	57.186205
100	1746	1.746	57.273769
102	1777.6	1.7776	57.380738
104	1809.6	1.8096	57.471264
106	1841.6	1.8416	57.558645
108	1873.3	1.8733	57.652271
110	1905.1	1.9051	57.739751
112	1936.5	1.9365	57.836303
114	1968	1.968	57.926829
116	1998.9	1.9989	58.031918
118	2030.3	2.0303	58.11949
120	2061.7	2.0617	58.204394
122	2092.2	2.0922	58.311825
124	2123.2	2.1232	58.402411
126	2154	2.154	58.495822
128	2184.5	2.1845	58.594644
130	2215.5	2.2155	58.677499
132	2245.8	2.2458	58.776383
134	2276.2	2.2762	58.870047
136	2306.8	2.3068	58.95613
138	2337.3	2.3373	59.042485
140	2367.1	2.3671	59.1441
142	2397.5	2.3975	59.228363
144	2427.2	2.4272	59.32762
146	2456.8	2.4568	59.426897

time t (sec)	volume (ml)	volume v (ltr)	t/v
148	2487.1	2.4871	59.507056
150	2516.6	2.5166	59.604228
152	2546.4	2.5464	59.692114
154	2576	2.576	59.782609
156	2605.5	2.6055	59.873345
158	2635.2	2.6352	59.957498
160	2664.7	2.6647	60.044283
162	2693.6	2.6936	60.14256
164	2723.2	2.7232	60.223267
166	2751.4	2.7514	60.332921
168	2781	2.781	60.409924
170	2809.5	2.8095	60.508987
172	2838.4	2.8384	60.59752
174	2867.2	2.8672	60.686384
176	2896.3	2.8963	60.767186
178	2924.1	2.9241	60.873431
180	2953.3	2.9533	60.948769
182	2981.6	2.9816	61.041052
184	3009.9	3.0099	61.131599
186	3038.8	3.0388	61.208372
188	3066.2	3.0662	61.313678
190	3094.8	3.0948	61.393305
192	3122.5	3.1225	61.489191
194	3150.2	3.1502	61.583392
196	3178.5	3.1785	61.664307
198	3206.4	3.2064	61.751497
200	3234.1	3.2341	61.841007
202	3261.7	3.2617	61.930895
204	3288.9	3.2889	62.026817
206	3316.7	3.3167	62.109929
208	3344.2	3.3442	62.197237
210	3371.3	3.3713	62.290511
212	3398.4	3.3984	62.382298
214	3425.6	3.4256	62.470808
216	3452.6	3.4526	62.561548
218	3479.7	3.4797	62.649079
220	3506.7	3.5067	62.737046
222	3533.2	3.5332	62.83256
224	3560.1	3.5601	62.919581

time t (sec)	volume (ml)	volume v (ltr)	t/v
226	3586.7	3.5867	63.010567
228	3613.2	3.6132	63.101959
230	3639.6	3.6396	63.193758
232	3665.9	3.6659	63.28596
234	3692.3	3.6923	63.375132
236	3718.6	3.7186	63.464745
238	3744.9	3.7449	63.553099
240	3770.8	3.7708	63.646971
242	3796.7	3.7967	63.739563
244	3822.7	3.8227	63.829231
246	3848.5	3.8485	63.921008
248	3874.6	3.8746	64.006607
250	3900.2	3.9002	64.099277
252	3926.2	3.9262	64.184198
254	3951.4	3.9514	64.281014
256	3976.9	3.9769	64.371747
258	4002.6	4.0026	64.458102
260	4027.8	4.0278	64.551368
262	4053.3	4.0533	64.638689
264	4078.3	4.0783	64.732854
266	4103.7	4.1037	64.819553
268	4128.7	4.1287	64.911473
270	4153.5	4.1535	65.005417
272	4178.7	4.1787	65.092014
274	4203.3	4.2033	65.186877
276	4228.7	4.2287	65.268286
278	4253.2	4.2532	65.362551
280	4278	4.278	65.451145
282	4302.6	4.3026	65.541765
284	4327.3	4.3273	65.629838
286	4351.7	4.3517	65.721442
288	4376.1	4.3761	65.812024
290	4400.5	4.4005	65.901602
292	4424.8	4.4248	65.991683
294	4449	4.449	66.082266
296	4473.3	4.4733	66.170389
298	4497.4	4.4974	66.260506
300	4521.5	4.5215	66.349663
302	4545.4	4.5454	66.440797

time t (sec)	volume (ml)	volume v (ltr)	t/v
304	4569.1	4.5691	66.533891
306	4592.9	4.5929	66.624573
308	4616.9	4.6169	66.71143
310	4640.5	4.6405	66.803146
312	4664.1	4.6641	66.893935
314	4687.7	4.6877	66.983809
316	4711.3	4.7113	67.072782
318	4734.8	4.7348	67.162288
320	4758.1	4.7581	67.253736
322	4781.4	4.7814	67.344292
324	4804.8	4.8048	67.432567
326	4827.9	4.8279	67.524182
328	4851.1	4.8511	67.613531
330	4874.3	4.8743	67.702029
332	4897.1	4.8971	67.795226
334	4920.2	4.9202	67.883419
336	4943	4.943	67.974914
338	4966	4.966	68.062827
340	4988.7	4.9887	68.154028
342	5011.5	5.0115	68.243041
344	5034	5.034	68.33532
346	5056.7	5.0567	68.424071
348	5079.3	5.0793	68.513378
350	5101.7	5.1017	68.604583
352	5124.2	5.1242	68.69365
354	5146.6	5.1466	68.783274
356	5168.7	5.1687	68.87612
358	5191	5.191	68.965517
360	5213.1	5.2131	69.056799
362	5235.4	5.2354	69.144669
364	5257.3	5.2573	69.237061
366	5279.3	5.2793	69.327373
368	5301.3	5.3013	69.416935
370	5323.2	5.3232	69.507063
372	5344.8	5.3448	69.600359
374	5366.6	5.3666	69.690307
376	5388.3	5.3883	69.780821
378	5409.9	5.4099	69.871902
380	5431.4	5.4314	69.963545

time t (sec)	volume (ml)	volume v (ltr)	t/v
382	5453.1	5.4531	70.051897
384	5474.5	5.4745	70.143392
386	5495.8	5.4958	70.235453
388	5517.2	5.5172	70.325527
390	5538.5	5.5385	70.416178
392	5559.7	5.5597	70.507401
394	5580.8	5.5808	70.599197
396	5601.9	5.6019	70.690302
398	5623.1	5.6231	70.779463
400	5644.1	5.6441	70.870467
402	5665	5.665	70.962048
404	5685.8	5.6858	71.054205
406	5706.7	5.7067	71.144444
408	5727.4	5.7274	71.236512
410	5748.1	5.7481	71.327917
412	5768.7	5.7687	71.419904
414	5789.5	5.7895	71.508766
416	5809.9	5.8099	71.601921
418	5830.3	5.8303	71.694424
420	5850.8	5.8508	71.785055
422	5871.2	5.8712	71.876277
424	5891.5	5.8915	71.96809
426	5911.7	5.9117	72.06049
428	5932	5.932	72.151045
430	5952	5.952	72.244624
432	5972.1	5.9721	72.336364
434	5992.2	5.9922	72.427489
436	6012.2	6.0122	72.519211
438	6032.1	6.0321	72.611528
440	6052	6.052	72.703239
442	6071.8	6.0718	72.795547
444	6091.6	6.0916	72.887255
446	6111.3	6.1113	72.979562
448	6131	6.131	73.071277
450	6150.7	6.1507	73.162404
452	6170.2	6.1702	73.255324
454	6189.7	6.1897	73.347658
456	6209.1	6.2091	73.440595
458	6228.6	6.2286	73.531773

time t (sec)	volume (ml)	volume v (ltr)	t/v
460	6247.9	6.2479	73.624738
462	6267.2	6.2672	73.71713
464	6286.5	6.2865	73.808956
466	6305.5	6.3055	73.903735
468	6324.7	6.3247	73.995605
470	6343.8	6.3438	74.088086
472	6362.8	6.3628	74.181178
474	6381.8	6.3818	74.273716
476	6400.7	6.4007	74.366866
478	6419.6	6.4196	74.459468
480	6438.5	6.4385	74.551526
482	6457.2	6.4572	74.645357
484	6476.1	6.4761	74.736338
486	6494.7	6.4947	74.830246
488	6513.4	6.5134	74.922468
490	6532	6.532	75.015309
492	6550.4	6.5504	75.109917
494	6569	6.569	75.201705
496	6587.4	6.5874	75.295261
498	6605.8	6.6058	75.388295
500	6624.1	6.6241	75.481952
502	6642.4	6.6424	75.575093
504	6660.6	6.6606	75.668859
506	6678.7	6.6787	75.763247
508	6697	6.697	75.85486
510	6715	6.715	75.949367
512	6733.1	6.7331	76.042239
514	6751.1	6.7511	76.135741
516	6769.1	6.7691	76.228745
518	6786.9	6.7869	76.323506
520	6804.8	6.8048	76.416647
522	6822.7	6.8227	76.5093
524	6840.4	6.8404	76.603707
526	6858.1	6.8581	76.697628
528	6875.8	6.8758	76.791064
530	6893.4	6.8934	76.885137
532	6911	6.911	76.97873
534	6928.5	6.9285	77.07296
536	6946	6.946	77.166715

time t (sec)	volume (ml)	volume v (ltr)	t/v
538	6963.4	6.9634	77.261108
540	6980.8	6.9808	77.355031
542	6998.2	6.9982	77.448487
544	7015.4	7.0154	77.54369
546	7032.7	7.0327	77.637323
548	7049.9	7.0499	77.731599
550	7067	7.067	77.826518
552	7084.1	7.0841	77.920978
554	7101.1	7.1011	78.016082
556	7118.2	7.1182	78.109634
558	7135.2	7.1352	78.203835
560	7152.1	7.1521	78.298682
562	7168.9	7.1689	78.394175
564	7185.7	7.1857	78.489222
566	7202.4	7.2024	78.584916
568	7219	7.219	78.681258
570	7235.6	7.2356	78.777157
572	7252	7.252	78.874793
574	7268.5	7.2685	78.970902
576	7284.7	7.2847	79.069831
578	7301	7.301	79.167237
580	7317.1	7.3171	79.266376
582	7333.1	7.3331	79.366162
584	7348.9	7.3489	79.467675
586	7364.6	7.3646	79.569834
588	7380.2	7.3802	79.672638
590	7395.7	7.3957	79.776086
592	7410.9	7.4109	79.882335
594	7426.1	7.4261	79.98815
596	7441	7.441	80.096761
598	7455.8	7.4558	80.206014
600	7470.7	7.4707	80.313759
602	7485.4	7.4854	80.423224
604	7499.8	7.4998	80.535481
606	7502.5	7.5025	80.773076
608	7502.6	7.5026	81.038573

A.10 MF-MFI sample data for Sand

time t (sec)	volume (ml)	volume v (ltr)	t/v
0	0		
2	47.3	0.0473	42.283298
4	83.5	0.0835	47.904192
6	119.6	0.1196	50.167224
8	155.6	0.1556	51.413882
10	191.3	0.1913	52.273915
12	226.2	0.2262	53.050398
14	260.6	0.2606	53.72218
16	294.4	0.2944	54.347826
18	327.8	0.3278	54.911531
20	360.9	0.3609	55.417013
22	393.6	0.3936	55.894309
24	426	0.426	56.338028
26	458.2	0.4582	56.74378
28	490.2	0.4902	57.119543
30	521.9	0.5219	57.482276
32	553.3	0.5533	57.834809
34	584.6	0.5846	58.159425
36	615.5	0.6155	58.489033
38	646.3	0.6463	58.796225
40	676.9	0.6769	59.092924
42	707.2	0.7072	59.38914
44	737.5	0.7375	59.661017
46	767.4	0.7674	59.942664
48	797.3	0.7973	60.203186
50	827	0.827	60.459492
52	856.6	0.8566	60.705113
54	886	0.886	60.948081
56	915.3	0.9153	61.182126
58	944.1	0.9441	61.43417
60	972.9	0.9729	61.671292
62	1001.8	1.0018	61.888601
64	1030.4	1.0304	62.111801
66	1058.8	1.0588	62.334719
68	1087.1	1.0871	62.551743

time t (sec)	volume (ml)	volume v (ltr)	t/v
70	1115.3	1.1153	62.763382
72	1143.3	1.1433	62.975597
74	1171.2	1.1712	63.18306
76	1199	1.199	63.386155
78	1226.7	1.2267	63.585229
80	1254.5	1.2545	63.770426
82	1281.9	1.2819	63.967548
84	1309.1	1.3091	64.166221
86	1336.4	1.3364	64.35199
88	1363.5	1.3635	64.539787
90	1390.5	1.3905	64.724919
92	1417.3	1.4173	64.912157
94	1444.5	1.4445	65.07442
96	1470.9	1.4709	65.266164
98	1497.5	1.4975	65.442404
100	1523.9	1.5239	65.621104
102	1550.5	1.5505	65.785231
104	1576.8	1.5768	65.956367
106	1602.8	1.6028	66.134265
108	1629.1	1.6291	66.294273
110	1655.1	1.6551	66.461241
112	1681	1.681	66.627008
114	1707.3	1.7073	66.772096
116	1732.4	1.7324	66.959132
118	1758.4	1.7584	67.10646
120	1783.9	1.7839	67.268345
122	1809.2	1.8092	67.43312
124	1834.9	1.8349	67.578615
126	1859.7	1.8597	67.752863
128	1884.9	1.8849	67.908112
130	1910.4	1.9104	68.048576
132	1935.4	1.9354	68.202955
134	1960.4	1.9604	68.353397
136	1985.4	1.9854	68.50005
138	2010.2	2.0102	68.649886
140	2035.3	2.0353	68.785928
142	2059.6	2.0596	68.945426
144	2084.3	2.0843	69.087943
146	2108.6	2.1086	69.240254

time t (sec)	volume (ml)	volume v (ltr)	t/v
148	2133.3	2.1333	69.376084
150	2157.4	2.1574	69.528136
152	2182	2.182	69.660862
154	2206.3	2.2063	69.800118
156	2230.4	2.2304	69.942611
158	2254.2	2.2542	70.091385
160	2278.3	2.2783	70.227801
162	2302.1	2.3021	70.370531
164	2326	2.326	70.507309
166	2349.8	2.3498	70.64431
168	2373.6	2.3736	70.778564
170	2397.6	2.3976	70.904238
172	2420.9	2.4209	71.047957
174	2444.5	2.4445	71.1802
176	2467.8	2.4678	71.318583
178	2491.2	2.4912	71.451509
180	2514.6	2.5146	71.581961
182	2537.6	2.5376	71.721311
184	2561.2	2.5612	71.841324
186	2584.4	2.5844	71.970283
188	2607	2.607	72.11354
190	2630.4	2.6304	72.23236
192	2653.5	2.6535	72.357264
194	2676.3	2.6763	72.488137
196	2698.8	2.6988	72.62487
198	2722	2.722	72.740632
200	2744.5	2.7445	72.873019
202	2767.2	2.7672	72.997976
204	2790	2.79	73.11828
206	2812	2.812	73.257468
208	2834.7	2.8347	73.376371
210	2856.9	2.8569	73.506248
212	2879.8	2.8798	73.616223
214	2901.7	2.9017	73.749871
216	2923.9	2.9239	73.873935
218	2945.6	2.9456	74.008691
220	2968.3	2.9683	74.116498
222	2990.3	2.9903	74.240043
224	3012.4	3.0124	74.359315

time t (sec)	volume (ml)	volume v (ltr)	t/v
226	3034.4	3.0344	74.479304
228	3056.1	3.0561	74.604889
230	3077.8	3.0778	74.728702
232	3099.8	3.0998	74.843538
234	3121.6	3.1216	74.961558
236	3143.4	3.1434	75.077941
238	3165	3.165	75.197472
240	3186.5	3.1865	75.317747
242	3207.8	3.2078	75.441112
244	3229	3.229	75.56519
246	3250.6	3.2506	75.678336
248	3272.3	3.2723	75.787672
250	3293.3	3.2933	75.9117
252	3314.7	3.3147	76.02498
254	3336	3.336	76.139089
256	3356.9	3.3569	76.260836
258	3378.1	3.3781	76.374293
260	3399.3	3.3993	76.486335
262	3420.4	3.4204	76.599228
264	3441.2	3.4412	76.717424
266	3462.1	3.4621	76.831981
268	3483.2	3.4832	76.940744
270	3504	3.504	77.054795
272	3524.6	3.5246	77.171878
274	3545.5	3.5455	77.28106
276	3565.8	3.5658	77.401986
278	3586.6	3.5866	77.510734
280	3607.1	3.6071	77.624685
282	3627.8	3.6278	77.733061
284	3648.1	3.6481	77.848743
286	3668.4	3.6684	77.963145
288	3688.9	3.6889	78.072054
290	3709.4	3.7094	78.17976
292	3729.6	3.7296	78.292578
294	3749.8	3.7498	78.404182
296	3769.9	3.7699	78.516672
298	3790.4	3.7904	78.619671
300	3810.7	3.8107	78.725693
302	3830.3	3.8303	78.844999

time t (sec)	volume (ml)	volume v (ltr)	t/v
304	3850.3	3.8503	78.954887
306	3870.5	3.8705	79.059553
308	3890.5	3.8905	79.167202
310	3910.3	3.9103	79.277805
312	3930.2	3.9302	79.385273
314	3950.1	3.9501	79.491658
316	3969.9	3.9699	79.598982
318	3989.6	3.9896	79.707239
320	4009.2	4.0092	79.816422
322	4029	4.029	79.920576
324	4048.5	4.0485	80.029641
326	4068.1	4.0681	80.13569
328	4087.6	4.0876	80.242685
330	4107.1	4.1071	80.348665
332	4126.5	4.1265	80.455592
334	4146.1	4.1461	80.557632
336	4165.4	4.1654	80.664522
338	4184.4	4.1844	80.776216
340	4203.9	4.2039	80.877281
342	4223.1	4.2231	80.983164
344	4242.2	4.2422	81.09
346	4261.4	4.2614	81.193974
348	4280.6	4.2806	81.297014
350	4299.6	4.2996	81.402921
352	4318.8	4.3188	81.504122
354	4338	4.338	81.604426
356	4356.5	4.3565	81.716975
358	4375.5	4.3755	81.819221
360	4394.3	4.3943	81.924311
362	4413.3	4.4133	82.024789
364	4431.9	4.4319	82.131817
366	4450.8	4.4508	82.232408
368	4469.5	4.4695	82.335832
370	4488.1	4.4881	82.440231
372	4506.9	4.5069	82.540105
374	4525.5	4.5255	82.642802
376	4544	4.544	82.746479
378	4562.4	4.5624	82.851131
380	4581.2	4.5812	82.947699

time t (sec)	volume (ml)	volume v (ltr)	t/v
382	4599.6	4.5996	83.0507
384	4618	4.618	83.15288
386	4636.3	4.6363	83.256045
388	4654.7	4.6547	83.356607
390	4673	4.673	83.458164
392	4691.3	4.6913	83.558928
394	4709.6	4.7096	83.658909
396	4727.8	4.7278	83.759888
398	4746	4.746	83.860093
400	4764	4.764	83.963056
402	4782.1	4.7821	84.063487
404	4800.3	4.8003	84.161407
406	4818.2	4.8182	84.263833
408	4836.2	4.8362	84.363757
410	4854.2	4.8542	84.462939
412	4872.1	4.8721	84.563125
414	4890.1	4.8901	84.660845
416	4907.8	4.9078	84.76303
418	4925.6	4.9256	84.862758
420	4943.4	4.9434	84.961767
422	4961.1	4.9611	85.061781
424	4978.9	4.9789	85.159373
426	4996.6	4.9966	85.257975
428	5014.2	5.0142	85.357584
430	5031.9	5.0319	85.454798
432	5049.4	5.0494	85.554719
434	5067	5.067	85.65226
436	5084.4	5.0844	85.752498
438	5102	5.102	85.848687
440	5119.4	5.1194	85.947572
442	5136.8	5.1368	86.045787
444	5154.2	5.1542	86.143339
446	5171.5	5.1715	86.241903
448	5188.8	5.1888	86.339809
450	5206.1	5.2061	86.437064
452	5223.3	5.2233	86.535332
454	5240.6	5.2406	86.631302
456	5257.6	5.2576	86.731589
458	5274.9	5.2749	86.826291

time t (sec)	volume (ml)	volume v (ltr)	t/v
460	5292	5.292	86.923658
462	5309.1	5.3091	87.020399
464	5326.1	5.3261	87.118154
466	5343	5.343	87.216919
468	5360.1	5.3601	87.311804
470	5377.1	5.3771	87.40771
472	5393.9	5.3939	87.506257
474	5410.8	5.4108	87.602573
476	5427.7	5.4277	87.698288
478	5444.6	5.4446	87.79341
480	5461.4	5.4614	87.889552
482	5478.2	5.4782	87.985105
484	5494.9	5.4949	88.081676
486	5511.5	5.5115	88.179262
488	5528.3	5.5283	88.273068
490	5544.8	5.5448	88.371086
492	5561.5	5.5615	88.465342
494	5578	5.578	88.562209
496	5594.6	5.5946	88.656919
498	5611.1	5.6111	88.752651
500	5627.6	5.6276	88.847821
502	5644.1	5.6441	88.942435
504	5660.4	5.6604	89.039644
506	5676.9	5.6769	89.133154
508	5693.3	5.6933	89.227689
510	5709.5	5.7095	89.32481
512	5725.9	5.7259	89.418257
514	5742.2	5.7422	89.51273
516	5758.4	5.7584	89.608225
518	5774.6	5.7746	89.703183
520	5790.8	5.7908	89.79761
522	5807	5.807	89.89151
524	5823.2	5.8232	89.984888
526	5839.2	5.8392	90.080833
528	5855.2	5.8552	90.176254
530	5871.4	5.8714	90.268079
532	5887.3	5.8873	90.364004
534	5903.6	5.9036	90.453283
536	5919.3	5.9193	90.551248

time t (sec)	volume (ml)	volume v (ltr)	t/v
538	5935.3	5.9353	90.644112
540	5951.1	5.9511	90.739527
542	5967.1	5.9671	90.831392
544	5982.9	5.9829	90.925805
546	5998.7	5.9987	91.019721
548	6014.5	6.0145	91.113143
550	6030.3	6.0303	91.206076
552	6046	6.046	91.300033
554	6061.7	6.0617	91.393503
556	6077.4	6.0774	91.486491
558	6093	6.093	91.580502
560	6108.7	6.1087	91.672533
562	6124.2	6.1242	91.767088
564	6139.9	6.1399	91.858174
566	6155.3	6.1553	91.953276
568	6170.9	6.1709	92.044921
570	6186.3	6.1863	92.139082
572	6201.8	6.2018	92.231288
574	6217.4	6.2174	92.321549
576	6232.5	6.2325	92.418773
578	6248	6.248	92.509603
580	6263.4	6.2634	92.601462
582	6278.7	6.2787	92.694348
584	6294	6.294	92.786781
586	6309.3	6.3093	92.878766
588	6324.6	6.3246	92.970306
590	6339.8	6.3398	93.062873
592	6354.9	6.3549	93.156462
594	6370.2	6.3702	93.24668
596	6385.3	6.3853	93.339389
598	6400.4	6.4004	93.431661
600	6415.5	6.4155	93.523498
602	6430.6	6.4306	93.614904
604	6445.6	6.4456	93.707335
606	6460.7	6.4607	93.797886
608	6475.7	6.4757	93.889464
610	6490.6	6.4906	93.982066
612	6505.6	6.5056	94.072799
614	6520.5	6.5205	94.164558

time t (sec)	volume (ml)	volume v (ltr)	t/v
616	6535.4	6.5354	94.255899
618	6550.2	6.5502	94.348264
620	6565.1	6.5651	94.438775
622	6579.9	6.5799	94.530312
624	6594.7	6.5947	94.621438
626	6609.5	6.6095	94.712157
628	6624.2	6.6242	94.803901
630	6639	6.639	94.893809
632	6653.6	6.6536	94.986173
634	6668.3	6.6683	95.076706
636	6682.9	6.6829	95.168265
638	6697.5	6.6975	95.259425
640	6712.1	6.7121	95.350188
642	6726.7	6.7267	95.440558
644	6741.2	6.7412	95.531953
646	6755.7	6.7557	95.622955
648	6770.2	6.7702	95.713568
650	6784.7	6.7847	95.803794
652	6799.1	6.7991	95.895045
654	6813.5	6.8135	95.98591
656	6827.9	6.8279	96.076392
658	6842.3	6.8423	96.166494
660	6856.6	6.8566	96.25762
662	6871	6.871	96.346966
664	6885.3	6.8853	96.437338
666	6899.6	6.8996	96.527335
668	6913.8	6.9138	96.618357
670	6928.1	6.9281	96.707611
672	6942.3	6.9423	96.797891
674	6956.4	6.9564	96.889196
676	6970.6	6.9706	96.978739
678	6984.8	6.9848	97.067919
680	6998.8	6.9988	97.159513
682	7012.9	7.0129	97.249355
684	7027	7.027	97.338836
686	7041	7.041	97.429342
688	7055	7.055	97.51949
690	7069	7.069	97.60928
692	7083	7.083	97.698715

time t (sec)	volume (ml)	volume v (ltr)	t/v
694	7097	7.097	97.787798
696	7111	7.111	97.876529
698	7125.2	7.1252	97.962162
700	7139.6	7.1396	98.044708
702	7153.7	7.1537	98.131037
704	7155.9	7.1559	98.380357

A.11 MF-MFI sample data for GAC

time t (sec)	volume (ml)	volume v (ltr)	t/v
0	0		
2	47	0.047	42.5532
4	94	0.094	42.5532
6	141	0.141	42.5532
8	186.6	0.1866	42.8725
10	228	0.228	43.8596
12	268.6	0.2686	44.6761
14	308.8	0.3088	45.3368
16	348.9	0.3489	45.8584
18	388.8	0.3888	46.2963
20	428.4	0.4284	46.6853
22	468.1	0.4681	46.9985
24	507.5	0.5075	47.2906
26	546.8	0.5468	47.5494
28	586.2	0.5862	47.7653
30	625.3	0.6253	47.977
32	664.3	0.6643	48.171
34	703.3	0.7033	48.3435
36	742.1	0.7421	48.511
38	780.9	0.7809	48.6618
40	819.5	0.8195	48.8103
42	857.9	0.8579	48.9568
44	896.5	0.8965	49.0798
46	935	0.935	49.1979
48	973.3	0.9733	49.3168

time t (sec)	volume (ml)	volume v (ltr)	t/v
50	1011.5	1.0115	49.4315
52	1049.7	1.0497	49.538
54	1087.8	1.0878	49.6415
56	1125.7	1.1257	49.7468
58	1163.7	1.1637	49.841
60	1201.7	1.2017	49.9293
62	1239.5	1.2395	50.0202
64	1277.1	1.2771	50.1135
66	1314.9	1.3149	50.1939
68	1352.4	1.3524	50.281
70	1389.8	1.3898	50.367
72	1427.4	1.4274	50.4414
74	1464.6	1.4646	50.5257
76	1501.9	1.5019	50.6026
78	1538.8	1.5388	50.6888
80	1575.8	1.5758	50.7679
82	1612.7	1.6127	50.8464
84	1649.7	1.6497	50.9183
86	1686.4	1.6864	50.9962
88	1723.4	1.7234	51.0619
90	1760.1	1.7601	51.1335
92	1796	1.796	51.2249
94	1832.8	1.8328	51.2876
96	1869.2	1.8692	51.3589
98	1905.7	1.9057	51.4247
100	1941.8	1.9418	51.4986
102	1978	1.978	51.5672
104	2014.2	2.0142	51.6334
106	2049.8	2.0498	51.7124
108	2085.8	2.0858	51.7787
110	2121.7	2.1217	51.8452
112	2156.9	2.1569	51.9264
114	2192.9	2.1929	51.986
116	2228.5	2.2285	52.053
118	2264.2	2.2642	52.1155
120	2299.1	2.2991	52.1943
122	2335.2	2.3352	52.2439
124	2370.1	2.3701	52.3185
126	2405.1	2.4051	52.3887

time t (sec)	volume (ml)	volume v (ltr)	t/v
128	2439.5	2.4395	52.4698
130	2474.7	2.4747	52.5316
132	2509.7	2.5097	52.5959
134	2544.4	2.5444	52.6647
136	2579.2	2.5792	52.7295
138	2613.5	2.6135	52.8028
140	2648.1	2.6481	52.8681
142	2683	2.683	52.9258
144	2717.3	2.7173	52.9938
146	2751.8	2.7518	53.0562
148	2786	2.786	53.1228
150	2820.3	2.8203	53.1858
152	2854.1	2.8541	53.2567
154	2888.3	2.8883	53.3186
156	2922.4	2.9224	53.3808
158	2956.4	2.9564	53.4434
160	2990.2	2.9902	53.5081
162	3024.6	3.0246	53.5608
164	3058.2	3.0582	53.6263
166	3092	3.092	53.6869
168	3124.9	3.1249	53.7617
170	3158.8	3.1588	53.8179
172	3192.5	3.1925	53.8763
174	3225.7	3.2257	53.9418
176	3258.9	3.2589	54.006
178	3292.4	3.2924	54.0639
180	3326	3.326	54.1191
182	3359	3.359	54.1828
184	3392	3.392	54.2453
186	3425.6	3.4256	54.2971
188	3465	3.465	54.2569
190	3491.5	3.4915	54.4179
192	3524.3	3.5243	54.4789
194	3557.3	3.5573	54.5357
196	3590	3.59	54.5961
198	3622.7	3.6227	54.6554
200	3655.5	3.6555	54.7121
202	3687.9	3.6879	54.7737
204	3719.9	3.7199	54.8402

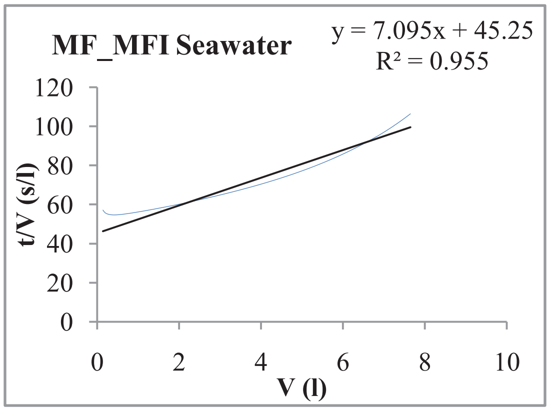
time t (sec)	volume (ml)	volume v (ltr)	t/v
206	3752.5	3.7525	54.8967
208	3784.9	3.7849	54.9552
210	3817.1	3.8171	55.0156
212	3849.1	3.8491	55.0778
214	3881.3	3.8813	55.1362
216	3913.5	3.9135	55.1936
218	3945.5	3.9455	55.2528
220	3977.2	3.9772	55.3153
222	4009.1	4.0091	55.374
224	4040.8	4.0408	55.4346
226	4072.3	4.0723	55.4969
228	4103.9	4.1039	55.5569
230	4135.2	4.1352	55.62
232	4166.7	4.1667	55.6796
234	4198	4.198	55.7408
236	4229.5	4.2295	55.7986
238	4260.5	4.2605	55.862
240	4291.2	4.2912	55.9284
242	4322.2	4.3222	55.99
244	4353.2	4.3532	56.0507
246	4383.9	4.3839	56.1144
248	4414.5	4.4145	56.1785
250	4445.1	4.4451	56.2417
252	4475.6	4.4756	56.3053
254	4505.4	4.5054	56.3768
256	4536.3	4.5363	56.4337
258	4566.3	4.5663	56.5009
260	4596.4	4.5964	56.566
262	4626.7	4.6267	56.6278
264	4656.5	4.6565	56.6949
266	4686	4.686	56.7648
268	4715.6	4.7156	56.8326
270	4745.1	4.7451	56.9008
272	4774.8	4.7748	56.9657
274	4804.2	4.8042	57.0334
276	4833.1	4.8331	57.1062
278	4862.8	4.8628	57.1687
280	4891.2	4.8912	57.2457
282	4920.8	4.9208	57.3078

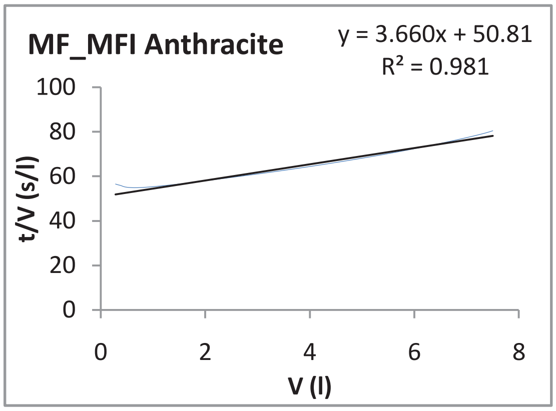
time t (sec)	volume (ml)	volume v (ltr)	t/v
284	4949.5	4.9495	57.3795
286	4978.4	4.9784	57.4482
288	5007	5.007	57.5195
290	5035.5	5.0355	57.5911
292	5064	5.064	57.6619
294	5092.5	5.0925	57.732
296	5120.5	5.1205	57.8069
298	5148.6	5.1486	57.8798
300	5176.8	5.1768	57.9509
302	5204.5	5.2045	58.0267
304	5232.8	5.2328	58.0951
306	5260.4	5.2604	58.1705
308	5288.2	5.2882	58.2429
310	5315.6	5.3156	58.3189
312	5343	5.343	58.3942
314	5370.6	5.3706	58.4665
316	5397.7	5.3977	58.5435
318	5424.9	5.4249	58.6186
320	5451.9	5.4519	58.6951
322	5478.9	5.4789	58.7709
324	5505.7	5.5057	58.8481
326	5532.4	5.5324	58.9256
328	5559.2	5.5592	59.0013
330	5585.7	5.5857	59.0794
332	5612	5.612	59.1589
334	5638.4	5.6384	59.2367
336	5664.5	5.6645	59.3168
338	5690.4	5.6904	59.3983
340	5716.4	5.7164	59.478
342	5744.1	5.7441	59.5394
344	5769.8	5.7698	59.6208
346	5795.4	5.7954	59.7025
348	5821.1	5.8211	59.7825
350	5846.5	5.8465	59.8649
352	5871.7	5.8717	59.9486
354	5897.1	5.8971	60.0295
356	5922.1	5.9221	60.1138
358	5947	5.947	60.1984
360	5971.8	5.9718	60.2833

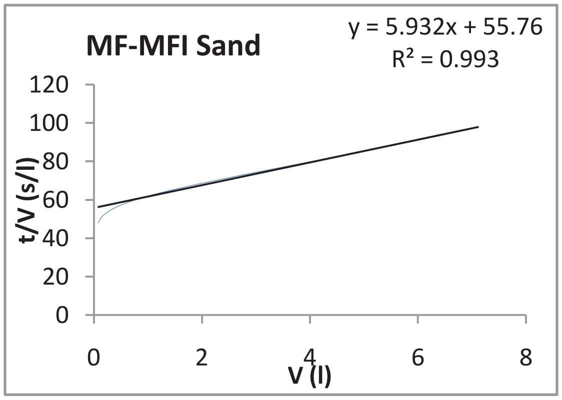
time t (sec)	volume (ml)	volume v (ltr)	t/v
362	5996.3	5.9963	60.3706
364	6021.2	6.0212	60.4531
366	6045.7	6.0457	60.5389
368	6070.1	6.0701	60.625
370	6094.2	6.0942	60.7135
372	6118.3	6.1183	60.8012
374	6142.5	6.1425	60.8873
376	6166.4	6.1664	60.9756
378	6190.2	6.1902	61.0643
380	6213.9	6.2139	61.1532
382	6237.5	6.2375	61.2425
384	6260.9	6.2609	61.333
386	6284.2	6.2842	61.4239
388	6307.5	6.3075	61.5141
390	6330.6	6.3306	61.6055
392	6353.6	6.3536	61.6973
394	6376.6	6.3766	61.7884
396	6399.3	6.3993	61.8818
398	6422.1	6.4221	61.9735
400	6444.6	6.4446	62.0675
402	6467.1	6.4671	62.1608
404	6489.5	6.4895	62.2544
406	6511.7	6.5117	62.3493
408	6533.9	6.5339	62.4436
410	6555.9	6.5559	62.5391
412	6577.8	6.5778	62.6349
414	6599.6	6.5996	62.7311
416	6621.2	6.6212	62.8285
418	6642.9	6.6429	62.9243
420	6664.4	6.6644	63.0214
422	6685.8	6.6858	63.1188
424	6707.1	6.7071	63.2166
426	6728.1	6.7281	63.3165
428	6749.2	6.7492	63.4149
430	6770.1	6.7701	63.5146
432	6790.8	6.7908	63.6155
434	6811.4	6.8114	63.7167
436	6831.8	6.8318	63.8192
438	6852.1	6.8521	63.922

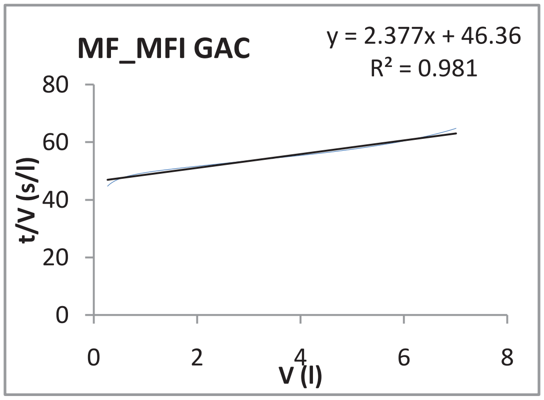
time t (sec)	volume (ml)	volume v (ltr)	t/v
440	6872.3	6.8723	64.0251
442	6892.2	6.8922	64.1305
444	6912	6.912	64.2361
446	6931.8	6.9318	64.3412
448	6951.2	6.9512	64.4493
450	6970.6	6.9706	64.5569
452	6989.7	6.9897	64.6666
454	7008.7	7.0087	64.7766
456	7027.4	7.0274	64.8889
458	7046.2	7.0462	64.9996
460	7064.7	7.0647	65.1125
462	7078.4	7.0784	65.269
464	7080.4	7.0804	65.533
466	7080.6	7.0806	65.8136
468	7080.9	7.0809	66.0933

A.12 Sample MF-MFI calculation figure









APPENDIX – B: COMPARATIVE STUDY ON IN - LINE FLOCCULATION AND SPIRAL - FLOCCULATION FOLLOWED BY MEDIA FILTRATION AS A PRE-TREATMENT OF SEAWATER

B.1 Headloss development and efficiency in terms of turbidity removal for In-line Flocculation

Filter Media	Flocculant dose (mg-Fe^{3+}/L)	Velocity (m/h)	Time (hr)	Turbidity NTU	Turbidity removal (%)	Final headloss development (cm)	Remarks
Sand	0	5	0	0.26	39.53	27.50	SW - 0.43 NTU
			1	0.22	48.84	28.00	
			2	0.21	51.16	28.00	
			3	0.20	53.49	28.00	
			4	0.20	53.49	28.00	
			5	0.20	53.49	29.00	
			6	0.19	55.81	31.00	

Filter Media	Flocculant dose (mg-Fe^{3+}/L)	Velocity (m/h)	Time (hr)	Turbidity NTU	Turbidity removal (%)	Final headloss development (cm)	Remarks
Sand	1	5	0	0.24	45.45	23.00	SW - 0.44 NTU
			1	0.23	47.73	23.50	
			2	0.23	47.73	25.50	
			3	0.24	46.59	35.00	
			4	0.23	48.86	38.00	
			5	0.21	52.27	43.50	
			6	0.19	57.95	46.00	
Sand	3	5	0	0.18	60.23	50.00	SW - 0.44 NTU
			1	0.16	63.64	52.00	
			2	0.15	65.91	65.00	
			3	0.12	72.73	71.00	
			4	0.12	72.73	74.00	
			5	0.13	70.45	81.00	
			6	0.11	74.32	88.50	
Sand	5	5	0	0.14	66.67	53.50	SW - 0.42 NTU
			1	0.14	66.67	80.00	Back wash done at 2.5 hour and 5 hr for sand
			2	0.12	71.43	114.00	
			3	0.13	69.05	138.50	
			4	0.10	76.67	168.00	
			5	0.11	73.81	186.00	
			6	0.11	73.81	205.00	

Filter Media	Flocculant dose (mg-Fe^{3+}/L)	Velocity (m/h)	Time (hr)	Turbidity NTU	Turbidity removal (%)	Final headloss development (cm)	Remarks
Sand	3	10	0	0.17	61.36	95.50	SW - 0.44 NTU
			1	0.16	63.64	130.00	Backwash done at every hour for sand
			2	0.16	64.77	175.50	
			3	0.15	65.91	206.50	
			4	0.15	67.05	235.50	
			5	0.15	67.05	272.00	
			6	0.14	67.27	324.00	
Anthracite	0	5	0	0.29	32.56	6.50	SW - 0.43 NTU
			1	0.27	37.21	6.50	
			2	0.27	38.37	6.50	
			3	0.26	39.53	6.50	
			4	0.25	41.86	7.00	
			5	0.24	44.19	7.50	
			6	0.23	46.51	8.00	
Anthracite	1	5	0	0.25	42.27	7.00	SW - 0.44 NTU
			1	0.24	45.45	14.00	
			2	0.25	43.18	16.50	
			3	0.25	43.18	20.50	
			4	0.24	45.45	25.50	
			5	0.24	46.59	29.00	
			6	0.21	53.41	37.00	

Filter Media	Flocculant dose (mg-Fe^{3+}/L)	Velocity (m/h)	Time (hr)	Turbidity NTU	Turbidity removal (%)	Final headloss development (cm)	Remarks
Anthracite	3	5	0	0.20	55.68	10.00	SW - 0.44 NTU
			1	0.19	56.82	16.50	
			2	0.18	59.09	25.00	
			3	0.15	65.91	36.00	
			4	0.13	70.45	44.50	
			5	0.12	72.73	51.50	
			6	0.12	72.73	62.00	
Anthracite	5	5	0	0.18	57.14	16.00	SW - 0.42 NTU
			1	0.18	57.14	18.50	
			2	0.17	59.52	31.00	
			3	0.16	61.90	38.00	
			4	0.13	69.05	44.50	
			5	0.12	71.43	51.00	
			6	0.12	71.43	74.00	
Anthracite	3	10	0	0.20	54.55	42.50	SW - 0.44 NTU
			1	0.19	56.82	50.00	Bach wash done after 3 hr
			2	0.18	59.09	85.00	
			3	0.17	61.36	120.00	
			4	0.17	62.50	125.50	
			5	0.17	62.50	138.00	
			6	0.16	63.18	148.00	

B.2 Efficiency in terms of UF-MFI for In-line Flocculation

Filter Media	Flocculant dose (mg-Fe^{3+}/L)	Velocity (m/h)	UF-MFI (0-3 hr) (s/L^2)	UF-MFI (3-6 hr) (s/L^2)	UF-MFI removal (0-3 hr) (%)	UF-MFI removal (3-6 hr) (%)
Sand	0	5	6350	6049	45.21	47.80
	1	5	4936	4287	57.41	63.01
	3	5	3360	3754	71.01	67.61
	5	5	4902	3627	57.70	68.70
	3	10	2688	4913	76.81	57.61
Anthracite	0	5	6061	5342	47.70	53.90
	1	5	3754	3105	67.61	73.21
	3	5	4218	3754	63.60	67.61
	5	5	1691	3754	85.41	67.61
	3	10	3198	4913	72.40	57.61

B.3 DOC removal and fractionation of organic matter presented in seawater and effluent from different Inline-flocculation filtration

Filter Media	Time	Velocity (m/h)	Flocculant dose (mg-Fe^{3+}/L)	DOC (mg/L)	HOC (mg/L)	CDOC (mg/L)	Bio-polymers (mg/L)	Humic substances (mg/L)	Building blocks (mg/L)	LMW neutrals and acids (mg/L)
	Raw Seawater			2.79	0.97	1.82	0.11	0.44	0.08	1.19
Sand	1 hr	5	0	2.70	0.77	1.93	0.07	0.44	0.08	1.34
				3.23	20.62	-	36.36	-	-	-
	6 hr	5	0	2.12	0.77	1.35	0.07	0.44	0.08	0.76
				24.01	20.62	25.82	36.36	-	-	36.13
Sand	1 hr	5	1	2.14	0.55	1.59	0.15	0.45	0.19	0.80
				23.30	43.30	12.64	-	-	-	32.77
	6 hr	5	1	2.00	0.47	1.53	0.12	0.44	0.18	0.79
				28.32	51.55	15.93	-	-	-	33.61
Sand	1 hr	5	3	1.59	0.36	1.23	0.08	0.37	0.12	0.66
				43.01	62.89	32.42	27.27	15.91	-	44.54
	6 hr	5	3	1.31	0.31	1.00	0.06	0.37	0.09	0.48
				53.05	68.04	45.05	45.45	15.91	-	59.66

Filter Media	Time	Velocity (m/h)	Flocculant dose (mg-Fe^{3+}/L)	DOC (mg/L)	HOC (mg/L)	CDOC (mg/L)	Bio-polymers (mg/L)	Humic substances (mg/L)	Building blocks (mg/L)	LMW neutrals and acids (mg/L)
Sand	1 hr	5	5	1.57	0.42	1.15	0.07	0.54	0.09	0.45
				43.73	56.70	36.81	36.36	-	-	62.18
	6 hr	5	5	1.53	0.41	1.12	0.06	0.50	0.08	0.48
				45.16	57.73	38.46	45.45	-	-	59.66
Sand	1 hr	10	3	1.86	0.37	1.49	0.05	0.56	0.10	0.78
				33.33	61.86	18.13	54.55	-	-	34.45
	6 hr	10	3	1.74	0.27	1.47	0.05	0.56	0.09	0.77
				37.63	72.16	19.23	54.55	-	-	35.29
Anthracite	1 hr	5	0	2.16	0.67	1.49	0.08	0.39	0.07	0.95
				22.58	30.93	18.13	27.27	11.36	12.50	20.17
	6 hr	5	0	2.22	0.69	1.53	0.10	0.40	0.08	0.95
				20.43	28.87	15.93	9.09	9.09	0.00	20.17
Anthracite	1 hr	5	1	1.65	0.43	1.22	0.06	0.38	0.14	0.64
				40.86	55.67	32.97	45.45	13.64	-	46.22
	6 hr	5	1	1.91	0.64	1.27	0.07	0.38	0.15	0.67
				31.54	34.02	30.22	36.36	13.64	-	43.70
Anthracite	1 hr	5	3	1.60	0.42	1.18	0.06	0.37	0.15	0.59
				42.65	56.70	35.16	45.45	15.91	-	50.42
	6 hr	5	3	1.76	0.52	1.24	0.06	0.42	0.10	0.66
				36.92	46.39	31.87	45.45	4.55	-	44.54

Filter Media	Time	Velocity (m/h)	Flocculant dose (mg-Fe^{3+}/L)	DOC (mg/L)	HOC (mg/L)	CDOC (mg/L)	Bio-polymers (mg/L)	Humic substances (mg/L)	Building blocks (mg/L)	LMW neutrals and acids (mg/L)
Anthracite	1 hr	5	5	1.61	0.22	1.09	0.07	0.45	0.12	0.45
				42.29	77.32	40.11	36.36	-	-	62.18
	6 hr	5	5	1.63	0.22	1.39	0.07	0.55	0.12	0.65
				41.58	77.32	23.63	36.36	-	-	45.38
Anthracite	1 hr	10	3	1.42	0.22	1.20	0.06	0.50	0.08	0.56
				49.10	77.32	34.07	45.45	-	-	52.94
	6 hr	10	3	1.76	0.24	1.53	0.06	0.60	0.09	0.78
				36.92	75.26	15.93	45.45	-	-	34.45

B.4 Headloss development and efficiency in terms of turbidity removal for Spiral Flocculation

Filter Media	Flocculant dose (mg-Fe^{3+}/L)	Velocity (m/h)	Time (hr)	Turbidity NTU	Turbidity removal (%)	Final headloss development (cm)	Remarks
Sand	3	5	0	0.16	62.62	54.50	SW - 0.42 NTU
			1	0.14	66.67	58.00	Head loss in spiral flocculator = 4cm
			2	0.20	52.38	60.00	G=13.6 $S^{-}1$
			3	0.12	71.43	65.00	Q=21.2 ml/min
			4	0.13	69.05	69.00	
			5	0.08	81.43	70.00	
			6	0.14	66.67	72.00	
Anthracite	3	5	0	0.15	64.29	5.00	SW - 0.42 NTU
			1	0.15	64.29	5.50	Head loss in spiral flocculator = 4cm
			2	0.14	66.67	6.00	G=13.6 $S^{-}1$
			3	0.16	62.86	6.20	Q=21.2 ml/min
			4	0.15	64.29	6.50	
			5	0.12	71.43	7.00	
			6	0.19	54.76	7.50	

Filter Media	Flocculant dose (mg-Fe^{3+}/L)	Velocity (m/h)	Time (hr)	Turbidity NTU	Turbidity removal (%)	Final headloss development (cm)	Remarks
Sand	3	10	0	0.15	62.44	50.00	SW - 0.41 NTU
			1	0.10	76.83	56.00	Head loss in spiral flocculator = 8cm
			2	0.10	76.83	66.00	G= 27.33S^{-}1
			3	0.14	65.85	80.00	Q=42.4 ml/min
			4	0.15	63.41	85.50	
			5	0.14	65.85	92.50	
			6	0.15	64.63	102.00	
Anthracite	3	10	0	0.20	53.86	15.00	SW - 0.44 NTU
			1	0.15	66.36	17.00	Head loss in spiral flocculator = 8cm
			2	0.15	65.91	20.00	G= 27.33S^{-}1
			3	0.20	54.55	23.00	Q=42.4 ml/min
			4	0.20	54.55	27.50	
			5	0.19	56.82	29.00	
			6	0.18	59.09	31.00	

B.5 Efficiency in terms of UF-MFI for Spiral Flocculation

Filter Media	Flocculant dose (mg-Fe^{3+}/L)	Velocity (m/h)	UF-MFI (0-3 hr) (s/L^2)	UF-MFI (3-6 hr) (s/L^2)	UF-MFI removal (0-3 hr) (%)	UF-MFI removal (3-6 hr) (%)
Sand	3	5	3453	5771	70.20	50.20
	3	10	3905	5133	66.30	55.71
Anthracite	3	5	5075	2943	56.21	74.61
	3	10	4067	4647	64.91	59.90

B.6 DOC removal and fractionation of organic matter presented in seawater and effluent from different Spiral-flocculation filtration

Filter Media	Time	Velocity (m/h)	Flocculant dose (mg-Fe^{3+}/L)	DOC (mg/L)	HOC (mg/L)	CDOC (mg/L)	Bio-polymers (mg/L)	Humic substances (mg/L)	Building blocks (mg/L)	LMW neutrals and acids (mg/L)
	Raw Seawater			2.07	0.38	1.69	0.21	0.58	0.17	0.76
Sand	1 hr	5	3	1.37	0.05	1.32	0.08	0.52	0.11	0.61
				33.82	86.84	21.89	61.90	10.34	35.29	19.74
	6 hr	5	3	1.29	0.09	1.20	0.06	0.52	0.11	0.51
				37.68	76.32	28.99	71.43	10.34	35.29	32.89
Sand	1 hr	10	3	1.39	0.11	1.28	0.08	0.53	0.08	0.59
				32.85	71.05	24.26	61.90	8.62	52.94	22.37
	6 hr	10	3	1.13	0.09	1.04	0.06	0.49	0.06	0.43
				45.41	76.32	38.46	71.43	15.52	64.71	43.42
Anth	1 hr	5	3	1.18	0.10	1.08	0.05	0.47	0.05	0.51
				43.00	73.68	36.09	76.19	18.97	70.59	32.89
	6 hr	5	3	1.26	0.12	1.14	0.07	0.53	0.05	0.51
				39.13	68.42	32.54	66.67	8.62	70.59	32.89
Anth	1 hr	10	3	1.06	0.08	0.98	0.05	0.42	0.09	0.42
				48.79	78.95	42.01	76.19	27.59	47.06	44.74
	6 hr	10	3	1.18	0.10	1.08	0.04	0.43	0.07	0.54
				43.00	73.68	36.09	80.95	25.86	58.82	28.95

APPENDIX – C: PERFORMANCE OF TITANIUM SALTS COMPARED WITH FECL$_3$ FOR SEAWATER REVERSE OSMOSIS PRE - TREATMENT

C.1 Turbidity, UV and DOC removal efficiency for TICL$_4$ at pH 5 – 9

pH	5
Seawater turbidity	6.15
DOC	2.45
UV	0.0436

Dose mg/l	pH	Turbidity	UV	DOC	Zeta potential	Turbidity removal %	UV removal %	DOC removal %
1	4.45	2.74	0.02	1.45	1.64	55.45	45.41	40.82
5	3.13	3.17	0.02	0.90	-1.80	48.46	61.70	63.27
10	2.87	5.30	0.02	0.86	-0.81	13.82	62.84	64.90
15	2.75	8.75	0.02	0.90	-0.61	-42.28	61.47	63.27
20	2.62	10.00	0.02	0.95	1.04	-62.60	59.86	61.22
30	2.40	25.20	0.02	0.95	-0.47	-309.76	60.32	61.22

pH	6.00
Seawater turbidity	6.30
DOC	1.90
UV	0.03

Dose mg/l	pH	T30	UV	DOC	Zeta potential	Turbidity removal %	UV removal %	DOC removal %
1	6.00	2.25	0.03	1.60	-11.63	64.29	16.00	15.79
5	5.63	1.74	0.02	1.13	6.23	72.38	41.54	40.53
10	4.93	2.61	0.01	0.75	-5.13	58.57	58.77	60.53
15	3.58	2.50	0.02	0.83	4.50	60.32	53.54	56.32
20	3.07	3.29	0.02	1.20	-3.33	47.78	38.46	36.84
30	2.56	6.90	0.02	0.83	-9.24	-9.52	53.54	56.32

pH	7.00
Seawater turbidity	6.70
DOC	2.90
UV	0.05

Dose mg/l	pH	T30	UV	DOC	Zeta potential	Turbidity removal %	UV removal %	DOC removal %
1	6.57	2.16	0.03	1.82	-4.13	67.76	40.58	37.24
5	6.16	1.57	0.02	1.45	-2.20	76.57	53.98	50.00
10	5.91	1.59	0.03	1.55	1.24	76.27	49.32	46.55
15	5.72	1.77	0.02	1.20	0.37	73.58	60.97	58.62
20	5.26	2.05	0.02	1.42	0.28	69.40	54.95	51.03
30	2.83	4.07	0.02	0.97	-2.76	39.25	66.99	66.55

pH	8.00
Seawater turbidity	6.67
DOC	2.30
UV	0.04

Dose mg/l	pH	T30	UV	DOC	Zeta potential	Turbidity removal %	UV removal %	DOC removal %
1	7.35	3.02	0.03	1.82	0.96	54.72	22.11	20.87
5	6.61	2.28	0.03	1.57	-0.16	65.82	32.91	31.74
10	6.18	2.02	0.02	1.32	-5.15	69.72	44.72	42.61
15	5.88	1.94	0.01	0.73	-1.30	70.91	68.09	68.26
20	5.58	2.86	0.01	0.80	3.68	57.12	63.82	65.22
30	3.37	2.94	0.01	0.65	-2.99	55.92	77.39	71.74

pH	9.00
Seawater turbidity	6.67
DOC	2.30
UV	0.04

Dose mg/l	pH	T30	UV	DOC	Zeta potential	Turbidity removal %	UV removal %	DOC removal %
1	8.71	2.46	0.03	1.64	-2.75	63.12	30.65	28.70
5	8.26	2.02	0.03	1.73	6.85	69.72	26.63	24.78
10	7.92	2.42	0.02	1.36	-1.55	63.72	42.46	40.87
15	7.33	2.99	0.02	1.43	1.91	55.17	40.20	37.83
20	6.89	2.44	0.02	1.25	1.95	63.42	48.49	45.65
30	6.20	1.83	0.01	0.73	-5.52	72.56	67.09	68.26

C.2 Turbidity, UV and DOC removal efficiency for Ti $(SO_4)_2$ at pH 5 – 9

pH	5
Seawater turbidity	6.1
DOC	2.6
UV	0.0435

Dose mg/l	pH	T30	UV	DOC	Zeta potential	Turbidity removal %	UV removal %	DOC removal %
1	5.00	4.13	0.03	1.85	1.23	32.30	26.21	28.85
5	4.19	1.68	0.02	1.35	3.64	72.46	48.05	48.08
10	3.30	2.60	0.02	1.25	-0.25	57.38	53.33	51.92
15	3.12	4.18	0.02	0.95	1.70	31.48	59.54	63.46
20	2.97	7.00	0.02	0.90	0.51	-14.75	62.07	65.38
30	2.65	11.20	0.02	1.28	-0.21	-83.61	51.49	50.77

pH	6.00
Seawater turbidity	6.00
DOC	1.70
UV	0.03

Dose mg/l	pH	T30	UV	DOC	Zeta potential	Turbidity removal %	UV removal %	DOC removal %
1	6.00	4.85	0.03	1.65	-2.82	19.17	3.47	2.94
5	5.97	1.67	0.02	1.43	-3.15	72.17	17.71	15.88
10	5.85	1.39	0.02	1.25	4.72	76.83	28.47	26.47
15	5.67	1.80	0.02	1.07	-0.69	70.00	35.07	37.06
20	5.32	2.09	0.02	1.00	0.41	65.17	38.19	41.18
30	3.42	2.37	0.02	1.25	-0.21	60.50	29.17	26.47

pH	7.00
Seawater turbidity	5.90
DOC	1.98
UV	0.03

Dose mg/l	pH	T30	UV	DOC	Zeta potential	Turbidity removal %	UV removal %	DOC removal %
1	6.73	3.49	0.03	1.75	2.15	40.85	12.61	11.62
5	6.56	1.69	0.03	1.55	-3.53	71.36	24.34	21.72
10	6.35	1.58	0.02	1.23	1.16	73.22	38.71	37.88
15	6.16	1.89	0.02	1.30	0.01	67.97	36.95	34.34
20	6.01	1.97	0.02	1.15	-0.43	66.61	43.40	41.92
30	5.30	2.26	0.02	1.00	-1.61	61.69	47.51	49.49

pH	8.00
Seawater turbidity	6.35
DOC	1.75
UV	0.03

Dose mg/l	pH	T30	UV	DOC	Zeta potential	Turbidity removal %	UV removal %	DOC removal %
1	7.64	4.26	0.03	1.65	-4.25	32.91	6.71	5.71
5	6.92	1.70	0.03	1.53	-5.10	73.23	15.10	12.57
10	6.70	1.96	0.02	1.42	-3.36	69.13	22.48	18.86
15	6.55	1.93	0.02	1.35	-0.70	69.61	25.17	22.86
20	6.42	1.87	0.02	1.42	-1.50	70.55	22.48	18.86
30	5.87	1.93	0.02	0.96	-6.44	69.61	44.63	45.14

pH	9.00
Seawater turbidity	6.86
DOC	1.97
UV	0.03

Dose mg/l	pH	T30	UV	DOC	Zeta potential	Turbidity removal %	UV removal %	DOC removal %
1	8.88	3.30	0.03	1.85	4.84	51.90	7.08	6.09
5	8.66	1.78	0.03	1.73	-2.58	74.05	13.57	12.18
10	8.47	1.65	0.03	1.67	3.99	75.95	15.63	15.23
15	8.08	2.00	0.03	1.65	-5.44	70.85	16.52	16.24
20	7.82	2.13	0.03	1.52	2.93	68.95	23.89	22.84
30	6.87	3.45	0.02	1.30	3.42	49.71	36.28	34.01

C.3 Turbidity, UV and DOC removal efficiency for $FeCl_3$ at pH 5 – 9

pH	5
Seawater turbidity	6.29
DOC	2
UV	0.0343

Dose mg/l	pH	T30	UV	DOC	Zeta	Turbidity removal %	UV removal %	DOC removal %
1	5.00	1.98	0.03	1.65	-0.68	68.52	18.08	17.50
5	4.95	1.62	0.02	0.90	-2.92	74.24	51.31	55.00
10	4.82	2.39	0.02	0.83	1.09	62.00	55.98	58.50
15	4.31	2.46	0.02	1.35	-0.63	60.89	35.86	32.50
20	3.85	3.45	0.02	1.28	0.44	45.15	38.19	36.00
30	3.23	10.80	0.03	1.82	4.57	-71.70	3.79	9.00

pH	6.00
Seawater turbidity	6.40
DOC	2.60
UV	0.04

Dose mg/l	pH	T30	UV	DOC	Zeta	Turbidity removal %	UV removal %	DOC removal %
1	6.14	1.86	0.03	1.64	0.48	70.94	34.29	36.92
5	6.13	1.83	0.02	1.50	-1.22	71.41	40.71	42.31
10	6.11	1.80	0.02	1.42	2.76	71.88	45.00	45.38
15	6.06	1.79	0.02	1.25	-0.48	72.03	50.95	51.92
20	5.97	1.80	0.02	1.32	-1.83	71.88	48.33	49.23
30	5.90	1.59	0.02	0.95	1.10	75.16	59.05	63.46

pH	7.00
Seawater turbidity	6.54
DOC	1.88
UV	0.03

Dose mg/l	pH	T30	UV	DOC	Zeta	Turbidity removal %	UV removal %	DOC removal %
1	6.97	2.05	0.03	1.64	-1.67	68.65	13.25	12.77
5	6.91	1.79	0.02	1.50	-1.84	72.63	21.45	20.21
10	6.90	1.64	0.03	1.55	-1.74	74.92	20.82	17.55
15	6.83	1.53	0.02	1.35	-2.92	76.61	29.97	28.19
20	6.82	1.64	0.02	1.36	-2.70	74.92	29.02	27.66
30	6.64	1.66	0.02	1.20	-2.49	74.62	36.91	36.17

pH	8.00
Seawater turbidity	6.67
DOC	1.90
UV	0.03

Dose mg/l	pH	T30	UV	DOC	Zeta	Turbidity removal %	UV removal %	DOC removal %
1	7.58	1.80	0.03	1.85	-0.99	73.01	2.16	2.63
5	7.49	1.53	0.03	1.73	0.03	77.06	9.57	8.95
10	7.34	1.53	0.03	1.62	-3.40	77.06	15.74	14.74
15	7.20	1.78	0.02	1.45	2.59	73.31	25.93	23.68
20	7.10	1.72	0.03	1.50	-1.30	74.21	22.84	21.05
30	6.87	2.08	0.02	1.20	0.52	68.82	38.89	36.84

pH	9.00
Seawater turbidity	6.22
DOC	2.12
UV	0.04

Dose mg/l	pH	T30	UV	DOC	Zeta	Turbidity removal %	UV removal %	DOC removal %
1	8.80	2.05	0.04	2.05	0.44	67.04	3.01	3.30
5	8.76	1.39	0.03	1.65	-4.63	77.65	24.86	22.17
10	8.62	1.80	0.03	1.80	1.75	71.06	10.93	15.09
15	8.53	1.88	0.03	1.77	0.12	69.77	17.49	16.51
20	8.68	1.93	0.03	1.82	-0.20	68.97	15.03	14.15
30	8.31	1.35	0.03	1.82	-2.34	78.30	15.30	14.15