

**Faculty of Science and Engineering
Department of Civil Engineering**

**Investigation on Fouling of Membranes for Wastewater Treatment
and Reuse**

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**This thesis is presented for the Degree of
Doctor of Philosophy
of
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Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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Abstract

Federation and Millennium droughts are the worst on record for Australia since settlement. Scarce rain in most of the densely populated regions across the country increased pressure on water during the Millennium drought. While this has triggered conservation measures, there has also been a diversification of water supply options. Specifically recycled water has emerged as an alternative source of water to fulfil requirements of industries (Western Corridor Recycled Water Project, South East Queensland) and also to facilitate indirect potable water (Groundwater replenishment, Western Australia). Purified recycled water is produced with tertiary treatment of wastewater using membrane filtration technology such as ultra-filtration (UF), nano-filtration (NF) and reverse osmosis (RO) membranes are commonly employed to facilitate this level of advance treatment. One of the major limitations of membranes is fouling. Membrane fouling can result in water production losses, integrity losses, poor water quality and higher energy and chemical costs. Chemicals that are used to control fouling on the other hand can have an impact on membrane integrity shortening its effective usage.

Pre-treatment of feed streams prior to membrane filtration is commonly used to reduce membrane fouling. In this study, both biological and physicochemical pre-treatments were investigated against membrane performance. Biological activated carbon (BAC) was used to facilitate biological pre-treatment and enhanced coagulation and magnetic ion exchange resin (MIEX) were used to facilitate physicochemical pre-treatment. The fundamental aspects of biological and physicochemical treatments were initially analysed in terms of dissolved organic carbon (DOC) removal. Subsequently the influence of their combined use was examined for DOC removal. Compared to individual pre-treatment, the combined pre-treatment resulted in an enhance removal of DOC. Specifically BAC treatment after physicochemical treatment of secondary wastewater effluent (SWWE)

facilitated preferential removal of low molecular weight DOC fractions. This combined treatment option also was noted to increase the average Stokes radius number average molecular weight of dissolved organic matter (DOM). Thus, contrary to the conventional focus, i.e. to reduce membrane fouling by reducing DOC using pre-treatment, this study focused on reducing membrane fouling by combing pre-treatment options in different arrangements such to induce change on DOC to prevent its entry into membrane pores.

Two pre-treatment combinations (biological/physicochemical and physicochemical/biological) were examined for their anti-fouling properties. Of the two combinations, physicochemical/biological combination effectively reduced fouling of both NF and UF membranes and this was found to be a result of an induced change on DOM, i.e. an increase of average Stokes radius and number average molecular weight of DOM. The reduced fouling on NF and UF membranes with the physicochemical/biological combination wasn't largely a result of an overall DOC reduction; it was primarily due to the reduction/conversion of specific low molecular weight DOM from SWWE. In fact, the biological/physicochemical combination resulted in a better overall DOC removal to that of its counterpart (physicochemical/biological) but failed to facilitate higher stable flux.

Accordingly this study for the first time have demonstrated the need for a change of mind set from trying to remove all DOC in SWWE to reduce fouling to only target specific DOC fractions that causes pore constriction and irreversible fouling. In this instance the combined used of physicochemical/biological pre-treatment did facilitate removal/conversion of specific DOC foulants and there is opportunity to further manipulate the operation of BAC such to achieve further stabilization and higher flux from membranes without compromising membrane integrity.

List of Publications

Journal articles forming chapters of the thesis

1. Aryal, A., Sathasivan, A. and Adhikari, R.A. (2011) Evidence that BAC treatment enhances the DOC removal by enhanced coagulation. *Desalination* 280(1-3), 326-331.
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Additional publications relevant to the thesis but not included as chapters

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Abbreviations

ATR-FTIR	Attenuated total reflection- Fourier transform infrared spectroscopy
BAC	Biological activated carbon
BWTP	Beenyup wastewater treatment plant
DBP	Disinfection by products
DI	Deionized
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EBCT	Empty bed contact time
EC	Enhanced coagulation
EfOM	Effluent organic matter
GAC	Granular activated carbon
HA	Humic acid
HMW	Higher molecular weight
LC-OCD	Liquid chromatography–organic carbon detection
LMW	Lower molecular weight
MF	Microfiltration
MIEX	Magnetic ion exchange resin
MW	Molecular weight

MWCO	Molecular weight cut off
NDMA	Nitrosodimethyldiamine
NF	Nanofiltration
NMR	Nuclear magnetic resonance
NOM	Natural organic matter
NP	Non-polar
NS	Non-sorbable
PAC	Powdered activated carbon
RO	Reverse osmosis
SS	Suspended solids
SWWE	Secondary wastewater effluent
TOC	Total organic carbon
UF	Ultrafiltration

Chapter 1

Introduction

1.1 Background

Water is a fugitive resource, flowing through space and time, upon which all social and economic activities and ecosystem functions depend. The global volume of water is very large, but only 2.5% is fresh water and it is unevenly distributed. Of concern is that, the global population is continuously on the rise and expected to exceed 9 billion by 2050 (UNESCO 2012, UNHABITAT 2010). The combination of a growing population, increased demand for resources and improving standards of living places increasing pressure on the water supplies required for domestic, agricultural and industrial purposes.

Australia is one of the driest countries in terms of drinking water resources. According to the Water Authority of Western Australia (WA), the demand for public water supply is growing as a result of significant population growth in the Perth metropolitan area. However, Perth's rainfall, and potential surface water catchment has undergone a significant reduction since the 1970s. Average flow to dams in the years 1911-1974 was 338 GL/year, and 167 GL/year in the years 1975-2001. Surface water deficits are being met by additional demands on groundwater, but increased use of groundwater from existing aquifers could result in a draw-down that may be detrimental to the environment. The winter of 2001 produced a surface water inflow of only 30 GL. The WA Water Corporation supplies 250 GL/year potable water to Perth, and receives 100 GL sewage per year into its seven metropolitan sewage water treatment plants. Only 3.3% of Perth's wastewater is recycled, mostly within Perth's sewage treatment plants, but some is indirectly accessed via groundwater by Alcoa at Kwinana (Radcliffe 2004). This indicates the sustainability limits to Perth's current water resources management.

Many countries around the world such as India, Ethiopia, Kenya, and Nigeria are likely to run short of water in the next 25 years. China has already faced chronic water problem (Hinrichsen et al. 1998, Tibbetts 2000). Similarly, the United Arab Emirates, Saudi Arabia, Kuwait, and Bahrain largely depend on sea water desalination as there is virtually no fresh water source available to meet the water demand of the existing population (Postel 1997). Spain has recently witnessed severe water shortages (Martin-Rosales et al. 2007). These are a just few examples indicating the severity of the water crisis around the globe.

In this context, the development of a sustainable alternative water resource is essential in order to prevent the degradation and shortage of water in both dry and densely populated areas of the world. Domestic wastewater contains more than 99% water and less than 1% solids (Shon et al. 2004). So, wastewater reuse could be a promising means of overcoming the potential pressure on water resources due to human intervention. The membrane filtration process can produce water that meets stringent quality requirements by being free of pathogenic microorganisms and organic and inorganic contaminants (Mulder 1996). A broad range of water types such as municipal wastewater, brackish water and sea water can be purified by employing membrane technology.

However, membrane fouling is a persistent problem faced by many water utilities, incurring higher operational costs and compromising treatment efficiency, leading to questions about the sustainability of membrane filtration. Membrane fouling is the blockage of pores by foulants such as organics, minerals, colloids, microbial contaminants, and particles on the membrane surface or by cake formation (Song 1998). The major membrane fouling mechanisms are generally referred to as scaling, particulate fouling, organic fouling and biofouling.

Scaling and particulate fouling are respectively the result of inorganic compounds and colloidal matter (Vrouwenvelder and van der Kooij 2003). Organic fouling results from the accumulation of dissolved organic matter (DOM) in the feed water in and on the membrane pores, and biofouling may arise during the long-term operation of membranes as a result of deposited organics and the microbial

population (Kang et al. 2004). The organic fouling classification overlaps those of colloidal fouling and biofouling. In addition to macro molecules, organic foulants can include organic colloids. Moreover, biofouling can be considered a biotic form of organic fouling while organic matter originating from microbiologically-derived cellular debris can be considered an abiotic form of biofouling (Amy 2008).

Membrane fouling is dependent on many parameters such as membrane characteristics, source or feed water characteristics and the hydrodynamic condition of the system. Of these, feed water characteristics are highly influential and complicated aspects of membrane fouling (Cuperus and Smolders 1991, Jarusutthirak and Amy 2001, Tang et al. 2007). Effluent organic matter (EfOM) is ubiquitous in secondary wastewater effluent (SWWE) and is considered to be an important factor in membrane fouling. It can be composed of different types of bulk organic matter, natural organic matter (NOM) dominated by humic substances, algal organic matter consisting of extracellular and intracellular molecule and cellular debris, and EfOM consisting of background NOM with soluble microbial products (SMPs) (Amy 2008, Fan et al. 2008, Jarusutthirak et al. 2002).

A long life span of membrane and low operational costs are only possible if the impact of organic matters responsible for fouling can be minimized beforehand. This research makes an in-depth assessment of DOM removal in SWWE particularly the employment of pre-treatment to reduce organic fouling of membranes. The pre-treatment options included in this study are biological activated carbon (BAC), enhanced coagulation (EC) and magnetic ion exchange resin (MIEX). Despite vast efforts to reduce membrane fouling, for instance, by improving membrane properties and the pre-treatment of feed water, fouling is still the major fundamental challenge in water treatment industries (Amy, 2008, Shon et al. 2004).

Both individual and combined pre-treatments to reduce membrane fouling have been investigated by many researchers in the past (Fabris et al. 2007, Jung et al. 2006, Li and Chen 2004, Shon et al. 2004). However, their anti-fouling properties through systematic and synergistic DOM removal remain poorly understood. Thus, this research aims to attain DOM residual reduction and maintain a suitable size of

dominant DOM residuals which can be retained on the surface of membrane to avoid pore blocking and hence reduce membrane fouling. The expected outcome of this research is a better understanding of pre-treatment strategies that reduce membrane fouling for efficient wastewater treatment and reuse.

1.2 Objectives and Scope of the Study

This research makes an in-depth assessment of organic matter removal by employing pre-treatment to reduce organic fouling of membrane. Various pre-treatment strategies were investigated for the removal of DOM as well as the alteration of their physical properties in SWWE. These two fundamental aspects were then investigated with respect to reduction of membrane fouling, for the development of efficient wastewater recycling techniques. The overall aim of this research can be summarized as follows:

1. To investigate the combination of BAC with EC or MIEX for enhanced organic removal and to develop a pre-treatment strategy to synergize organic matter removal over a wide spectrum of dissolved organic carbon (DOC).
2. To evaluate the individual and combined pre-treatment strategies against membrane fouling in order to understand the fouling mechanism through systematic and synergistic DOM removal
3. To identify the organic compounds, particular groups or molecular characteristics responsible for membrane fouling in order to gain better understanding of membrane fouling that can be employed in future research and applications.

1.3 Research Significance

Previous studies have investigated the performance of various biological and physicochemical pre-treatments for the removal of DOM from SWWE and to reduce membrane fouling. In many instances, these pre-treatments are simply employed in combination to maximize organics removal, but this is often inhibited by a lack of understanding of the synergistic effect. By contrast, this study investigated the ability

of biological treatment to induce changes in DOM geometry, in addition to DOM removal. The fundamental behaviour of BAC was then further explored to synergize DOM removal along with other physicochemical pre-treatments and to reduce membrane fouling. The significant points of the research outcomes are:

- Successful conversion of the non-coagulable fraction into a coagulable fraction in SWWE with the help of microbial activity in the BAC bed. The finding was further verified for the conversion of the MIEX non-amenable fraction into an amenable fraction. This noble finding was then employed to synergize BAC with EC or MIEX treatment for the removal of additional DOC which otherwise remained unaffected by individual pre-treatment.
- The ability of BAC treatment to induce changes in DOM geometry in addition to DOM removal is reported in contrast to previous research. This property of BAC was employed to understand and reduce membrane fouling in SWWE.
- This study helps water utilities to identify the better pre-treatment strategies for efficient organic removal or for membrane fouling reduction in wastewater recycling and reuse

1.4 Research Approach

The research was undertaken in two different steps as presented in Figure 1.1. The performance of pre-treatment was evaluated first in terms of EfOM removal from SWWE. BAC was investigated both alone and in combination with EC and MIEX to synergize the removal of organic matter. Different pre-treatments and their combinations were employed in order to understand the role of microbial activity in enhanced organics removal. The second part of this research investigated the fundamental mechanism of microbial activity in reducing fouling of ultrafiltration (UF) and nanofiltration (NF) membranes. The outcome of the research is grouped in five different chapters as presented in Figure 1.2.

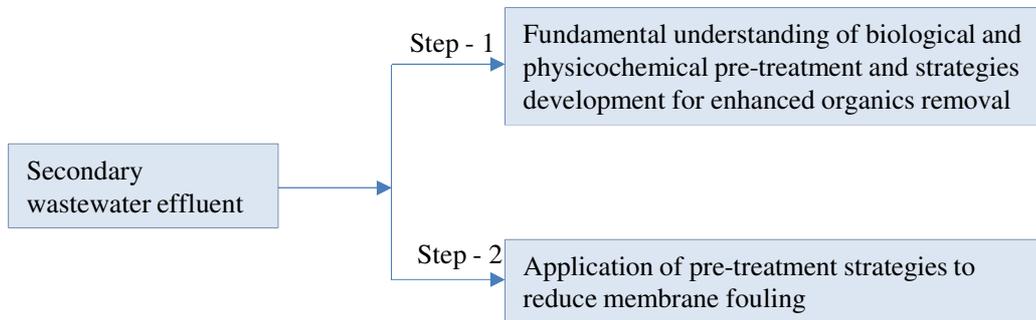


Figure 1.1: Research approach taken in the dissertation

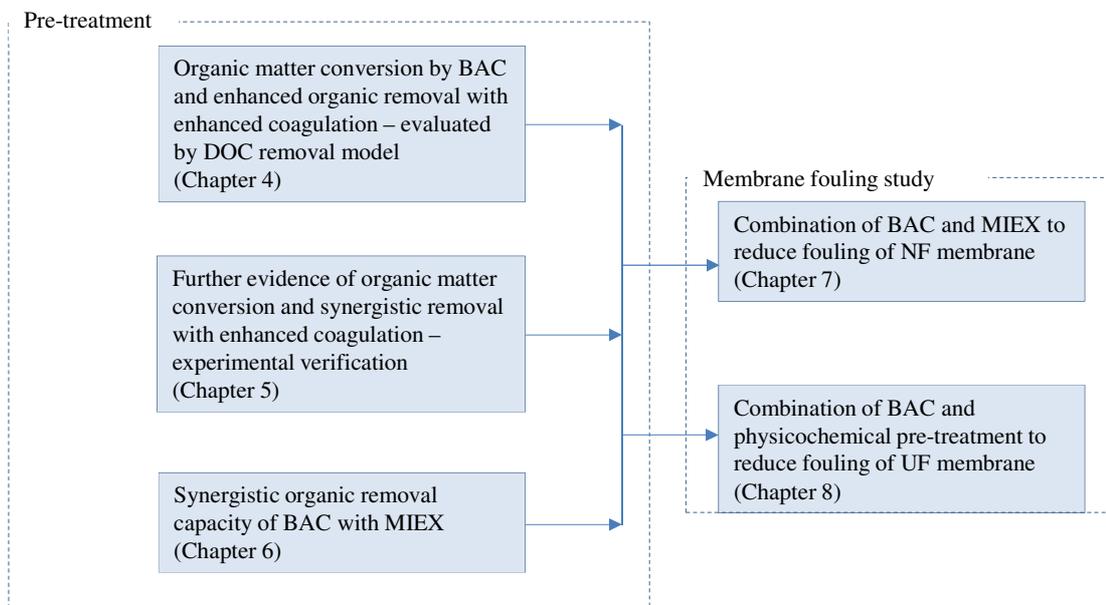


Figure 1.2: Primary area of research presented in this dissertation

The dissertation is presented in nine chapters including this introductory first chapter. Chapters 4 to 8 are written as stand-alone chapters and each chapter is either already published or has been submitted to peer-reviewed journals for publication. However, to facilitate the flow in reading common materials and methods are presented prior to these chapters. An overview of the work presented in each chapter is briefly described as follows.

Chapter 2 presents a comprehensive survey of the literature associated with the present work. The history and development of membrane filtration along with associated fouling mechanisms are reviewed in detail. The chapter also discusses various pre-treatment techniques employed in previous studies to reduce organic matter and subsequent membrane fouling emphasizing on their limitations in order to identify the scope of the present work.

Chapter 3 provides details on sample sources and common methodologies of pre-treatment and analysis undertaken in this research. It also provides an outline of experimental set-up, the BAC reactor set-up and the analytical parameters investigated.

Chapter 4 investigates the evidence that BAC treatment enhances the DOC removal by enhanced coagulation. The EC model is employed to show the crucial role of biological activity in enhancing the performance of coagulant in organic matter removal.

The evidence of organic matter conversion observed in Chapter 4 is further investigated in terms of experimental observation in Chapter 5 to verify the conclusions obtained from DOC modelling and to quantify the synergistic DOC removal obtained by the combination of BAC and EC.

Similarly, Chapter 6 investigates the importance of the combination order in enhancing EfOM removal by combining BAC and MIEX in order to show the ability of BAC to synergizing DOC removal when used with other physicochemical treatments.

Chapter 7 discusses the combined BAC and MIEX pre-treatment of SWWE to reduce fouling of NF membranes.

Similarly, chapter 8 investigates combined BAC and physicochemical pre-treatment of SWWE to reduce fouling of UF membranes. The experimental findings obtained from pre-treatment are further verified with organic matter of different fractions using the molecular weight cut off fractionation technique.

A summary of the research work, the conclusions, and recommendations for further studies are presented in Chapter 9.

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Chapter 2

Literature Review

2.1 Introduction

The application of membranes in water treatment and recycling has increased continuously over the past few years because of improved membrane design, smaller foot print and stringent quality requirements in terms of potable and industrial water use. However, membrane fouling remains a fundamental drawback that limits its ultimate potential. Membrane fouling is associated with many factors such as membrane characteristics, source or feed water characteristics and hydrodynamic conditions. Among them, the organic constituents present in secondary wastewater effluent (SWWE), known as effluent organic matters (EfOM), and their complex interplay are considered to be important factors. Thus, a detailed, cross-disciplinary exploration of fractional organic matter is required to understand the fundamentals of foulants and their removal prior to membrane filtration. On this basis, this chapter aims to reinforce critical points from the previous research to provide a background for the current investigation.

2.2 Membrane Filtration: History and Development

Membrane filtration is generally defined as a selective barrier between two phases. The perm-selective barrier allows some species such as water to permeate through them while selectively retaining other dissolved species such as ions. Thus, a membrane has the ability to transport one component more readily than another due to differences in physical and/or chemical properties between the membrane and the permeating components, when a driving force is applied. The membrane filtration process is characterized by the fact that the feed stream is divided into two streams, the retentate or concentrate, and the permeate (Figure 2.1), implying that either the concentrate or the permeate stream is the product (Kucera 2010, Mulder 1996).

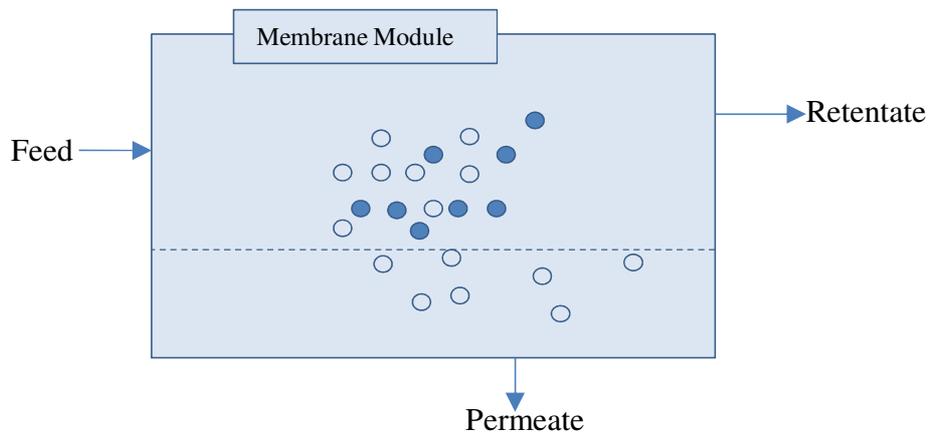


Figure 2.1: Schematic representation of a membrane filtration process

The systematic study of semi-permeable membranes can be traced back to 1748 when Abbe Nollet observed the phenomenon of osmosis (Cheryan 1998). Later, Pfeffer and Traube studied this phenomenon using ceramic membrane in the 1850s. Even towards the middle of 18th century membrane phenomena were observed and studied primarily to elucidate the barrier properties and related phenomena rather than to develop membranes for technical and industrial applications. Many years passed with scientific study, and the first commercial membranes for practical applications were manufactured by Sartorius in Germany (Zsigmondy 1918, 1922), although its products were mostly used in research laboratories. During World War II, damage to German distribution networks by bombing raids led to the development of techniques for rapid analysis for bacteria in water supplies. Thus, Sartorius membranes were employed as an effective method to cultivate microorganisms in drinking water. This was the first large-scale application of microfiltration (MF) membranes (Simon 2011).

In the late 1950s the basis for modern-day reverse osmosis (RO) was introduced by research with cellulose acetate membranes (Reid and Breton 1959), which showed their capacity for producing potable water from saline solutions. However, the crucial breakthrough in industrial membrane applications was achieved by the development of asymmetric membranes by Loeb and Sourirajan (1960, 1963). These membranes were comprised of a very thin, dense top layer ($< 0.5 \mu\text{m}$) with a

supporting porous sub layer of 50-200 μm thick. Loeb and Sourirajan's membrane preparation method had a great influence on the development of RO, ultrafiltration (UF), MF and gas separation membranes.

In the early 1970s, researchers made rapid progress in the development of commercially-viable RO membranes. During this time, thin film composite membranes were introduced with continuous improvement on water flux and rejection properties and reduction in feed pressure. Table 2.1 lists the development of some membrane processes that can also be found in more detail in several reviews (Baker 2004, Bøddeker 1995, Glater 1998).

Table 2.1: Development of (technical) membrane processes (Mulder, 1996)

Membrane Process	Country	Year	Application	Scale
Microfiltration	Germany	1920	laboratory use (bacteria filter)	small
Ultrafiltration	Germany	1930	laboratory use	small
Haemodialysis	Netherlands	1950	artificial kidney	small
Electrodialysis	USA	1955	desalination	industrial
Hyperfiltration	USA	1960	sea water desalination	industrial
Ultrafiltration	USA	1960	concentration of macromolecules	industrial
Gas separation	USA	1979	hydrogen recovery	industrial
Membrane distillation	Germany	1981	concentration of aqueous solutions	industrial
Pervaporation	Germany/ Netherlands	1982	dehydration of organic solvents	industrial

Membrane operation can be classified based on various parameters such as nature, porous or non-porous, morphology or structures and transport phenomenon. Along with these criteria, membrane separation can be broadly classified into high pressure and low pressure-driven membranes where the driving force is a pressure difference across the membrane. MF and UF are normally considered to be low pressure-driven membranes while NF and RO are high pressure-driven membranes (Figure 2.2). MF can remove particle sizes from 0.1 to 0.5 μm while UF can remove particles of 0.005 to 0.05 μm . Similarly, NF can effectively remove divalent ions and colour (0.5 to 10 nm) while the RO membrane is designed to remove both mono and divalent ions (<0.5 nm) for more than 99%. Thus, RO is widely used in sea water desalination and wastewater recycling while UF and MF are used in food and bioprocessing.

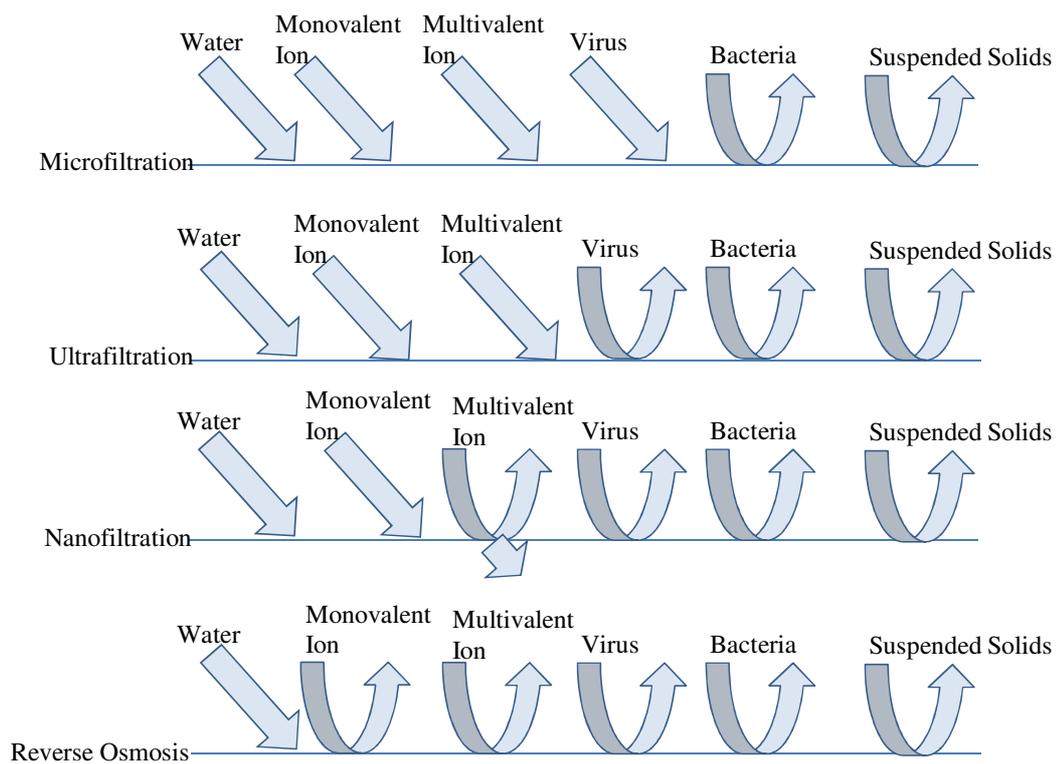


Figure 2.2: Scheme of different pressure-driven membrane filtration process and rejection capacities

2.3 Membrane Fouling

Despite the promising attributes of membranes in discriminating impurities from water, they are plagued by the single, critical problem of fouling. The term membrane fouling generally refers to flux decline resulting from clogging of membrane pores by deposits of undesirable organic and inorganic matter present in the water on and inside the membrane pores (Crozes et al. 1993).

Based on the particle deposition on or inside the membrane, fouling is classified as external (cake layers) and internal (pore blocking) as presented in Figure 2.3a (Chan and Chen 2001, Tarleton and Wakeman 1994). Similarly, the fouling is considered reversible if the membrane regains most of its permeability with hydraulic backwash. However, with an increase in filtration cycles, membrane fouling in general is not totally reversible and the membrane loses its permeability even after backwashing, resulting in significant flux decline (Figure 2.3b) (Crozes et al. 1993). Based on the mechanism, fouling can further be classified into scaling, particulate fouling, organic fouling and biofouling. Scaling and particulate fouling are the result of inorganic compounds (Vrouwenvelder and van der Kooij 2003) while organic and biofouling are caused by an abundance of organic matter and microbial activity (Kang et al. 2004).

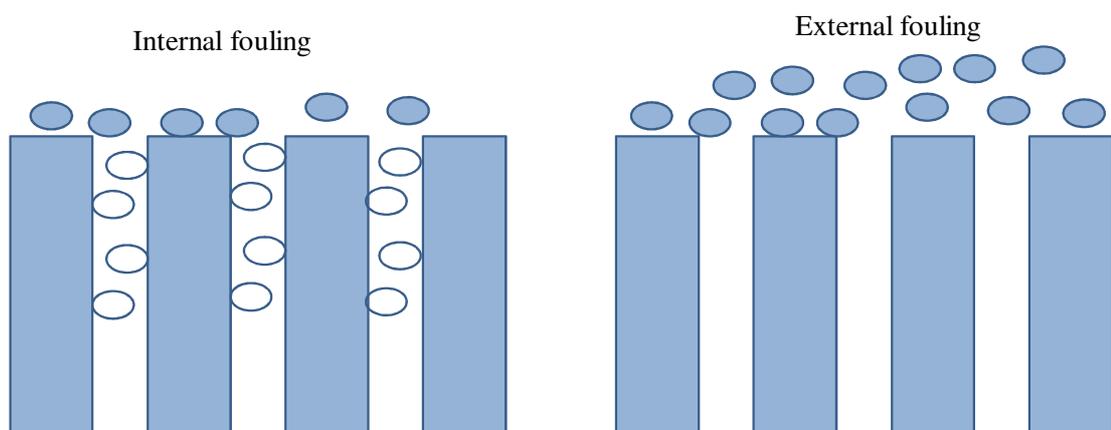


Figure 2.3a: Internal and external fouling

Membrane fouling is governed by many factors such as membrane and solute characteristics, membrane surface charge and hydrophobicity, hydrodynamic conditions and the presence of organic matter in feed water (Cuperus and Smolders 1991, Hong and Elimelech 1997, Jarusutthirak and Amy 2001, Seidel and Elimelech 2002, Tang et al. 2007). Of these, the presence of organic constituents in the water is the most complicated problem (Cuperus and Smolders 1991, Jarusutthirak and Amy 2001, Tang et al. 2007).

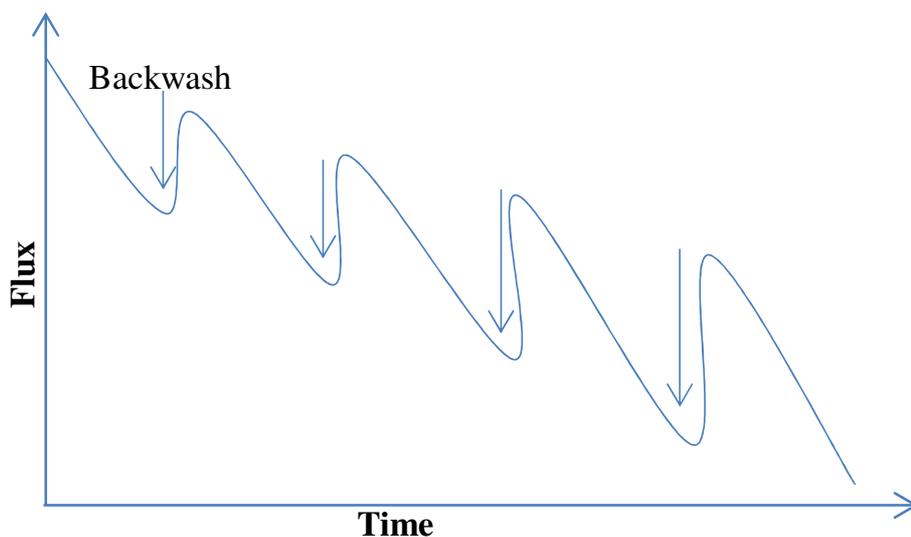


Figure 2.3b: Reversibility of membrane filtration

In wastewater treatment, the presence of EfOM is one of the major problems in membrane fouling. EfOM can be composed of different types of bulk organic matter, natural organic matter (NOM) dominated by humic substances, algal organic matter consisting of extracellular and intracellular molecule and cellular debris, and EfOM consisting of background NOM with soluble microbial products (SMPs) (Amy 2008, Fan et al. 2008, Jarusutthirak et al. 2002). Their presence in the feed stream eventually results in a loss of productivity and frequent membrane replacement (Clech et al. 2006). Thus, an improvement in membrane filtration performance is possible if the organic compounds responsible for fouling can either be removed or changed their fundamental behaviour with the membrane.

2.3.1 EfOM and Membrane Fouling

Previous studies have taken various approaches towards understanding EfOM-membrane behaviour with the aim of reducing membrane fouling (Figure 2.4). Considerable effort has gone into the characterization of organic matter and identification of foulants in SWWE to understand the influence of each of the fractions upon membrane fouling. According to Filloux et al. (2012) humic substances, protein and polysaccharides like substances in SWWE largely contributes towards membrane fouling. Jarusutthirak et al. (2002) examined the fouling of membranes using synthetic derivatives of humic substances, protein and polysaccharides and made similar observations. By characterising the organic matter in SWWE as hydrophobic and hydrophilic, many previous studies have been able to demonstrate that hydrophobic fractions contribute more towards fouling than hydrophilic fractions (Nilson and DiGiano 1996, Shon et al. 2006a, Yoon et al. 2005). However, hydrophilic fractions have also been found to be influential in membrane fouling (Cho et al. 1998, Fan et al. 2001, Lee et al. 2001). Table 2.2 presents similar observations arising from many other studies attempting to identify specific foulants.

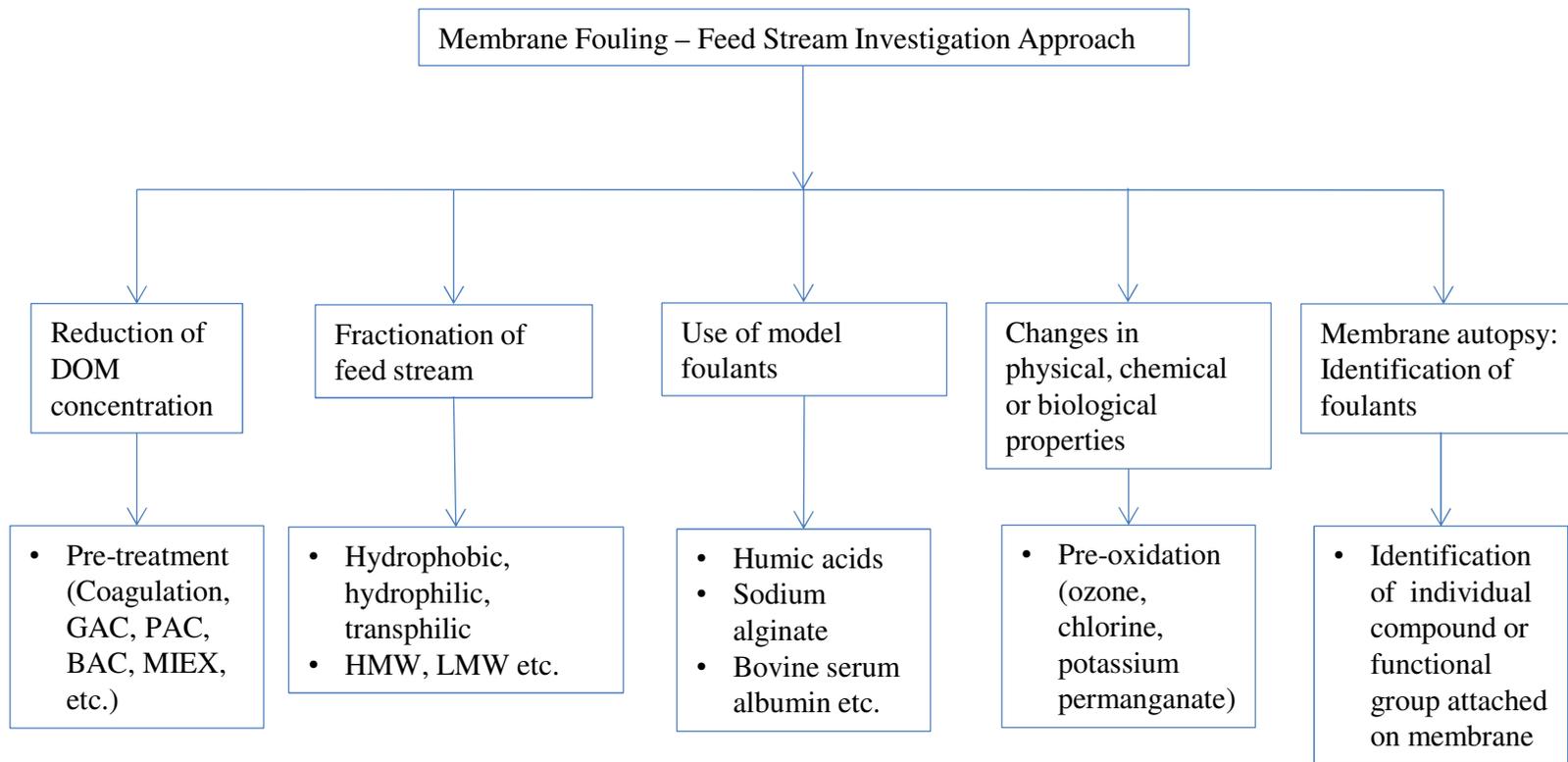


Figure 2.4: Approaches taken to understanding fouling in previous literature

Table 2.2: Organic fractions identified as a membrane foulants

SN	Organic Source	Membrane Used	Major Foulants	Reference
1	Surface water	MF, NF	NOM fraction between 1 μ m and 100 kDa	(Howe et al. 2006)
		UF	Polysaccharides-like compounds, iron and manganese	(Kimura et al. 2004a)
		MF, UF	Polysaccharides, proteins and peptidoglycans enriched in amino sugars	(Amy 2008)
		UF	High molecular weight neutral, hydrophilic neutral > hydrophobic acids > transphilic acid > hydrophilic charged	(Fan et al. 2001)
2	Drinking water	UF, NF	Hydrophobic and hydrophilic	(Cho et al. 1998)
		NF	High hydrophilicity and high MW values, protein and/or saccharides like substances	(Park et al. 2006)
		UF, NF	Carbohydrates as dominant membrane foulant, adsorption of hydrophobic (humic-like) components with small molecular weight followed by hydrophilic (carbohydrate-like) compounds with larger molecular weight on the membrane surface	(Yamamura et al. 2007)
3	SWWE	UF, NF	Protein, polysaccharides, amino sugars	(Jarusutthirak et al. 2002)

SN	Organic Source	Membrane Used	Major Foulants	Reference
		MF, UF	HMW organic material (40-70 kDa) comprised of hydrophilic components such as SMP and protein	(Fan et al. 2008)
		NF, RO	Polysaccharides, organic sulfonic acids, silicate colloids with a diverse amount of carboxylates, esters and primary and secondary amide groups	(Xu et al. 2006)
4	River water	NF	Humic macromolecules with higher hydrophobicity than hydrophilic fraction	(Nilson and DiGiano 1996)
		UF	Humic acid>fulvic acid	(Jucker and Clark 1994)
		UF	Hydrophilic>hydrophobic>transphilic	(Zularisam et al. 2007)
5	Ground Water	UF	Negatively charged carboxylic and phenolic group	(Lee et al. 2001)

Although, examining the impact of individual organic matter fractions enables the advancement of fundamental knowledge, studying their combined influence is perhaps more relevant to developing strategies to minimize membrane fouling. Previous studies have demonstrated that fouling from exposure to dissolved organic matters (DOM) was far more severe than the sum of fouling from each independent DOM fractions (Bonnélye et al. 2008, Drewes and Fox 1999, Gao et al. 2011). In a similar study, Braghetta et al. (1998) suggests that fractionation of organic matter into hydrophobic or hydrophilic fractions may not be the right approach as their interaction has a significant influence on membrane fouling behaviour with bulk DOM solutions. Jermann et al. (2007) studied a similar phenomenon by using

polysaccharides and humic acid solution, showing that both components acted synergistically, possibly through mutual interaction, resulting in more severe, irreversible fouling than with the individual fractions. These observations show that membrane fouling mechanisms yet remain complex and not fully understood.

These studies clearly show that it is hard to specify a particular treatment method for the reduction of membrane fouling. However, there are a few general approaches normally used to reduce membrane fouling, as presented in Figure 2.5. Among others, the pre-treatment of feed water is a commonly used approach and will be investigated in this dissertation.

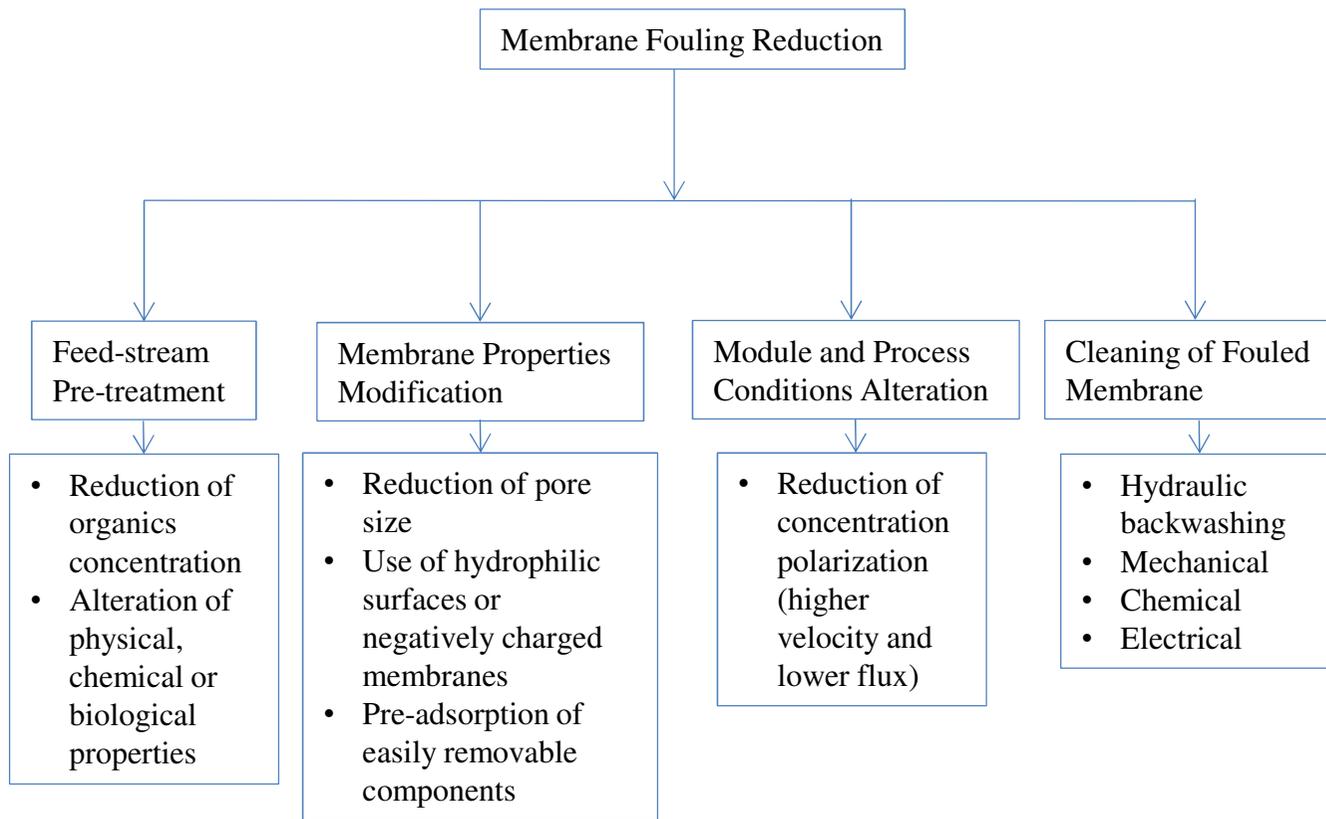


Figure 2.5: Fouling mitigation measures (Mulder 1996)

2.4 Feedwater Pre-treatment

Pre-treatment of the feed stream has long been used to reduce membrane fouling either by reducing the concentration of organic matter or by altering the physical, chemical or biological properties of the organic matter in the feed water. Changes to physical property increase the size of aquatic substances facilitating their removal at the UF membrane or with the aid of an upstream separation process (e.g., sedimentation and filtration). An increase in the size of aquatic substances also prevents membrane pore blockage and contributes towards the formation of a cake layer, resulting in fouling that is less severe and more reversible (Huang et al. 2009). Similarly, changing the chemical properties of SWWE using oxidants, coagulants and adsorbents (cation/anion exchange) not only reduces the foulants but can also reduce the affinity of adsorption to the membrane surface, thus reducing fouling (Gao et al. 2011, Heng et al. 2008). Biological treatment methods, on the other hand, facilitate the removal of biodegradable organic compounds, reducing both reversible and irreversible fouling of membranes (Hallé et al. 2009).

In recent years, numerous pre-treatments such as enhanced coagulation, activated carbon adsorption, MIEX and ozonation have been investigated with the aim of reducing membrane fouling (Fabris et al. 2007, Jung et al. 2006, Li and Chen 2004). A few widely used pre-treatment types investigated in this study are reviewed in terms of organics removal and subsequent membrane fouling reduction.

Activated Carbon

Activated carbon is highly effective for wastewater treatment by removing the majority of organic constituents from SWWE. It is normally used either as granular activated carbon (GAC) or as powdered activated carbon (PAC). Removal of DOM by activated carbon largely depends on surface chemistry and the pore size distribution of the activated carbon as this affects the process of adsorption (Kilduff et al. 1996). It shows a strong affinity for the removal of hydrophobic organic compounds even at lower concentrations (Jacangelo et al. 1995). A previous study

has shown the effectiveness of PAC for the removal of phenols, volatile acids, aromatic and aliphatic organics (Aktaş and Çeçen 2007).

Biological activated carbon (BAC) has been used extensively for the removal of dissolved organics from water and wastewater. Carbon beds and pores are utilized as a habitat for bacteria, with the organic matter present in water providing a source of nutrients for them. A theoretical representation of the BAC process is presented in Figure 2.6. During the first phase (Phase A), most of the removal occurs through physical adsorption while bacteria colonize the GAC surface. Afterwards, physical adsorption and the biological degradation process operate in parallel, but biological activity increases while the physical adsorption process gradually decreases (Phase B). Then, it reaches a final, steady Phase C. During this phase, the majority of organic matter removal occurs by biological oxidation due to the already acclimatized bacteria in the BAC bed (Her et al. 2007, Xiaojian et al. 1991).

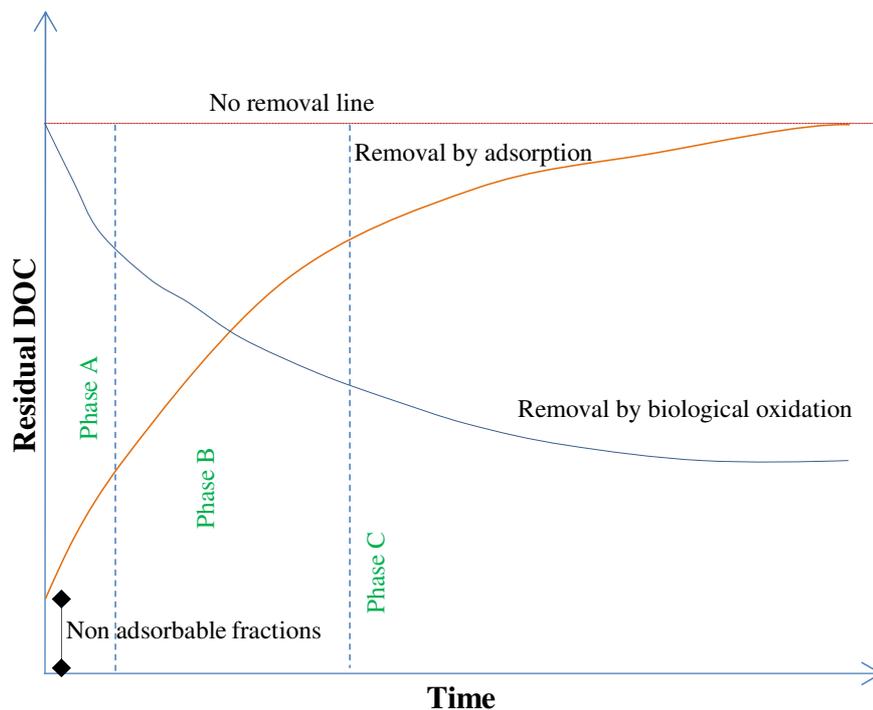


Figure 2.6: Theoretical representation of the BAC process

BAC utilizes microorganisms to regenerate the activated carbon while the carbon bed is in operation (Kimura et al. 2004b, Lee et al. 2004). Bio-regeneration is a phenomenon caused by the combined biological and activated carbon-adsorption process (Aktaş and Çeçen 2007), facilitating higher biological reaction rates (Howe and Clark 2002, Kimura et al. 2004b). Thus, microorganisms establish a natural biofilm extending its life span significantly (Scholz and Martin 1997) and offering a more economical treatment process.

BAC facilitates the removal of a wide range of organics. Previous research shows that BAC effectively removes potentially carcinogenic but biologically resistant compounds by adsorption and biological removal of lower molecular weight (LMW) oxygenated compounds that would otherwise be partially removed by activated carbon alone (Ying and Weber 1979). Similarly, Tsuno et al. (2006) observed the removal of both phenol and tetrachloroethylene, and chloroacetaldehyde regardless of their strong and weak adsorption affinity respectively.

BAC also shows a capacity to remove disinfection by-products such as halo acetic acid (HAA₅) and nitrosodimethylamine (NDMA) through biodegradation process. Despite the hydrophilic nature of NDMA, one study shows its reduction by more than 90% (Asami et al. 2009, Kim and Kang 2008). Pre-oxidation with ozone increases the bio-degradable fraction of dissolved organic carbon (DOC), facilitating its removal by BAC in ozone/BAC combination (Kim et al. 1997, Shon et al. 2006b). These studies show the diverse capabilities of BAC for a wide range of organics removal, which could be employed to improve the performance of membrane filtration as well.

Magnetic Ion Exchange Resin (MIEX)

MIEX, on the other hand, is an efficient technology developed for the removal of DOC from various water sources. MIEX is micro sized resin, macro porous and strong base made from a moderately cross-linked acrylic skeleton, which contains quaternary amine functional groups that provide the charged sites (Slunjski et al. 2000). The beads are much smaller than conventional resin beads at around 180 µm,

which provides a much greater surface area for high DOC exchange and rapid exchange kinetics (Hammann et al. 2004). The high density and magnetic properties of the resin provide rapid clarification following the contact stage. Furthermore, almost 95% of the resin can be recycled back to the contractor for regeneration by concentrated brine solution (Ray et al. 2002).

MIEX works on a principle different to that of coagulation, which relies on adsorption or hydrophobic interaction (See Figure 2.7) (Tan et al. 2005). Negatively charged DOC is removed from water by exchanging it with a chloride ion on the active sites on the resin surface (Hammann et al. 2004). This is based on the character of humic substances as weak organic acids. The process is reversible and this is considered to be its main advantage over other DOC removal processes as shown in Figure 2.7. Further, this exchange cycle is based on the high affinity of anionic resins for DOC, allowing DOC to be removed from raw waters and other naturally occurring anions (Slunjski et al. 2000).

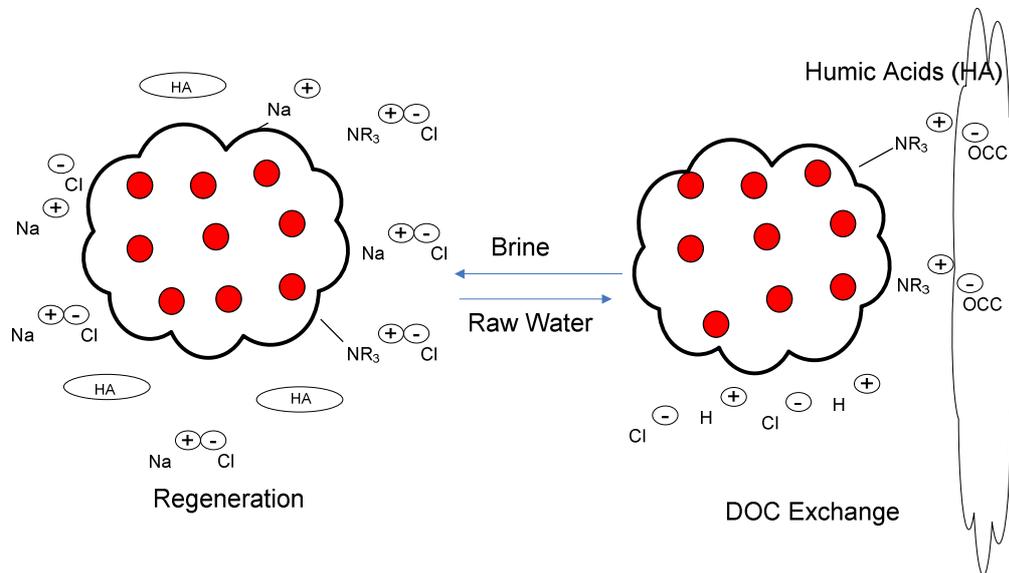


Figure 2.7: Chemistry of DOC exchange

MIEX effectively removes both hydrophilic and hydrophobic organic fractions (Son et al. 2005). Previous studies show a much higher removal efficiency of these compounds compared to coagulation (Allpike et al. 2005, Boyer and Singer 2005).

MIEX also works well in combination with other physicochemical treatments. Better DOC removal than enhanced coagulation was obtained in combination with coagulation and reduced the coagulant dose by up to 75% for the given DOC removal (Fearing et al. 2004, Morran et al. 2004).

Past research shows the effectiveness of MIEX for the removal of LMW compounds. Allpike et al. (2005) show the effective removal of smaller anionic species that contains carboxylic groups. This is in agreement with another study that showed the ability of MIEX to remove organic compounds between 500 and 1500 Da (Graham 1999). MIEX also facilitates the removal of fulvic acids having LMW (800 Da) (Fearing et al. 2004). Zhang et al. (2006) observed a similar capacity of MIEX to remove the majority of LMW compounds within a range of 500-1000 Da.

Enhanced Coagulation

Enhanced coagulation is an important process in water and wastewater treatment due to its ability to remove particles and a variety of inorganic and organic compounds. During the process, coagulant destabilizes colloidal particles of very small size that carry an electrical charge in aqueous solution (Johnson and Amirtharajah 1983). These colloidal particles in wastewater mostly carry a negative electrical charge in aqueous solution. The primary charges on the particle are counter-balanced by the charge in the aqueous phase, resulting in an electric double layer at every interface between solid and water. The forces of diffusion and electrostatic attraction spread the charge in the water around each particle in a diffusion layer (Hundt and O'Melia 1988). During this process colloids continuously change chemically, overcoming the forces that maintain a stable suspension and promoting aggregation and the formation of larger particles called floc. Finally, removal of organic matter occurs through four primary mechanisms; enmeshment, adsorption, charge neutralization/destabilization and complexation/precipitation (Amirtharajah and Mills 1982, Duan and Gregory 2003, Gregor et al. 1997, Hu et al. 1999, Randtke 1988,). These mechanisms are presented conceptually in Figure 2.8.

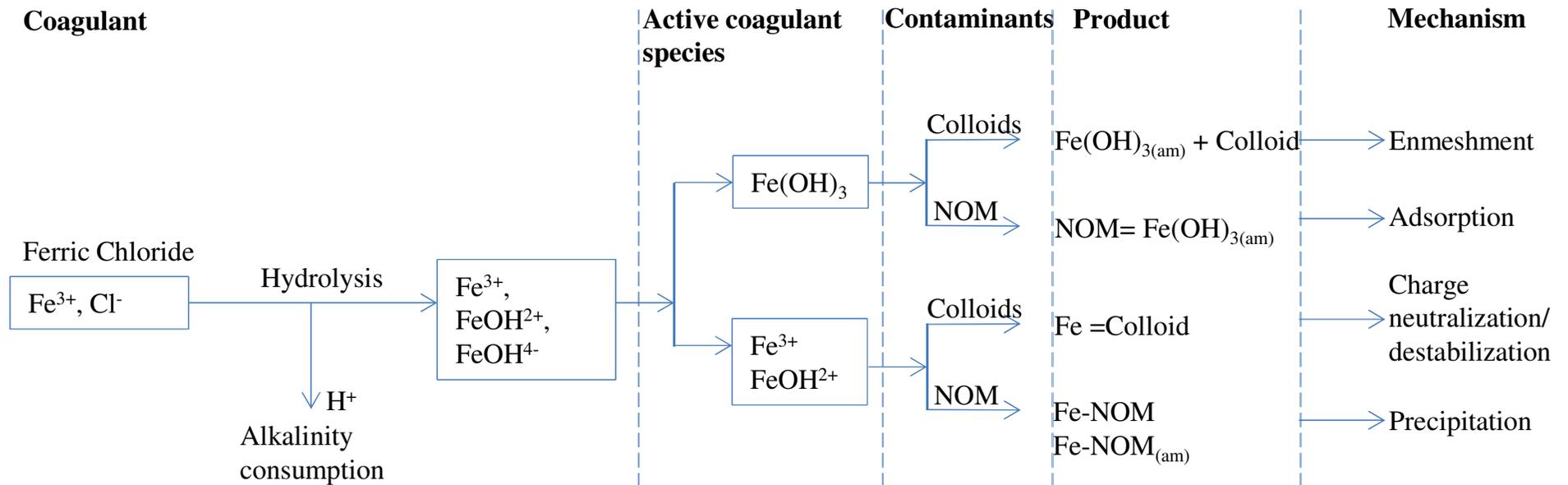


Figure 2.8: Conceptual view of coagulation

The effectiveness of coagulation in wastewater treatment depends on the surface charge of colloids, the charge of organic matter functional groups, solubility, and molecular size of the organic matter (Urfer et al. 1997). Similarly, pH conditions, coagulant dosage and the concentration of DOM itself are also highly influential factors in coagulation (Johnson and Amirtharajah 1983).

The coagulation process preferentially removes HMW organic matter and compounds that are hydrophobic in nature. It is equally effective in removing low charge density humic acids (Collins et al. 1986, Randtke 1988, Hayes et al. 1989, Krasner and Amy 1995). These characteristic are consistent with the observation that coagulation removes a quantity of organic matter from water containing relatively high hydrophobic organic concentrations than from water with low hydrophobic organic concentrations (Persson et al. 2006).

2.5 Pre-treatment and Membrane Fouling Reduction: Previous Effort

Past research has exploited the unique properties of various pre-treatment strategies and their affinity for particular groups of organic compounds alone or in combination to reduce membrane fouling. Coagulation has been widely used as a cost-effective physicochemical pre-treatment process to reduce contaminants prior to membrane filtration (Bérubé et al. 2002, Gao et al. 2011). Kim et al. (2005) obtained significant improvements in flux in MF and UF by coagulation of SWWE. Few other studies also show coagulation to be an effective pre-treatment for both SWWE and surface water to reduce fouling of MF or UF membranes (Carroll et al. 2000, Haberkamp et al. 2007, Laine et al. 1989, Lee et al. 2005, Shon et al. 2004,). Adsorbents such as GAC or PAC have also proven effective in removing certain contaminants that foul UF membranes (Lorain et al. 2007, Tsujimoto et al. 1998). Pianta et al. (1998) shows stable UF membrane performance with the use of PAC treatment in spring water.

Pre-treatment with oxidants such as ozone, permanganate and chlorine suppresses microbial growth and changes the structure, concentration and properties of organic matter reducing both organic and biofouling of membranes (Gao et al. 2011, Kim et al. 1997). Similarly, the use of MIEX facilitates the removal DOM and reduces the

fouling of MF membranes (Boyer and Singer 2006, Dixon et al. 2010). Kim and Dempsey (2010) have demonstrated the effectiveness of MIEX pre-treatment for the use of both MF and UF membrane with SWWE.

Biological pre-treatment of source water is not only cost-effective but also reduces membrane fouling. Shon et al. (2004) have shown that BAC treatment minimizes the fouling on RO membranes. While the above pre-treatment options have proven to individually minimize membrane fouling, previous research has also investigated their potential to reduce membrane fouling in combination. Shon et al. (2004) have shown that coagulation used in combination with PAC adsorption, leads to improved UF membrane performance. In a similar investigation, GAC in combination with Floc-Ads also improved UF membrane performance (Shon et al. 2005). Fabris et al. (2007) investigated the combination of MIEX with coagulation and observed reduction of short-term MF membrane fouling.

Despite these promising characteristics in separating organic impurities from water and consequent improvement in membrane performance, the pre-treatments possess some limitations. The removal capacity of activated carbon decreases gradually as adsorbed organics increase, so that it needs to be either replaced or regenerated. Furthermore, adsorption capacity is reduced after each regeneration cycle (Aktaş and Çeçen 2007, Maloney et al. 1983). The cost-effectiveness of exploiting physical adsorption alone is therefore still under scrutiny. On the other hand, BAC offers consistent DOC removal for a long time but organics removal during the steady stage is very limited. Similarly, there are residual fractions that cannot be removed during both MIEX and the coagulation process irrespective of the increased dose, and which potentially act as foulants in membrane filtration (Howe and Clark 2006, Humbert et al. 2007). As a result, membrane fouling remains ubiquitous in the long run even after pre-treatment and despite some improvement (Carroll et al. 2000, Fabris et al. 2007, Schlichter et al. 2004, van der Hoek et al. 1999).

These studies clearly indicate that membrane fouling is a complex phenomenon and the difficulties in developing proper strategies to reduce fouling demonstrate inadequate knowledge of the interaction between organic matter and membranes.

While advances in fouling research are needed for better membrane design and to develop effective strategies to pre-treat feed streams, continuing efforts to maximize the removal of organic matter using existing pre-treatment are important.

Previous studies investigated various biological and physicochemical pre-treatments for the removal of DOM as they are the principal factors in membrane fouling. While removal efficiencies have been shown to be significantly improved by these pre-treatments, little research has been carried out to understand the fundamentals of biological treatment and its role in enhancing organic removal with other physicochemical treatments and its effect on membrane fouling reduction. The current research aims to investigate the effect of microbial activity in a BAC treatment for the enhanced removal of DOM when used in combination with EC or MIEX treatment. With a fundamental understanding of bulk dissolved organics removal and the structural changes to the organics resulting from microbial activity in BAC bed, further investigation is carried out in combination with EC or MIEX pre-treatment in order to better understand the fouling mechanism and hence to reduce fouling of UF and NF membranes.

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Chapter 3

Material and Methods

3.1 Source Water, Sample Collection and Preservation

3.1.1 Description of the Studied System

Secondary wastewater effluent (SWWE) from Beenyup Wastewater Treatment Plant (BWTP), Perth, Western Australia was used during this study period. The wastewater comes predominantly from household kitchens, bathrooms, toilets and laundries. The BWTP serves Perth's rapidly developing northern suburbs from Quinns Beach through to Scarborough and inland through Dianella and Bayswater to the foothills east of Midland (Figure 3.1). The treatment plant has a current capacity of 120 million litres per day with a treatment target of 200 million litres per day, serving a population of 1.1 million people. The wastewater treatment plant was engineered to biologically remove nitrogen and dissolved organic carbon (DOC) from influent wastewater. Neither chemical nor biological methods were employed to remove phosphorus from influent waters.

3.2 Stock Chemical Solutions, Sampling Containers and Glassware Preparation

Stock solution for all chemicals were prepared using analytical-grade chemicals in reverse osmosis (RO) treated water (Ibis IS0006, Ibis Technology, Australia) or Milli-Q water (PURELAB UHQ II, Milli-Q water unit, Australia). The water had a dissolved organic carbon (DOC) and conductivity of <0.1 mg/L and <1 μ S/cm respectively. Sample containers were cleaned with 10% sodium hypochlorite solution followed by RO treated water to ensure they were free from chlorine.

The samples were collected in 20 L black plastic containers with air-tight plastic covers. Collected SWWE was transported to the laboratory at Curtin University, Western Australia, and was stored at 4°C. The samples were left at room temperature

of around 25°C for 24 h prior to experimentation. Samples were collected regularly from the wastewater treatment plant based on the requirements of BAC reactor and other experiments, in order to avoid long storage periods.

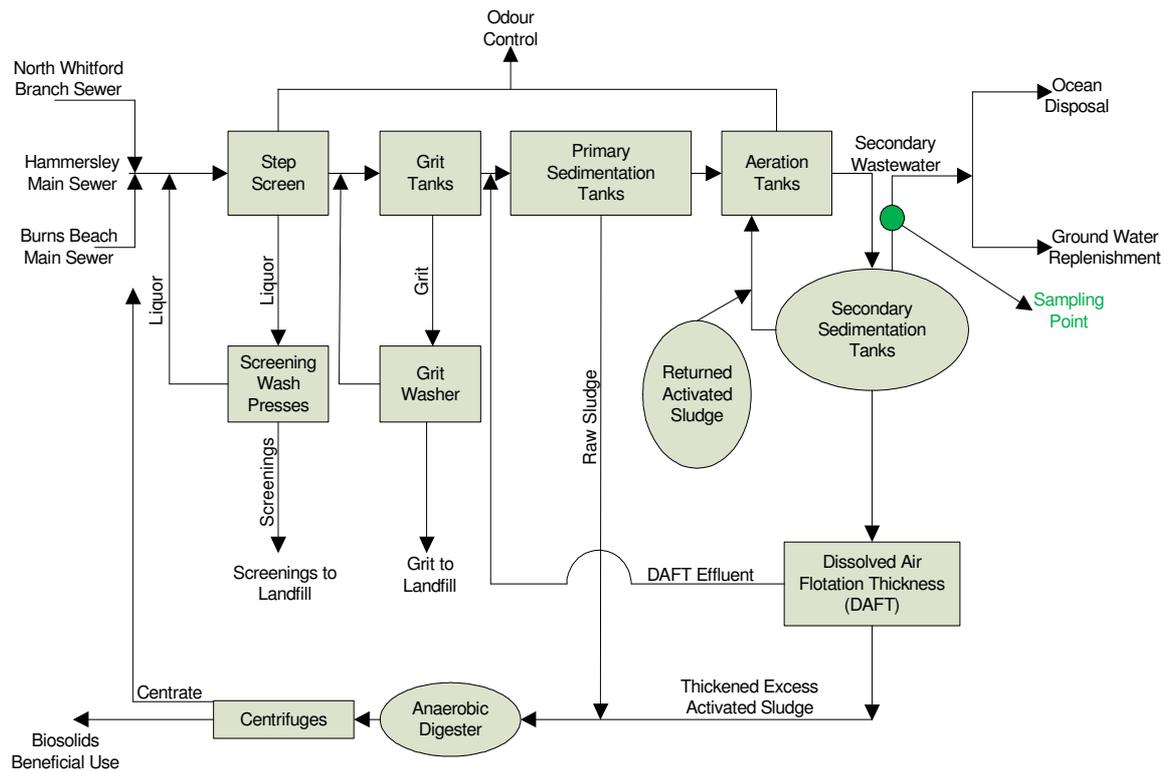


Figure 3.1: Flow chart for the BWTP

3.3 Description of BAC Reactor System Set-up

The biological activated carbon (BAC) filter column was operated as a continuous flow reactor. The reactor was designed with three different ports for feeding wastewater, bed cleaning and outlet for the collection of BAC effluent as illustrated in Figure 3.2. The diameter of both columns was 3.9 cm. The granular activated carbon (GAC) (Rowe Scientific, Australia) used in the experiment was washed several times with DI water (PURELAB UHQ II Milli-Q Water Unit, Australia, which had a DOC and conductivity of <0.1 mg/L and <1 µS/cm respectively) and

dried in an oven at 105 °C for 24 h to ensure that all the GACs were free from ash and other impurities before use. Afterwards, the GAC was cooled to room temperature before being packed into columns. The physical properties of GAC are presented in Table 3.1.

Table 3.1: Physical properties of GAC

Iodine number (mg/(g.min))	Maximum ash content (%)	Maximum moisture content (%)	Bulk density (kg/m³)	BET surface area (m²/gm)	Average pore diameter (A₀)
798	5	5	748	1144	26.28

Two reactor columns, each with a bed depth of 15 cm (180 cm³ of GAC) were connected in series and operated for different empty bed contact times (EBCT) based on the nature of the experiments, (Further explained in each respective chapter). A variable speed peristaltic pump was used to feed into the first column. Afterwards, effluent flowed under gravity from one column to another, and the final BAC effluent was collected in the collection tank. The water was fed drip by drip into the air space in the top of the columns to allow contact with oxygen as shown in Figure 3.2. The treated water was collected from the port placed at the bottom of the column. To ensure contact of water with the entire BAC bed, effluent was extracted from a level 1 cm above the upper BAC level in the reactor using a plastic pipe connected to the bottom outlet of the column. As a result, the whole BAC bed was operating under fully submerged conditions. Backwash was carried out monthly with SWWE in order to avoid physical clogging of the BAC bed.

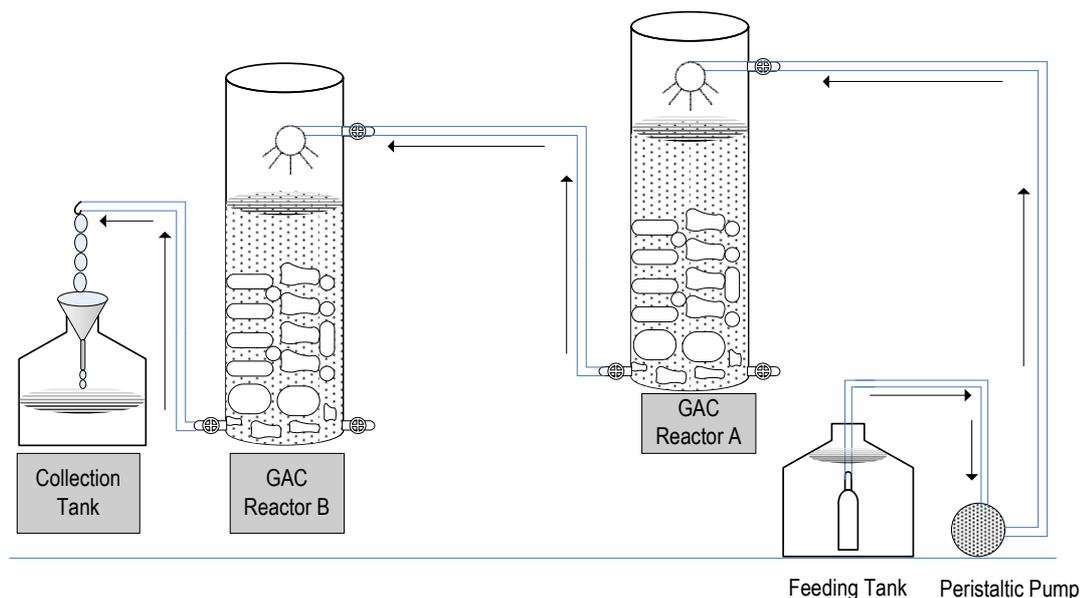


Figure 3.2: BAC reactors in series

3.4 Analytical Measurements

Based on the nature of the experiments, various techniques were used for the measurement of DOM and its fractionation. Figure 3.3 presents a brief simple diagram of the analytical measurements and instruments used during this investigation. The details of each method are described in detail in their respective chapters.

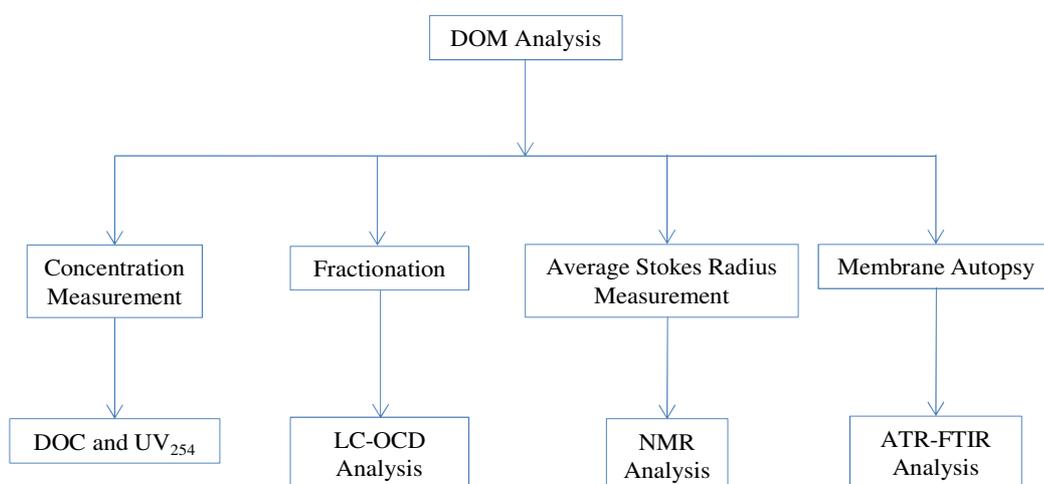


Figure 3.3: Analytical techniques used in this dissertation

Chapter 4

Evidence that BAC Treatment Enhances the DOC Removal by Enhanced Coagulation

Abstract

Effluent organic matter (EfOM) in secondary wastewater effluent (SWWE) contains a wide range of organic compounds, which vary depending on the performance of the wastewater treatment plant. The removal of EfOM is required for various reuse/recycling applications. This study investigates the effectiveness of combining biological activated carbon and enhanced coagulation (BAC/EC) by modelling dissolved organic carbon (DOC) removal resulting from EC of SWWE and BAC effluent obtained at different empty bed contact times (EBCT). The results suggest that BAC significantly reduced the coagulant non-sorbable DOC concentration which otherwise remained unaffected by the EC/BAC combination. Further, the non-sorbable concentration decreased with increased EBCT. This clearly indicates the crucial role of biological activity in increasing the performance of the coagulant.

Key Words: BAC, Pre-treatment, Enhanced Coagulation, DOC removal

4.1 Introduction

Wastewater reuse is increasingly seen as an essential strategy for better use of limited fresh water resources (Shon et al. 2005). However, the wide range of organic compounds present in SWWE makes treatment less effective (Jarusutthirak et al. 2002). Thus, the application of various pre-treatment techniques for the removal of DOC, an indicator of organic compounds, is a subject of primary interest for sustainable wastewater reuse.

Coagulation is an important process in water treatment due to its ability to remove particles and a variety of inorganic and organic compounds. It is more effective in removing higher molecular weight (HMW) organic compounds than lower molecular

weight (LMW) ones (Collins et al. 1986, Croue et al. 1999, Liang and Singer 2003, Matilainen et al. 2002, White et al. 1997). Similarly, a higher percentage removal of UV₂₅₄ than the corresponding removal of total organic carbon indicates the removal of hydrophobic substances that belonging to humic acid groups. This could be removed effectively by EC (Edzwald et al. 1985, Owen et al. 1995, White et al. 1997).

Based on specific coagulant preference, DOC can be conceptually divided into sorbable and non-sorbable (NS) fractions (Kastl et al. 2004). The sorbable fractions are comprised of humic acid (HA) and non-polar (NP) fractions. HA removal varies with pH but NP removal does not depend on pH (Kastl et al. 2004). Based on these assumptions, the following expressions can be formulated for initial fractions:

$$DOC_{\text{nonsorb}} = f_{\text{nonsorb}} \times DOC_0 \quad (1)$$

$$DOC_{\text{ha},0} = f_{\text{ha}} \times DOC_0 \quad (2)$$

$$DOC_{\text{nonpolar},0} = f_{\text{nonpolar}} \times DOC_0 \quad (3)$$

$$f_{\text{nonsorb}} + f_{\text{ha}} + f_{\text{nonpolar}} = 1 \quad (4)$$

Where, DOC_{nonsorb} is non sorbable DOC, DOC_{nonpolar} is non-polar DOC, DOC_0 is initial DOC concentration, DOC_{ha} is humic acid compound group, f_{ha} is humic acid fraction, f_{nonpolar} is non polar fraction and f_{nonsorb} is described as non-sorbable fraction.

Higher coagulant doses help to obtain f_{nonpolar} and f_{nonsorb} fractions while f_{ha} fraction can be determined by using a wide range of pH. Further, the removal of non-polar and humic acid fraction can be described by the Langmuir adsorption isotherm. Then, the final DOC remaining in the water can be described as follows:

$$DOC_{\text{mod}} = DOC_{\text{nonsorb}} + [HA]_t + [A^-]_t + DOC_{\text{nonpolar},t} \quad (5)$$

Where, DOC_{mod} is the predicted remaining DOC and subscripts 't' refers to the concentration in water

BAC offers an economic solution for the removal of organic matter from wastewater (Dussert and VanStone 1994). In this process, beds and pores of carbon are utilized

as a habitat for bacteria by providing them with the organic matter present in water as a source of nutrients (Xiaojian et al. 1991). The microorganisms eventually establish a natural biofilm during bioregeneration and significantly extend the operational life of the BAC bed (Scholz and Martin 1997). Further, adsorption of less biodegradable organics and degradation by microorganisms on the carbon bed result in higher biological reaction rates on activated carbon (Graham et al. 1996, Rice and Robson 1982, Weber and Ying 1977).

In addition, BAC effectively reduces the potential for formation of disinfection by products (DBPs) by reducing the hydrophilic natural organic matters (NOM) fractions (Asami et al. 2009, Kelven et al. 1996,). Further, BAC removes nitrosodimethylamine and haloacetic acid (HAA₅) (respectively more than 90% and 99%) (Kim and Kang 2008), indicating its effectiveness in removing hydrophilic compounds that would otherwise remain unaffected by the use of coagulant alone.

Previous investigations clearly show the preference of BAC and coagulation over different groups of organic compounds and their removal capacity. Traditionally, BAC has been used after coagulation as a polishing treatment for additional DOC removal. However, the enhanced DOC removal potential that could be obtained by using BAC prior to coagulation has not been well investigated. This study therefore investigates the BAC/EC combination for enhanced removal of organic matter by quantifying fractional DOC removal using the EC DOC removal model which helped in elucidating the mechanism.

4.2 Materials and Methods

4.2.1 Experimental Design

The investigation was undertaken in three steps. In the first step, individual BAC performance was evaluated under two different EBCTs (B20 and B40) (Table 4.1). Long-term biofilter experiment was conducted with SWWE, maintaining 20 min EBCT in each column. Columns were operated for more than 3 months. In the second step, the performance of EC on SWWE was investigated for various pH

levels (5 - 9) and coagulant doses (1.25 - 160 mg/L). The third step studied the combination of these two processes (BAC followed by EC. Afterwards, the efficiency of each process was analyzed either in terms of residual DOC or in terms of sorbable and non-sorbable DOC fractions predicted by using equation 5 (Kastl et al. 2004).

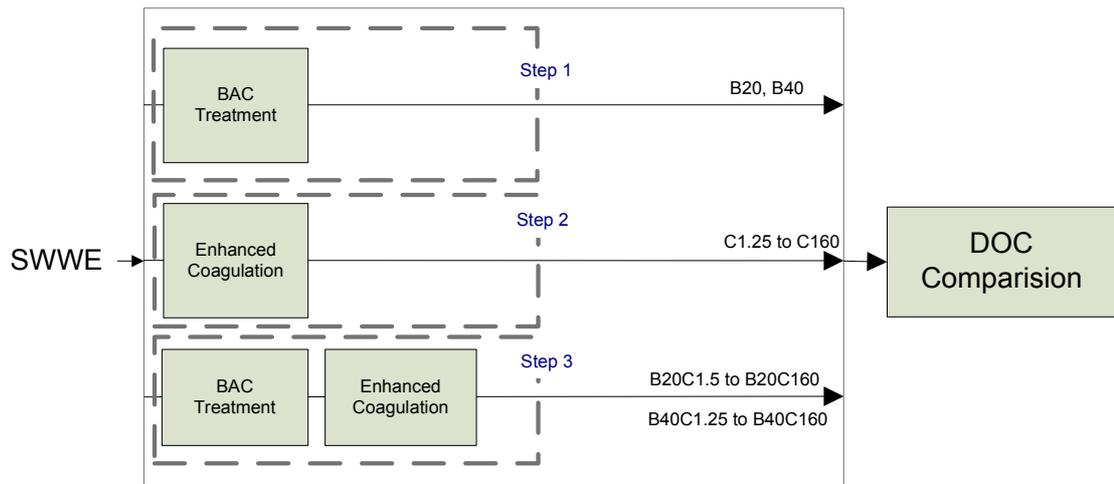


Figure 4.1: Experimental flow chart

4.2.2 BAC Treatment and Reactor Set-up

Details of the BAC reactor set-up are presented in Chapter 3 (Section 3.3, Figure 3.2). Two reactor columns were connected in series and operated at 20 min EBCT each. Thus, 40 min EBCT was achievable in one single run. For an EBCT of 20 min (B20), only the first column was used, while both columns were used to obtain 40 min (B40).

4.2.3 Enhanced Coagulation

EC was undertaken by applying ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) as a Ferric at various doses of 1.25 mg/L–160 mg/L (C1.25 to C160) before and after the BAC treatment under different pH ranges (5–9). Three types of experiments; constant pH–varying dose, constant dose–varying pH and varying dose–pH were undertaken to clarify the dependence of DOC removal on pH and coagulant dose. Samples were subjected to

mixing upon addition of coagulant and pH was adjusted continuously using sodium hydroxide and sulphuric acid, each of 1M concentration. The jar test was carried out following the standard protocol representing the coagulation and flocculation process consisting of rapid mixing at 200 rpm for the first 2 min and 20 rpm for last 20 min. A settling period of 30 min was employed for the separation of flocculated particles prior to filtration.

4.2.4 Analytical Measurements

Two parameters, mainly DOC and UV₂₅₄ were measured for all of the samples in this investigation. DOC was measured using a 5310C laboratory Total Carbon Analyzer connected to an auto-sampler. As samples were analysed after filtering through 0.45 µm cellulose acetate filter paper (GE Water and Process Technologies, Cat. No. A04SP04700, Acetate plus supported), the measured value is the DOC. This machine uses UV persulphate oxidation for the measurement of DOC and has an analytical range of 30 µg/L to 50 mg/L within the measurement error of 5%. Prior to filtration of samples, the filter medium was pre-washed with Milli-Q water (PURELAB UHQ II Milli-Q water unit, Australia). The Milli-Q water had a DOC and conductivity of <0.1 mg/L and <1 µS/cm respectively. UV absorbance was measured using a Helios Gamma Spectrophotometer (Thermoelectron) and measured for filtered samples as above. The optical design of this instrument is single beam Seya Namioka monochromator and gives a 0.05% error in measurement. The pH adjustment was carried out by using a portable pH meter (HACH 40d) and electrode (PHC101, Hach).

4.3 Results and Discussion

4.3.1 Source Water

The SWWE used in this study was from a municipal wastewater treatment plant (Beenyup, Western Australia). The plant uses a secondary treatment process, to biologically remove nitrogen and DOC from influent wastewater. Neither chemical

nor biological methods were employed to remove phosphorus from influent waters. The SWWE characteristics of this plant are reported in Table 4.1.

Table 4.1: Water quality characteristics of Beenyup SWWE

	Temp (°C)	pH	EC ^a (µS/cm)	UV ₂₅₄ (per cm)	mg/L				
					DOC	DO ^b	SS ^c	NH ₃ .N	NO ₃ .N
	26.5	7.2	1357	0.203	7.84	7.8	9.0	0.295	10.69
Average	±	±	±	±	±	±	±	±	±
	2.12	0.14	7.77	0.009	2.49	0.14	0.28	0.037	0.763

^aElectrical conductivity ^bDissolved oxygen; ^cSuspended solids

4.3.2 Performance of BAC and DOC Removal

The long-term performance of BAC was observed using SWWE. As shown in Figure 4.2, the overall removal of DOC for the first day was around 83%. However, the removal efficiency decreased gradually during the first week of operation indicating possible role of physical adsorption as a removal mechanism. It can be clearly seen that, the rate of decrease in DOC removal efficiency is highest during the first week. Despite the drop in physical adsorption, DOC removal tended to stabilize after the first week of operation. This is in agreement with previous studies showing that the biological process gradually becomes dominant over physical adsorption in removing organic carbon in the BAC bed (Hoang et al. 2008, Servais et al. 1994).

Table 4.2: DOC and UV removal after BAC treatment

	2009*		2010	
	DOC (mg/L)	UV _{254_1cm}	DOC (mg/L)	UV _{254_1cm}
SWWE	9.47	0.21	10.6	0.206
B20	7.43	0.169	8.3	0.172
B40	6.5	0.142	7.84	0.150

* Sampling year

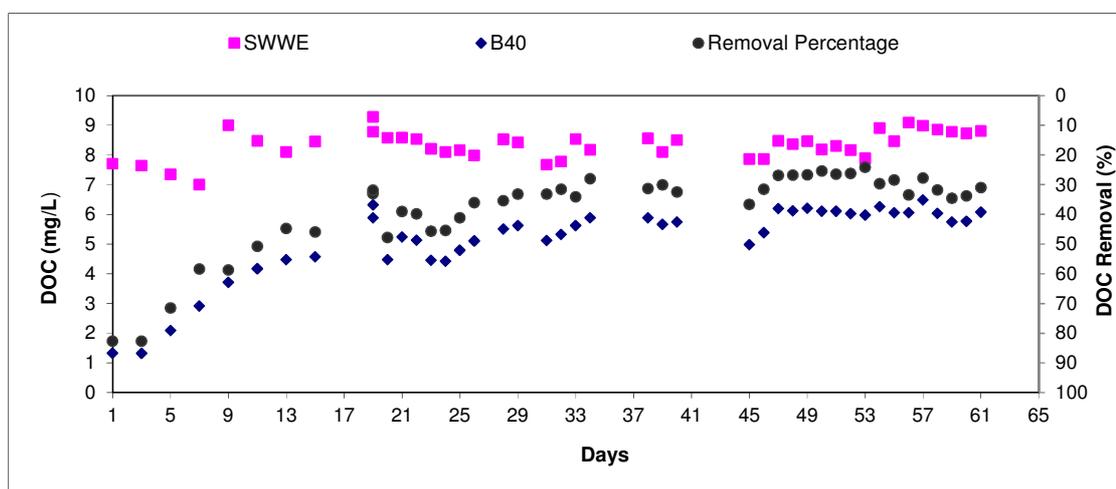


Figure 4.2: Long-term performance of BAC (40 min EBCT)

Afterwards, experiments were undertaken with two different SWWE samples having DOC values of 9.47 mg/L and 10.60 mg/L. As presented in Table 4.2, the percentage removal of DOC was found to be higher in the first column than in the second one in both samples. It reduced from 9.47 to 7.43 mg/L in the first column for 20 min EBCT. This further reduced to 6.5 mg/L on increasing the EBCT by another 20 min in the second column, accounting for 31% DOC removal overall. A similar removal trend was obtained in the sample with higher DOC, although relatively less DOC (around 26%) was removed under the same conditions. The trend for UV removal was also observed to be similar to DOC removal.

4.3.3 Enhanced Coagulation and DOC Removal

This step involved the performance evaluation of EC on SWWE in terms of DOC removal. SWWE samples having lower and higher DOC values of 5.17 mg/L and 10.6 mg/L respectively were investigated. The results obtained from the jar tests for pH 5 and 9 (respectively the lowest and highest ends of the range used) are presented in Figure 4.3 for both samples. The DOC in the low source DOC sample was reduced to 2.4 mg/L with 80 mg/L coagulant at pH 5. On doubling the coagulant dose, DOC values further decreased to 2.05 mg/L, accounting for an overall DOC removal of 60%. Similarly, DOC in the high source DOC sample was reduced to 4.4 mg/L and then further to 3.72 mg/L, resulting in a marginally higher removal efficiency of 65% than in the low source DOC sample. However, the removal trend in both samples remained the same. For both samples, a coagulant dose of 80 mg/L was not sufficient to meet the coagulant demand, as DOC removal increased by nearly 10% on doubling the coagulant dose to 160 mg/L, regardless of the source DOC. Although further reduction may be achieved by increasing the coagulant dose, the highest dose was maintained at 160 mg/L.

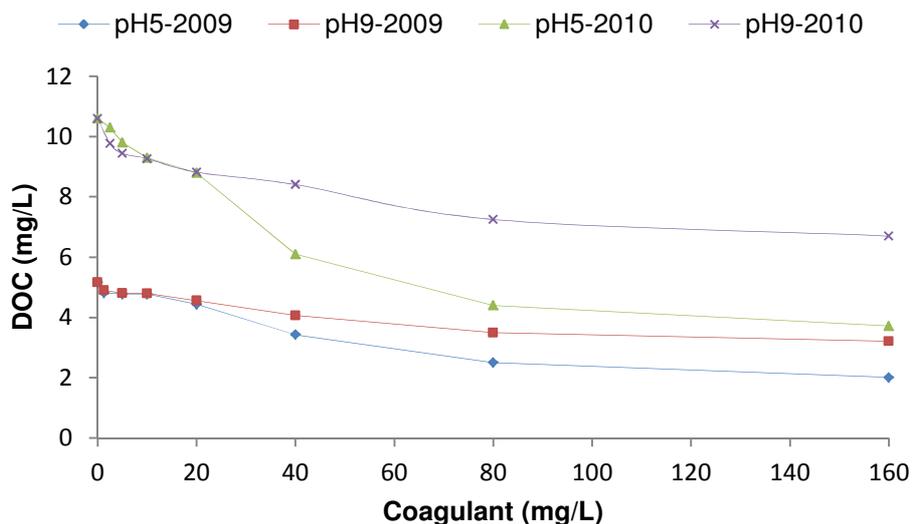


Figure 4.3: DOC removal in SWWE by enhanced coagulation

4.3.4 EC of BAC Effluent (BAC/EC Combination): Do They Aid Each Other?

To evaluate the combined effect, SWWE (10.6 mg/L) and B40 samples were subjected to EC. The results obtained for pH 5 with two higher coagulant doses are presented in Figure 4.4. As can be seen, the DOC was reduced to 2.39 mg/L when 80 mg/L coagulant was added to the BAC treated water. This was further reduced to 2.26 mg/L on doubling the coagulant dose with overall removal efficiency of 79% from SWWE suggesting that same amount of coagulant performs better on BAC treated water.

The increased removal efficiency of the coagulant is possibly due to two main reasons. Firstly, BAC may absorb certain portion of EfOM present in SWWE that cannot otherwise be removed by EC. Secondly, microbial activity inside the BAC bed may have converted non-coagulable organic carbon into coagulable organic carbon. However, the residual DOC alone is not sufficient to conclude that increased removal was due to reduced DOC in the BAC effluent or the associated microbial activity inside the BAC bed. This is because removal obtained at a particular dose of coagulant and pH does not represent the full spectrum of sorbable and non-sorbable fractions present in the water. Thus, in order to clearly understand the synergistic mechanism, coagulation was carried out in SWWE and B20 and B40 effluents. The investigation was undertaken twice at two different times of the year. The DOC removal model (Kastl et al. 2004) was applied for each condition as this model (equation 5) could effectively calculate the sorbable and the non-sorbable DOC fractions present in the water.

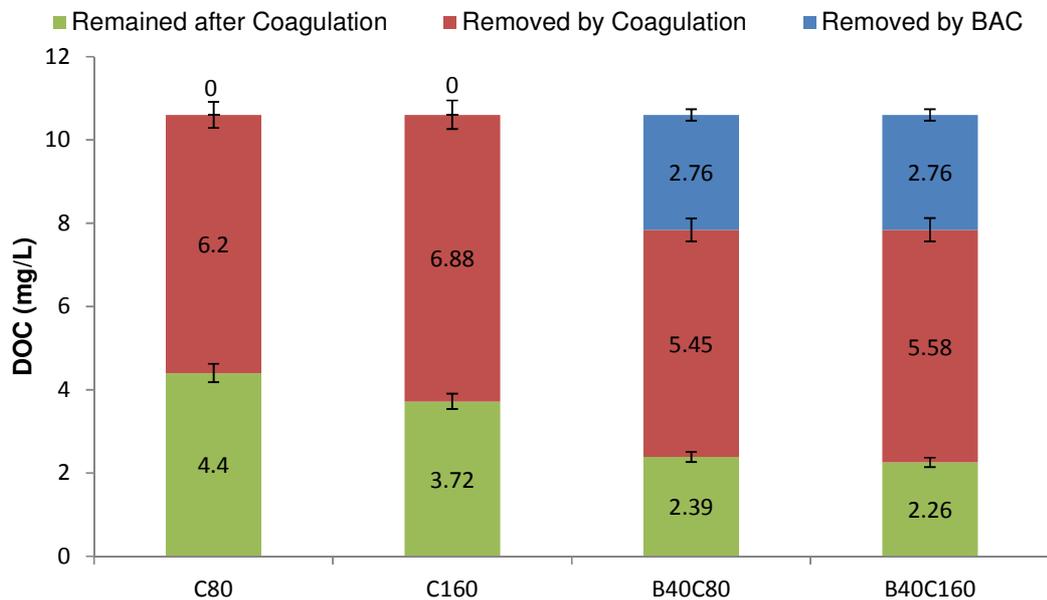


Figure 4.4: Performance of the BAC/EC combination and EC alone in removing coagulable organic carbon

4.3.5 Model Fitting the Experimental Data

The resulting DOC values obtained from EC prior to and after the BAC treatment for five different conditions were fitted to the model. The model was originally developed for two Australian waters—Happy Valley and North Richmond water but was later tested for 17 US waters (Kastl et al. 2004). It had never been applied to SWWE. Thus, the validity of the model for SWWE and BAC-treated effluent was tested, followed by analysis of combined the effect of BAC/EC using the parameters obtained from the model.

All of the appropriate coefficients were estimated as to minimize error. The relative adsorption constant (K) was found to be close to 1 as in the original model; i.e., humic acid groups and non-polar groups assumed to show the same adsorption activity on a given floc surface (Kastl et al. 2004). By this procedure, unique parameter values of adsorption capacity (a), adsorption constant (b), humic acid

fraction (f_{ha}), non-polar fraction (f_{np}) and dissociation constant of humic acid (pK_a) (log of k_a) were obtained for both SWWE and BAC-treated water.

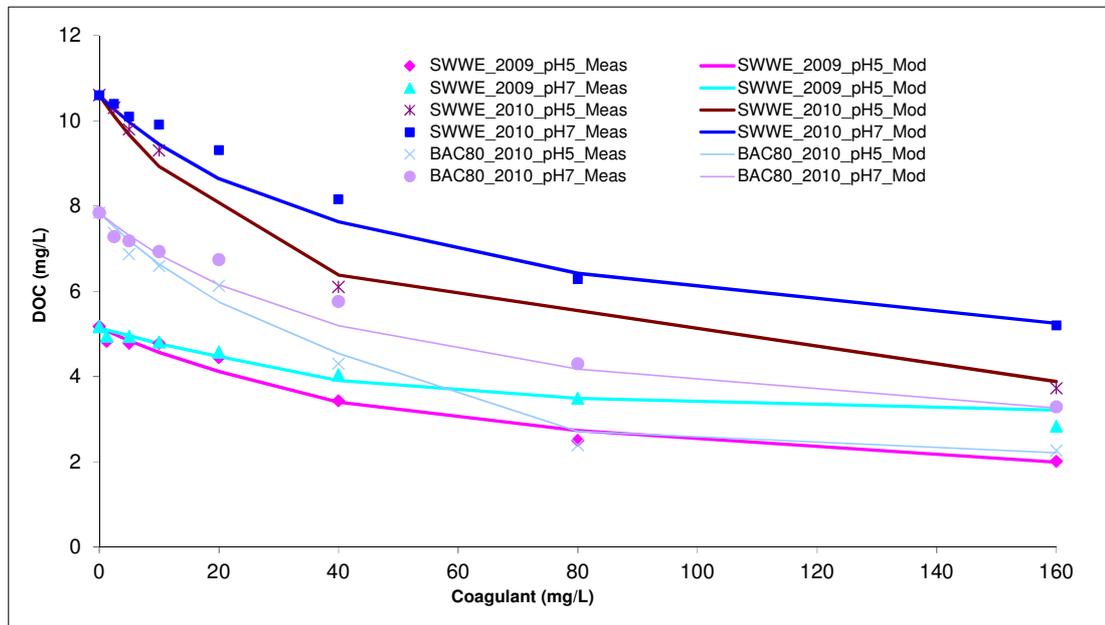


Figure 4.5: Residual DOC for different coagulant doses

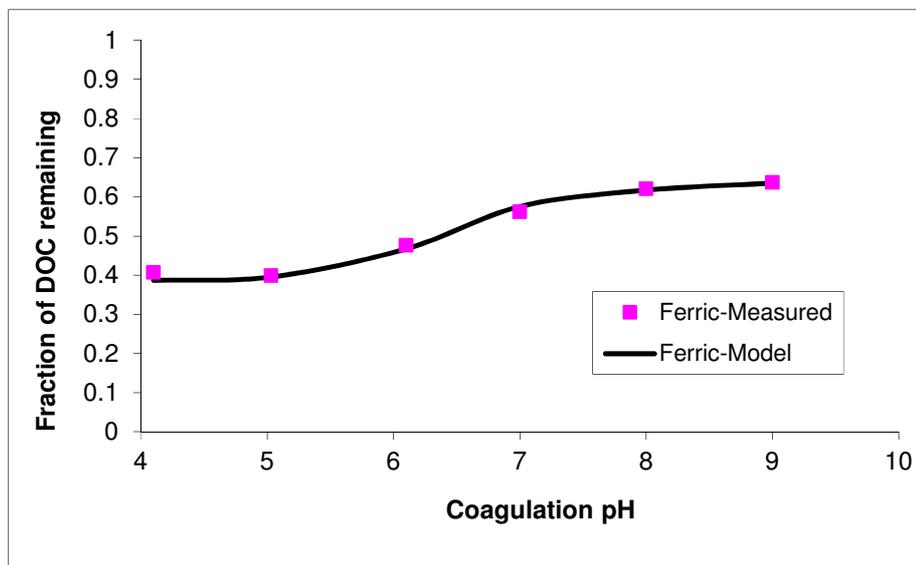


Figure 4.6: pH dependence of the fraction of DOC remaining for SWWE 2009

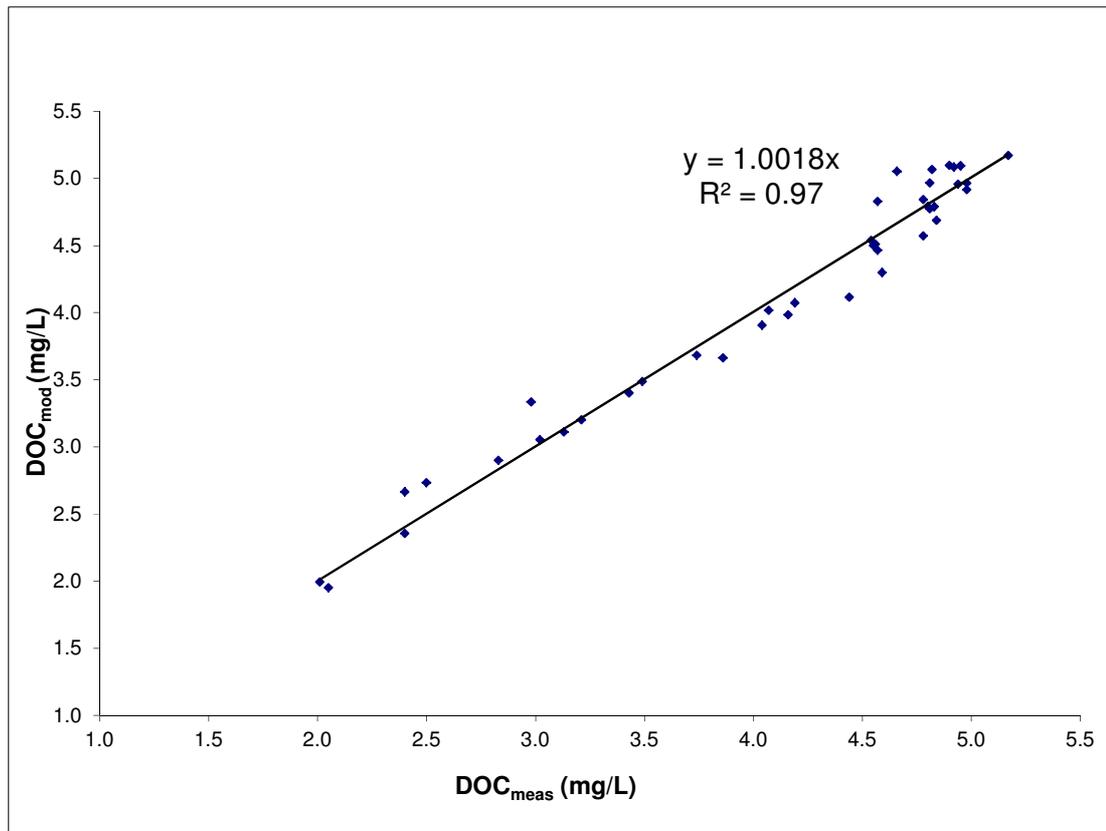


Figure 4.7: Measured final DOC vs. model-predicted final DOC for SWWE 2009

The model outputs for SWWE and BAC-treated waters for five different conditions are presented in Table 4.3 and compared with the parameters calculated for the original model (Happy Valley). The fitting obtained is also presented in Figures 4.5, 4.6 and 4.7. Jar test results were described well by the fitted model offering R^2 values of 0.94–0.98 and standard deviation of errors 0.16–0.33mg/L. This is comparable to values obtained in the original model (R^2 of 0.99 and standard deviation of error 0.22mg/L) in all different conditions. Similarly, the maximum error predicted was found to be between 8.05 and 10.64% and the standard deviation of errors between 3.9 to 6.07% which is even better than the original model that found them to be 12.2 and 6.15%. Figures 4.5 and 4.6 illustrate the predicted DOC against the measured results. As can be seen, the predicted DOC results are very close to the actual ones. However, in the lower range of coagulant dosing, the deviation between the model

and measured values was consistently higher, indicating that other mechanisms might play a role in altering the behaviour of coagulant.

Table 4.3: Comparison of model parameters and errors with original model

	Happy Valley	SWWE 2009**	B40 2009	SWWE 2010	B20 2010	B40 2010
Initial DOC (mg/L)	9.2	5.17	6.4	10.6	8.3	7.84
a*-mg DOC/meq coagulant	9.8	92	13	150	80	50
b-(L/mg-DOC) ⁻¹	19	0.0105	0.2	0.01	0.019	0.026
f _{sorbable} DOC fraction	0.749	0.83	0.92	0.78	0.83	0.94
f _{ha} DOC fraction	0.400	0.34	0.32	0.32	0.3	0.24
f _{nonpolar} DOC fraction	0.349	0.49	0.6	0.46	0.53	0.7
pK _a	4.30	5.82	6.46	6.16	6	5.5
∑(error in DOC prediction) ²	1.331	1.07	1.42	3.37	3.22	3.46
Number of experimental Data	27	41	30	33	30	35
R ²	0.991	0.97	0.98	0.97	0.94	0.96
Standard deviation of errors in prediction (%)	6.15	4.22	5.64	3.9	5.46	6.07
Standard deviation of errors in	0.22	0.16	0.22	0.32	0.33	0.31

	Happy Valley	SWWE 2009**	B40 2009	SWWE 2010	B20 2010	B40 2010
prediction (mg/L DOC)						
Maximum error in DOC prediction (%)	12.2	10.64	12.68	8.05	9.71	11.92
Maximum error in DOC prediction (mg/L)	0.41	0.39	0.41	0.67	0.58	0.59
Estimated potential experimental error if instrumental errors are combined (mg/L DOC)**	0.61	0.25	0.29	0.41	0.35	0.33

**sampling year *a - adsorption capacity in mg-DOC/meq coagulant; b - adsorption constant mL/mg-

DOC, DOC - dissolved organic carbon; f_{ha} - humic acid fraction; $f_{nonpolar}$ - nonpolar fraction, $f_{sorbable}$ - sorbable fraction, *Error in prediction is the difference found between each measured and modelled data, **Estimated potential experimental error is calculated by adding maximum error that can occur if pH measurement is 0.1 unit in error and DOC measurement error (larger of 0.05 or 3% of DOC)

Further investigation showed that suspended solids present in SWWE interfere with the removal efficiency of coagulant in the lower dose range (Aryal et al. 2011). Despite this abnormality, the model fitted very well. These observations show the validity of the model for all five different conditions used for wastewater as well. Thus, it was applied in addition to direct measurement of residual DOC, particularly to quantify the changes in sorbable fraction and resulting amenability towards coagulant resulted due to BAC treatment.

4.3.6 Amenability Analysis: Evidence of Increased Sorbability

Figure 4.8 illustrates the sorbable (HA and NP) and NS DOC concentration present in SWWE and BAC effluent (sample set 2010). These values were obtained by multiplying the original DOC (see Table 4.2) by the respective sorbable and non-sorbable fractional values obtained from parameter fitting (Table 4.3). It clearly reveals that for an EBCT of 20 and 40 min, non-sorbable DOC concentration was reduced to 1.4 mg/L and 0.47 mg/L respectively from 2.3 mg/L, measured in the untreated SWWE. This means the total non-sorbable fraction that was 22% in SWWE respectively decreased to 17% and 6% after BAC treatment. This was mainly associated with non-polar fractional concentration (from 47% to 53% and 70%). A similar phenomenon was also observed in the 2009 sample set (Table 4.3).

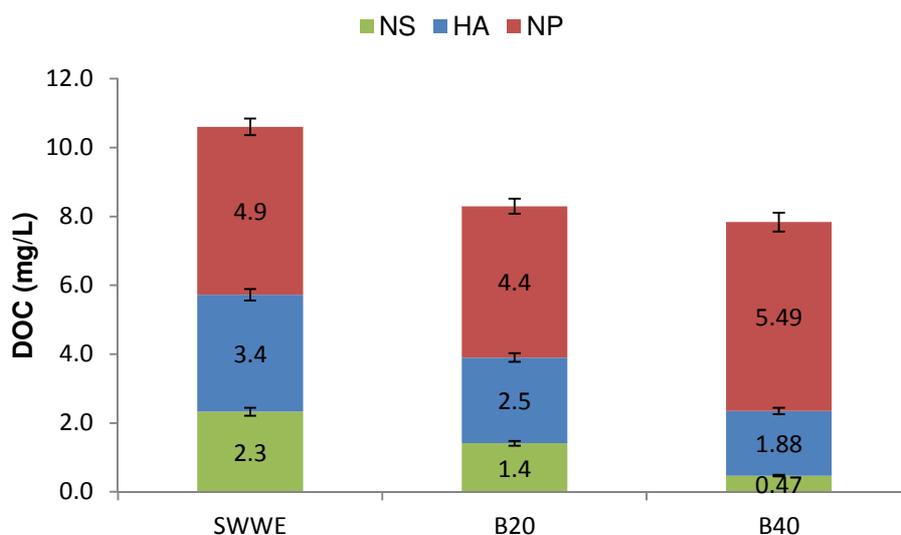


Figure 4.8: Effect of BAC treatment on sorbability

From Table 4.2, it can be seen that DOC in the 2010 samples decreased from 10.6 mg/L to 8.3 mg/L and then to 7.8 mg/L by 20 and 40 min EBCT respectively, implying that minimal DOC reduction was obtained by increasing EBCT from 20 to 40 min. However, the reduction in the sorbable fraction was 0.93 (1.4–0.47) mg/L. This is very much different from the reduction in DOC of 0.5 (8.3–7.8) mg/L.

Decreased non-sorbable and increased sorbable DOC concentrations resulting from increased EBCT indicates the role of microbial activity in the BAC bed. This is in agreement with previous studies reporting that BAC is suspected to preferentially remove hydrophilic fractions and there is a possibility that soluble microbial products (SMPs) are released during passage through the BAC (Carlson and Amy 2000, Namkung and Rittmann 1986). Those SMPs have been shown to be a HMW sorbable compound and preferentially removed by coagulant (Kastl et al. 2004, Randtke 1988). As a result, the model also showed a reduction in the non-sorbable fraction. This indicates that microbes in the BAC bed utilize the non-sorbable fraction as their substrate and release SMPs or HMW compounds to be removed by coagulants. Although detailed investigations are needed to identify the SMP or HMW compounds in particular, the analysis still supports the known hypothesis that SMPs are released by microbes and increased retention time can increase the release of SMPs and sorption of non-sorbable DOC fractions.

4.5 Conclusions

This research was undertaken to reduce the DOC present in SWWE using BAC and EC as a pre-treatment. BAC followed by EC were tested under for various conditions and analyzed in terms of DOC removal. Additionally, a model was applied to observe the quantitative effect of biological treatment over EC. The results showed an enhanced performance of coagulation on BAC-treated effluent. The experimental results obtained during this investigation help to draw following conclusions:

- The DOC model prepared for Australian/US drinking water also fits very well for SWWE and helps to quantify the sorbable and non-sorbable fractions of DOC.
- The reduction of the non-sorbable fraction with an associate increase in the sorbable fraction clearly indicates the ability of BAC treatment to aid the coagulation process by adsorbing non-sorbable fractions and/or by releasing coagulable fractions from the microbes in the bed.

4.6 Acknowledgements

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Chapter 5

Synergistic Effect of Biological Activated Carbon and Enhanced Coagulation in Secondary Wastewater Effluent Treatment

Abstract

The use of secondary wastewater effluent (SWWE) is an essential strategy for making better use of limited water resources. However, a wide range of organic compounds eventually renders them unsuitable for recycling. In water treatment processes, biologically activated carbon (BAC) is adopted after physicochemical treatment. However, the effectiveness of such a combination for treating SWWE remains poorly understood. This study investigates the effectiveness of different combinations - BAC/enhanced coagulation (EC) or EC/BAC - especially in terms of dissolved organic carbon (DOC) removal. The results show that there is a distinct advantage to adopting the BAC/EC combination rather than EC/BAC, as microbes in BAC not only remove non-coagulable compounds but also synergize removal efficiency by releasing coagulable fractions.

Keywords: BAC, DOC removal, Enhanced Coagulation

5.1 Introduction

Wastewater reuse offers one of the best alternatives for better use of limited fresh water resources (Shon et al. 2004). However, its wide application is still limited as effluent organic matter (EfOM) significantly reduces the efficiency of various post-treatment processes resulting in problems such as increased chemical demand and membrane fouling. Thus, the efficient removal of EfOM is essential for sustainable wastewater reuse.

Coagulation by ferric salt is an effective technique for removing organic matter in wastewater treatment (Kastl et al. 2004, Shin et al. 2008). It preferentially removes organic matter having higher molecular weight (HMW) and compounds that are hydrophobic in nature. It is also effective in removing low charge density humic acids (Collins et al. 1986, Hayes et al. 1989, Krasner and Amy 1995, Randtke 1988). This characteristic of ferric salt coagulation is consistent with the observation that greater removal of EfOM is achieved by coagulation in water containing relatively high hydrophobic organic concentrations than in water with low hydrophobic organic concentrations (White et al. 1997).

These observations indicate that there could be residual fractions that cannot be removed by coagulant irrespective of the increased dose. The remaining portion is reported to contain mainly hydrophilic compounds which are also responsible for reducing the efficiency of various post-treatment processes such as membrane filtration (Amy et al. 1992, Lee et al. 2001) and disinfection (Jjemba et al. 2010). In addition, an increased dose of coagulant ultimately leads to the production of excessive sludge that must be disposed of (Jarvis et al. 2008). Thus, maximizing the removal efficiency for a given dose of coagulant is highly important for sustainable wastewater reuse.

BAC offers an economic solution for the removal of dissolved organics from wastewater. In this process, beds and pores of carbon are utilized as a habitat for bacteria by making the organic matter present in water available as nutrients for them (Xiaojian et al. 1991). BAC normally utilizes microorganisms to regenerate the activated carbon while the carbon bed is in operation (Perrotti and Rodman 1974, Rice and Robson 1982). The microorganisms establish a natural biofilm during bioregeneration mode and significantly extend the life span of carbon bed (Scholz and Martin 1997). Thus, adsorption of less biodegradable organics and degradation by microorganisms occur simultaneously on the carbon bed resulting in higher biological reaction rates (Rice and Robson 1982, Weber and Ying 1977).

Further, BAC is more effective in removing lower molecular weight (LMW) organic compounds than HMW organic compounds (Matilainen et al. 2002). Disinfection by-

products (DBPs) such as N-Nitrosodimethylamine (NDMA) with an extremely hydrophilic nature were also found to be removed by more than 90% (Asami et al. 2009) demonstrating the capacity of BAC to remove non-coagulable organic compounds.

Previous studies have investigated the individual and combined performances of BAC and EC in terms of DOC removal. A reduction of non-coagulable DOC as a result of microbial activity during BAC treatment has been demonstrated using a mathematical model for DOC removal (Aryal et al. 2011). However, knowledge of the removal mechanism of the combination has been inhibited by a lack of understanding of synergistic effects. This chapter investigates synergistic DOC removal using BAC and EC in combination. Further, it shows the ability of the BAC treatment to convert non-coagulable DOC into coagulable DOC with the help of microbial activity enhancing the performance of EC in SWWE treatment.

5.2 Materials and Methods

5.2.1 Experimental Design

SWWE with a DOC concentration of 8.5 mg/L was used in this study. Figure 5.1 illustrates the approach taken to study and evaluate the performance of different pre-treatment methods. Four different treatment methods, either individually or in combination, were studied to understand their effectiveness in DOC removal.

Run 1: Enhanced Coagulation

EC was undertaken for various doses (expressed as mg/L of ferric ion (Fe^{3+})) of ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in two different ranges (1.25–160 mg/L and 20–320 mg/L) (C1.25 to C160 and C20 to C320). Samples were subjected to mixing upon addition of coagulant and pH was adjusted using sodium hydroxide and sulphuric acid, each of 1M concentration. The standard jar test protocol consisting of rapid mixing at 200 rpm for the first 2 min followed by 20 rpm for the next 20 min was

adopted. A settling period of 30 min was employed to allow the separation of flocculated particles prior to filtration.

Run 2: BAC Treatment and Reactor Set-up

Details of the BAC reactor set-up are presented in Chapter 3 (Section 3.3, Figure 3.2). For this experiment, two reactor columns each with 20 min empty bed contact time (EBCT) were operated as a continuous reactor. Thus, 40 min EBCT (B40) was achievable in one single run. This was considered to be first cycle. To obtain 80 min EBCT, effluent obtained from the 40 min EBCT (the first cycle) was collected. The B40 effluent alone was then fed again through the system (beds connected in series), instead of SWWE. The BAC effluent obtained during this second cycle is reported as an EBCT of 80 min (B80).

Run 3: Biological Activated Carbon/Enhanced Coagulation

Run 3 consisted of an initial BAC step followed by enhanced coagulation. Two different EBCTs of 40 and 80 min were individually subjected to different coagulant doses (1.25–160 mg/L) (B40C1.25 to B40C160 and B40C1.25 to B80C160) and different pH (5–9) in order to understand the effectiveness of microbial activity in the BAC/EC combination in terms of DOC removal.

Run 4: Enhanced Coagulation/Biological Activated Carbon/Enhanced Coagulation

Run 4 consisted of an initial enhanced coagulation of SWWE and a subsequent BAC treatment followed by EC again. It was undertaken to investigate whether the enhanced DOC removal in the BAC/EC combination is a result of adsorption or conversion of non-coagulable DOC or both. Thus, SWWE was first treated with a pre-determined coagulant dose in order to remove all coagulable fractions. The coagulant dose was progressively increased until residual DOC levels remained constant. Afterwards, the coagulated effluent was filtered through 0.45µm filter paper (Cellulose Acetate filter paper (GE Water and Process Technologies, Cat. No.

A04SP04700, Acetate plus supported)) to remove all the flocs. As pH had been reduced to 5 during coagulation, it was re-adjusted back to the original SWWE pH (7.37) to ensure a favourable environment for the microbial community prior to BAC treatment. Further, nutrients for the bacteria were supplemented by adding phosphorus (1:100 Carbon to Phosphorous) (Sathasivan et al. 1997) as it had been removed during coagulation (Sathasivan et al. 1998) leaving less than 5 µg/L PO₄-P in the water. Potassium di-hydrogen phosphate was used as a source of phosphorus to prepare stock solution (1 g/L).

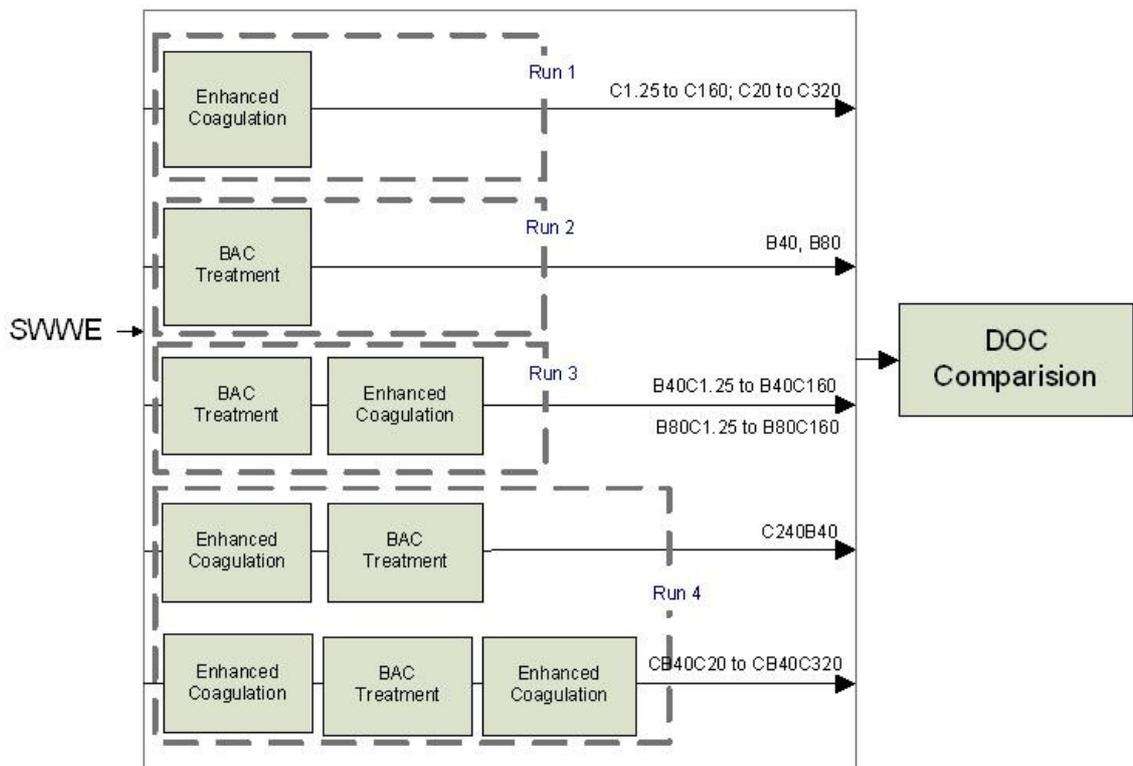


Figure 5.1: Experimental flow chart

The BAC bed was flushed with Milli-Q water (PURELAB UHQ II Milli-Q water unit, Australia) followed by feed water itself prior to sending the coagulated effluent. Afterwards, nutrient and pH-adjusted coagulated effluent with only non-coagulable DOC was subjected to BAC treatment at an EBCT of 40 min. Around 2 L of BAC effluent was discarded to avoid possible contamination on switching feed water.

Then effluent obtained from the EC/BAC combination was again subjected to coagulation (CB40C20 to CB40C320 mg/L) at pH 5.

5.2.2 Analytical Measurements

DOC was considered to be a major analytical parameter and measured using a 5310C laboratory GE Total Organic Carbon Analyzer connected to an autosampler. As samples were analyzed after filtering through the 0.45 μm Cellulose Acetate filter paper (GE Water and Process Technologies, Cat. No. A04SP04700, Acetate plus supported), the measured value is the DOC. This machine uses UV persulphate oxidation for the measurement of DOC. This instrument has an analytical range of 30 $\mu\text{g/L}$ to 50 mg/L within the measurement error of 5%. Prior to filtration of the sample, the filter medium was pre-washed with Milli-Q water (PURELAB UHQ II Milli-Q water unit, Australia). The Milli-Q water had a DOC and conductivity of <0.1 mg/L and <1 $\mu\text{S/cm}$ respectively. The pH and dissolved oxygen (DO) was measured using a Hach pH and DO meter (HACH 40d) and electrode (PHC101, Hach) respectively. The pH probe was calibrated using Hach buffer solution of three different ranges of pH (4, 7 and 9) prior to the experiment.

Similarly, number average molecular weight (M_n) in SWWE and BAC-treated effluent was analyzed by using size exclusion chromatography with continuous $\text{UV}_{254\text{nm}}$ and organic carbon detection (LC-OCD system model 8, based on the Grantzel thin film reactor developed by DOC-Labor, Dr. Huber Karlsruhe/Germany; SEC column: Toyopearl HW-50S weak cation exchange gel filtration column, Tosoh Bioscience, Tokyo Japan). The qualitative analysis is based on size exclusion chromatography (SEC) to separate different classes of dissolved organic materials (organic acids, bases, and neutral species). SEC separates components on the basis of their molecular size. In addition to the organic carbon detector, LC-OCD uses UV detection and determines the spectral absorption coefficient (SAC) at 254 nm to complete the information about the analyzed wastewater samples.

5.3 Results and Discussion

5.3.1 Source Water

The SWWE from Beenyup Wastewater Treatment Plant (BWTP), Western Australia was used in this investigation. The wastewater came predominantly from household kitchens, bathrooms, toilets and laundries. The plant uses a secondary treatment process, to biologically remove nitrogen and dissolved organic carbon from influent wastewater. Neither chemical nor biological methods were employed to remove phosphorus from influent waters. The SWWE characteristics of this plant during the time of this experiment are reported in Table 5.1.

Table 5.1: Water quality characteristics of Beenyup SWWE

	Temp (°C)	pH	UV ₂₅₄ (per cm)	mg/L					
				DOC	DO ^b	SS ^c	NH ₃ -N	NO ₃ -N	PO ₄ -P
	24	7.35	0.203	8.5	7.8	9.2	0.028	11.25	8.2
Average	±	±	±	±	±	±	±	±	±
	2.16	0.16	0.007	0.50	0.18	0.22	0.002	0.20	0.28

^aElectrical Conductivity; ^bDissolved oxygen; ^cSuspended solids

5.3.2 Individual Performance of EC and BAC

Although DOC can be effectively removed by EC, there remains some portion that can be detrimental to other post-treatment processes such as membrane filtration and disinfection. The EC jar test results obtained for various pH and coagulant doses (Run 1) are presented in Figure 5.2. The DOC in SWWE was reduced from 8.5 mg/L to 3.56 mg/L with 80 mg/L coagulant at pH 5. An increased coagulant dose further

reduced DOC although the additional removal achieved was minimal beyond 80 mg/L. Similarly, pH manipulation from 5 to 4 resulted in no additional DOC removal. Thus, pH 5 was used as an effective pH for the remaining experiments. From these observations, it is clear that 80 mg/L at pH 5 significantly reduces the residual DOC. However, if all coagulable DOC has to be removed, a higher coagulant dose needs to be applied. These results are consistent with previous studies (Kastl et al. 2004).

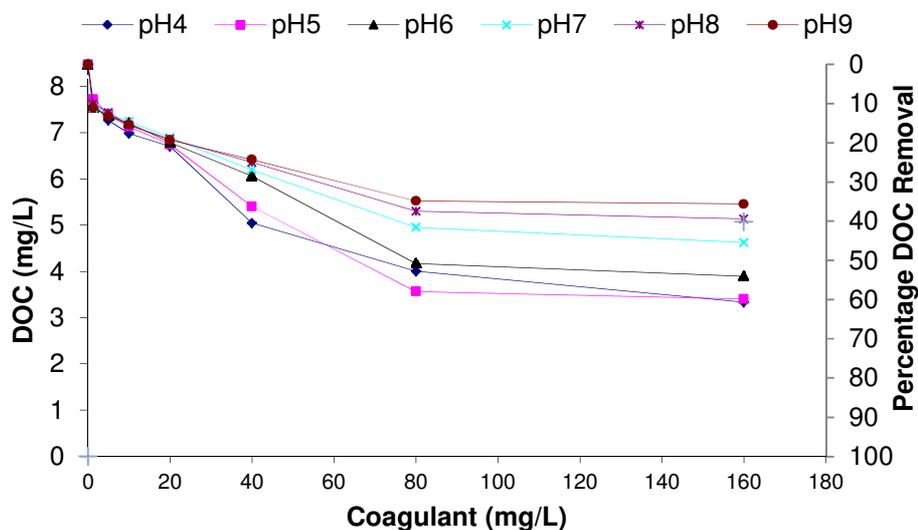


Figure 5.2: DOC removal from SWWE by EC

Similarly, the long-term performance of BAC showed stabilization of DOC removal at around 30% for B40 water (Run 2). The DOC removal for the first day was around 83% (Figure 4.1; Chapter 4) but decreased gradually, signifying physical adsorption as a major removal mechanism in the initial period. It stabilized afterwards and reached a steady state with an average of 30% removal once microbial activities became dominant over physical adsorption. This is in agreement with previous studies (Hoang et al. 2008, Servais et al. 1994). However, an increase in EBCT achieved higher DOC removal. It is evident from Figure 5.3b that the steady state DOC removal efficiency increased from 32 to 45% for B80 water.

5.3.3 Performance of the BAC/EC Combination

Having established that EC or BAC left substantial amount of residual DOC in the treated water, it is necessary to understand how well they perform in combination. The BAC/EC combination was investigated at two different EBCTs (B40 and B80). As illustrated in Figure 5.3b, B40 removed around 32% DOC and the removal further increased with an increase in EBCT. EC of BAC treated effluent (Figure 5.1, Run 3) was investigated as presented in Figure 5.3a. It is evident that DOC remained stable at 2.5 mg/L after the addition of 240 mg/L coagulant in SWWE but decreased further to 1.26 mg/L in B40 effluent. EC was even more effective in B80 effluent as DOC decreased to 1.14 mg/L at a coagulant dose of 160 mg/L. This further reduction in DOC that was initially non-coagulable could only be possible if BAC removes it either by adsorption or by conversion into a coagulable form. These possibilities are discussed further below.

5.3.4 Performance of the EC/BAC Combination

Having shown the effectiveness of the BAC/EC combination, the EC/BAC combination was investigated to determine whether BAC adsorbs non-coagulable fractions by applying higher doses than those used in Run 1 (Figure 5.1, Run 4). The maximum coagulable organics in SWWE were determined by employing coagulant doses of 20–320 mg/L at pH 5. As mentioned in the previous section, DOC remained constant at 2.5 mg/L at coagulant doses above 240 mg/L, indicating that this dose is the minimum required to remove all coagulable fractions (Figure 5.3a). Thus, the BAC feed containing only non-coagulable DOC was prepared by dosing with 240 mg/L (C240) coagulant.

This non-coagulable (mostly hydrophilic) fraction (2.5 mg/L) of DOC was filtered through the BAC reactor at an EBCT of 40 min (Figure 5.1, Run 4). The DOC decreased further by 30% to 1.73 mg/L (Figure 5.3b). This indicates that BAC could remove non-coagulable DOC by adsorption. However, it still remained unclear

whether BAC converts non-coagulable DOC to coagulable DOC at the same time. Hence, a further experiment was carried out.

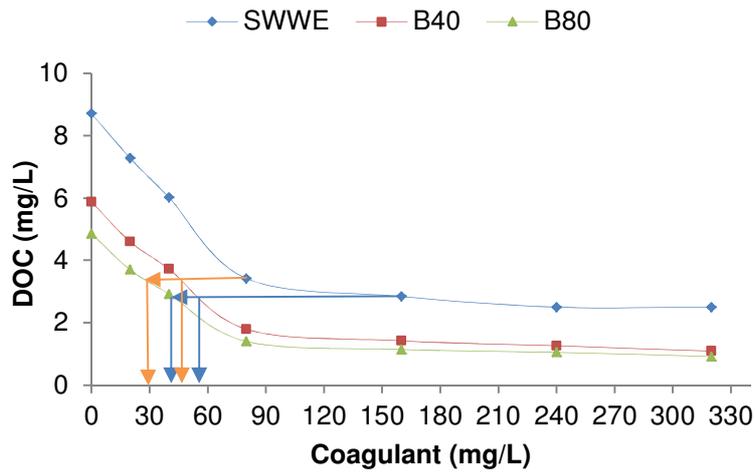


Figure 5.3a: Performance of the BAC/EC combination

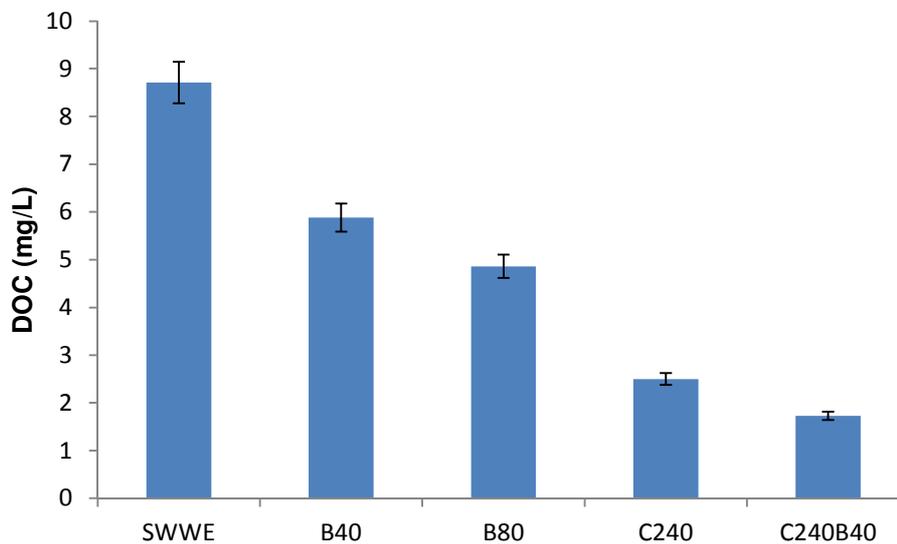


Figure 5.3b: Performance of BAC and the EC/BAC combination

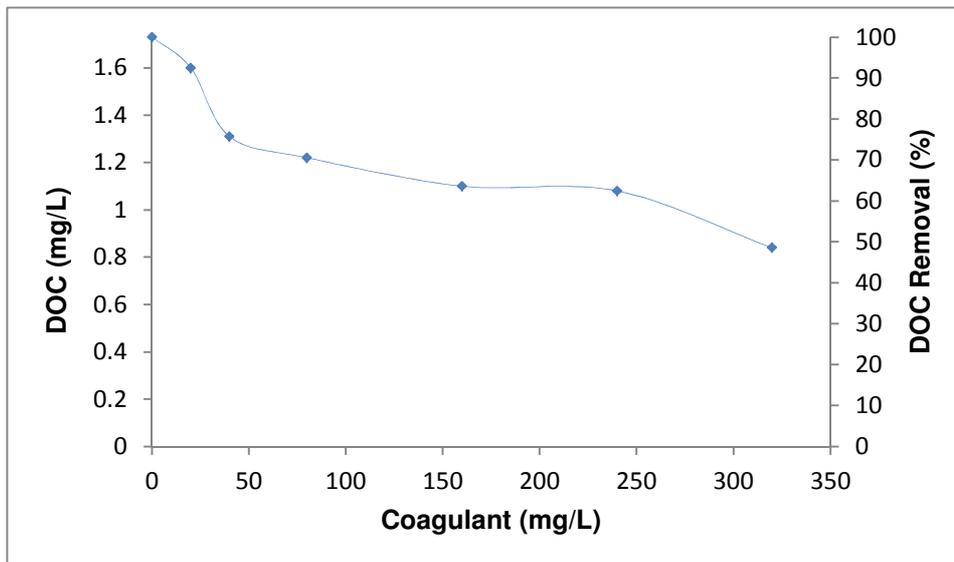


Figure 5.3c: EC/BAC/EC combination (EC performance on BAC effluent fed with only non-coagulable DOC)

5.3.5 EC/BAC/EC: Verification of Enhanced Performance of Coagulant on BAC Effluent

The EC/BAC/EC combination (Figure 5.1, Run 4) was investigated by again performing EC on the BAC effluent (DOC 1.73 mg/L) obtained after feeding with non-coagulable (mostly hydrophilic) DOC. This was based on the assumption that if increased removal efficiency in BAC/EC compared to the EC/BAC combination is only a result of the adsorption of non-coagulable DOC in the BAC bed, then residual DOC in the EC/BAC effluent should still be non-coagulable. A range of coagulant doses was applied to investigate this. The results (Figure 5.3c) reveal evidence of coagulable DOC being reduced with an increase in coagulant dose. This clearly indicates the generation of coagulable DOC after BAC treatment. This could be caused by the formation of compounds similar to the coagulable HA fractions (Kastl et al. 2004) formed during BAC filtration of water.

Evidence of the increase in number average molecular weight (M_n) in the BAC bed was further obtained with the help of LC-OCD analysis. M_n value in SWWE (486 g/mol) continuously increased to 605 and 619 g/mol respectively with EBCTs of 40

and 80 min in BAC bed and coagulation is better in removing higher molecular weight compounds (Randtke 1988). These results clearly indicate the role of microbial activity in the BAC bed in producing coagulable DOC from non-coagulable DOC. BAC synergized the DOC removal achieved by EC by generating more coagulable DOC in addition to adsorption, thus making BAC/EC more effective than EC/BAC.

5.4 Why BAC Prior to EC?

The previous section clearly shows the effectiveness of the BAC/EC combination in enhancing DOC removal. However, in order to understand the practicability of the combination, this section investigates removal below the 160 mg/L coagulant dose. Figure 5.3a shows the improved performance of coagulant in BAC effluent throughout the applied dose range. The residual DOC that was at 2.84 mg/L (33%) prior to BAC decreased to 1.42 mg/L (24%) for the same dose of coagulant (160 mg/L) after BAC treatment. Further analysis showed that the DOC removal efficiency obtained by 60 mg/L coagulant in BAC effluent was equivalent to 160 mg/L in SWWE reducing the necessary coagulant dose by 63%. This could also be useful in reducing the sludge produced for the given amount of DOC removal. In summary, BAC is effective in combination with EC as it enhances the amenability of organics for removal by coagulation as well as absorbing organics and bringing down the coagulant dose required for EC alone.

5.5 Conclusions

The results clearly show that the BAC/EC combination synergized the DOC removal performance for two main reasons. The BAC adsorbs some of the fraction that cannot be removed by EC and at the same time converts non-coagulable DOC to coagulable DOC by microbial activity. As a result, the BAC/EC combination proved to be more promising than the EC/BAC combination in terms of synergistic organics removal from the SWWE. However, further investigation is necessary into

comparing the capital and operating costs of optimized BAC/EC with those of EC/BAC.

5.6 Acknowledgements

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Chapter 6

Importance of the Order in Enhancing EfOM Removal by Combination of BAC and MIEX

Abstract

Biological activated carbon (BAC) is an operationally simple treatment which can be employed to remove effluent organic matter (EfOM) from secondary wastewater effluent (SWWE). Unfortunately, BAC removes only a limited amount of dissolved organic carbon (DOC). Thus, maximizing DOC removal from SWWE using BAC is a major concern in wastewater reuse. This study has investigated a hybrid system of BAC and Magnetic Ion Exchange Resin (MIEX) for the enhanced removal of DOC. Performance of both BAC prior to MIEX (BAC/MIEX) and the reverse combination (MIEX/BAC) were evaluated in terms of DOC removal. The BAC/MIEX combination showed a much better DOC removal due to microbial activity in the BAC bed converting MIEX-non-amenable DOC to MIEX-amenable DOC. As a result, the BAC/MIEX combination synergized DOC removal. In addition, BAC was also found to be highly effective in reducing the MIEX dose required for a given removal of DOC from SWWE.

Keywords: Biological Activated Carbon, DOC Removal, MIEX

6.1 Introduction

Increasing water demand resulting from increased domestic and industrial consumption is leading to potential water shortages in many parts of the world. The removal of EfOM from SWWE is therefore receiving greater attention in order to develop wastewater recycling as an alternative water source. However, the presence of a wide range of organic compounds in the water, usually measured as DOC, makes this process more complicated and necessitates further intensive treatment.

Various treatment processes have been studied in the past. They include enhanced coagulation (EC), activated carbon adsorption, BAC, MIEX and ozonation. While DOC removal by coagulation is a promising alternative, it produces sludge that needs disposal (Jarvis et al. 2008) and requires a large sedimentation tank for settlement. In addition, it offers limited DOC removal due to the presence of non-sorbable fractions (Kastl et al. 2004). By comparison, BAC and MIEX offer a better solution (Scholz and Martin 1997, Slunjski et al. 2000), although their application needs further improvement.

The activated carbon adsorption process can be highly effective in removing the majority of organics from SWWE (Shon et al. 2005). However, their cost-effectiveness in exploiting physical adsorption alone is still under scrutiny. BAC offers an economic solution to remove DOC from wastewater. Beds and pores of carbon are utilized as a habitat for bacteria with the organic matter present in the water acting as a source of nutrients for them (Xiaojian et al. 1991). BAC normally utilizes microorganisms to regenerate the activated carbon while the carbon bed is in operation (Perrotti and Rodman 1974, Rice and Robson 1982). The microorganisms establish a natural biofilm during bioregeneration mode and significantly extend the life span of the carbon bed (Scholz and Martin 1997). Furthermore, adsorption of less biodegradable organics and degradation by microorganisms can occur simultaneously on the carbon bed, resulting in higher biological reaction rates (Rice and Robson 1982, Weber and Ying 1977).

MIEX, on the other hand, has emerged as an effective alternative treatment technology for the removal of organic contaminants from SWWE. It is a micro sized strong base resin with ammonium functional groups, consisting of a macro-porous, poly-acrylic structure (Slunjski et al. 2000). It effectively removes wide ranges of organic carbon of both hydrophilic and hydrophobic fraction from the water because of its anion exchange properties (Jarvis et al. 2008, Son et al. 2005). MIEX treatment has been found to be effective when followed by coagulation, reducing coagulant

doses by up to 75% and reducing organic carbon residuals (Morran et al. 2004, Fearing et al. 2004).

Pre-oxidation with ozone prior to BAC treatment is considered to be an effective option for removing a wide range of organics (Chen et al. 2007). However, it involves a complicated ozonation process followed by adsorption and biodegradation, and is still not fully effective in removing DOC (Takeuchi et al. 1997). In this context, a treatment combination with a lower chemical requirement and sludge disposal, with a simple treatment protocol for the removal of a wide range of organic carbons is a priority for sustainable wastewater reuse.

While removal efficiencies have been shown to be significantly improved by combining resin pre-treatments with other physico-chemical treatment, little research has been carried out to understand its effectiveness in combination with biological treatment using BAC. Thus, the principal objective of this paper is to investigate the removal of DOC from SWWE using BAC and MIEX in combination. A direct comparison was made between the MIEX/BAC and BAC/MIEX combinations. Further investigation was carried out to understand the role of microbial activity in the BAC bed in enhancing the performance of MIEX in SWWE treatment.

6.2 Materials and Methods

6.2.1 Experimental Design

SWWE with a DOC concentration of 9.04 mg/L was used in this experiment. The performances of BAC and MIEX both individually and in combination were investigated as presented in Figure 6.1. The experiment was repeated with SWWE with a source DOC of 7.83 mg/L (Appendix 1) following the same experimental protocol, but only the results from first set are discussed in detail in this chapter.

Run 1: MIEX Sampling and Treatment

The MIEX resin with a size of 150 to 180 μm in size was obtained from Orica Watercare, Australia and delivered in slurry form in a plastic container. The plastic

container contained approximately 90% v/v (based on settled resin volume in the water carrier). The regenerated MIEX doses were manipulated first by vigorously shaking the plastic container and then filling a 10-50 ml graduated syringe with the slurry. Specific concentrations mainly over two different ranges (0.2–3.2% v/v (M0.2 to M3.2) and 0.2–8.0% v/v (M0.2 to M8.0)) were applied based on the nature of investigations. Samples were put into a jar tester and stirred at 150 rpm for 20 min. The samples were then allowed to settle for 5 min before filtration.

Run 2: BAC Treatment and Reactor Set-up

Details of BAC reactor set-up are presented in Chapter 3 (Section 3.3, Figure 3.2). Two reactor columns were connected in series and operated at 20 min empty bed contact time (EBCT) each. Thus, 40 minutes EBCT (B40) was achievable in a single run. Once the BAC performance was stable in terms of DOC removal, 10 min EBCT (B10) was obtained by adjusting the feed discharge into the first column by using a peristaltic pump. The whole experiment was undertaken with BAC effluent obtained after 10 weeks and 12 months of operation in order to verify the consistency of results. The experimental results obtained for the BAC effluent after 12 months of operation are provided in Appendix 1.

Run 3: BAC/MIEX Treatment Combination

Run 3 investigated the combination of BAC followed by MIEX treatment. Two different EBCTs of 10 min and 40 min were individually subjected to various MIEX doses (0.2–3.2% v/v) (B10M0.2 to B10M3.2 and B40M0.2 to B40M3.2) in order to understand the effectiveness of microbial activity for DOC removal in the BAC/MIEX combination.

Run 4: MIEX/BAC/MIEX Treatment Combination

This step tested the combination of MIEX-treated SWWE followed by BAC treatment. The MIEX/BAC combination was then followed by a MIEX treatment in order to show the generation of the MIEX-amenable fraction out of the non-amenable fraction. The SWWE was first treated with a pre-determined MIEX dose in order to remove all MIEX amenable fractions. The MIEX dose was progressively

increased until residual DOC remained constant. MIEX-treated effluent was then filtered through 0.45 µm filter paper to remove all the residual MIEX resins.

In order to avoid possible contamination, the BAC bed was flushed with DI water followed by MIEX-treated water (2 L each). Afterwards, the MIEX-treated SWWE only with the MIEX non-amenable fraction was subjected to BAC treatment at an EBCT of 40 min. BAC effluent obtained during this process (M6.4B40) was again subjected to MIEX treatment (0.2–3.2% v/v) (M6.4B40M0.2 to M6.4B40M3.2) after discarding the first 2L of M6.4B40-treated effluent.

6.2.2 Analytical Measurements

DOC was considered to be the major analytical parameter and measured using a GE 5310C laboratory Total Carbon Analyzer connected to an autosampler. As samples were analyzed after filtering through 0.45 µm Cellulose Acetate filter paper (GE Water and Process Technologies, Cat. No. A04SP04700, Acetate plus supported), the measured value is the DOC. The total carbon analyzer uses UV persulphate oxidation for the measurement of DOC, and has an analytical range of 30 µg/L to 50 mg/L within the 5% measurement error. Prior to the filtration of the sample, the filter medium was pre-washed with Milli-Q water (PURELAB UHQ II Milli-Q water unit, Australia). The Milli-Q water had a DOC and conductivity of <0.1 mg/L and <1 µS/cm respectively.

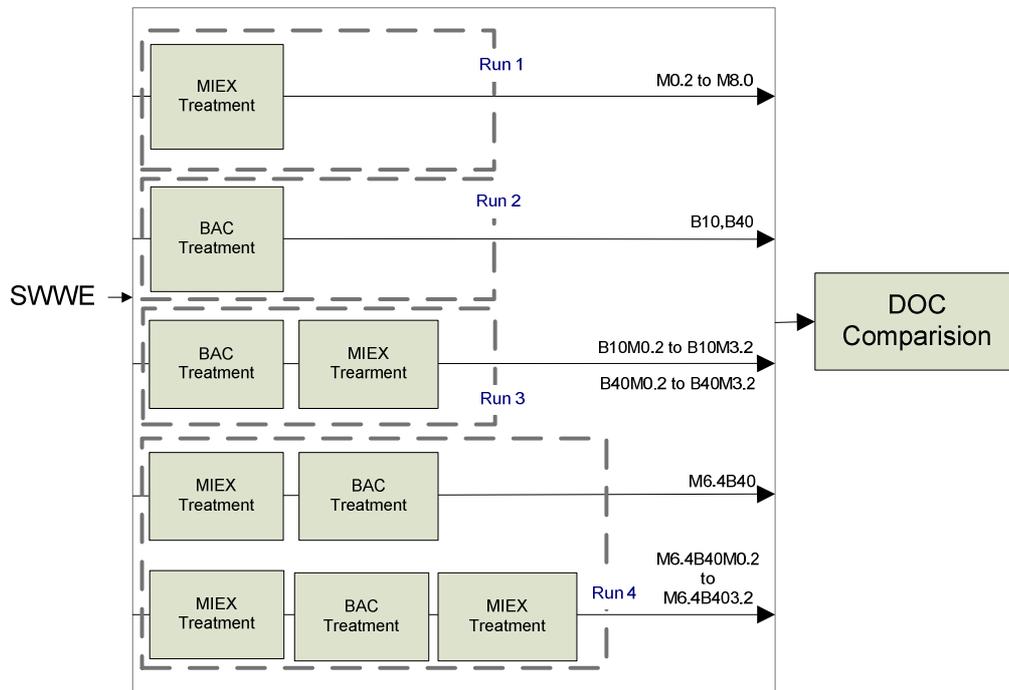


Figure 6.1: Experimental flow chart

6.3 Results and Discussion

6.3.1 Source Water Characteristics

The SWWE used in this study was from a municipal wastewater treatment plant (Beenyup, Western Australia). The plant uses a secondary treatment process to biologically remove nitrogen and DOC from influent wastewater. Neither chemical nor biological methods were employed to remove phosphorus from influent waters. The water quality characteristics of this water are presented in Table 6.1.

Table 6.1: Water Quality Characteristics of Beenyup SWWE

	Temp (°C)	pH	EC ^a (µS/ cm)	UV ₂₅₄ (per cm)	mg/L				
					DOC	DO ^b	SS ^c	NH ₃ -N	NO ₃ -N
Average	26.5	7.2	1356.5	0.201	8.16	7.8	9.0	0.287	7.74
	±	±	±	±	±	±	±	±	±
	2.12	0.14	7.78	0.005	0.47	0.14	0.28	0.388	2.60

^aElectrical Conductivity; ^bDissolved Oxygen, ^cSuspended Solids

6.3.1 Individual Performance of MIEX and BAC

Investigations of the effectiveness of MIEX in treating SWWE have shown that it cannot fully remove DOC despite its ability to remove both hydrophobic and hydrophilic fractions (Son et al. 2005). The results obtained from the jar test (Figure 6.2) clearly indicate an increase in DOC removal with increases in both resin contact time and dose. DOC decreased to 5.46 mg/L (39%) with the addition of 1.6% v/v MIEX concentration during the first 5 min of mixing. It decreased by 56% after a two-fold increase in MIEX. As illustrated in Figure 6.2, DOC decreased further after an increase in resin contact time to 20 min, with an overall removal of 60% and signs of stabilization thereafter, clearly indicating that a 3.2% v/v concentration of MIEX over 20 min achieves most of the DOC removal. A resin contact time of 20 min was therefore employed for the remaining experiments. However, more MIEX with a longer contact time is necessary for the removal of all MIEX-amenable DOC.

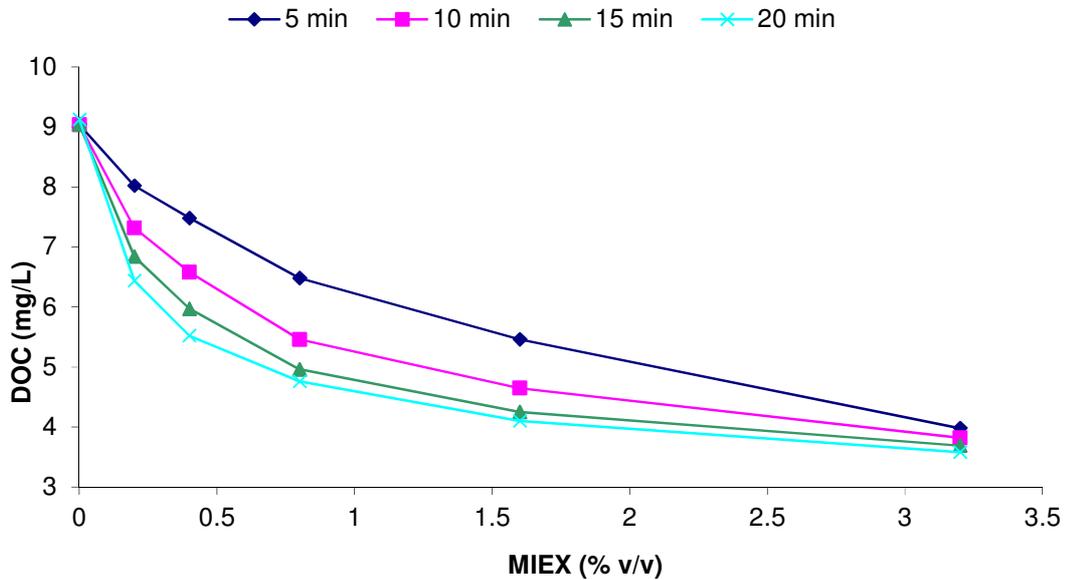


Figure 6.2: Performance of MIEX in SWWE

As explained earlier in Chapter 4, BAC was investigated for its long-term performance, and stable DOC removal was obtained after four weeks of operations, once microbes were acclimatized. DOC removal for the first day was around 83% (Figure 4.1; Chapter 4). However, this decreased gradually thereafter, indicating the possible role of physical adsorption as a removal mechanism. Despite the drop in physical adsorption, DOC removal reached a steady state with an average of 30% removal once microbial activity became dominant. This is in agreement with previous studies that have shown that the biological process gradually becomes dominant over physical adsorption in removing organic carbon in a BAC bed (Hoang et al. 2008).

6.3.2 Performance of BAC/MIEX Combination

The results of individual BAC and MIEX treatments showed substantial residual DOC in treated water, indicating the need to determine whether their performance in combination might remove more. This was investigated by subjecting SWWE first to BAC under two different EBCTs (Figure 6.3; 6.4) in order to analyze the effect of

microbial activity on MIEX performance. As shown in Figure 6.3, B10 removed around 17% DOC and this increased with an increase in EBCT.

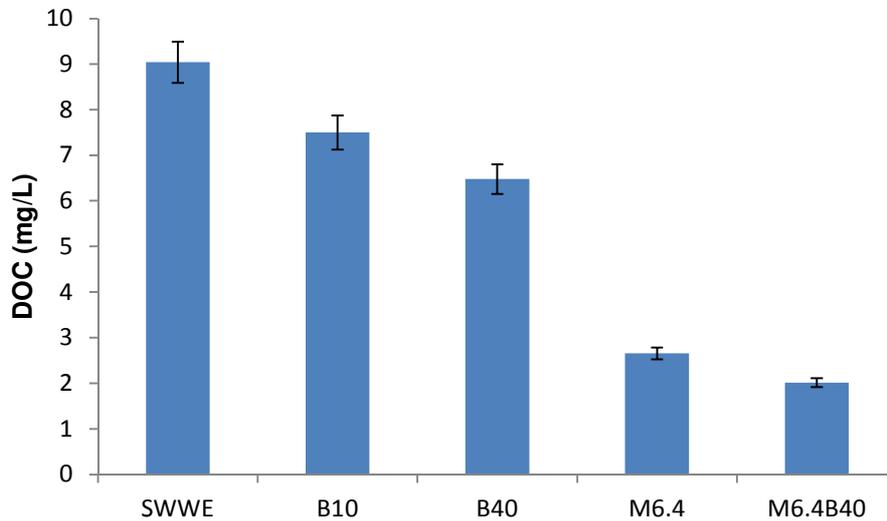


Figure 6.3: BAC performance prior to and after the MIEX

The B10 and B40 effluents were then subjected to MIEX treatment (Run 2). Figure 6.4 compares the DOC removal efficiency of MIEX for SWWE and BAC effluent. It clearly shows that there is no further DOC removal with an increase in MIEX dose beyond 6.4%, and residual DOC remained constant at 2.61 mg/L. However, in B10 effluent, residual DOC decreased to 2.42 mg/L just with 3.2% v/v MIEX concentration. It decreased further to 1.96 mg/L in a B40 effluent, indicating the possible role of microbial activity in the BAC bed. However, it was not yet clear whether this was a result of microbial activity or simply an adsorption of MIEX non-amenable fractions on the BAC bed. Thus, these possible mechanisms were investigated further.

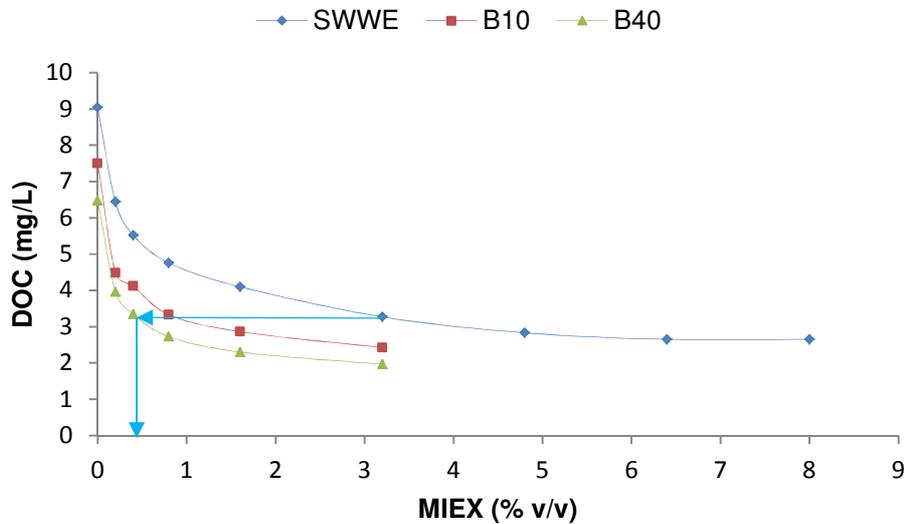


Figure 6.4: Performance of MIEX under various conditions

6.3.3 Performance of MIEX/BAC Combination

Having determined the effectiveness of the BAC/MIEX combination this section investigates the MIEX/BAC combination to find out whether BAC adsorbs MIEX non-amenable fractions. This was done in two steps. The SWWE was first subjected to successive MIEX concentrations (0.2–8.0% v/v) in order to understand the ultimate capacity of MIEX for DOC removal. The BAC feed was prepared by using a 6.4% v/v MIEX concentration as the DOC remained constant at 2.65 mg/L thereafter.

In the second step of Run 3, effluent with only the MIEX non-amenable fraction was then filtered through BAC at an EBCT of 40 min. As illustrated in Figure 6.3, additional treatment further reduced DOC to 2.01 mg/L by 25%, clearly indicating the ability of BAC to remove MIEX non-amenable fractions by adsorption. However, it still unclear whether increased DOC removal in the BAC/MIEX combination was only a result of adsorption, or BAC released some MIEX-amenable fraction from the residual non-amenable fraction at the same time. Hence, this was investigated further.

6.3.4 MIEX/BAC/MIEX: Verification of Enhanced Performance of MIEX on BAC Effluent

The MIEX/BAC/MIEX combination (Run 3) was investigated by subjecting the BAC effluent (2.01 mg/L) obtained after feeding with MIEX non-amenable DOC to MIEX treatment again. This was based on the assumption that if the higher removal efficiency of the BAC/MIEX combination compared to the MIEX/BAC combination is only a result of the adsorption of non-amenable DOC in the BAC bed, then residual DOC in the MIEX/BAC effluent should still be non-amenable to MIEX. Hence, a range of MIEX doses was applied to investigate this. The results showed the evidence of MIEX-amenable DOC decreasing with an increase in MIEX dose (Figure 6.5). This implies that the microbial activity inside the BAC bed is significant in converting non-amenable DOC into amenable DOC in addition to adsorption, which otherwise could not be removed by MIEX again.

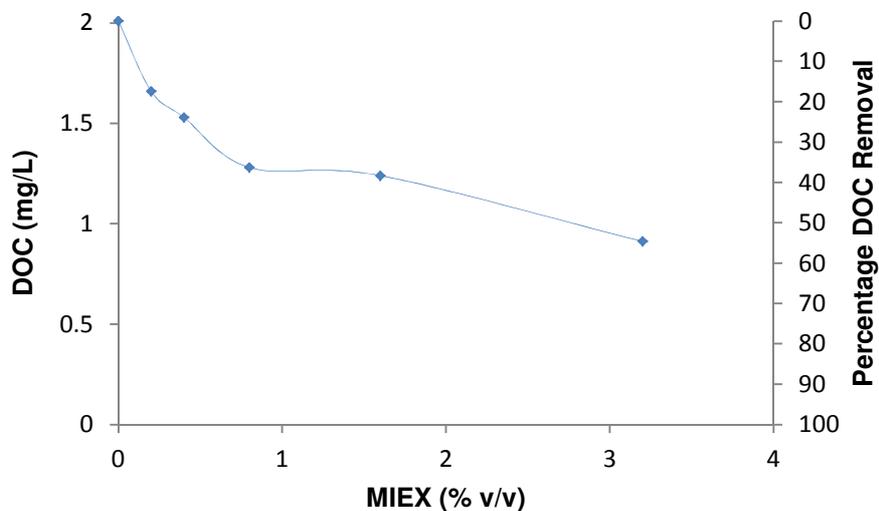


Figure 6.5: MIEX performance on BAC effluent fed with MIEX non-amenable fraction alone

6.3.5 Effectiveness of BAC/MIEX Order

The previous section clearly shows the synergistic effect of the BAC/MIEX combination on enhancing DOC removal. In order to understand the practicability of the combination, this section deals with the range of 3.2% v/v of MIEX concentration. Figure 6.6 juxtaposes the effectiveness of the BAC/MIEX and MIEX/BAC combinations. Both combinations were tested on the same source water and residual DOC. The EBCT in the BAC reactor was kept constant (40 min) while MIEX concentration was varied. The MIEX/BAC combination consumed 6.4% v/v MIEX concentration to obtain residual DOC of roughly around 2 mg/L. However, this same residual DOC was obtained using only half the concentration of MIEX (3.2% v/v) in the BAC/MIEX combination, indicating that BAC/MIEX is a more efficient combination than MIEX/BAC.

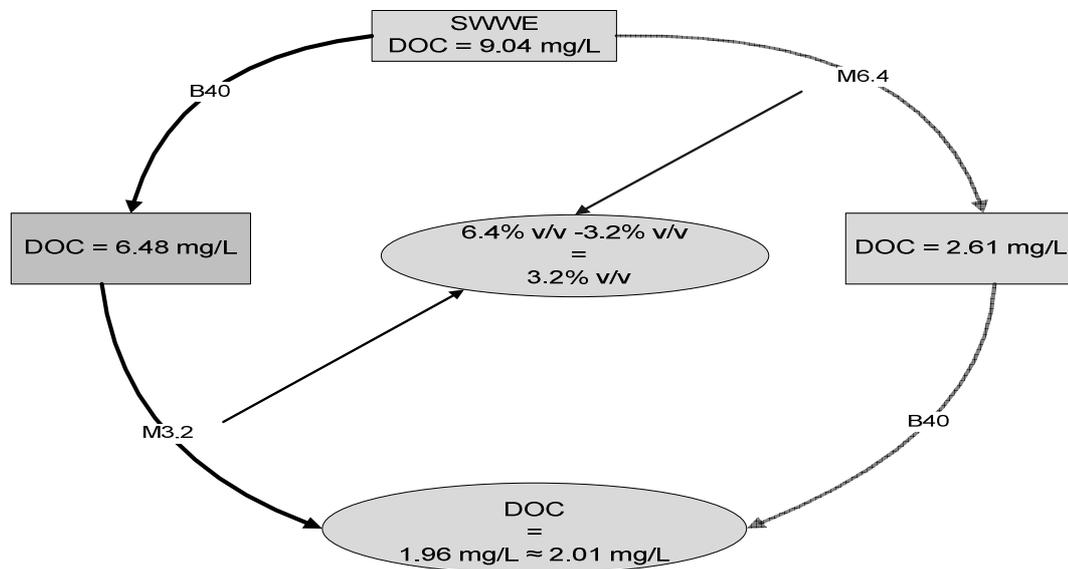


Figure 6.6: Effectiveness of BAC/MIEX vs. MIEX/BAC combination

Similarly, as illustrated in Figure 6.4, the efficiency obtained by 0.8% v/v MIEX concentration in B10 effluent is equal to the efficiency of 3.2% v/v concentration in SWWE. With increased EBCT, in B40 effluent the MIEX concentration further

decreased to 0.4% v/v with a reduction in MIEX dose of up to 87% for the removal of the given DOC. This is indeed a small amount to treat SWWE, as Wanneroo Treatment Plant (Perth, Western Australia) normally uses MIEX concentrations up to 2.0% v/v in order to treat ground water with DOC 8-10 mg/L to bring it up to drinking water quality standards.

The whole investigation was repeated by subjecting SWWE (DOC 7.83 mg/L), collected during a different time of year, to the BAC bed after 12 months of operation. The results confirmed the effectiveness of the BAC/MIEX combination (B40 and M3.2) with a substantial reduction in residual DOC (1.31 mg/L) and saving in MIEX dose of 85%. This indicates that although BAC offers very limited DOC removal when used alone, it is effective in synergizing the DOC removal to be removed by MIEX. This unique feature could be harnessed in various water treatment applications such as membrane fouling reduction, disinfection reduction and ground water recharge with proper optimization, although it needs further investigation.

Further, SWWE can be directly treated using the BAC/MIEX combination without any pre-treatment such as pH adjustment. Thus, compared to other treatments such as coagulation and ozone/BAC, it requires no chemicals. In addition to this, both BAC and MIEX can be regenerated for reuse. BAC can be regenerated continuously by microbial activity and needs only a nominal maintenance such as periodic back wash of the bed once a month in order to avoid physical clogging of the bed.

Previous investigations with MIEX showed nearly same removal efficiency even after 10 cycles of regeneration (Zhang et al. 2006). It can be used for at least 550 cycles without any mechanical damage to the resin or decrease in adsorption along with resin recovery rates of more than 99.9% (Bourke et al. 1999). Thus, MIEX offers a reversible DOC removal mechanism with reduced sludge production unlike in enhanced coagulation. In addition, it removes a significant amount of DOC from SWWE while using less chemicals without a complicated operating procedure, and with lower energy requirements unlike ozone/BAC and membrane treatment respectively. The generation of brine solution as a result of MIEX regeneration is a

clear disadvantage. However, the BAC/MIEX combination substantially reduces the MIEX dose required for a given DOC removal, which reduces the MIEX regeneration cycle, and consequently reduces the amount of brine solution to be disposed of.

6.4 Conclusions

Performance of both BAC and MIEX were investigated alone and in combination to determine their effectiveness in removing DOC removal from SWWE. Experimental results showed that BAC/MIEX offers reversible DOC removal with a substantial reduction in sludge to be disposed of unlike enhanced coagulation. Similarly, it does not demand excessive use of chemicals compared to the Ozone/BAC process. These benefits could be instrumental in developing cost-effective and reversible DOC removal techniques in water treatment utilities although further detailed investigation with different types of SWWE is needed to better understand the process. The major experimental findings of this experiment are as follows.

1. The BAC/MIEX combination is highly effective compared to the MIEX/BAC combination as MIEX gains synergistic benefit of the microbial activity occurring in BAC pre-treatment for enhanced and additional DOC removal.
2. BAC enhances the performance of MIEX by the adsorption of DOC that cannot be removed by MIEX and by converting MIEX non-amenable DOC to amenable DOC through microbiological activity inside the BAC bed.
3. For a given DOC removal, BAC pre-treatment could mean a saving in MIEX dose up to 87%, consequently reducing the number of MIEX regeneration cycles.

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Chapter 7

Combined BAC and MIEX Pre-treatment of Secondary Wastewater Effluent to Reduce Fouling of Nanofiltration Membranes

Abstract

Two different materials, biological activated carbon (BAC) and magnetic ion exchange resin (MIEX) were used to pre-treat secondary wastewater effluent (SWWE). The individual and combined effects of pre-treatment were checked against a nanofiltration membrane. BAC pre-treated water facilitated a lower but steady flux while MIEX treated water resulted in a higher flux but rapidly declined. The combined use of these pre-treatments on the other hand was able to increase average flux from 58-67% to 80-89%. Of the two possible pre-treatment combinations, MIEX/BAC combination was far superior at reducing membrane fouling. Measurement of average Stokes radius (m) and number average molecular weight (M_n) respectively by nuclear magnetic resonance (NMR) and liquid chromatography organic carbon detection (LC-OCD) revealed that the microbial activity of BAC has the ability to increase the size of dissolved organic matter (DOM) in SWWE. Further, the analysis of dissolved organic carbon (DOC) fractionations indicated the ability of BAC to specifically reduce lower molecular weight (LMW) neutral fraction (<350 Da) of DOC. Hence, the removal of LMW neutral fractions and an increase of average stokes radius (m) and the number average molecular weight (M_n) of DOC appear important to facilitate a long-term stable flux. Specifically, the combined MIEX/BAC pre-treatment appear to target and reduce the foulants in SWWE largely responsible for the reduction of flux in nanofiltration membranes.

Keywords: Biologically Activated Carbon, Membrane Fouling, MIEX, Hybrid Pre-treatment, Advanced wastewater treatment

7.1 Introduction

The use of membrane processes for water treatment extends back several decades. However, the use of membrane filtration for treatment of SWWE has gained interest only in the recent past due to a shift towards a true urban water cycle to deal with the water and energy crisis. One of the benefits of membrane filtration of SWWE is the removal of organic contaminants (Diagne et al. 2012). The organic contaminants however induce microbial adhesion, gel layer formation, and solute adhesion that irreversibly block the pores of the membrane, reducing its permeability and overall performance (Sablani et al. 2001). The blockage of a membrane, which is also referred to as fouling, needs to be mitigated in order to effectively use membranes with re-cycled wastewaters. Pre-treatment of feed streams has shown promise in reducing membrane fouling. Pre-treatment is carried out to achieve two objectives: (1) to eliminate penetration of colloidal particles or organic matters into membrane pores and (2) to modify the membrane deposit characteristics of organic matter (Fritzmann et al. 2007, Redondo and Lomax 2001).

In recent years, numerous pre-treatments such as enhanced coagulation, activated carbon adsorption, MIEX, and ozonation have been investigated with the aim of reducing membrane fouling (Fabris et al. 2007, Jung et al. 2006, Li and Chen 2004). Coagulation reduces fouling on membranes due to its ability to remove higher molecular weight organic compounds (Carroll et al. 2000, Laine et al. 1989,). MIEX, on the other hand, is effective at removing both hydrophobic and hydrophilic organic fractions (Jarvis et al. 2008, Son et al. 2005). Granular activated carbon (GAC) can facilitate both physicochemical and biological removal of DOC (Shon et al. 2004, Shon et al. 2005). Pre-oxidation with ozone increases the biodegradable fraction of DOC facilitating its removal by BAC in the ozone/BAC combination (Kim et al. 1997). Although these pre-treatments facilitate some improvements to membrane performance (in terms of flux) as a result of DOC reduction, membrane fouling remains problematic (Carroll et al. 2000, Fabris et al. 2007, Schlichter et al. 2004, van der Hoek et al. 1999).

To develop effective pre-treatment strategies and membranes that resist fouling, several studies focused on characterizing the organic matter in feed waters (e.g. size (particulated, colloidal, and dissolved); volatility; polarity (hydrophobic, transphilic, hydrophilic); acid, base, neutral characteristics; and precipitation or flocculation upon acidification) (Cho et al. 1998, Gur Reznik et al. 2008, Howe et al. 2006). Compared to hydrophilic fractions, the hydrophobic fractions of organic matter were found to severely foul membranes (Nilson and DiGiano 1996, Yoon et al. 2005, Shon et al. 2006). However, in the absence the of hydrophobic compounds, hydrophilic compounds (e.g. polysaccharides, urea), colloids and other macromolecular organic compounds (non-humic) appear to act as foulants (Cho et al. 1998, Fan et al. 2001, Lee et al. 2001, Shon et al. 2004).

These observations suggest that organic fouling of membranes is complex and the knowledge around organic matter–membranes interaction in particular is limiting. While advances in fouling research are needed to better design membranes and develop effective strategies to pre-treat feed streams, continuing efforts to maximize the removal of organic matter using existing pre-treatment are important. The combined use of existing pre-treatments technologies has recently been examined and holds much promise for effective removal of organics from feed waters (Aryal et al. 2011, Aryal et al. 2012). The combined use of BAC and ferric coagulant offer both hydrophobic and hydrophilic organic carbon removal. The BAC/MIEX combination also effectively removes a range of DOC which MIEX or BAC alone fail to remove (Aryal and Sathasivan 2011). These studies demonstrate that combinations of BAC and physicochemical treatments (in the proper order) possess the ability to remove more or a wider range of organic fractions from feed waters.

While the combined effect of BAC and physicochemical treatment to remove a range of organic fractions from feed waters has been demonstrated, its impact on membrane performance is yet to be investigated. This study aims to investigate membrane performance when BAC and MIEX are used in combination to pre-treat feed waters.

7.2 Materials and Methods

7.2.1 The Membrane Filtration Process for SWWE Treatment

SWWE having a DOC concentration of 9.4 ± 1.725 mg/L was used in this study. Figure 7.1 illustrates the approach taken to study membrane performance with different pre-treatment methods. Four different pre-treatment methods either individually or in combination were studied to examine membrane fouling and the effectiveness of pre-treatment was measured in terms of membrane flux decline.

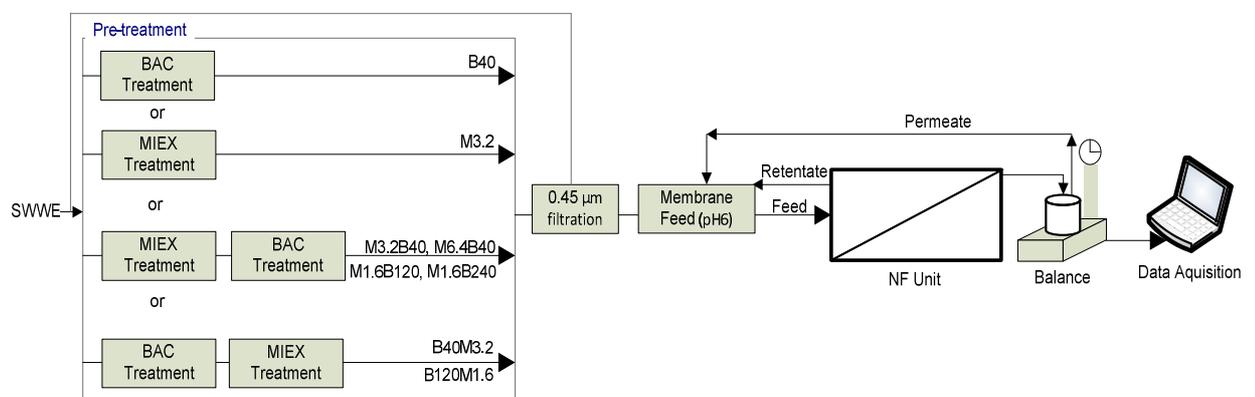


Figure 7.1: Monitoring membrane performance with different SWWE pre-treatment methods

Method -1: BAC Treatment

Details of the BAC reactor set up are presented in Chapter 3 (Section 3.3, Figure 3.2). The BAC filter column was operated as a continuous flow reactor using a variable speed peristaltic pump adjusted to achieve an empty bed contact time (EBCT) of 40 minutes (B40). When EBCTs of 120 min (B120) and 240 min (B240) were required, the BAC filter effluent was re-circulated three and six times over respectively through the same BAC filter. Additional information about the operation of the BAC filter column can be found elsewhere (Aryal et al. 2012).

Method -2: Ion Exchange Treatment

The regenerated ion exchange resin (MIEX, Orica Watercare, Australia) was composed of 150–180 μm size beads and was at an initial concentration of 90% v/v (based on settled resin volume). In this study, depending on the experiment a resin concentration of 1.6%, 3.2% and 6.4% v/v (M1.6, M3.2 and M6.4 respectively) was applied and mixing was carried out at 150 rpm with a detention time of 30 min to facilitate the exchange of DOC into the resin. Subsequently mixing was stopped and the resin was allowed to settle for 5 min prior to recovery of treated water.

Method -3: Ion Exchange/BAC Treatment Combination

This combination consisted of an initial ion exchange and a subsequent BAC treatment. In order to determine the minimum resin concentration required to achieve a maximum DOC removal, the resin dose was progressively increased until the residual DOC remained constant. Resin concentrations of 3.2% and 6.4% v/v were used to perform the ion exchange/BAC pre-treatment combination (M3.2B40, M6.4/B40). However, in the M6.4B40 combination, a higher dose of MIEX removed phosphate (0.2 mg/L) in addition to DOC (See Appendix 3). Thus, in order to ensure sufficient microbial activity in the BAC bed, M6.4 effluent was supplemented with phosphate (2 mg/L) followed by BAC treatment at an EBCT of 40 min. The combination was further investigated by progressively increasing EBCT in the BAC bed using two different MIEX/BAC combinations (M1.6B120 and M1.6B240) in order to understand the effect of BAC treatment on membrane fouling.

Method -4: BAC/Ion Exchange Combination Treatment

The combined treatment consisted of an initial BAC and a subsequent ion exchange treatment. Initially, BAC-treated water at an EBCT of 40 min was subjected to an ion exchange treatment (M3.2). Afterwards, the combined pre-treated membrane feed (B40M3.2) was compared against individual BAC (B40), ion exchange (M3.2) and M6.4/B40 combination (obtained from Methods 1, 2 and 3) in order to determine the

most effective order of the BAC and MIEX combination. This was also investigated with increased EBCT at the BAC bed followed by reduced MIEX concentration (B120M1.6)

7.2.3 Nanofiltration (NF)

To elucidate the effective DOC removal by the four pre-treatment methods, the pre-treated effluents were first individually subjected to 0.45 μm pore size filtration (GE Water and Process Technologies, Cat. No. A04SP04700, Acetate plus supported) to remove particulate matter. Subsequently, the filtered pre-treated effluents were subjected to NF. A NTR 729HF polyvinyl alcohol/polyamide NF membrane with a 700 Da molecular weight cut off (Nitto Denko Corp., Japan) was housed in a cross flow NF unit. For each of the pre-treatment methods investigated, a new membrane sheet with an effective membrane area of 0.008 m^2 was used. The NF membrane was first subjected to pre-compaction for 24 h at room temperature with RO-treated water (Ibis IS0006, Ibis Technology, Australia). The pre-compaction of the membrane was carried out with trans-membrane pressures (0.5 or 1 MPa) used for the fouling test. On completion of pre-compaction, fouling tests were carried out by switching the feed line from RO water to a feed tank containing 12 L of pre-treated SWWE. The feed water was adjusted to pH 6 (to achieve better flux (Aryal et al. 2010)) with the help of sodium hydroxide or sulphuric acid each at 1M concentration, and measured by using a portable pH meter (HACH 40d) and electrode (PHC101, Hach). Subsequently, the fouling experiments were carried out for up to 131 hours at 0.5 MPa and 1 MPa. The higher trans-membrane pressure was used in order to determine the maximum extent of fouling resulting from the BAC/MIEX or MIEX/BAC combinations beyond the range that was obtained at a trans-membrane pressure of 0.5 MPa. The permeate flux was evaluated in terms of normalized flux (J/J_0), where J is a permeate flux for SWWE or pre-treated water and J_0 is a permeate flux for RO water. The RO-treated water had a DOC and conductivity of <0.1 mg/L and $<1\mu\text{S/cm}$ respectively. The filtration for the fouling test was carried out in a recycle mode. The retentate was continuously returned. In order to maintain the same concentration in the feed stream, the permeate was recycled back to feed tank

periodically (prior to accumulation of less than 800 ml) by using a peristaltic pump. A similar approach has been taken by several studies to maintain concentrations in the feed stream (Shon et al. 2004, Haberkamp et al. 2008). The permeate was continuously measured and recorded using an electronic balance (Shimadzu, UW8200S) and a computer. During experiments no backwashing of the membrane was carried out.

7.2.4 Analytical Parameter Measurement

The DOC concentration was measured using a TOC Analyzer connected to an autosampler (TOC-LCSH/CSN Model, Shimadzu Co., Kyoto, Japan). Samples were first filtered through 0.45 μm pore size filter media (GE Water and Process Technologies, Cat. No. A04SP04700, Acetate plus supported) prior to DOC measurement. All the standards and blanks were first acidified using HCl to a pH of 2.2–2.5. Calibration of the TOC instrument was carried out by using potassium hydrogen phthalate standards (1–25 mg/L). The correlation coefficient (r^2) of the calibrations was > 0.99 at all times. According to the manufacturer, the instrument has a measurement range of 4 $\mu\text{g/L}$ to 30,000 mg/L. Similarly, the phosphorus measurement was carried out using an Aquakem 200 (Thermo Scientific, Finland), high precision wet chemistry analyzer. The instrument had a lower detection limit of 0.002 mg/L. The measurement error of this instrument was $\pm 1.5\%$ (95% confidence level).

7.2.5 Size Exclusion Chromatography

The DOC fractionation of the SWWE and pre-treated water was performed using size exclusion chromatography with continuous UV_{254nm} and organic carbon detection (LC-OCD system model 8, based on the Grantzel thin film reactor developed by DOC-Labor, Dr. Huber Karlsruhe/ Germany; SEC column: Toyopearl HW-50S weak cation exchange gel filtration column, Tosoh Bioscience, Tokyo/Japan). LC-OCD provides an account of the molecular weight (M_n) distribution and separates DOC into five different fractions namely: biopolymers,

humic substances, building blocks, LMW acids and LMW neutral. The fractionation was based on steric interactions over a wide range of molecular weights and quantification used inline detectors: organic carbon detector (OCD) and ultraviolet absorbance detector (UVD). 1000 μ L of the diluted samples were first eluted with phosphate buffer (28 mM, pH 6.6) at a flow rate of 1.1 mL/min. Before introducing them to the column the samples were filtered using a 0.45 μ m pore size filter (GE Water and Process Technologies, Cat. No. A04SP04700, Acetate plus supported) and a portion was bypassed to measure the DOC content by the non-purgeable organic detection method. The fractions from the column were first measured by UVD followed by OCD. The International Humic Substance Society (IHSS) Suwanee River reference material, humic acid (HA) and fulvic acids were used as reference samples. The chromatograms obtained were interpreted using the DOC-Labor ChromCALC software program.

7.2.6 ^1H PGSE Nuclear Magnetic Resonance (NMR) Analysis

The ^1H PGSE NMR diffusion experiments were performed on a Bruker Advance 500MHz spectrometer at 500 MHz using a TXI high-resolution probe equipped with a gradient coil. The analysis was carried out at 25° C using a modified PGSTE-WATERGATE method (Stokes 1856, Zheng et al. 2008a, Zheng et al. 2008b). Typical acquisition parameters adopted in this analysis included a spectral width of 10 kHz, free induction decay digitized into 9 k data points, $\pi/2$ pulse lengths 8.15 μ s, 32768 scans, 128 dummy scans, and recycle-delay of 1 s. Diffusion measurements were performed by linearly incrementing gradient strength (g_1) from 0.26 to 0.56 T/m, with $g_2=0.21$ T/m, a gradient length (δ) of 0.003 s and a diffusion time (Δ) of 0.03 s. The self-diffusion coefficient and Stokes radius of molecules or colloids was calculated by using the Stokes-Einstien-Sutherland equation (Einstien 1905, Sutherland 1905, Zheng and Price 2012). OriginPro 8.6 (OriginLab) was used for all diffusion data analysis. Further details of the modified PGSTE-WATERGATE method can be found elsewhere (Zheng and Price 2012).

7.2.7 Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) Studies

The ATR-FTIR technique was used to investigate functional groups and molecular structures on fouled and non-fouled membrane surfaces. Both new and used membranes were dried at room temperature. Subsequently, the membrane surface was pressed tightly against a crystal plate (ZnSe crystal). A Perkin-Elmer 100 FTIR apparatus equipped with a HeNe (helium compound with neon–1:1) laser as a radiation source, deuterated triglycine sulphate as a detector, and optical KBr as a beam splitter was employed. It was operated as an internal reflection element at a nominal angle of incidence of 45°. The ATR was used for recording the IR spectra of the sample. The measurements were carried out in the mid-infrared range from 4000 cm^{-1} to 650 cm^{-1} . The resolution was set to 4 cm^{-1} , and 16 scans were recorded to average each spectrum. This was further processed against FTIR and base line correction was carried out using the Spectrum software (6.3.4).

7.3 Results and Discussion

7.3.1 Source Water

The SWWE used in this study was from a municipal wastewater treatment plant (Beenyup, Western Australia). The plant uses a secondary treatment process, to biologically remove nitrogen and dissolved organic carbon from influent wastewater. Neither chemical nor biological methods were employed to remove phosphorus from influent waters. The SWWE characteristics of this plant are reported in Table 7.1.

Table 7.1: General characteristics of SWWE used in the investigation

Parameters	pH	mg/L								
		SS ^a	BOD ^b	COD ^c	NH ₃ ⁺ -N	NO ₂ ⁻ -N	NO ₃ ⁻ -N	TON ^d	DON ^e	PO ₄ ⁻³ -P
Average	7.1	10.15	4.5	33.13	2.13	0.17	12.92	2.59	1.52	8.63
	±	±	±	±	±	±	±	±	±	±
	0.16	4.74	2.38	5.04	1.70	0.04	1.42	0.67	0.25	0.99

^a Suspended solids; ^b Biological oxygen demand; ^c Chemical oxygen demand; ^d Total organic nitrogen; ^e Dissolved organic nitrogen

7.3.2 Effectiveness of the Pre-treatment on Nanofiltration

The effectiveness of the four pre-treatments was evaluated by monitoring fouling on a nanofiltration membrane. The normalized flux profiles obtained for the four pre-treatment methods are given in Figure 7.2a. By the end of nanofiltration, the normalized flux for SWWE remained at 43% showing fouling of the membrane. The normalized flux for the B40 and M3.2 pre-treated waters were 56% and 61% respectively. Despite a lower average normalized flux, BAC-treated water showed a steady normalized flux as opposed to MIEX-treated water (Figure 7.2a). As can be seen from Table 7.2, the difference in the average normalized flux between first and the last 20 hours of operation for the M3.2 treated water is much higher (16%) compared to B40 treated water (6%). It appears that BAC could achieve a better performance in a long run while MIEX is better for a short run only.

These results indicate the limitations that exist with BAC or MIEX treatment. With the BAC treatment resulting in a steady flux and, MIEX treatment facilitating a higher flux, a combined use of the two treatment methods was hypothesized to increase the flux whilst reducing the membrane fouling. The effectiveness of pre-

treatment was then investigated by employing B40M3.2 and M3.2B40 combinations keeping both EBCT in BAC bed and MIEX dose a constant. The M3.2B40 combination increased the normalized flux to 89% (Figure 7.2a). As shown in Table 7.2, the flux decline between first and the last 20 hours for both M3.2B40 and B40M3.2 treated water remained roughly 3%, highlighting the significance of pre-treatment combinations (BAC and MIEX) to enhance membrane performance (Table 7.2). However, out of the two combinations, MIEX/BAC appeared to be more effective in terms of average normalized flux (89%) than BAC/MIEX (normalized average flux 79%). To determine whether MIEX or BAC was contributing towards this difference, DOC removal was maximized by increasing MIEX dose in MIEX/BAC combination. This was primarily determined by systematically increasing the MIEX dose and a dose of 6.4% was determined to be sufficient to remove all MIEX-amenable DOC from SWWE. The M6.4B40 combination yielded an average normalized flux of 83% (Figure 7.2a), which is less than M3.2B40 pre-treatment combination. M6.4B40 combination resulted in a lower average normalized flux even when the residual DOC after the combined pre-treatment was 3% less. This observation shows the more influential role of BAC compared to the MIEX to maintain a better flux in a MIEX/BAC combination.

As the BAC treatment appeared to enhance membrane performance, the influence of BAC was further examined by lowering the MIEX concentration and by increasing the EBCT of the BAC treatment (B120M1.6 and M1.6B120 combinations). In order to further understand the extent of fouling beyond a trans-membrane pressure of 0.5 MPa, these investigations were carried out at a trans-membrane pressure of 1 MPa. As shown in Figure 7.2b, B120M1.6 pre-treated water resulted in a rapid flux decline for the first 40 h, and thereafter a stable normalized flux of 40% was achieved. With M1.6B120 pre-treated water on the other hand, the rate of flux decline was considerably less. Despite a higher residual DOC of 3.64 mg/L in M1.6B120 pre-treated water, the reduction in flux was considerably less compared to that with B120M1.6 pre-treated water (DOC of 3.14 mg/L). When comparing the last 20 h of operation (Table 7.2), the normalized flux achieved using M1.6B120 is 40% superior to that of what was achieved with B120M1.6 pre-treated

water indicating MIEX/BAC order as the better one compared to the BAC/MIEX order to reduce the membrane fouling.

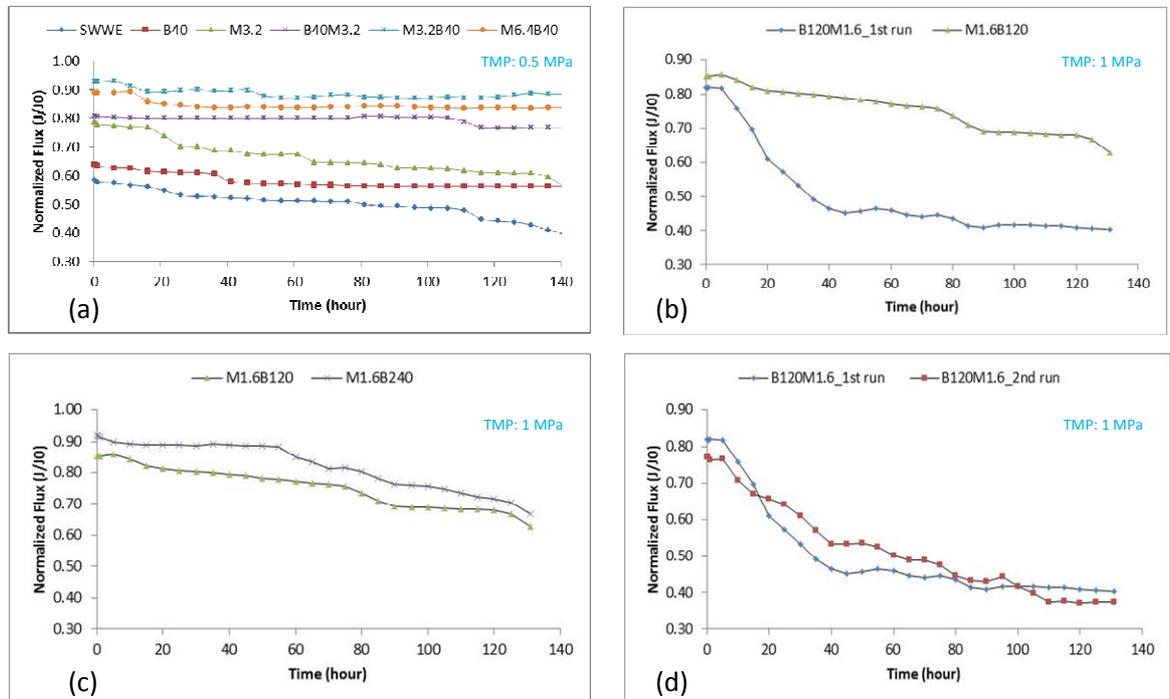


Figure 7.2: Normalized flux at trans-membrane pressure of (a) 0.5 MPa against various pre-treated sample; (b) 1 MPa for two different orders of BAC and MIEX pre-treatment in combination; (c) 1 MPa for two different MIEX/BAC pre-treatment combinations; (d) 1 MPa for same feed water (B120M1.6) but two consecutive tests with new sheet of membrane

7.3.3 EBCT on MIEX/BAC Combination and its Influence on Membrane Fouling

Once the MIEX/BAC order was determined to be the most effective pre-treatment combination, experiments were designed to investigate the effect of an extended EBCT on membrane fouling. As anticipated, the increase in EBCT from 120 min to 240 min in the MIEX/BAC combination also increased the normalized flux (Figure 7.3c). The average normalized flux for M1.6B120 treated water was around 75%. On doubling the EBCT this further increased to 82%. The 7% increase of average

normalized flux coincided with an additional 4% reduction of DOC. However, it is noteworthy to mention that B120M1.6 pre-treated water, even with a similar DOC concentration resulted in an average normalized flux which was 32% less to that observed with M1.6B240 pre-treated water. This suggests that DOC removal alone from source waters is not sufficient to manage fouling of membranes as expected.

MIEX/BAC pre-treated water has also allowed long-term maintenance of filtration efficiencies. Compared to the filtration efficiency of the first hour, the flux decline after 131 hours of operation with M1.6B120 and M1.6B240 pre-treated waters were 24% and 21% respectively. In contrast during a similar period of operation, the flux decline with B120M1.6 pre-treated water was approximately double (41%). Further, the average normalized flux (trans-membrane pressure 0.5 MPa) achieved using M3.2B40 pre-treated water is only marginally higher (7% higher) to that of average normalized flux (trans-membrane pressure 1 MPa) achieved using the M1.6B240 pre-treated water. This decline of flux could be a result of reversible fouling attributed to concentration polarization followed by gel or cake layer formation resulting from a higher trans-membrane pressure (Carroll et al. 2000, Zularisam et al. 2007). Further investigations are required to understand the exact nature of fouling at higher trans-membrane pressures.

7.3.4 Is Stabilization of Flux a Result of Foulant Exhaustion in Feed Water?

Declining of flux even with pre-treated waters is unavoidable particularly when membrane filtration is carried out over an extended period of time. The MIEX/BAC combined pre-treatments, specifically facilitated the maintenance of a stable flux over a relatively longer period of time (Figures 7.2a, 7.2b, 7.2c). The BAC/MIEX pre-treatment combination (B120M1.6), on the other hand, initially resulted in a rapid decrease of flux (i.e. approximately over the first 40 h) and subsequently achieved a stable flux of 40% for over 91 h. One could speculate that the observed flux stabilisation was a result of foulant exhaustion in feed water (due to recycle mode of operation returning permeate back to feeding tank). In order to explore whether the lack of foulants in feed water was the reason for the stable flux observed

the pre-treated water subjected to recycle mode of nanofiltration (for over 131 h) was re-exposed to a new nanofiltration membrane (for another 131 h). The new nanofiltration membrane showed a similar level of fouling during the first 40 h of operation (Figure 7.2d). This suggests that lack of foulants in source water is not the reason for the observed stable flux, after 40 h of membrane filtration.

Table 7.2: The impact of MIEX and BAC combined treatments on DOC removal and average normalized flux from a nanofiltration membrane

	Trans-membrane pressure (MPa)	DOC before treatment (mg/L)	DOC after pre-treatment (mg/L)	Percentage DOC removal	Average normalized flux percentage		
					During 131 h	During first 20 h	During last 20 h
M3.2B40	0.5	7.7	1.82	76	88.66 ± 0.02*	91.05 ± 0.02	87.64 ± 0.00
M6.4B40			1.61	79	84.63 ± 0.02	87.78 ± 0.02	83.52 ± 0.01
B40M3.2			1.28	83	79.61 ± 0.01	80.20 ± 0.00	76.86 ± 0.01
M3.2			2.17	72	67.38 ± 0.05	77.01 ± 0.01	61.00 ± 0.00
B40			5.48	29	58.31 ± 0.02	62.23 ± 0.01	56.25 ± 0.00
SWWE			-	-	50.88 ± 0.04	56.65 ± 0.01	44.85 ± 0.01
M1.6B240			1.0	11.86	3.2	73	82.16 ± 0.07
M1.6B120	3.64	69			75.46 ±	84.01 ±	66.91 ±

	Trans-membrane pressure (MPa)	DOC before treatment (mg/L)	DOC after pre-treatment (mg/L)	Percentage DOC removal	Average normalized flux percentage		
					During 131 h	During first 20 h	During last 20 h
					0.06	0.02	0.02
B120M1.6 2 nd run			2.42	80	51.48 ± 0.12	71.95 ± 0.04	37.59 ± 0.00
B120M1.6 1 st run			3.14	74	49.64 ± 0.13*	75.60 ± 0.07	40.40 ± 0.01

*standard deviation

7.3.5 Pre-treatment Methods and its Influence on DOC Fractions

In order to understand the effect of pre-treatment, LC-OCD analysis was performed to characterize the DOC composition in specific samples (Figure 7.3). B40 and M3.2 pre-treatments facilitated 64% and 66% removal of the hydrophobic fractions respectively. The removal efficiencies increased up to 79% and 81% when B40M3.2 and M6.4B40 pre-treatment combinations were used respectively. Compared to the M6.4B40, B40M3.2 was superior at removing biopolymers (100%), humic substances (99%) and building blocks (84%) of the hydrophilic fractions (Table 7.3). However, M6.4B40 outperformed B40M3.2 by facilitating an average normalized flux that was 7% higher. When removal of different DOC fractions were examined across the pre-treatment methods tested (Table 7.3), the improvement on the flux with M6.4B40 appear to be a result of the efficient removal of hydrophobic and LMW neutral fractions from SWWE.

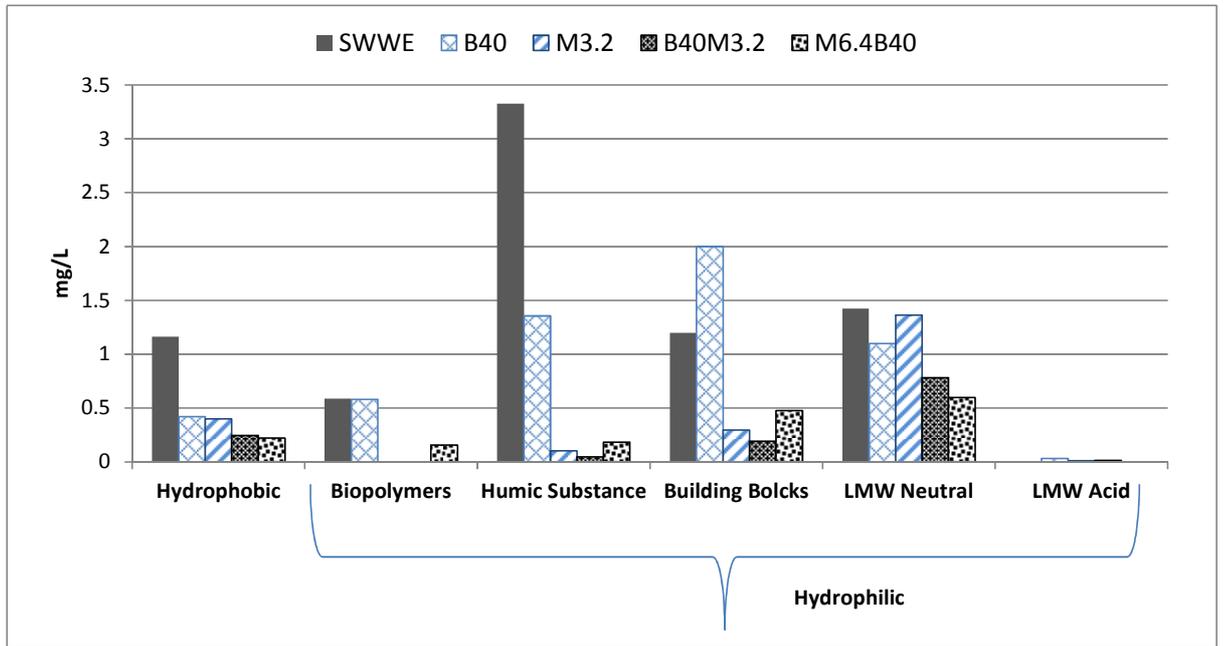


Figure 7.3: DOC fractionation of the samples (with source DOC 7.7 mg/L) after various pre-treatment used for membrane filtration at trans-membrane pressure of 0.5 MPa

Table 7.3: Percent removal / production of DOC fractions on pre-treatment of SWWE

	Overall DOC removal	Hydrophobic	Hydrophilic				Average normalized flux
			Biopolymers	Humic substance	Building blocks	LMW neutral	
M6.4B40	79%	81%	74%	95%	60%	58%	84%
B40M3.2	83%	79%	100%	99%	84%	45%	77%
B40	29%	64%	1%	59%	-67%	23%	56%
M3.2	72%	66%	100%	97%	75%	4%	61%

The overall removal of DOC fractions of B40 and M3.2 pre-treatments were similar to that of M6.4B40 and B40M3.2 pre-treatments respectively (Table 7.3). However, the average normalized flux (61%) was better with M3.2 treated water. Although the

average normalized flux was higher, there was a rapid decline in flux during the first and last 20 h of operation (i.e. from 77% to 61%) with M3.2 treated water. As oppose to a 16% drop only a 6% drop in normalized flux was observed for the same period with B40 treated water. When examining the hydrophilic compounds of M3.2 and B40 treated waters, the LMW neutral fraction appears largely removed in B40 treated water. Hence stable normalized flux observed in both B40 and M6.4B40 (Figure 7.2a) could be a result of the removal of LMW neutral fractions from SWWE. Previous studies also have shown the importance of removing the hydrophilic fractions to minimize membrane fouling (Lee et al. 2001, Fan et al. 2001). Accordingly, pre-treatment strategies appear best to target the removal of LMW neutral fractions as oppose to simply facilitating overall DOC removal in SWWE. The higher stable normalized flux observed with M6.4B40 even when the overall DOC removal was lesser compared to B40M3.2 treated water (Table 7.3) suggests the importance of targeted removal of specific DOC fractions from SWWE to minimize irreversible fouling of membranes. While this study has demonstrated the importance of removing the LMW neutral fractions to minimize membrane fouling, further research is required to confirm this observation.

7.3.6 Pre-treatment Methods and its Influence on Stokes Radius and Number Average Molecular Weight

The average Stokes radius of DOM was calculated to further understand the influence of pre-treatment methods on membrane performance. As shown in Table 7.4, microbial activity of BAC (B120 and B40) increased the average Stokes radius of DOM. However, B40M3.2 combination reduced the Stokes radius, below to that of SWWE. A similar phenomenon was observed in terms of number averaged molecular weight (M_n) during LC-OCD analysis. Considering that BAC is able to induce a change on DOM (i.e., increased the Stokes radius) and MIEX (anion exchange resin) is subsequently able to remove it. This suggests that DOM (of higher stokes radii) after BAC treatment is likely to be negatively charged. Effective removal of the negatively charged DOM (of higher stokes radii) by MIEX results in pre-treated water that has DOM of smaller stokes radii. An opposite combination

(M3.2B40) on the other hand will facilitate the maintenance of BAC transformed DOM (of higher Stokes radii) in pre-treated water.

The increase of number average molecular weight when subjected to the BAC treatment is consistent with the observations made by DOC fractionation. According to the LC-OCD measurements, MIEX was more effective towards the removal of higher molecular weight compounds and in contrast removal of the LMW neutrals was only feasible using BAC. Hence, MIEX treatment results in pre-treated water with DOM of lower number average molecular weight and BAC treated water results in pre-treated water that has DOM of higher number average molecular weight. The increase of Stokes radii and number average molecular weight after BAC treatment appear to reduce fouling of membrane possibly by minimising internal pore constrictions of membrane. When comparing B120M1.6 and M1.6B120 pre-treated waters, the 27% improvement observed in average normalized flux with the latter suggests the importance of managing Stokes radii and number average molecular weight of solutes to minimise fouling of membranes. However, further research is required to better understand how an increase of Stokes radii and number average molecular weight of source waters could reduce membrane fouling.

Table 7.4: Changes in Stokes radius (m) and number average molecular weight (Mn)

Sample	Average diffusion coefficient (m ² /s)	Average Stokes radius (m)	Number Average MW (g/mol)
SWWE	$5.4 \pm 0.3 \times 10^{-10}$	$4.6 \pm 0.2 \times 10^{-10}$	486
B40	$5.0 \pm 0.3 \times 10^{-10}$	$4.9 \pm 0.3 \times 10^{-10}$	605
B120	$3.8 \pm 0.2 \times 10^{-10}$	$6.5 \pm 0.3 \times 10^{-10}$	652
B40M3.2	$9.3 \pm 0.7 \times 10^{-10}$	$2.6 \pm 0.2 \times 10^{-10}$	254

7.3.7 Spectroscopic Analysis (ATR-FTIR)

Both new and used membrane surfaces were analysed for the functional groups employing ATR-FTIR spectroscopy (Figure 7.4). The main functional groups identified on a clean membrane were at 2967 cm^{-1} suggesting a coating layer of aliphatic hydrocarbon. Similarly, the peaks near 1584 , 1503 and 1488 cm^{-1} corresponds to aromatic compounds and weak peaks in the range of 1385 – 1365 were due to C-H symmetric deformation vibrations of $\text{C}(\text{CH}_3)_2$. The peaks between 1350 – 1280 cm^{-1} and 1180 – 1145 cm^{-1} respectively belong to the asymmetric and symmetric SO_2 stretching vibrations. Similarly, other functional groups present on new membranes included alcohols ($\text{R-CH}_2\text{-OH}$) and ethers (C-O-C) (corresponding to 1075 – 1000 cm^{-1} and 950 – 815 cm^{-1} respectively). These observations coincide with similar observations made by others (Tang et al. 2009).

A similar analysis to that on a clean membrane was carried out on membranes subjected to filtration with different pre-treated waters. As presented in Figure 7.4 few additional peaks compared to a clean membrane can be observed on these used membranes.

One of the major peaks was observed at 3287 cm^{-1} and corresponds to simple hydroxy compounds. Some broader peaks were also observed between 1200 – 1000 cm^{-1} . Additional, peaks at 1635 cm^{-1} represents functional groups that could possibly constitute polysaccharides or amino sugars-like compounds (Jarusutthirak et al. 2002). The peaks between 1040 and 1240 cm^{-1} show the presence of C-O bonds of ethers, carboxylic acids and polysaccharides (Cho et al. 1998, Zularisam et al. 2006). This indicates that residual humic fractions and polysaccharides-like substances are retained on all membranes regardless of the various pre-treatments used. A quantitative reduction of these fractions can be assumed to be important to reduce the membrane fouling. However, when FTIR spectra of different pre-treatments were compared against average normalized flux achieved, no correlation was observed between average normalized flux and peak area of FTIR. For instance based on FTIR even though B40M3.2 can be anticipated to result in a higher flux, a higher flux was

only observed with M3.2B40 pre-treated waters. Furthermore FTIR peaks observed with SWWE was consistently found even when M3.2B40 pre-treated water was used. Hence the analysis of membrane surface with FTIR alone may not facilitate a clear understanding about the manner in which different pre-treatments affected membrane fouling.

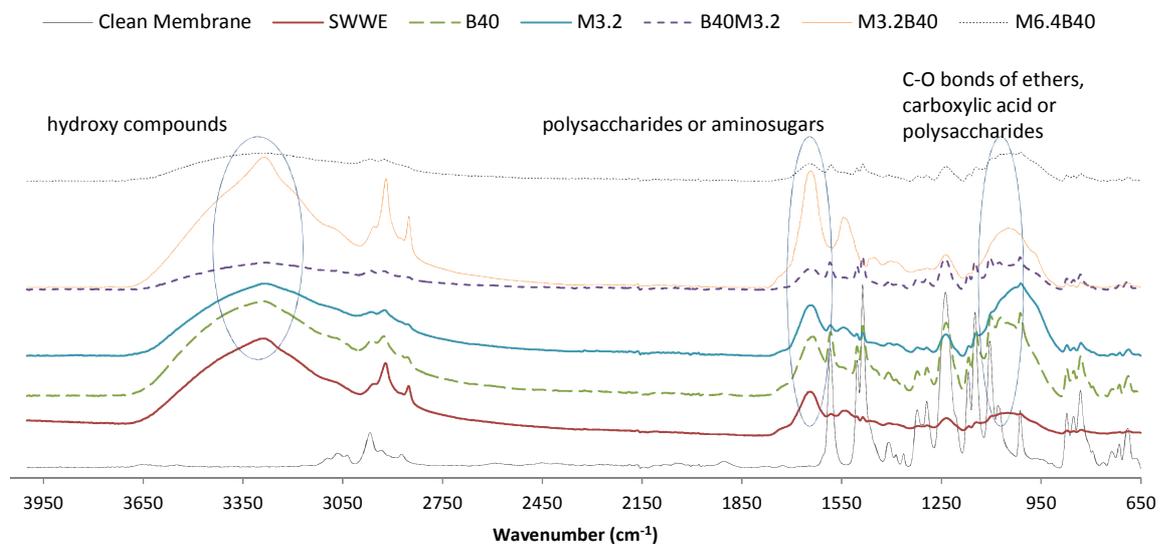


Figure 7.4: FTIR spectra of a clean membrane and of used membranes subjected filtration with different pre-treated waters at a trans-membrane pressure of 0.5 MPa

7.4 Conclusions

The investigation was undertaken in order to evaluate the individual and combined effect of BAC and MIEX to reduce membrane fouling and to understand the fouling mechanism. The experimental results suggest that combined use of BAC and MIEX is able to reduce membrane fouling provided the pre-treatment is carried out in its proper order. Although, long-term stability was achieved in the BAC/MIEX combination, it was less effective for reducing immediate fouling. However, the MIEX/BAC combination overcame this limitation and appeared far better than the

BAC/MIEX combination despite the higher residual DOC present in it. This could be attributed to the following reasons:

1. The MIEX/BAC combination is more effective in reducing the LMW neutral fraction (<350 Da) that is possibly contributing to membrane fouling
2. BAC plays an important role in increasing the average Stokes radius of DOM, reducing the probability of internal pore constriction and hence improving the membrane performance.

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Chapter 8

Combined BAC and Physicochemical Pre-treatment of Secondary Wastewater Effluent to Reduce Fouling of Ultrafiltration Membranes

Abstract

Biological activated carbon (BAC) as a pre-treatment has long been used to reduce dissolved organic matter (DOM) and corresponding membrane fouling reduction in secondary wastewater effluent (SWWE). However, the ability of BAC to convert or reduce lower molecular weight (LMW) into higher molecular weight (HMW) organic fractions and its implication against ultrafiltration (UF) is yet to be largely understood. This specific ability of BAC treatment was employed to understand membrane fouling in combination with physicochemical treatment (magnetic ion exchange resin (MIEX) or enhanced coagulation) using two different orders. The biological/physicochemical and physicochemical/biological orders were employed respectively to reduce and increase the average DOM size (Stokes radius or number average molecular weight) in feed water. Of the two combinations, physicochemical/biological order effectively reduced UF fouling and further improved with extended biological treatment despite the higher residual DOC possibly due to reduction in pore constriction facilitated by increased DOM size. Further investigation with successively reduced DOM size using molecular weight cut off (MWCO) by 17500 Da and 700 Da in SWWE or BAC treated water showed smaller DOM size more critical towards UF fouling and BAC's plays an instrumental role to reduce or convert smaller DOM to bring about better UF filtration performance.

Keywords: Biological activated carbon, Ultrafiltration, Membrane fouling

8.1 Introduction

UF membranes are increasingly used in wastewater recycling either to improve the quality of tertiary treated wastewater or as a pre-treatment step prior to reverse osmosis. These membranes are able to remove a wide range of organic matter. However, organic matter itself is largely responsible for UF membrane fouling (Jarusutthirak et al. 2002). Organic matter in SWWE is complex and is composed of refractory natural organic matter (NOM) (humic and fulvic acids, proteins and carbohydrates of various sizes etc.), synthetic organic compounds and soluble microbial products (Drewes and Fox 1999, Her et al. 2003). This organic matter in SWWE demands frequent backwashing of UF membranes reducing system productivity and increasing energy usage and operational costs (e.g. frequent replacement of membrane) (Clech et al. 2006). Frequent backwashing allows higher flux, but this is counter balanced with a loss of system productivity, highlighting the need to develop strategies to minimize organic fouling of UF membranes (Fritzmann et al. 2007).

Previous studies have investigated effluent organic matter (EfOM)-membrane interactions with the aim of understanding s fouling. Considerable effort has gone towards characterizing the organic matter in SWWE to understand the influence of each of the fractions towards membrane fouling. According to Filloux et al. (2012) humic substances, protein and polysaccharides-like substances in SWWE largely contributes towards membrane fouling. Having a similar view, Jarusutthirak et al. (2002) examined fouling of membranes using synthetic derivatives of humic substances, protein and polysaccharides and made similar observations. Characterizing the organic matter in SWWE as hydrophobic and hydrophilic, other researchers were able to demonstrate that hydrophobic fractions contribute towards fouling than hydrophilic fractions (Nilson and DiGiano 1996, Shon et al. 2006, Yoon et al. 2005). However, the hydrophilic fractions also contribute towards membrane fouling (Cho et al. 1998, Fan et al. 2001, Lee et al. 2001).

Examining the impact of individual organic matter fractions enables the advancement of fundamental knowledge, but when fouling of a membrane estimated in terms of a sum of fouling brought about by each independent fractions is compared with membrane fouling observed with a cocktail of DOM, the latter was found to result in severe fouling conditions (Bonnélye et al. 2008, Gao et al. 2011, Law et al. 2010). Accordingly, DOM fractionation alone may not explain fundamentals behind membrane fouling. Thus, studying the combined influence is perhaps more relevant in developing effective pre-treatment strategies for understanding and to minimizing membrane fouling.

Reducing DOM in source waters has often been the focus to reduce membrane fouling and the impact of each of the pre-treatment methods (physical, chemical and biological) appear different. Enhanced coagulation (EC) is a cost effective physicochemical pre-treatment process used to reduce contaminants prior to UF (Bérubé et al. 2002, Gao et al. 2011). Powdered or granular activated carbon (PAC or GAC)-like adsorbents, which have a relatively large specific surface area, have also proven effective in removing certain fractions that foul UF membranes (Lorain et al. 2007, Tsujimoto et al. 1998). Pre-treatment with oxidants (e.g. ozone, permanganate and chlorine) on the other hand, suppresses microbial growth and changes the structure, concentrations and properties of organic matter reducing both organic and biological fouling of membranes (Gao et al. 2011, Kim et al. 1997). MIEX on the other hand facilitates the removal of negatively charged DOM through ion exchange, and has shown to reduce hydraulically irreversible membrane fouling fractions from source waters (Boyer and Singer 2006, Dixon et al. 2010). Unlike physicochemical pre-treatment methods, BAC treatment appear to specifically reduce LMW organic fractions responsible for fouling and also bring about change to organic matter in source by increasing the average Stokes radius (m) of DOM.

The combined influence of MIEX and the BAC to successfully reduce fouling of membranes has been demonstrated, but the exact manner by which fouling is minimized, still remains unclear. The objectives of this study are in three fold: (1) To examine whether the influence of pre-treatments are universal across membranes (i.e.

across a nano and an ultrafiltration membrane). (2) To examine whether different physicochemical pre-treatments brings about distinctive combined influences with BAC on an ultrafiltration membrane. (3) To systematically validate the influence of LMW organic fractions on membrane fouling.

8.2 Materials and Methods

8.2.1 The Membrane Filtration Process for SWWE Treatment

SWWE with a DOC concentration of 8.14 mg/L or 11.86 mg/L was used in this study. Figure 8.1 illustrates the approach taken to studying membrane performance with different pre-treatment methods. The membrane fouling was investigated by employing four different pre-treatment approaches (individual or in combination). The fouling was also examined using source waters subjected to the specific MWCO. The effectiveness of pre-treatment was measured in terms of membrane flux decline following procedures detailed in past literature (Fonseca et al. 2007, Haberkamp et al. 2008).

Method -1: BAC: Biological Treatment

Details of the BAC reactor setup are presented in chapter 3 (Section 3.2.1, Figure 3.2). The BAC filter column was operated in a continuous mode using a variable speed peristaltic pump with the speed of the pump being adjusted to achieve an empty bed contact time (EBCT) of 120 min (B120). When EBCTs of 240 min (B240) or 360 min (B360) were required, the BAC filter effluent was re-circulated twice or three times through the same BAC filter. Additional information about the operation of the BAC filter column can be found in Chapter 6, Section6.2.

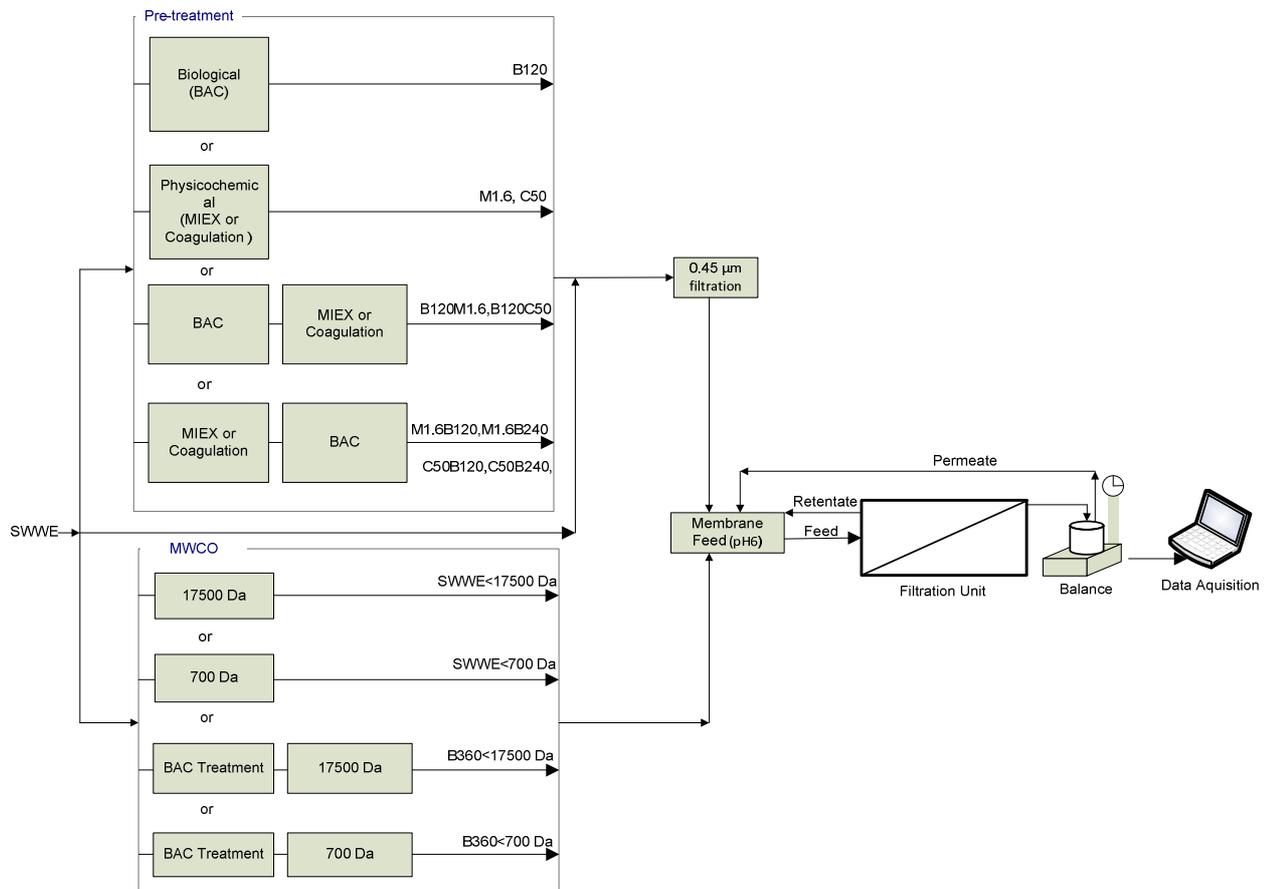


Figure 8.1: Monitoring membrane performance with different SWWE pre-treatment and MWCO methods

Method -2: Ion Exchange or Enhanced Coagulation: Physicochemical Treatment

The regenerated ion exchange resin (MIEX, Orica Watercare, Australia) was composed of 150–180 µm size beads and was at an initial concentration of 90% v/v (based on settled resin volume). In this study an optimized resin concentration of 1.6% v/v (M1.6) was applied (Appendix 3) and mixing was carried out at 150 rpm providing a detention time of 30 min to facilitate the exchange of DOC into the resin. Subsequently mixing was stopped and the resin was allowed to settle for 5 min prior to recovery of treated water.

EC was carried out using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and an optimized ferric ion (Fe^{3+}) concentration of 50 mg/L (C50) was applied (Appendix 4). EC was carried out at pH 5 and was controlled using a pH meter (HACH 40d), electrode (PHC101, Hach) and acid (1 M sulphuric acid) and base (1 M sodium hydroxide) solutions. The jar test protocol included rapid mixing (200 rpm) for 2 min, slow mixing (20 rpm) for 20 min and no mixing (settling) for 30 min.

Method -3: Ion Exchange or EC/BAC Combination: Physicochemical/Biological Treatment Combination

This combination consisted of an initial physicochemical treatment and a subsequent BAC treatment (EBCT of 120 min). A resin concentration of 1.6% v/v or a coagulant dose of 50 mg/L was used to perform the ion exchange/BAC and the EC/BAC treatment combinations (M1.6/B120 and C50/B120) respectively. In order to understand the impact of extended biological treatment, physicochemically treated effluents were biologically treated (EBCT of 240 min) for an additional period of time (M1.6B240 and C50B240). EC with FeCl_3 removes phosphate (Zhou et al. 2008) in addition to DOM and the impact of lower phosphorus concentrations on BAC and on membrane performance was investigated by examining the EC/BAC combination supplemented with phosphate (C50_PO₄B120). A phosphate concentration of 2.5 mg/L was applied prior to BAC treatment.

Method -4: BAC/ Ion Exchange or EC Combination Treatment: Biological/Physicochemical Treatment Combination

The combined treatment consisted of an initial BAC and a subsequent ion exchange treatment or coagulation. 120 min EBCT BAC treatment (B120) was individually subjected to ion exchange (M1.6) or coagulation (C50) in order to prepare B120M1.6 or B120C50 combinations respectively.

Method -5: Molecular Weight Cut Off

MWCO filtration of the feed water was performed by using UF (NTR 7410) and NF (NTR 729 HF) membranes (Nitto Denko Corp., Japan) having MWCO of 17500 Da and 700 Da respectively. SWWE and B360 pre-treated water were independently subjected to a MWCO of 17500 Da and 700 Da. In order to ensure the maximum effect of BAC treatment, 320 min EBCT was used for the experiment (see Appendix 5). Specifically 24 L of SWWE or B360 water was used to produce 12 L of the MWCO filtration waters (i.e. SWWE<17500 Da, SWWE<700 Da, B360<17500 Da and B360<700 Da).

8.2.3 Ultrafiltration

To elucidate the effectiveness of pre-treatment methods, the pre-treated effluents except the MWCO fractionated sample were first individually subjected to 0.45 μm pore size filtration (GE Water and Process Technologies, Cat. No. A04SP04700, Acetate plus supported) to remove particulate matters. Subsequently, the filtered pre-treated effluent samples were subjected to UF. A NTR 7410 UF membrane (Sulfonated polysulfones) with a 17500 Da MWCO (Nitto Denko Corp., Japan) was housed in a cross flow UF unit. For each of the pre-treatment methods investigated, a new membrane sheet having an effective membrane area of 0.008 m^2 was used. The UF membrane was first subjected to pre-compaction until reaching a steady-state (less than 5% of flux variation) RO water flux (Ibis IS0006, Ibis Technology, Australia) (for 6 h) at room temperature. The pre-compaction of the membrane was carried out with a trans-membrane pressure (0.3 MPa) used for fouling tests. On completion of pre-compaction, fouling tests were carried out by switching the feed line from RO water to a feed tank that contained 12 L of pre-treated SWWE. The feed water pH was adjusted to a value of 6 using a portable pH meter (HACH 40d) and electrode (PHC101, Hach). Subsequently, the fouling experiments were carried out for 24 h at a trans-membrane pressure of 0.3 MPa. The permeate flux was evaluated in terms of normalized flux (J/J_0), where, J is the permeate flux for SWWE or pre-treated water and J_0 is the permeate flux for RO water. The RO-treated water

had a DOC and conductivity of <0.1 mg/L and <1 μ S/cm respectively. The filtration for fouling test was carried out in a recycle mode. The retentate was returned continuously. In order to maintain similar concentrations in a feed stream, the permeate was recycled back to the feed tank periodically (prior to accumulation of 800 ml). A similar experimental approach has also been taken by previous studies to successfully maintain concentrations in feed streams and examine membrane fouling (Fonseca et al. 2007, Haberkamp et al. 2008, Shon et al. 2004). The permeate flux was continuously measured and recorded using an electronic balance (Shimadzu, UW8200S) and a computer. During the experiments no backwashing of the membrane was carried out.

8.2.4 Analytical Parameter Measurement

All the samples (except MWCO fractionated samples) were filtered through 0.45 μ m pore size filter media (GE Water and Process Technologies, Cat. No. A04SP04700, Acetate plus supported) prior to DOC and UV absorbance (UV_{254}) measurements. The DOC concentration was measured using a TOC Analyzer connected to an auto sampler (TOC-L_{CSH/CSN} Model, Shimadzu Co., Kyoto, Japan). All the standards and blanks were first acidified using HCl to a pH of 2.2–2.5. Calibration of the TOC instrument was carried out by using potassium hydrogen phthalate standards (1–25 mg/L). The correlation coefficient (r^2) of the calibrations was > 0.99 at all times. According to the manufacturer, the instrument has a measurement range of 4 μ g/L to 30,000 mg/L.

UV absorbance (UV_{254}) of DOM was carried out using a Helios Gamma Spectrophotometer (Thermoelectron). According to the manufacturer, the instrumental error is 0.05%. The analysis of phosphorus in collected samples was carried out using an Aquakem 200 (Thermo Scientific, Finland), high precision wet chemistry analyzer. The instrument had a lower detection limit of 0.002 mg/L. The measurement error of this instrument was $\pm 1.5\%$ (95% confidence level).

8.2.5 Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) Studies

The ATR-FTIR technique was used to investigate functional groups and molecular structures on a fouled and non-fouled membrane surface. Both new and used membranes were dried at room temperature. Subsequently, the membrane surface was pressed tightly against a crystal plate (ZnSe crystal). A Perkin-Elmer 100 FTIR apparatus equipped with a HeNe (helium compound with neon–1:1) laser as a radiation source, deuterated triglycine sulphate as a detector, and optical KBr as a beam splitter was employed. It was operated as an internal reflection element at a nominal angle of incidence of 45°. The ATR was used to record IR spectra of samples. The measurements were carried out in the mid-infrared range from 4000 cm^{-1} to 650 cm^{-1} . The resolution was set to 4 cm^{-1} , and 16 scans were recorded to average each spectrum. This was further processed against FTIR and base line correction was carried out using the Spectrum software (6.3.4).

8.3 Results and Discussion

8.3.1 Source Water

The SWWE that was subjected to pre-treatment was collected from Beenyup Wastewater Treatment plant (Western Australia). The wastewater treatment plant was engineered to biologically remove nitrogen and dissolved organic carbon from influent wastewater. Neither chemical nor biological methods were employed to remove phosphorus from influent waters. The SWWE characteristics of this plant are reported in Table 8.1.

Table 8.1: General characteristics of SWWE used in the investigation

Parameters	pH	mg/L							
		SS ^a	BOD ₅ ^b	COD ^c	NH ₄ ⁺ -N	NO ₂ ⁻ -N	NO ₃ ⁻ -N	DON ^d	PO ₄ ⁻³ -P
Average	7.32	13.70	4.50	33.13	0.028	0.001	13.47	1.52	8.63
	±	±	±	±	±	±	±	±	±
	0.2	0.68	2.38	5.04	0.05	0.00	0.016	0.033	0.242

^a Suspended solids; ^b Biological oxygen demand; ^c Chemical oxygen demand; ^d Dissolved organic nitrogen

8.3.2 The Influence on Flux with BAC and/or MIEX Pre-treatment

The impact of physicochemical and biological pre-treatment strategies was first evaluated individually and subsequently in combination to monitor fouling of UF membranes. The normalized flux obtained during the experiments is presented in Figure 8.2. By the end of filtration, the normalized flux for SWWE was at 33% showing rapid membrane fouling. With M1.6 pre-treated water, normalized flux remained similar to SWWE with a minor improvement during the first hour of operation (Figure 8.2a; Table 8.2). The normalized flux against B120 and B120M1.6 pre-treated water was at 42% and 41% respectively. Despite achieving a significant removal of DOC, the B120M1.6 pre-treated water (Table 8.2) fouled the UF membrane more than B120 pre-treated waters. According to past literature, the BAC/MIEX pre-treatment combination is able to facilitate the removal of HMW organic carbon (Aryal and Sathasivan 2011, Aryal et al. 2012). The remaining LMW organic matter then can be hypothesized to enter the pores of the UF membrane and clog its passage resulting in a significant decrease of membrane flux. The reverse order, i.e. M1.6/B120 combination resulted in an increase in normalized flux (53%). When the EBCT was increased from 120 min (M1.6B120) to 240 min (M1.6B240) the normalized flux further increased up to 69%. This observation could be a result of BACs' ability to remove or transform LMW organic matter over to HMW

compounds preventing its entry into UF membranes, reducing pore constriction or blockage.

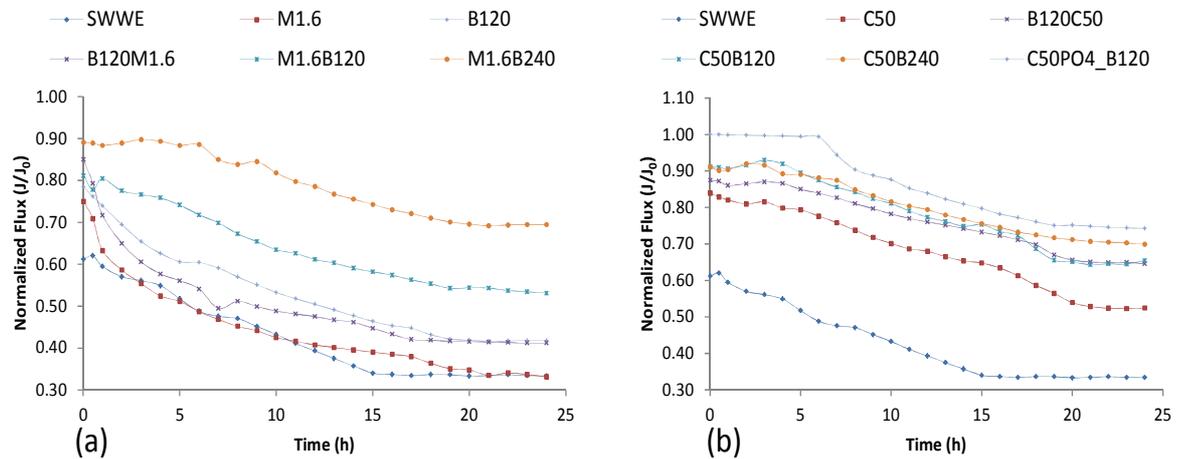


Figure 8.2: Pre-treatment of SWWE and its influence on normalized flux (a) BAC and/or MIEX pre-treatment (b) BAC and/or EC pre-treatment

8.3.3 The Influence on Flux with BAC and/or EC Pre-treatment

The impact of BAC on UF membrane performance was also examined in combination with EC using normalized flux (Figure 8.2b). EC (C50) resulted in a flux of 52% after 24 h of filtration. When BAC was combined with EC (B120/C50) the average normalized flux further increased to 65%. The reverse combination (C50/B120), although expected to further improve the normalized flux only showed a slight improvement during the first few hours of filtration and the overall performance was similar to the B120/C50 combination. This is in contrast to the MIEX/BAC combination, which outperformed the BAC/MIEX combination by almost 12%. An increase in EBCT to 240 min in the C50/B240 combination failed to show any improvement to the average normalized flux, suggesting poor microbial activity in the BAC bed. When SWWE subjected to EC was examined, it was noted that PO₄³⁻-P concentration in the pre-treated water was very low (0.02 mg/L). Phosphorus is a major essential element for microbial growth and the failure of the BAC bed is likely to be due to the non-availability of phosphorus for microbial

growth. Once phosphorus was supplemented (2.5 mg/L) upon EC (C50), the C50_PO₄/B120 combination was able to achieve average normalized flux of 74% and outperformed the B120/C50 combination as anticipated.

8.3.4 The Residual Organic Matter Concentrations in Pre-treated Waters and its Influence on Flux

The effect of BAC or MIEX either individual or in combination was investigated in terms of DOC and reduction in UV absorbance. The percentage reduction in UV absorbance was higher than corresponding DOC removal but both showed a similar removal trend (Table 8.2). The overall DOC removal with pre-treatment combinations were in the order of B120/M1.6 > M1.6/B120 > M1.6/B240 > M1.6 > B120 (Table 8.2) while an increase of average normalized flux against the UF membrane on the other hand were in the order of M1.6/B240 > M1.6/B120 > B120 > B120/M1.6 > M1.6. MIEX pre-treatment (M1.6) reduced DOC by 63% and an average normalized flux of 45% was achieved. BAC/MIEX combination (B120/M1.6) on the other hand reduced the DOC further down to 87%, but only a marginal improvement to average normalized flux (51%) was observed. Once the same BAC/MIEX combination was used in reverse order (M1.6/B120), an average normalized flux of 64% was achieved. However, the DOC removal achieved was marginally less (85%) compared to BAC/MIEX combination. Doubling the EBCT (M1.6/B240) resulted in no additional DOC removal but significantly increased the average normalized flux (79%).

Similar observations were made when combinations of BAC and EC were used to pre-treat SWWE. EC alone (C50) reduced the DOC by 61% and an average normalized flux of 68% was achieved. When B120/C50 combination was used, a reduction in DOC down to 89% was achieved and the average normalized flux increased up to 77%. A marginal increase (79%) was observed with a reverse combination (C50/B120) and approximately the same amount of DOC was removed (84%). Doubling the EBCT further (C50/B240), did neither remove additional DOC nor improve flux. Supplementing phosphorous deficiencies of pre-coagulated water

enhanced BAC pre-treatment (C50_PO₄B120) and an average normalized flux of 87% was achieved compared to lower 79% with C50/B120. The results demonstrate that the increased average normalized flux is not entirely a result of an overall reduction of DOC.

Table 8.2. DOC removal, reduction of UV254 absorbance and flux recovery with pretreated waters

Pre-treatment	DOC and UV ₂₅₄ in SWWE	DOC after pre-treatment (mg/L)	UV ₂₅₄ After pre-treatment (cm ⁻¹)	Average normalized flux (%)		
				24 h	0-6 h	18-24 h
B120M1.6	8.14 mg/L and 0.19 cm ⁻¹	1.06 (87%) [†]	0.0138 (93%)	51.44±0.12	66.17±0.11	41.37±0.00
M1.6B240		1.22 (85%)	0.0188 (90%)	79.40±0.08	88.91±0.00	69.52±0.00
M1.6B120		1.23 (85%)	0.0186 (90%)	64.40±0.09	76.89±0.03	53.87±0.01
M1.6		3.05 (63%)	0.0417 (78%)	45.08±0.11	59.42±0.10	34.03±0.01
B120		5.41 (33%)	0.1004 (47%)	53.89±0.11	68.39±0.07	41.81±0.00
B120C50		0.9 (89%)	0.0190 (90%)	76.61±0.10	86.19±0.01	65.34±0.01
C50_PO ₄ B120		1.19 (85%)	0.0211 (89%)	86.57±0.10	99.73±0.00	74.71±0.00
C50B240		1.31 (84%)	0.0209 (89%)	80.50±0.08	90.17±0.01	70.71±0.01
C50B120		1.36 (83%)	0.0191 (90%)	78.68±0.10	90.76±0.02	64.89±0.01
C50		3.15 (61%)	0.0706 (63%)	68.33±0.11	81.02±0.02	53.39±0.02

[†] Standard deviations

8.3.5 The Importance to Target LMW Fractions during Pre-treatment of SWWE

With above pre-treatment strategies suggesting the importance to remove or convert LMW compounds in source waters over to HMW compounds to reduce pore constriction of the UF membranes, specific MWCO filters were used to further consolidate this hypothesis. Two MWCO filters were used to generate pretreated

waters with DOC of molecular weight of 17500 Da and below or 700 Da and below. According previous chapter (Chapter 7), flux stabilization of a nano-filtration membrane is associated with the removal of LMW DOM fractions (<350 Da) from source waters. Pre-filtration of SWWE using 17500 Da and 700 Da MWCO membranes do not facilitate the removal of these LMW DOM fractions and the reduced normalized fluxes (70% & 74% respectively, Figure 8.3) observed for the both of these two pre-treatments further consolidate the findings of previous chapter (Chapter 7). The 4% increase of average normalized flux with the 700 Da MWCO pre-filtered water is likely to be a result of an 86% removal of DOC from SWWE. The 17500 Da MWCO pre-filter on the other hand only managed to remove 40% of DOC from SWWE. Even with an additional 46% of DOC removal, the 700 Da MWCO pre-filtered water only could facilitate a 4% increase of average normalized flux. This observation highlights the importance to remove the LMW DOC fractions (<700 Da) in source waters to manage fouling of membranes.

Pre-treatment of SWWE using BAC with an EBCT of 360 min (B360) alone resulted in an average normalized flux (82%) that was ~10% superior to the flux achieved with SWWE pre-filtered using 17500 Da and 700 Da MWCO membranes. Even having the same MWCO of 17500 Da, the UF membrane failed to produce a higher flux with 17500 Da MWCO membrane pre-filter water. SWWE pre-filtration using a 17500 Da MWCO membrane resulted in a 40% removal of DOC and a 56% DOC removal was achieved when pre-treatment was with B360. This additional 16% DOC removal, may have contributed towards the improved normalized flux (82%) observed with B360 pre-treated waters. However, even with an 86% DOC removal, the 700 Da MWCO membrane failed to produce a pre-filtered water that could facilitate a higher average normalized flux (74%). Hence the increase of flux with B360 pretreated water is likely to be due to the biological removal of LMW DOC fractions (< 700 Da) from SWWE. Similar observations were made on repeating the experiments (see Appendix 2).

When B360 pre-treated water was subjected to a 17500 Da MWCO membrane filtration, a 54% overall DOC removal (i.e. compared to DOC of SWWE) was

observed and a similar removal was observed also with just a B360 pre-treatment. When average normalized flux with B360 pre-treated water and B360<17500 Da pre-filtered water was compared, B360<17500 Da pre-filtered water resulted in a 6% increase. The final DOC concentration in B360<17500 Da pre-filtered water was 55% less to that of B360 pretreated water and this low DOC concentration is likely to have resulted in the 6% increase of average normalized flux. When DOC removal between B360<17500 Da pre-filtered water and B360<700 Da pre-filtered water was examined, an additional 42% reduction in DOC was observed in B360<700 Da pre-filtered water. Even with an extra removal of DOC, the average normalized flux (86%) remained similar to what was observed with B360<17500 Da pre-filtered water (88%).

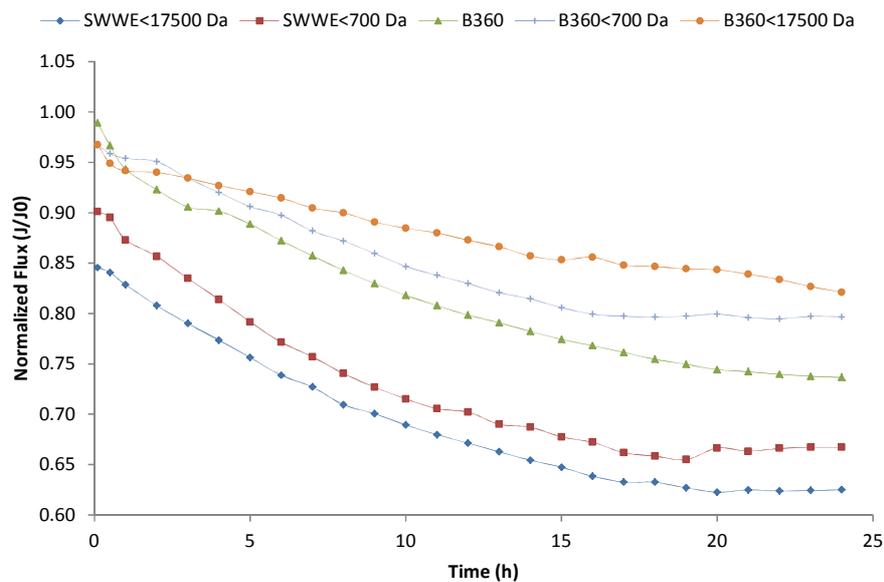


Figure 8.3: Pre-filtration of SWWE using MWCO membranes and its influence on normalized flux

Overall these experiments demonstrate the importance to selectively remove LMW (<700 Da) DOM to minimize membrane fouling. While an overall reduction of DOM is also important to sustain a long-term stable flux (by reducing the cake layer formation), to reduce pore constriction or blockage of UF membranes, the removal of

LMW DOM (<700 Da) appears more critical. BAC although not able to significantly reduce DOM present in SWWE appear to selectively remove or convert LMW organic matter into HMW organic matter facilitating a higher flux with both nano and ultrafiltration membranes.

Table 8.3: DOC removal, reduction of UV₂₅₄ absorbance and flux recovery with pre-filtered waters

Pre-treatment	DOC and UV ₂₅₄ in SWWE	DOC after pre-treatment (mg/L)	UV ₂₅₄ After pre-treatment (cm ⁻¹)	Average normalized flux (%)		
				24 h	0-6 h	18-24 h
SWWE (<17500 Da)	11.86 mg L ⁻¹ and 0.201 cm ⁻¹	7.07 (40%)*	0.108 (46%)	69.90±0.08	79.76±0.04	62.46±0.00
SWWE (<700 Da)		1.38 (86%)	0.015 (92%)	73.52±0.08	84.22±0.05	66.42±0.00
B360		5.17 (56%)	0.066 (67%)	82.41±0.08	92.38±0.04	74.16±0.00
B360 (<17500 Da)	5.17 mg L ⁻¹ and 0.066 cm ⁻¹	2.35 (54%)	0.018 (72%)	88.32±0.04	93.69±0.04	83.47±0.01
B360 (<700 Da)		1.36 (74%)	0.006 (91%)	85.51±0.06	93.61±0.03	79.69±0.00

*Percentage removal

8.3.6 Analysis in Terms of Stokes Radius and Number Averaged Molecular Weight

The effect on Stokes radius and number average molecular weights resulting from the BAC pre-treatment was investigated in our previous study. As shown in Table 8.4, microbial activity in the BAC bed at an EBCT of 40 and 120 min (B40 and B120) increased the average Stokes radius of DOM. However, B40 followed by 3.2% MIEX concentration (B40M3.2) reduced the average Stokes radius of aquatic substances even smaller to that of SWWE. A similar phenomenon was observed in terms of number averaged molecular weight (M_n) during LC-OCD analysis.

Table 8.4: Changes in Stokes radius (m) and number average molecular weight (M_n) (Chapter 7)

Sample	Average Stokes radius (m)	Number Average MW (g/mol)
B40M3.2	$2.6 \pm 0.2 \times 10^{-10}$	254
SWWE	$4.6 \pm 0.2 \times 10^{-10}$	486
B40	$4.9 \pm 0.3 \times 10^{-10}$	605
B120	$6.5 \pm 0.3 \times 10^{-10}$	652

The BAC/MIEX combination maximized DOM removal but failed to reduce residual DOM having smaller stokes radii or number average molecular weight. This likely facilitated the entry of DOM into the UF membrane causing pore constriction and blockage resulting in a flux decline. The DOM with higher stokes radii or number average molecular weight resulting in after BAC treatment on the other hand are likely to prevent pore constriction or blocking of UF membranes and may contribute towards the formation of a cake layer instead results in a form of fouling that is less severe and reversible (Figure 8.4). Considering the effect of coagulation on normalized flux was similar to that of MIEX, the influence brought about by coagulation on average Stokes radius and number average molecular weight could be essentially similar to observations made with MIEX.

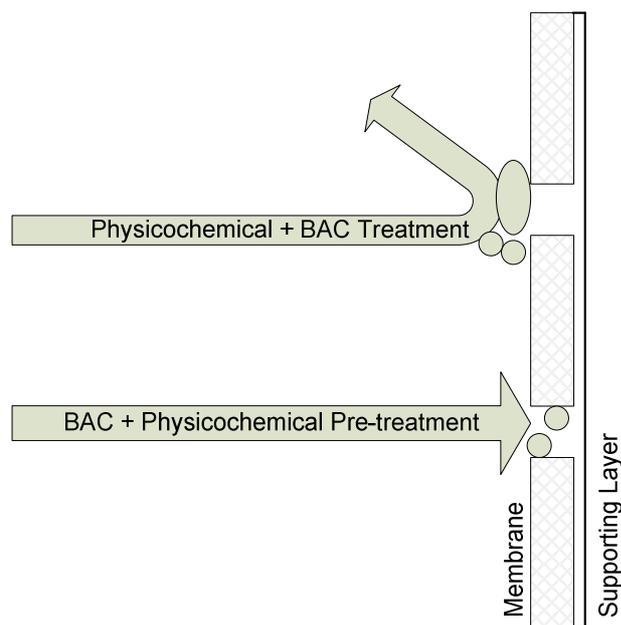


Figure 8.4: Conceptual representation of BACs' effect on membrane fouling reduction

8.3.7 Membrane Analysis: FTIR Analysis

Clean and fouled UF membrane surfaces were analyzed for functional groups using ATR-FTIR spectroscopy (Figure 8.5a, 8.5b and 8.5c). The main functional groups identified on clean membrane were aromatic ($1625\text{--}1590\text{ cm}^{-1}$ and $1525\text{--}1470\text{ cm}^{-1}$) and sulphur group (CO-SO₂-OC at $1415\text{--}1390\text{ cm}^{-1}$; C-SO₂-OC at $1375\text{--}1335\text{ cm}^{-1}$; C-SO₂-C at $1340\text{--}1290\text{ cm}^{-1}$; N=S=O at $1300\text{--}1230$; C-SO₂-C at $1200\text{--}1050\text{ cm}^{-1}$ and C-SO₂-C at $1165\text{--}1120\text{ cm}^{-1}$). Similarly, other functional groups present in the membrane were ether (C-O-C at $1125\text{--}1090\text{ cm}^{-1}$), alcohol (R-CH₂-OH) and ether (C-O-C at $950\text{--}815\text{ cm}^{-1}$). These observations coincide with observations made by a previous study (Shon et al. 2004). A similar characterization of functional groups was performed on the surface of fouled membranes exposed to different pre-treated waters. As shown in Figures 8.5a, 8.5b and 8.5c, a couple of additional peaks appeared as a result of organic matter adsorption on membrane surfaces. One of the major peaks was observed between $3700\text{--}3000\text{ cm}^{-1}$ that corresponds to stretching vibration of N-H or o-H. Similarly, another functional group was evident at 1650 cm^{-1}

¹ that corresponds to C=O stretching vibration of soluble proteins (Chittur 1998, Huang et al. 2013).

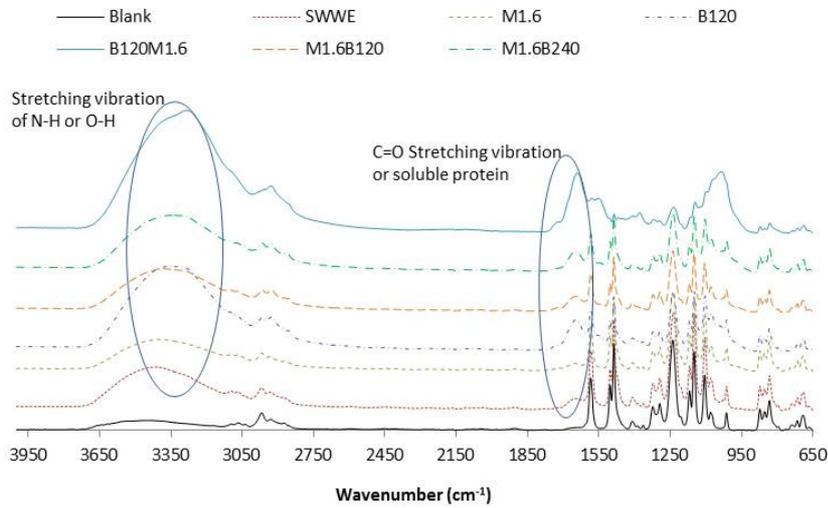


Figure 8.5a: FTIR spectra of clean membrane and used membrane (BAC and MIEX)

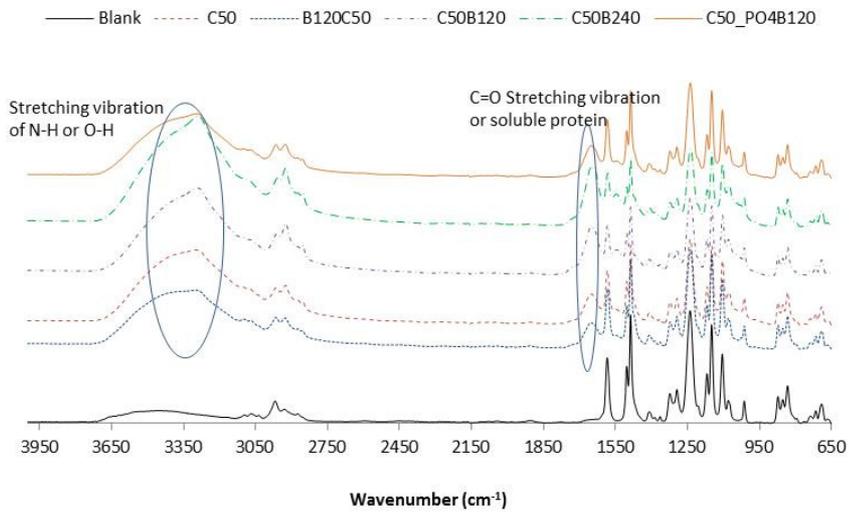


Figure 8.5b: FTIR spectra of clean membrane and used membrane (BAC and EC)

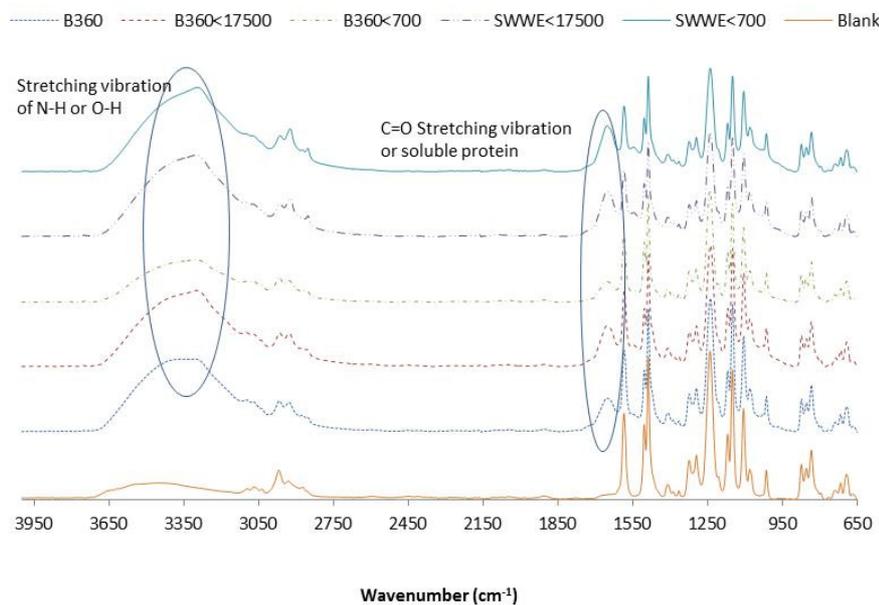


Figure 8.5c: FTIR spectra of clean and used membrane (MWCO fractionated BAC and SWWE Sample)

This analysis demonstrates the presence of the same functional groups on UF membranes exposed to both SWWE, pre-treated water and MWCO fractionated water sample. Although organic matter with similar characteristics deposited on membrane surfaces when exposed to different pre-treated waters, their influence on flux reduction was different. Previous studies have identified specific functional groups or compounds such as carboxylic acid, humic substances, polysaccharides, biopolymers or proteins as severe foulants (Cho et al. 1998, Jarusutthirak et al. 2002, Zularisam et al. 2006). However, this study indicates that even organic matter having the same functional groups could have different behaviours on a UF membrane and perhaps the geometry of the organic compounds is contributory towards this difference in behavior.

Lowering the concentration of residual organic matter in the feed streams is important to reduce the extent of the external cake layer and intensity of internal fouling (Duclos-Orsello et al. 2006, Sablani et al. 2001). Considering that it is the molecular weight and size of DOM that governs irreversible fouling of a membrane,

even a lower residual organic matter concentration in a feed could result in fouling of membranes. As demonstrated in this study, BACs' ability of removing LMW DOM and also producing DOM of higher Stokes radii and molecular weight could be effectively used in conjunction with physicochemical pre-treatments to reduce UF membrane fouling in terms of reduced cake layer formation and internal pore blockage.

8.4 Conclusions

This investigation was undertaken to explore the beneficial use of BAC in combination with other physicochemical pre-treatment methods to understand fouling of UF membranes. The major conclusions of the study are summarized below:

1. Microbial activity in the BAC bed could be utilized to manipulate the size of DOM in combination with physicochemical pre-treatment
2. The ability of BAC to increase the average Stokes radius or number average molecular weight can be employed to stabilize the performance of UF membrane
3. The MIEX/BAC or EC/BAC order of pre-treatment is more effective in reducing UF fouling than the BAC/MIEX or BAC/EC respectively.
4. A decrease in DOC concentrations does not necessarily reduce fouling on UF membranes.

8.5 Acknowledgements

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8.6 References

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Chapter 9

Summary Discussion and Recommendations

9.1: Summary and Discussion

Fouling of membranes by raw and pre-treated secondary wastewater effluent (SWWE) was investigated in order to reduce the fouling of ultrafiltration (UF) and nanofiltration (NF) membranes. Biological activated carbon (BAC) was applied as a biological pre-treatment option and enhanced coagulation (EC) by ferric chloride and magnetic ion exchange resin (MIEX) were applied as physicochemical pre-treatments. Both individual and combined effects of the pre-treatments were investigated in terms of organic matter removal and membrane fouling reduction.

The research was divided into two parts. The first part investigated individual pre-treatments and their combined influence on dissolved organic carbon (DOC) removal. In the second part of the thesis, pre-treatment (individual and combined) of secondary wastewater and its influence on membrane (NF & UF) fouling was examined.

Primarily, BAC and enhanced coagulation was examined to reduce dissolved organic matter (DOM) in SWWE. A DOC removal model was used to estimate the non-coagulable fraction of SWWE after each successive BAC treatment. This facilitated an understanding on enhanced coagulation. The non coagulable fraction of SWWE was 22%. When SWWE was subjected BAC treatment with empty bed contact times (EBCTs) of 20 and 40 min, enhanced coagulation was able to facilitate removal of the non-coagulable fraction down to 17% and 6% respectively. Similarly the non-polar fraction that can be removed by coagulation increased from 47% to 53% and 70% with increasing EBCTs.

The investigations carried out to examine the individual and combined influence of pre-treatments revealed that the BAC/EC order was more effective compared to the EC/BAC order in terms of organics matter removal. Analysis showed that the

BAC/EC combination synergized the performance based on two main reasons. The BAC adsorbs some of the fractions that cannot be removed by enhanced coagulation. At the same time it converts non-coagulable DOC to coagulable DOC by microbial activity and increases the performance of subsequent coagulation process. Additionally, the BAC/EC significantly decreased the amount of coagulant dose required to remove a given quantity of DOC. Specifically, to achieve a DOC removal efficiency similar to that of 160 mg/L of coagulant, a pre-treatment with the BAC (EBCT 80 min) followed by 60 mg/L of coagulant is sufficient and this in essence could reduce the coagulation costs by 63%. This in turn would also reduce the amount of chemical sludge produced, contributing towards an overall reduction of sludge disposal costs.

Similar to BAC/EC combination, BAC/MIEX combination was also found equally effective in terms of additional organic matter removal. The MIEX/BAC combination failed to bring about removal efficiency similar to that of the BAC/MIEX. Analysis showed that BAC significantly increases the efficiency of the MIEX treatment. Specifically, to achieve DOC removal efficiency similar to that of 3.2% v/v MIEX, a pre-treatment with the BAC (EBCT 40 min) followed by 0.4% v/v MIEX is sufficient and this in essence could reduce operational cost of MIEX by 87%. Similar to with the coagulation this in turn would reduce the need for frequent regeneration of MIEX and consequently would reduce brine requirements and its disposal.

The characteristics of organic matter before and after BAC treatment revealed changes to average Stokes radius and number average molecular weight of DOM. Both parameters increased with increased EBCT of BAC bed indicating BACs' ability to remove/convert lower molecular weight (LMW) organic compound into higher molecular weight (HMW) organic compound. Subsequently physicochemical pre-treatment processes were able to easily remove the HMW organic compounds from SWWE.

The individual and combined impact of pre-treatment was assessed against NF and UF membranes. The MIEX/BAC combined pre-treatment was able to reduce

membrane fouling and also facilitate long-term steady flux. Over the duration of 131 h, the flux decline against a NF membrane was only 5% at a trans-membrane pressure of 0.5 MPa. The MIEX/BAC order of pre-treatment was observed to effectively remove LMW neutral fraction (350 Da) and other individual and combined MIEX and BAC treatments didn't appear to specifically target this LMW neutral fraction of SWWE. In addition, BAC treatment was also observed to increase the average Stokes radius and number average molecular weight of DOM in SWWE. This change in DOM may have prevented pore constriction and the blockage of membranes. The BAC induced change on DOM in SWWE appear important to reduce membrane fouling as flux decline on membrane was reduced (i.e. an increase of normalized flux) with increasing EBCT of MIEX/BAC pre-treatment combination. Overall the influence of MIEX/BAC combination on both UF and NF membrane was similar with both resulting in higher long-term stable flux.

The influence of EC/BAC combined pre-treatment on UF membrane was also similar to that of the MIEX/BAC combined pre-treatment. The BAC/EC or MIEX order combination pre-treatment although effective at reducing residual DOC in SWWE failed to facilitate higher or a long-term stable flux against an UF membrane. This signifies the importance of removing specific foulants that are responsible towards pore constrictions and blockage of membranes to enable a long-term stable flux. According to this thesis, although an overall reduction of DOM is important to maintain a reduced cake layer on the membrane (reversible fouling), specific reduction of LMW DOM from SWWE is important to prevent irreversible fouling of membranes.

In summary, the results of this thesis suggest that BAC treatment could be utilized both to increase the molecular size of dissolved organic matter removal and also to enhance DOC removal efficiencies of physicochemical pre-treatment methods. Further, based on requirement, combined BAC and physicochemical pre-treatment order could be manipulated such to either achieve very low DOM in SWWE or to achieve higher long-term stable flux from UF or NF membranes.

9.2 Recommendations for Future Research

During this course of this PhD, a number of other research questions were raised with regards to fractions of DOM and their contribution towards membrane fouling and this call for further investigations. The recommendations for future research in this field are described below:

- The thesis highlights changes to other DOC fractions (other than to LMW DOM) when combined physicochemical/BAC treatment is carried out on SWWE. Many studies in the past have categorised humic substances, polysaccharides, biopolymer etc. as a severe foulants. Hence, it would be interesting to explore the behaviour (fouling/non-fouling) of these individual foulant after BAC treatment against a NF or UF membrane.
- This study also indicated that microbial activities in BAC increase the number average molecular weight and average Stokes radius of DOM. The thesis suggests that the increase of number average molecular weight and average Stokes radius of DOM prevents pore constriction and blockage of membranes. Although indirect evidence suggest that this may well be the reason for the reduced fouling observed, obtaining direct evidence towards this with the aid of scanning electron microscopy would further advance knowledge about BAC and its pre-treatment mechanisms.
- This thesis focused on facilitating re-cycled water from SWWE. Hence all pre-treatment methods examined to reduce fouling of membranes were based on SWWE. The use of membranes is not limited to SWWE and for example is also applied with seawater and surface waters. Hence, the pre-treatment strategies detailed in this thesis to reduce fouling may be applicable to these source waters too. Systematic studies however, would be required to establish whether similar outcomes could be achieved with these source waters.

Appendix

Appendix 1: Performance of MIEX in SWWE and BAC effluent (12 months old BAC bed)

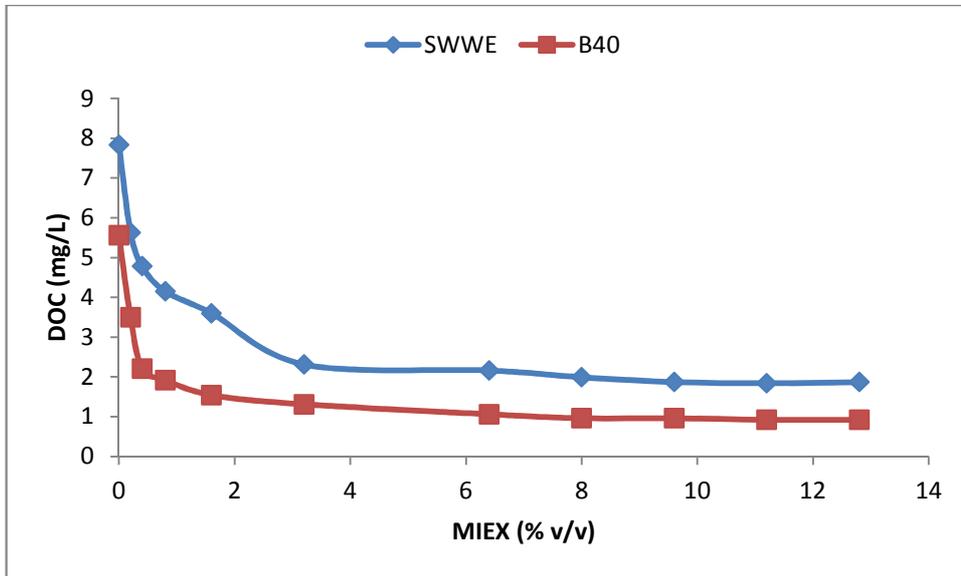


Figure A1.1: Performance of MIEX under different conditions

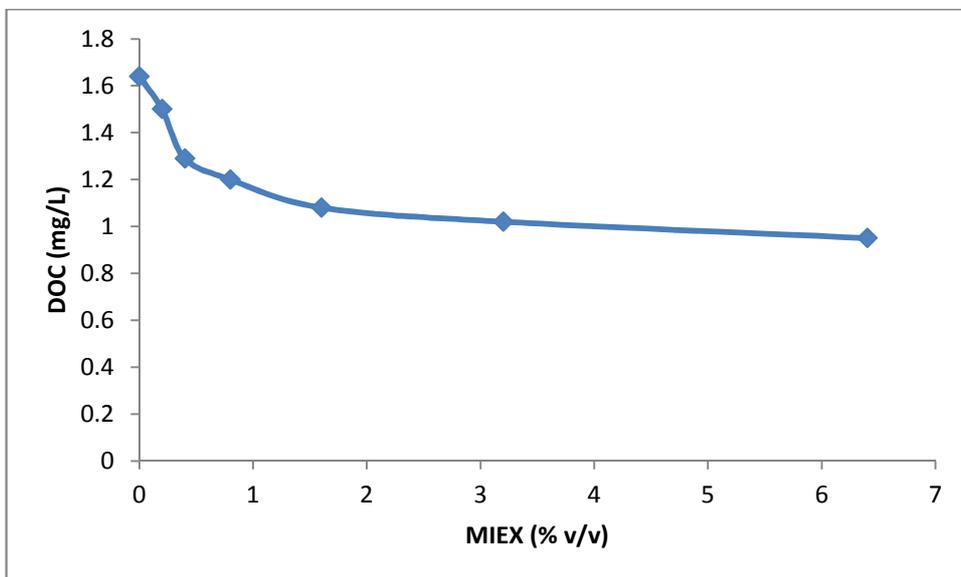


Figure A1.2: MIEX performance on BAC effluent fed with MIEX non-amenable fraction alone

Appendix 2: Normalized flux and organic matter removal for different MWCO fractionated samples

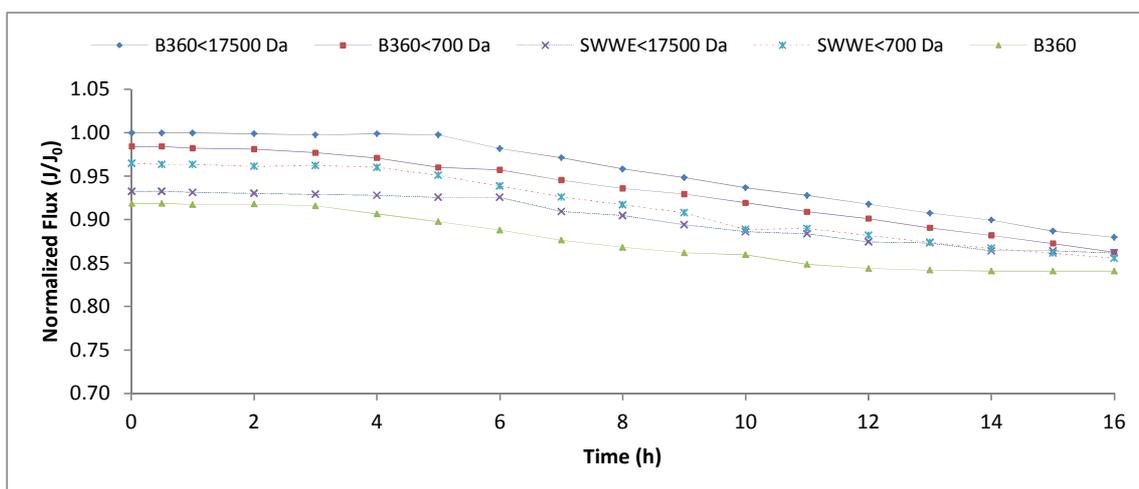


Figure A2.1: Normalized flux for different MWCO fractionated samples

Table A2.1: Removal of DOC and UV absorbance from SWWE in MWCO samples

Samples	DOC	UV _{254_1cm}
SWWE	8.57	0.184
B360	6.35	0.064
B360<17500 Da	3.85	0.059
B360<700 Da	1.47	0.006
SWWE<17500 Da	7.02	0.093
SWWE<700 Da	1.48	0.011

Appendix 3: Performance of MIEX in removing Phosphorus, DOC and UV absorbance

Table A3.1: Performance of MIEX in terms of Phosphorus removal

Sample	PO ₄ -P (mg/L)
SWWE	8.98
M1.6	2.95
M3.2	1.60
M6.4	0.20

Table A3.2: Performance of MIEX in terms of organic matter removal

Samples	DOC	UV _{254_1cm}
SWWE	8.14	0.190
M1.6	3.05	0.042
M3.2	2.43	0.035
M6.4	2.35	0.035

Appendix 4: Performance of enhanced coagulation in removing phosphorus, DOC and UV absorbance

Table A4.1: Performance of MIEX in terms of Phosphorus removal

Sample	PO ₄ -P (mg/L)
SWWE	8.98
C50	0.02
C100	0.013
C150	0.001

Table A4.2: Performance of enhanced coagulation in terms of organic matter removal

Samples	DOC	UV _{254_1cm}
SWWE	8.14	0.190
C50	3.15	0.071
C100	2.65	0.056
C150	2.50	0.052

Appendix 5: Performance of BAC in removing DOC and UV absorbance

Samples	DOC	UV _{254_1cm}
SWWE	9.28	0.182
B120	7.43	0.113
B240	6.80	0.087
B360	5.87	0.089
B480	5.63	0.082
B500	5.53	0.076