An Investigation into Membrane Fouling from Algae-containing Waters

A Thesis submitted in fulfilment of the requirement for the Degree of

Master of Applied Science

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December, 2008

Declaration

I certify except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of this thesis is the result of work which has been carried out since the official commencement date of the approved research program; and, any editorial work, paid or unpaid, carried out by a third party is acknowledged.

Signed  ……..

on……05/08/09…..

Acknowledgements

The author would like to acknowledge the following people and organisations:

The CRC for Water Quality and Treatment for provision of a scholarship. The Smart Water Fund for provision of research funds for the WTP investigation.

Professor Felicity Roddick and Dr John Harris for being my supervisors and providing constructive comment and guidance throughout the project.

Dr Thang Nguyen and Dr Linhua Fan for support provided during the WTP investigation and assistance during the project. My fellow postgraduate students in the Water Research Team for their input, assistance and companionship.

Kylie Debono for allowing time off work to complete the thesis.

My parents, Lorensz and Sandra, for always being there for me and providing such loving support over the past 7 years, I couldn't have done it without you. My mates for providing such enjoyable distractions. My Lord for continually providing beyond my wants and expectations. And most importantly of all, my wife to be, Amy, your loving support and encouragement this last year has been overwhelming, you have played a significant role in completion of this thesis.

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Abbreviations

A_{254} = Absorbance at 254 nm
AOM = Algal organic matter
B1, B2… = Batch sample number
BTSE = Biologically treated sewage effluent
Chl-a = Chlorophyll a
C4 = Clarifier number 4 sample
Da = Daltons (molecular size)
DOC = Dissolved organic carbon
EEM = Excitation-Emission Matrix
EfOM = Effluent organic matter
EOM = Extracellular organic matter
HPI = Hydrophilic organic matter
HPO = Hydrophobic organic matter
HORS = Head of Road Storage
IOM = Intracellular organic matter
J = Permeate flux
J_o = Initial pure water flux through new membrane
J_Δ = Irreversible fouling resistance
MF = Microfiltration
LMH = L/m^2h
NOM = Natural organic matter
P10 = Lagoon pond 10
Raw = Sample prior to treatment
TOC = Total organic carbon
TPI = Transphilic organic matter
SMP = Soluble microbial products
UF = Ultrafiltration
WTP = Western Treatment Plant, Werribee, Victoria

Summary

Membrane treatment of surface water, and of secondary treated municipal wastewater for recycling, has rapidly become the treatment process of choice due to high levels of bacterial removal. A major disadvantage of the technology is membrane fouling which reduces water flux and thus reduces throughput and water recovery, leading to more frequent maintenance and greater plant downtime. Natural organic matter (NOM) is a constituent of surface waters and municipal wastewater, and can cause significant fouling of membranes. NOM can be allochthonous (from surface runoff and contains products from the degradation of vegetable and animal matter) and autochthonous (derived from sources within the water body, such as algae). Waters subject to algal blooms typically contain high concentrations of hydrophilic organic carbon compounds such as proteins and polysaccharides. These compounds have been found to contribute greatly to membrane fouling. In this study the fouling propensity, and the components of the fouling layer, for microfiltration (MF) and ultrafiltration (UF) membranes were characterised for samples taken from a wastewater treatment plant with lagoons prone to algal blooms and an algal culture.

Effluent from the Western Treatment Plant in Werribee, Victoria, Australia, was tested for fouling propensity. The plant uses a combined activated sludge–lagoon treatment (AS-lagoon) process. The lagoons are subject to occasional blue-green algal blooms hence filtration experiments using MF and UF membranes were conducted in a stirred cell system to determine the most suitable feed water supply for a future membrane filtration plant. It was found that clarified activated sludge effluent typically fouled both membrane types more rapidly than AS-lagoon treated effluent. This was attributed to the clarifier effluent sample containing higher concentrations of total organic carbon (TOC), particularly of hydrophilic (HPI) organic carbon, and suspended solids. Analysis by Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy and polymeric resin fractionation indicated proteins and polysaccharides were the major components of the foulant layers on the membranes.

Anabaena circinalis, a cyanobacterium commonly referred to as a blue-green alga, was cultured to ascertain differences in fouling propensity of organic carbon released by the cells during the growth phase (extracellular organic matter - EOM) and lytic phase (algal organic matter - AOM). Comparison of the flux rates for EOM and AOM solutions at the same concentration (5 ppm) showed that EOM had a greater fouling effect than AOM on the MF membrane, whereas the fouling rates were very similar for both sample types for the UF membrane. The EOM feed had a markedly higher proportion of hydrophilic to hydrophobic

components than the AOM feed. This is consistent with the excretion of proteins and polysaccharides by the algae as they grow, and their release of intracellular organic materials and cell wall constituents on lysis.

MF removed approximately 30% of the TOC, mainly hydrophilic compounds, from both the EOM and AOM solutions, indicating that the proteins and polysaccharides of large molecular size in this fraction were the main contributors to the fouling of the membrane. For UF, more TOC was removed from the AOM (70%) than from the EOM (53%). UF removed more hydrophilic organic compounds than MF, and gave significant removal of hydrophobic (ie., humic acid-like) material for both EOM and AOM. For the two membrane types, hydraulic cleaning and backwashing with Milli-Q water showed that irreversible fouling was an order of magnitude greater for AOM- than EOM-fouled membranes. This was attributed to differences in the characteristics of the hydrophilic fraction and the hydrophobic fraction. The concentration of the latter was higher in AOM and was almost completely removed by UF.

MF and UF of the HPI fractions (obtained by resin fractionation) of the EOM and AOM showed that flux reduction for both membrane types was not entirely due to the HPI fraction. For MF the fouling rate for the AOM-derived fraction was greater than for the EOM-derived fraction, whereas for UF, the fouling rate for the EOM-derived fraction was greater than for the AOM-derived fraction. This propensity for higher fouling rate and greater irreversible fouling was attributed to the higher content of hydrophobic compounds and/or the difference in the characteristics of at least some of the hydrophilic macromolecular compounds in the AOM.

These results show that although no algal bloom occurred in the Western Treatment Plant lagoons during the sampling period, such an event would likely have a significant impact on the fouling propensity of the lagoon effluent.

Chapter 1 - Introduction

1.1 Background

Microfiltration (MF) and ultrafiltration (UF) technologies are used in water treatment processes because of their high removal of pathogens and improved water quality (Glimenius, 1985; Vrouwenvelder et al., 1998; Goosen et al., 2004). However membrane fouling remains the biggest obstacle. Membrane fouling, caused by natural organic matter (NOM), results in reduced flux and plant downtime. NOM in water bodies is derived from two sources. Allochthonous NOM is organic matter introduced into the water body by surface runoff and contains products from degraded vegetable and animal matter. It is predominantly aromatic in character with high lignin content. Autochthonous NOM is derived from sources within the water body, such as algae, and is largely aliphatic with high concentrations of carboxylic acid functional groups (McKnight and Aiken, 1998; Pivokonsky et al., 2006; Lee et al., 2006a).

Western Treatment Plant (WTP), Victoria, Australia, is unusual as it uses a combined activated sludge–lagoon treatment (AS-lagoon) process. The sewage first passes through activated sludge ponds with anoxic and aeration zones after which the biologically treated effluent then passes through a clarifier and a chain of lagoons. The lagoons are subject to periodic blue-green algal blooms, particularly in the warmer months. There is interest in recycling the treated water, however, the salt content (1,800 $\mu S\ cm^{-1}$) is a limiting factor to the long term sustainable use of the recycled water. Trials have demonstrated that MF or UF can be used to pre-treat the effluent from the WTP prior to salt reduction via reverse osmosis (RO), however, it was observed that membrane fouling was a potential problem.

Algal blooms result in large amounts of autochthonous NOM being released into the water column. These compounds are typically hydrophilic and comprise proteins and polysaccharides (Her et al., 2004). Algae release two types of organic matter. As algal cells grow they excrete extracellular organic matter (EOM) into the water column. This comprises mostly protein- and polysaccharide–like compounds (Pivokonsky et al., 2006). As the cells lyse they begin to release intracellular compounds into the water column (Pivokonsky et al., 2006; Nguyen et al., 2005). The mixture of extracellular and intracellular compounds due to cell lysis is herein referred to as algal organic matter (AOM).

AOM compounds have been strongly associated with increased membrane fouling (Her et al., 2004; Park et al., 2006; Lee et al., 2008). For these experiments the authors used AOM extracted from freeze dried algal samples by sonication and/or grinding. At the time of the present study, no work had been published on the fouling propensity of EOM and AOM from a single algal culture for which the algal cells had not been freeze dried, ground, or sonicated.

1.2 Objectives

The primary objectives of this study were to:

- Investigate the fouling potential, and characterise the organic components of the membrane foulant layers, of clarified activated sludge and lagoon effluent obtained from the WTP.

- Investigate the fouling propensities of EOM and AOM derived from a blue-green algal culture as it passed through the growth cycle, ie., for which the cells had not been subject to physical disruption.

- Determine any difference in the fouling propensity of EOM and AOM and relate it to organic composition.

1.3 Thesis outline

The literature review, contained in Chapter 2, is presented in four subsections: description of natural and wastewater organic composition, elucidation of membrane fouling, influence of algae on membrane fouling, and characterisation of membrane fouling layers. The experimental materials and methods are described in Chapter 3. Experimental results are presented in two chapters. Membrane fouling by the clarifier and lagoon effluents from Western Treatment Plant is investigated in Chapter 4. Investigation of the fouling propensities of EOM and AOM derived from *Anabaena circinalis* is provided in Chapter 5. The conclusions and recommendations for further work are provided in Chapter 6.

Chapter 2 - Literature Review

2.1 Natural and Wastewater Organics

2.1.1 Origin and properties of NOM in natural waters

NOM is found in all natural water sources and is a complex matrix of organic compounds. NOM is derived from the degradation of vegetable and animal matter. It is a major contributor to problems associated with drinking water supply such as colour, odour, formation of disinfection by-products, biofilm growth, and membrane fouling (Stevens and Symonds, 1977; Malcolm, 1985; Gottschalk et al., 2000; Zularisam et al., 2006). Comprising mostly of carbon, oxygen, and hydrogen, NOM also contains nitrogen and sulphur at varying levels depending on its source (Croue et al., 2000). The composition of NOM can vary significantly depending on the environmental source, properties of the water body, and the chemical and biological degradation it has undergone (Wilson, 1988; McDonald et al., 2004). Due to the differences in origin and degradation processes, NOM is not identified by specific compounds but rather characterised by its properties (Drikas, 2003). Despite these complexities NOM can be categorised into two classes: allochthonous and autochthonous (McKnight and Aiken, 1998). Allochthonous NOM is organic matter that has been introduced to a body of water, generally through surface runoff. It is derived mostly from degraded terrestrial vegetable and animal matter and is predominantly aromatic; it has a high lignin content. Autochthonous NOM is derived from sources within the water body, such as algae, and is largely aliphatic with high concentrations of carboxylic acid functional groups (McKnight and Aiken, 1998; Pivokonsky et al., 2006; Lee et al., 2006a).

2.1.1.1 Characteristics

NOM is a complex heterogeneous mixture of molecules. These are commonly categorised into three major groups based on their abundance: humic (or hydrophobic) substances, hydrophilic (or transphilic) acids, and simple hydrophilic compounds (Thurman, 1985). However it should be noted that these categorisations are based on the overall properties of a molecule and that a single NOM molecule may have hydrophilic and hydrophobic structures. Typically humic acids make up the largest proportion of NOM, with proportions of transphilic acids and simple hydrophilic compounds varying with seasonal changes (Gjessing, 1975; Thurman, 1985; Drikas, 2003). However, water sources dominated by algal activity and little allochthonous NOM input, such as glacial lakes, have much higher concentrations of simple hydrophilic compounds (Lee et al., 2006a). Humic substances comprise mainly humic acids,

some fulvic acids and humin, and are hydrophobic due to their high molecular weight (MW) and high aromaticity (Croue, 1999; Zularisam et al., 2006). Transphilic acids comprise two major types: organic acids, such as volatile fatty acids and hydroxylic acids, and complex polyelectrolytic acids (Leenheer, 1981). Hydrophilic compounds are typically simple organic compounds such as carboxylic acids, amino acids, carbohydrates, and polysaccharides and have either a charged or neutral surface (Thurman, 1985; Drikas, 2003). Table 2.1 is a list of compounds associated with different organic fractions. Proteins are listed under hydrophobic bases; however proteins associated with autochthonous NOM, particularly AOM, are typically categorised as hydrophilic due to low aromaticity (Her et al., 2004; Lee et al., 2006a). However, Henderson et al. (2008) found that proteins made up the majority of the hydrophobic fraction in AOM.

Table 2.1: Chemical groups in NOM fractions (Edzwald, 1993)

Fraction	Chemical groups	
Hydrophobic:		
Acids	Strong	Humic and fulvic acids, high MW alkyl monocarboxylic and dicarboxylic acids, aromatic acids
	Weak	Phenols, tannins, intermediate MW alkyl monocarboxylic and dicarboxylic acids
Bases		Proteins, aromatic amines, high MW alkyl amines
Neutrals		Hydrocarbons, aldehydes, high MW methyl ketones and alkyl alcohols, ethers, furans, pyrroles
Hydrophilic:		
Acids		Hydroxylic acids, sugars, sulfonics, low MW alkyl monocarboxylic and dicarboxylic acids
Bases		Amino acids, purines, pyrimidines, low MW alkyl amines
Neutrals		Polysaccharides, low MW alkyl alcohols, aldehydes, ketones

2.1.2 Organic composition of treated wastewater

The effluent organic matter (EfOM) present in treated wastewater generally comprises some refractory NOM from the source water, refractory waste products, and breakdown products. However, for biologically treated sewage effluent (BTSE) the majority of EfOM is derived from microbial activity within the treatment plant (Noguera et al., 1994; Kou et al., 1996;

Barker et al., 1999). Microbes from the activated sludge treatment process excrete extracellular polymeric substances (EPS) and soluble microbial products (SMP). EPS constituents comprise mainly soluble and insoluble polysaccharides and proteins that cover the outer cell surface, providing an extracellular layer that aids in aggregation of cells, cellular adhesion to surfaces, protection from biocides, and retention of water and nutrients (Flemming and Wingender, 2001; Laspidou and Rittmann, 2001). SMP constituents comprise mostly soluble polysaccharides and proteins which are released by cells during cell lysis, cell membrane diffusion, and excretion (Namkung and Rittmann, 1986; Laspidou and Rittmann, 2001). The excretion of SMP and EPS means that BTSE generally contains a high proportion of hydrophilic compounds, about 59% (Shon et al., 2006).

2.2 Membrane Fouling

There are four types of membrane fouling in surface water treatment: organic fouling, biofouling, inorganic fouling or scaling, and particulate fouling. Of these, organic fouling is the most common and biofouling is the most severe (Goosen et al., 2004). Organic fouling is the adhesion and accumulation of organic compounds in the feed water to the membrane surface. Biofouling is the deposition and growth of microbes on the membrane surface. Inorganic scaling is the formation and accumulation of ionic crystals on the membrane surface, this only affects tight membranes such as for nanofiltration (NF) and reverse osmosis (RO) where membrane rejection of ions occurs (Goosen et al., 2004). Particulate fouling is the deposition of organic macromolecules or aggregates, greater than 0.45 μm, on the membrane surface which block the membrane pores (Goosen et al., 2004).

This study focuses on organic fouling, specifically the fouling of MF and UF membranes, and so this will be reviewed in the rest of this chapter.

There are three modes or mechanisms by which organic compounds can foul MF and UF membranes: surface fouling, cake filtration and pore plugging. These are influenced by the feed water pH, ionic concentration, organic compound composition, inorganic composition, and membrane surface charge (Goosen et al., 2004; Zularisam et al., 2006).

2.2.1.1 Surface Fouling

As feed water contaminants are rejected by the membrane, they concentrate at and adhere to the membrane surface. This is due to the surface charge of the membrane and contaminants (Section 2.2.2), friction resistance of the membrane, and permeate drag forces (Al-Ahmad et al., 2000; Goosen et al., 2004).

2.2.1.2 Cake Filtration

A gel-layer forms at the membrane surface as the concentration of constituents increases and they form weak intermolecular and ionic bonds. The reversible gel-layer increases permeate resistance resulting in a decline in flux and the cross-membrane passage of small contaminants (Al-Ahmad et al., 2000; Goosen et al., 2004). Backwashing or cross-flow pulsations can disperse and remove these weakly bonded structures; however they quickly form again so truly effective treatment involves regular cleaning regimes or chemical cleaning, which are sometimes disadvantageous for plant productivity and costs. As a consequence the feed water pressure is increased to maintain a consistent flux rate. High pressures result in aggregation of constituents (colloidal, macromolecular, and micromolecular organic compounds) at the membrane surface forming a cake-layer. At this point the fouling layer becomes strongly adhered to the membrane surface. Backwashing and cross-flow pulsations are effective in removing some of the cake-layer and chemical cleaning is often required. Invariably some foulants remain and the rate of flux decline increases after each cleaning process. Subsequent flux reduction leads to increased feed pressure, further compaction of the cake-layer and an irreversibly bound fouling layer (Goosen et al., 2004). Chen et al. (1997) reported the presence of a critical flux for the filtration of colloidal silica. When the critical flux was exceeded, the loosely held cake-layer (or gel-layer) forms a consolidated cake structure that is irreversible.

2.2.1.3 Pore Plugging

Flux decline is also caused by the blockage of pores within the membrane (pore plugging). Small particulate matter such as colloids are dragged through the membrane by permeate drag forces and can become stuck part way due to changes in pore size or pore morphology. The plugged pore means there is a reduction in flux.

Plugging can also be attributed to the surface accumulation of smaller particles within the pore which reduce the effective pore size causing particulates to become stuck (Comstock, 1982; Kilduff et al., 2005). Backwashing is effective in regaining most of the membrane flux by re-opening the pores. However it cannot remove all particulates or all of the organics adhered to the pore surface, and the reduction in pore size and distribution results in reduced flux and rapid fouling.

2.2.1.4 Mechanisms of MF and UF Fouling

Four filtration laws, developed by Hermia (1982), are commonly used to explain flux decline under constant pressure. Definitions of the principles of these laws are provided in Figure 2.1.

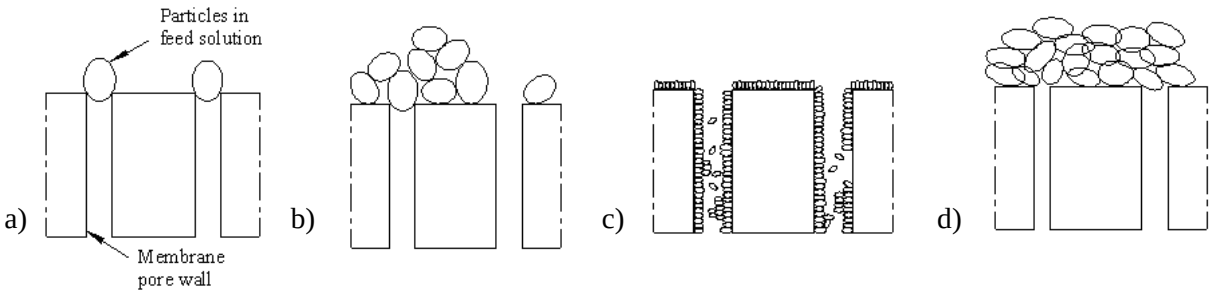


Figure 2.1: Schematic presentation of different membrane fouling models (Bowen et al., 1995) a) Complete blocking – Closing of pores by particles with no particle superimposition, b) Intermediate blocking – Closing of pores by particles with particle superimposition, c) Standard blocking – Deposition of particles smaller than the pore size onto the pore surface reducing the pore size, d) Cake filtration – Deposition of particles larger than the pore size onto the membrane surface(Ye et al., 2005)

After conducting low pressure filtration of alginate, Ye et al. (2005) tested these different filtration models to determine which fitted best. It was found that a MF membrane fitted two consecutive models: the standard blocking model followed by the cake filtration model. The standard blocking model fitted during the initial period of flux decline, where alginate particles accumulated within the membrane pores, eventually blocking them. After that the cake filtration model fitted. The blocked pores resulted in the formation of a cake layer at the membrane surface, providing increased trans-membrane pressure (TMP) and reduced flux. For an UF membrane the cake filtration model fitted the entire filtration run. The occurrence of pore blocking was either non-existent or of no measurable effect. The formation of a cake layer is virtually instantaneous on an UF membrane and is therefore the most significant factor in UF flux decline.

2.2.2 Surface Charge

The surface charge on the membrane and contaminants plays an important role in contaminant rejection and fouling potential. In general, membranes with high negative surface charge are good at rejection and less prone to fouling because fouling constituents comprise mostly hydrophobic and negatively charged compounds (Sadr Ghayeni et al., 1998; Goosen et al., 2004). Constituents with high negative surface charges, such as humic and fulvic acids, are

repelled by the negative charge on the membrane surface and so are well rejected and do not adhere to the membrane surface (Jarusutthirak et al., 2002).

2.2.2.1 Influence of Ionic Strength and pH

The strength of the repulsive force between membranes and contaminants can be reduced by increasing the ionic strength of the solution. Waters with high ion concentrations are more prone to fouling than similar waters with lower concentrations due to the build-up of counter ions around charged surfaces (Braghetta et al., 1997). Surfaces with a high negative charge will attract positive ions forming an electrical double layer. This build-up of positive ions attracts negative ions, and in turn more positive ions, into a region called the diffuse layer. The build-up of counter-charged ions effectively negates the long range repulsive force of the negatively charged surface from other negatively charged surfaces, therefore allowing possible attractive forces such as van der Waals forces to dominate. This interaction between repulsive and attractive forces is known as the Derjaguin-Landay-Verwey-Overbeek (DLVO) theory.

High ionic strength and low pH have similar effects on membrane surface behaviour and fouling. These variables reduce the electrostatic repulsive forces between the membrane surface and contaminants allowing the contaminants to concentrate at the membrane surface and foul the membrane. Reduced electrostatic repulsive forces within the membrane also cause the membrane to compress. This reduction in membrane volume and subsequent pore size results in reduced flux (Braghetta et al., 1997; Kilduff et al., 2005). Charge repulsion of functional groups on organic contaminants can also be reduced, allowing weaker attractive forces to dominate and increasing the compactness of cake-layers. Additionally, divalent cations can act as bridging ions between organic compounds. This can result in a more compact cake-layer with a higher resistance. The low pH and high ionic strength also cause an apparent shift in molecular weight of organic macromolecules by reducing the space between intermolecular bonds due to surface charge suppression. This results in increased passage of contaminants through the membrane. Passage of inorganic ions also increases as the repulsion forces that would ordinarily lead to the rejection of such ions are reduced (Braghetta et al., 1997; Kilduff et al., 2005).

2.3 Algae and Membrane Fouling

2.3.1 Definition of Algal Organic Matter

Algal-derived NOM is often referred to as algal organic matter and consists largely of hydrophilic (HPI) compounds (proteins and polysaccharides) and some hydrophobic (HPO) and transphilic (TPI) acids (Pivokonsky et al., 2006, Lee et al., 2006). These compounds are released into the water column by excretion of intracellular organics during the algal growth phase, and are commonly referred to as extracellular organic matter (EOM). During cell lysis intracellular organic compounds are released into the water column due to the breakdown and degradation of the cell walls; these organic compounds are commonly referred to as intracellular organic matter (IOM) (Nguyen et al., 2005; Pivokonsky et al., 2006; Lee et al., 2006). The combined presence of IOM and EOM in the water column caused by the growth and death phase of an alga is referred to as algal organic matter (AOM) in this thesis.

2.3.2 Algae and Flux Decline

2.3.2.1 Cellular Adhesion to Membranes

In a report issued by Montgomery Watson (1997) a number of surface water membrane filtration plants had operated consistently until the occurrence of an algal bloom. Once an algal bloom occurred the rate of membrane fouling increased significantly. In one instance an UF plant typically encountered significant flux decline after 34 days of operation, however after an algal bloom in the source water the operating time was reduced to less than 30 hours. In another case a MF plant went from 18-20 days of operation to 4-5 days after an algal bloom before cleaning was required.

Kwon et al. (2005) investigated the fouling effect of *Microcystis aeruginosa* (a blue-green alga) cells in the presence of NOM on an UF membrane. It was observed that the cells plus NOM had a significantly larger effect on flux decline than the NOM or cells individually. This suggests that interaction between the NOM and the EPS that cover the algal cells created a fouling layer with a much higher resistance and lower permeability.

Due to EPS, cellular adhesion to a membrane surface occurs very easily and the cells are very difficult to remove. Similar to algal cells, microbes also excrete EPS which is used as a colonising and protective device (Flemming and Wingender, 2001). The adhesion and cohesion forces of EPS are not due to covalent forces but weaker physicochemical forces. However, despite their weakness compared with C-C bonds, the total sum and number of

binding sites exceed that of covalent bonds making EPS gel-layers very difficult to remove (Flemming & Wingender, 2001). Even under conditions where permeate flow has been shut off so there is no physical force towards the membrane (ie., permeate drag force), microbes are found to irreversibly attach themselves (Kang et al., 2004; Wang et al., 2005). Hydraulic cleaning methods such as backwashing and forward flushing are effective in removing some of the adhered algal cells, resulting in a slight improvement in flux, whilst chemical cleaning provides better flux recovery but can damage the membrane (Montgomery Watson, 1997; Liang et al., 2008)

2.3.2.2 Dissolved and Colloidal AOM and Membrane Fouling

The removal of algal cells from a feed water may prevent cellular adhesion to the membrane, however organic compounds (e.g. AOM) released by cells into the water column have a significant impact on membrane fouling causing a decrease in flux. Lee et al. (2006a) conducted a series of filtration experiments with MF and UF membranes using whole water samples, dissolved organic fractions, and the colloidal fraction from lakes and reservoirs that was dominated by either allochthonous NOM, or autochthonous NOM (from frequent algal blooms), as well as a representative AOM sample derived through the grinding and sonication of a blue-green alga sample. It was reported that the colloidal fractions and AOM samples caused the most fouling on the membranes, compared with the dissolved organic fractions (hydrophobic, transphilic and hydrophilic organic fractions). The colloids from a reservoir subject to frequent algal blooms were found to cause the most significant fouling. Analysis of the membrane feed water solution, fouling layer, and membrane permeate confirmed that the protein- and polysaccharide-like compounds found in the AOM and colloidal samples contributed significantly to the increased fouling.

Her et al. (2004) conducted a series of filtration tests containing varying concentrations of Suwannee River humic acid and representative AOM samples derived through grinding, sonication, or liquid extraction using methanol, of a blue-green alga. As the concentration of AOM increased so too did the rate of fouling. It was determined by Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) analysis that the major constituents in the fouling layer were protein- and polysaccharide-like compounds, similar to those found in the AOM fraction, and not the humic acid (Her et al., 2004; Park et al., 2006). One reason for this is intermolecular bridging between proteins and/or polysaccharides due to the presence of divalent cations, particularly calcium, copper and iron. The bridging causes a well organised gel-layer to form at the membrane surface (Lee & Elimelech, 2006). This layer increases the

hydraulic resistance and subsequent flux decline. Gel-layer formation from divalent cations is more predominant for hydrophilic organic matter (ie., acid polysaccharides) than hydrophobic organic matter (ie., humic acid), because the cation complexes with the carboxylic group and forms bridges between the molecules (Lee & Elimelech, 2006).

The proteins and polysaccharides released during the growth and lysis phase of algal cells are similar in characteristics to those reported as significant contributors to fouling of hydrophilic filtration membranes (Her et al, 2004; Gabelich et al., 2004; Pivokonsky et al., 2006; Park et al., 2006)

2.4 Fouling Layer Characterisation

Organic fouling is a major form of membrane fouling affecting every water separation process from groundwater to seawater, drinking water to wastewater. Characterisation of the fouling components is difficult and complex due to the large number and range of compounds. Generally surface water contains a higher concentration of hydrophobic compounds (Thurman, 1985); consequently hydrophilic membranes are commonly used in membrane filtration plants (Goosen et al., 2004). This means that fouling is mainly caused by hydrophilic compounds (Fan et al., 2002; Zularisam et al., 2006), particularly colloidal particulates (Lee et al., 2006; Park et al., 2006). Separation of feed water constituents showed that these fractions foul hydrophilic membranes faster than hydrophobic and transphilic compounds. Various analyses showed these foulants as having high molecular weight and hydrophilicity, and saccharide- and protein-like substances similar to microbial by-products (Park et al., 2006). The complexity of NOM in surface water means comprehensive, multifaceted analysis is required to clearly identify the organic constituents. Below are a number of useful and commonly used analysis methods to identify membrane fouling layer constituents and characteristics.

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

ATR-FTIR provides information on the presence of functional groups within the clean membrane and fouling layer surface. This is useful in identifying which compounds may be present in the fouling layer. Park et al. (2006) identified functional groups associated with proteins and polysaccharides present in the fouling layer of membranes used to treat surface water from a freshwater lake. They found that these were similar in characteristics to the microbial by-product fractions from the same water. The formation of the fouling layer was

therefore attributed to the proteins and polysaccharides present in the microbial by-products. Numerous reports state similar findings of protein- and polysaccharide-like compounds, which were attributed to microbial by-products, in the fouling layer (Jarusutthirak et al., 2001; 2002; Her et al., 2004; Lee et al., 2006; Davey et al., 2006).

Table 2.2: Common IR spectra of AOM and algal cell surfaces (Her et al., 2004; Lee et al., 2006; Hung et al., 2006)

Bands (cm^{-1})	Associated group
3430	O-H alcohol
3300	N-H
2930	Aliphatic $-CH_2$ asymmetrical stretching
2850	Aliphatic $-CH_2$ symmetrical stretching
1720	C(=O)OH
1650	Amide I, primary peptide carbonyls, C=O
1515-1570	Amide II, C-N-H
1318	CH_3, aminosugars
1250	C-O, carboxylic
1000-1150	Polysaccharide-like

2.4.2 Dissolved Organic Carbon Fractionation

The use of Amberlite XAD resins to fractionate dissolved organic carbon (DOC) from water samples, based on the hydrophobic and hydrophilic properties of the constituents, has been extensively used (Mantoura and Riley, 1975; Leenheer et al., 1981; Aiken et al., 1992; Chow et al., 2004). Aiken et al. (1992) separated surface water samples into hydrophobic acids and more polar (transphilic) acids by sorbing and eluting the compounds onto Amberlite XAD-8 and Amberlite XAD-4 resins respectively. Using ^{13}C-NMR, they identified the hydrophobic acid fraction as mostly fulvic and humic acid and the transphilic acid as humic-like compounds; however they also noted that both fractions were very complex mixtures. The major difference between the two fractions was the transphilic acid had a larger proportion of carboxyl and heteroaliphatic carbon, and was less aromatic compared with the hydrophobic acid. Leenheer and Croue (2003) used XAD-8 and XAD-4 resins to characterise surface water samples. They noted that XAD-8 adsorbed humic components (ie., hydrophobic acids such as humic acids, fulvic acids, and tannins), XAD-4 absorbed more polar species, and non-

absorbed species (small organic acids, sugars, and possibly amino acids) were classed as hydrophilic compounds.

Fan et al. (2002) fractionated the DOC of surface water into hydrophobic acids (HPO), transphilic acids (TPI), hydrophilic charged compounds (CHA), and hydrophilic neutral compounds (NEU), using Supelite DAX-8 (which is comparable to Amberlite XAD-8), Amberlite XAD-4, and Amberlite IRA-958 resins respectively. The fractions were passed through hydrophilic and hydrophobic MF membranes. The order of fouling potential was reported to be similar for all membranes: NEU>HPO>TPI>CHA. The high fouling propensity of the NEU fraction was attributed to the high concentration of calcium and carbohydrates (ie., polysaccharides) in the fraction. The predominance of hydrophilic (HPI) compounds present in the fouling layer was reported by Park et al., (2006) further supporting the theory of higher fouling propensity for HPI compounds. However Shon et al. (2006) reported the HPO fraction had a higher fouling propensity on a hydrophobic UF membrane.

As reported by Fan et al. (2002), not all HPI compounds foul membranes rapidly. Lee et al. (2006a) separated surface water samples into HPO, TPI, HPI, and colloid fractions. They found colloids to be the main contributor to the fouling of hydrophilic and hydrophobic MF and UF membranes. The hydrophilic colloids contained polysaccharide- and protein-like compounds and were likely aggregated compounds rather than single molecules. Rapid fouling attributed to colloidal fractions has also been reported by Jarusutthirak et al. (2002) and Park et al. (2006).

2.4.3 Fluorescence Emission - Excitation Matrix (EEM) Spectroscopy

Fluorescence spectroscopy can be operated in a single scan mode or a 3D mode (EEM). Single scan modes operate as either a varying excitation wavelength with emission measured at a fixed wavelength, or a fixed excitation wavelength and emission measured at a varying wavelength. This method provides an overall view of features within a selected spectral range and is useful in quickly identifying previously standardised compounds. EEM operates by varying both the excitation and emission wavelengths, providing a three dimensional topographical graph of all fluorescing compounds within a sample (Her et al., 2003; Zepp et al., 2004; Sierra et al., 2005). Chen et al. (2003) conducted a comprehensive EEM study of NOM fractions and model compounds and proposed regional boundaries to classify EEM peaks (Figure 2.1). Regions I and II are associated with protein-like extracellular organic matter, which comprise aromatic amino acids. Region III is associated with fulvic acid-like

compounds. Region IV is associated with soluble microbial by-product-like compounds, mainly proteins and polysaccharides. Region V is associated with humic acid-like compounds. These regional boundaries are well supported by findings made in other investigations of NOM fractions and model compounds (McKnight et al., 2001; Her et al., 2003; 2004; Lee et al., 2006a).

It has been found that HPO fractions appear in Region V (humic acid-like), TPI in Regions IV & V (SMP- and humic acid-like), colloids in region IV, and extracted AOM in regions IV & V (Her et al., 2006; Lee et al., 2006a).

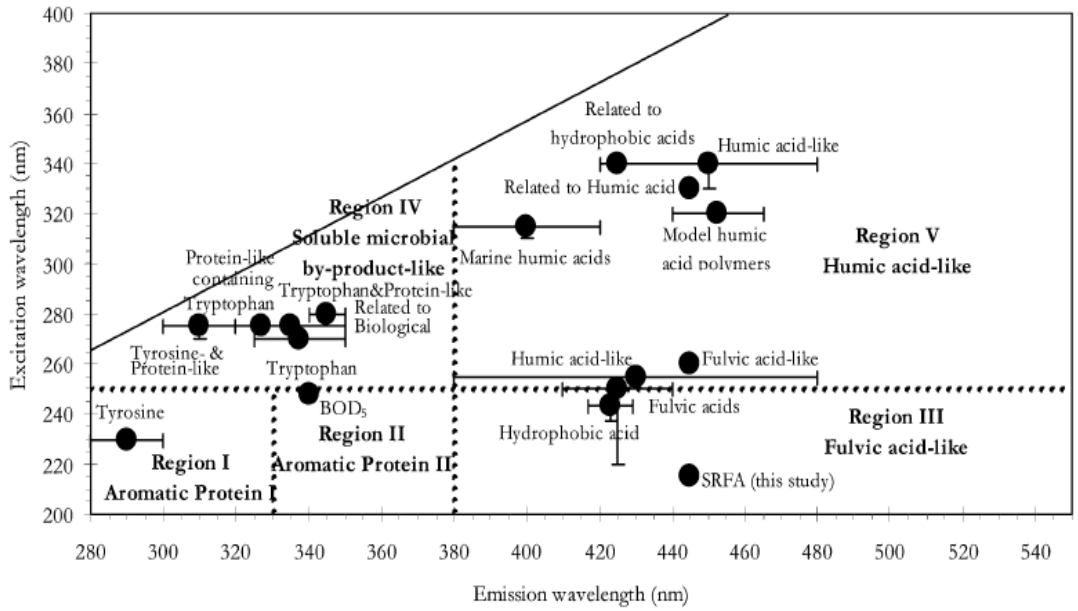


Figure 2.2: Excitation and emission wavelength boundaries for natural organic matter (Chen et al. 2003)

As previously stated, Lee et al. (2006a) found the colloidal fraction of surface water samples to cause rapid fouling of filtration membranes. EEM analysis of the colloids and an AOM sample with comparable fouling propensity, revealed a similar peak in Region IV suggesting that the polysaccharide-like compounds found in each sample were responsible for the increased fouling.

2.4.4 High Performance Size Exclusion Chromatography

High Performance Size Exclusion Chromatography (HPSEC) separates constituents within a sample by apparent molecular weight. Analysis of HPSEC fractions can be conducted by mass spectroscopy, DOC detection, UV absorbance, fluorescence, or a combination of these methods (Her et al., 2004; Habarou et al., 2005; Davey et al., 2006). Samples with high molecular weight compounds have been found to foul filtration membranes faster than

samples without, however this may change for membranes with smaller pore sizes (Lozier et al., 2007). These macromolecular compounds (greater than 10,000 Da) are associated with colloidal particles (Jarusutthirak et al., 2002; Her et al., 2004; Lee et al., 2006a). HPSEC analysis of fouling layer constituents show the strong presence of macromolecules (20,000 - 50,000 Da) which are similar in size to AOM, SMP and model protein compounds, suggesting that these colloids most likely originated from microbial activity and contain proteins and polysaccharides (Habarou et al., 2005; Park et al, 2006).

Analysis by HPSEC-UV is problematic as absorbance is generally measured at a wavelength of around 254 nm. Colloidal fractions do not absorb well at these wavelengths as they comprise proteins and polysaccharides which contain little to no UV-absorbing aromatic or conjugated bonds, compared with lower molecular weight compounds such as humic and fulvic acids (Zularisam et al., 2006). This means detection of polysaccharide peaks is difficult and DOC detection of HPSEC fractions is preferable.

2.4.5 Pyrolysis Gas Chromatography – Mass Spectroscopy

Pyrolysis Gas Chromatography – Mass Spectroscopy (PyroGC-MS) is useful in identifying molecular weight constituents by pyrolysis breakdown products (Davey et al,. 2006). Park et al. (2006) characterised AOM extracted from *Synedra* sp. by sonication, as having protein-related products, humic acid having polyhydroxyaromatic products, colloids having polysaccharide, protein, and amino sugar products, and SMP as having amino sugar products. They also identified the colloid products as similar to AOM and SMP products, and concluded that the colloids were derived from AOM and SMP.

PyroGC/MS analysis of MF and UF fouling layer constituents identified products of polysaccharides which corresponded to extracellular polymeric fractions, and amino sugar products (Habarou et al., 2005). Habarou et al. noted that the feed and permeate of a solution containing EPS were virtually identical, however the fouling layer contained a prominent amount of hydroxypropanone compared with cyclopentenone, indicating that a particular type of polysaccharide sorbed onto the membrane. They postulated that a lower molecular weight polysaccharide preferentially sorbed onto the surface of the membrane and was not recoverable by backwashing.

All these analysis methods provide specific information on constituents within a fouling layer and can be used to monitor the effectiveness of treatment processes.

2.4.6 Scanning Electron Microscopy (SEM)

SEM provides high resolution images of the physical appearance of the membrane and fouling layer surface. This is useful in analysing how a fouling layer is structured, the plugging of pores, and microbial colonisation (Sadr Ghayeni et al., 1999; Davey et al., 2006). Lee et al. (2004) observed a build-up of fouling material on the internal and external surface of a MF membrane, and the formation of globular fouling structures from filtering surface water. Davey et al. (2006) used SEM to investigate the inside surface of an UF membrane and found a build up of internal fouling material. Fan et al. (2008) investigated Al^{3+} and Fe^{3+} pretreatments of secondary treated effluent from a wastewater treatment plant and the effect on MF filterability, and showed structural differences in the cake-layer using an Environmental SEM. This type of SEM is useful for membrane analysis as other SEM techniques can result in changes in structure of the foulant layer through sample preparation such as drying.

2.5 Fouling Mitigation / Pre-treatment

The use of different membrane materials and surface modifications have been successful in reducing fouling in specific applications. The inclusion of a urea group in the surface of an RO membrane showed superior performance to similar membranes due to reduced adhesion of microbial cells (Ridgway et al. 1984; Flemming & Schaule, 1988; Jenkins & Tanner, 1998). Other surface modifications include UV-assisted photochemical graft polymerisation and polymerisation of acrylamine using argon and carbon dioxide plasmas (Escobar et al., 2005). These showed reduced fouling but also reduced permeability. Research is required to develop new surface modifications and membrane materials that reduce fouling, however it is not considered likely that one membrane type will sufficiently prevent fouling due to the variety of compounds found in all waters. Instead, pre-treatments are used to remove problematic compounds or alter their composition to reduce the likelihood of fouling.

Shon et al. (2004; 2005) tested a variety of pre-treatments on secondary sewage effluent. Flocculation using $FeCl_3$ was effective in removing the majority of larger MW hydrophobic organics and some smaller components. Adsorption with powdered activated carbon (PAC) further removed larger and smaller MW organics (90% TOC removal) leading to virtually no flux decline on a UF membrane (sulfonated polysulfone, 17.5 kDa MWCO).

Humbert et al. (2005) investigated a number of anion exchange resins for the removal of NOM from high DOC content surface water. MIEX and IRA938 resins exhibited the fastest

removal of NOM from water. MIEX was very effective in removing high molecular weight compounds as well as a large proportion of small molecular weight compounds that were refractory to coagulation/flocculation treatment. These findings are supported by Zhang et al. (2006). Dosing wastewater effluent with 10 mL/L MIEX was found to reduce DOC by 60% (Fan et al., 2008). HPSEC-Fluorescence conducted on MIEX-treated effluent suggested the presence of protein-like materials (Humbert et al., 2005) however these did not seem to have noticeable effect on flux decline (Fan et al., 2008).

Chapter 3 - Methods

3.1.1 Filtration experiments

Filtration experiments were conducted using an 8050 Amicon dead-end stirred cell unit which stirred at 240 rpm. Permeate volume was measured using an Ohaus Explorer bench top balance connected to a computer; weights were recorded using Ohaus Balance Talk software every 60 seconds. The 2 L feed tank was pressurised with nitrogen gas at 70 kPa for MF and 110 kPa for UF. These feed pressures were selected to correspond with previous pilot-plant investigations conducted at WTP.

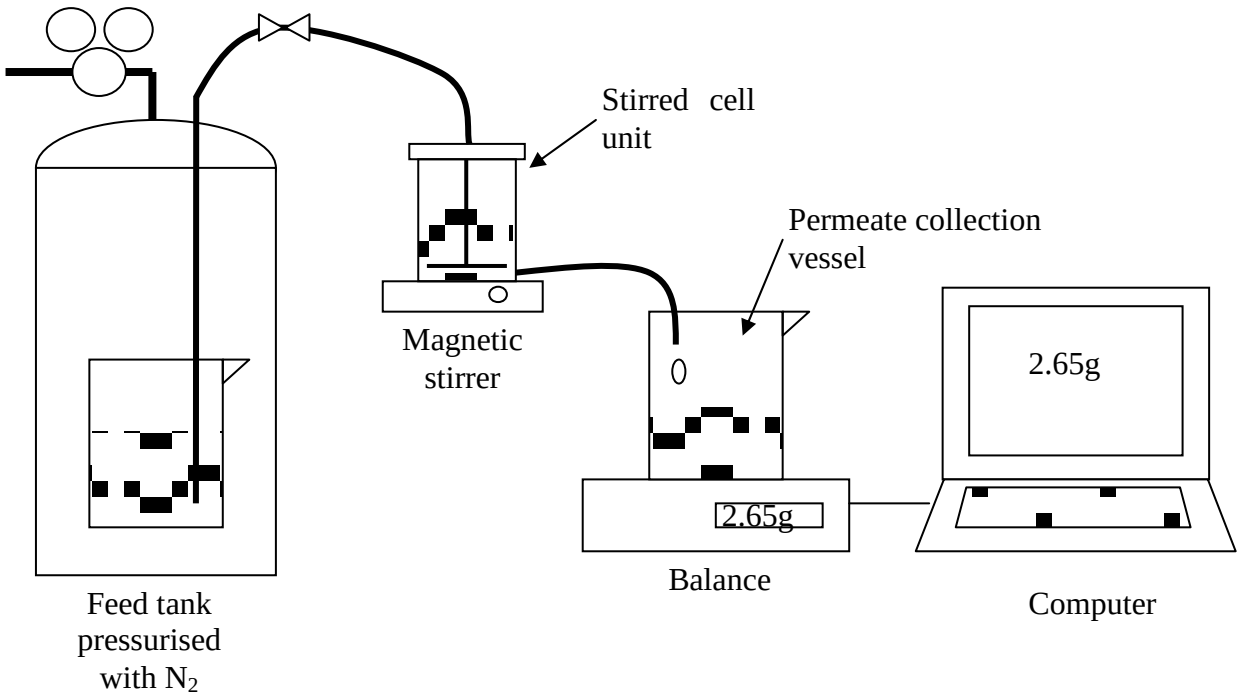


Figure 3.1: Schematic of dead-end stirred cell filtration rig

The unit was flushed twice with 1 L of Milli-Q water before and after every experiment to purge the system of residual sample. Membranes were placed in Milli-Q water with agitation for 24 hours prior to experiments. After membranes were fitted to the stirred cell unit they were flushed with 2 L of Milli-Q water at the relevant fixed pressure and the flux was recorded as "pure water flux" (J_o), 3700 ± 180 and 1500 ± 100 LMH for MF and UF respectively. Feed samples were at 19 ± 1 ^oC prior to commencement of filtration experiments. Permeates were collected in glass vials and kept at 4^oC, or in PET bottles where the solution was acidified with 2M HCl to pH 2 and kept at 4^oC prior to fractionation of organic carbon.

Membrane flux was determined as L/m^2hr, abbreviated to LMH, as per Equation 3.1. The change in flux (Eq. 3.1) was reported relative to specific permeate volume (L/m^2), or units of total organic carbon delivered to the membrane (g/m^2) as per Equations 3.2 and 3.3 respectively.

$$Flux\ (J) = \frac{\Delta V}{A \times \Delta t} \qquad \text{Equation 3.1}$$

$$Specific\ Permeate\ Volume\ (P_v) = \frac{V_t}{A} \qquad \text{Equation 3.2}$$

$$Delivered\ OC = TOC \times P_v \qquad \text{Equation 3.3}$$

where ΔV = change in volume of permeate over time, $V_2 - V_1$ (L)

A = area of membrane (m^2)

Δt = change in time, $t_2 - t_1$ (hours)

V_t = total volume of permeate at time t_n (L)

TOC = total organic carbon (g/L)

Additional to reporting flux, membrane resistance was determined. Membrane resistance was calculated as per Equation 3.4.

$$Resistance\ (R) = \frac{\Delta P}{J \times \mu} \qquad \text{Equation 3.4}$$

where R = membrane resistance (m^{-1})

ΔP = applied pressure (Pa)

J = permeate flux (m/s)

μ = viscosity of water (Pa.s)

3.1.2 Filtration Membranes

Membranes used in ultrafiltration experiments were polyethersulphone (PES) with 100 kDa nominal molecular weight cut-off (Biomax PB, Millipore). Microfiltration experiments were conducted using hydrophilic polyvinylidene fluoride membranes with 0.22 µm pore size (Durapore, Millipore). Prior to experiments these were wetted for 24 hrs with Milli-Q water and flushed with 2 L of Milli-Q water to remove any preservative agents and ensure compaction of membranes.

3.1.3 Irreversible Fouling Resistance – Backwashing

Once the flux declined to an equivalent of 55 L/m^{2}h (LMH) the membrane was hydraulically cleaned by surface washing using 20 mL of Milli-Q water at 40 kPa, and placed upside down in the stirred cell unit. The membrane was backflushed with 100 mL of Milli-Q water at 70 kPa for MF and 110 kPa for UF and returned to its previous orientation. Milli-Q water was then filtered at the appropriate pressure and the resistance of the cleaned membrane was measured (R_w). Irreversible fouling was determined by R_w - R_o and indicated the level of irreversible fouling propensity of the feed water. Each test was done in triplicate and ceased once carbon loading on the membrane was equal for all samples to provide comparable data.

$$\textit{Irreversible Fouling Resistance } (R_{irr}) = R_w - R_o \qquad \text{Equation 3.5}$$

Where R_o = Resistance through new membrane

R_w = Resistance through cleaned membrane

3.1.4 UV-vis absorbance (A_{254})

Absorbance at 254 nm was determined using a Unicam UV/vis Spectrometer UV2 using VisionPro software by ThermoSpectronic. Samples were filtered (0.45 µm cellulose acetate, Whatman) prior to analysis to remove interference by suspended matter.

3.1.5 Fluorescence analysis

Excitation-emission matrices (EEM) were prepared using a Perkin Elmer Luminescence Spectrometer LS50B and Perkin Elmer Fluorescence WinLab 1.0 software. Excitation range was 200-600 nm and emission range was 200-540 nm. Samples were filtered (0.45 µm cellulose acetate, Whatman) prior to analysis to remove absorbance interference by suspended matter.

3.1.6 Organic carbon analysis

Concentration of organic carbon was determined using a Sievers 820 TOC Analyzer. Triplicates of each sample were analysed in triplicate, therefore nine measurements were done on each sample and the averaged result reported.

Total organic carbon (TOC) is defined as the measurable concentration of organic carbon that passes through a 1 µm filter (Whatman GF/B).

Dissolved organic carbon (DOC) is defined as the measurable concentration of organic carbon that passes through a 0.45 µm filter (Whatman CA).

3.1.7 Total Suspended Solids

Total suspended solids was determined by mass difference. Two 300 mL glass beakers were cleaned as per section 3.1.14 and placed in a desiccator after firing to cool; they were then weighed on an analytical balance. A known volume of sample (200.0 mL) was passed through a 0.45 μm filter (Whatman CA), the permeate was decanted into one of the 300 mL beakers; two portions of 25 mL of Milli-Q water were used to rinse the filtration rig and decanted into the same beaker. An equal amount (200.0 mL) of unfiltered sample was decanted into the second 300 mL beaker. The beakers were sealed with aluminium foil and placed in an oven at 100 ^{o}C until no water was present in the beakers, and dried for a further 4 hrs to ensure adequate drying. The beakers were placed in a desiccator to cool and weighed using an analytical balance. The determination was done in triplicate. Total suspended solids was determined as per the equation below.

$$Total\ Suspended\ Solids (TSS) = \frac{(W_o - B_1) - (W_f - B_2)}{V} \qquad \text{Equation 3.6}$$

Were B_1, B_2 = weight of beaker

W_o = weight of B_1 with dried unfiltered sample

W_f = weight of B_2 with dried filtered sample

V = volume of sample (0.2000 L)

3.1.8 Fractionation of organic matter

The dissolved organic carbon (DOC) in samples was separated into hydrophobic (HPO), transphilic (TPI), and hydrophilic (HPI) fractions using polymeric resins (Leenheer et al.,1981; Cho et al., 2000). Supelite DAX-8 resin was used to remove HPO acids whilst Amberlite XAD-4 resin was used to remove TPI acids.

Prior to initial experimentation the resins were soaked in methanol and thoroughly washed with Milli-Q water to remove all residual organic material. The resins were then placed in individual 200 x 15 (i.d.) mm glass columns with sintered glass supports. Samples were prefiltered (0.45 μm cellulose acetate, Whatman), acidified to pH 2 with 2M HCl and passed through DAX-8 and XAD-4 columns in sequence using a peristaltic pump at 3 mL per minute. Samples of column effluents were collected in triplicate and analysed for DOC.

The fraction concentrations were calculated by difference of DOC concentration between effluents and the original prefiltered sample.

RAW = Original DOC Equation 3.7

HPO = RAW – DAX-8 column effluent DOC Equation 3.8

TPI = DAX-8 effluent DOC – XAD-4 column effluent DOC Equation 3.9

HPI = XAD-4 column effluent DOC Equation 3.10

After every experiment 200 mL of 0.1M NaOH was pumped through each of the columns to remove the surface bound organics followed by 1 L of Milli-Q water. The effluent DOC was measured and compared with the DOC of the Milli-Q water to ensure that no contamination between samples occurred.

3.1.9 High performance size exclusion chromatography – UV detection

The molecular weight distribution of UV-absorbing organics was determined using high performance size exclusion chromatography and detection at 260 nm (HPSEC-UV). The analyses for the WTP samples were done at the Australian Water Quality Centre, Adelaide, South Australia, using the method as per Buchanan et al., (2005), those for the algal samples were done at the Curtin Water Quality Research Centre, Curtin University of Technology, Western Australia. Samples were prefiltered (0.45 μm) to prevent clogging of the separation column.

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

ATR-FTIR analysis of membranes were conducted using a Perkin Elmer Spectrum 100 Fourier Transform Infrared with ATR attachment. Membranes were dried under sterile conditions and stored in a desiccator until analysis.

3.1.11 Environmental Scanning Electron Microscopy (ESEM)

ESEM analysis was conducted using an FEI Quanta 200 ESEM at the RMIT Microscopy and Microanalysis facility. Samples were analysed in ESEM mode (low vacuum, high humidity) allowing for analysis of hydrated membrane and fouling layers, therefore reducing the likelihood of compaction due to sample drying.

3.1.12 Cultivation of *Anabaena circinalis*:

An *Anabaena circinalis* (CS-code: 541/06) culture was obtained from CSIRO Microalgae Research Centre (Hobart, Tasmania, Australia). The growth medium was MLA (Bolch and Blackburn, 1996), prepared as per Appendix 2 with components as listed below. Inoculum volumes of 10 mL/L of growth medium were incubated in a growth cabinet at 22^{o}C under 24 hr illumination by two 1 m fluorescent tubes mounted on the door. Subcultures were made every 15-20 days. Samples were cultivated in 5 L erlenmeyer flasks and constantly aerated to ensure mixing and sufficient CO_2 levels. The air line was fitted with a charcoal filter and 0.45 µm filter to prevent pollutants and microbes from entering the cultures. All glassware was cleaned and autoclaved at 121^{o}C for 20 minutes prior to use. All subculturing, sample extraction and sample handling was conducted aseptically in an Email Bioair CWS sterile cabinet.

Table 3.1: MLA growth medium constituents

Chemical	**Concentration (mg/L)**
$MgSO_4.7H_2O$	49.4
$NaNO_3$	170
K_2HPO_4	69.6
H_3BO_3	2.47
Biotin	5×10^{-5}
Vitamin B_{12}	5×10^{-5}
Thiamine HCl	0.10
Na_2EDTA	4.36
$FeSO_2.7H_2O$	1.625
$NaHCO_3$	0.60
$MnCl_2.4H_2O$	0.36
$CuCl_2.2H_2O$	6.83×10^{-4}
$ZnCl_2$	1.043×10^{-3}
$CoCl_2.6H_2O$	1.0×10^{-3}
$Na_2MoO_4.2H_2O$	6.0×10^{-4}

3.1.13 Measurement of Chlorophyll-a

The method for chlorophyll-a measurement was adapted from ESS Method 150.1 (Wisconsin State Lab, 1991). A sample was passed through a 1 μm glass fibre filter (Whatman GF/B). The filter was then placed in a light-proof container with 20 mL of 90% acetone and left for 24 hrs at 4°C. The solvent solution was then warmed to room temperature and transferred into a 25 mL volumetric flask, the filter was rinsed with a small volume of fresh solvent which was then added to the flask, and the solution was made up to the mark. The solution was then filtered (0.45 μm PVDF, Millipore) to remove suspended matter. Absorbance was measured at 630, 645, and 663 nm using a Unicam UV/vis Spectrometer UV2 and a 5 cm sample cell. The absorbance was also measured at 750 nm to determine if turbidity correction was required. The concentration of chlorophyll-a was determined by the following equation:

$$Chl-a\ (\mu g/L) = \frac{[11.64(Abs_{663}) - 2.16(Abs_{645}) + 0.10(Abs_{630})]\,E(F)}{V(L)} \qquad \text{Equation 3.11}$$

Where F = *Dilution factor*

E = *Volume of acetone used for extraction (mL)*

V = *Volume of water filtered (L)*

L = *Cell path length (cm)*

3.1.14 Glassware

All glassware was prepared by cleaning with Decon 90, rinsing with deionised water, soaking overnight in 5% nitric acid, rinsing with DI water, and firing at 550°C for 4 hrs and then sealed before use. Only analytical glassware was not fired.

3.1.15 Milli-Q water

All references to Milli-Q water refer to high purity water produced by a Millipore Elix10 unit (EC > 18 mΩ, TOC < 8 ppb).

Chapter 4 - Membrane Filtration of Wastewater

4.1 Introduction

Recycling treated wastewater by means of membrane technology is attractive due to its ability to remove particulates, bacteria, viruses, and ions. However, due to high concentrations of EfOM membrane fouling is an inherent problem.

At the Western Treatment Plant (WTP) in Werribee, Victoria, the influent wastewater consists of domestic and industrial waste. The wastewater is diverted into one of two treatment trains: 25 West or 55 East. These treatment trains are similar in design concept but have slight operational and pond size differences (Figure 4.1 and Appendix 1). Influent passes through anoxic and aerobic ponds before undergoing activated sludge treatment, after which it is clarified. The clarified effluent is transferred to a series of large ponds, or lagoons, for further treatment by microbes, phytoplankton and zooplankton, solar radiation, and aeration through wave action. The lagoon treated effluent is either transferred to the receiving effluent reuse channel (a 6 km channel/pipeline) and thence to the head of road storage (HORS) for disinfection and recycling, or discharged into Port Phillip Bay. The process at WTP is unusual due to the sequential activated sludge and lagoon treatments.

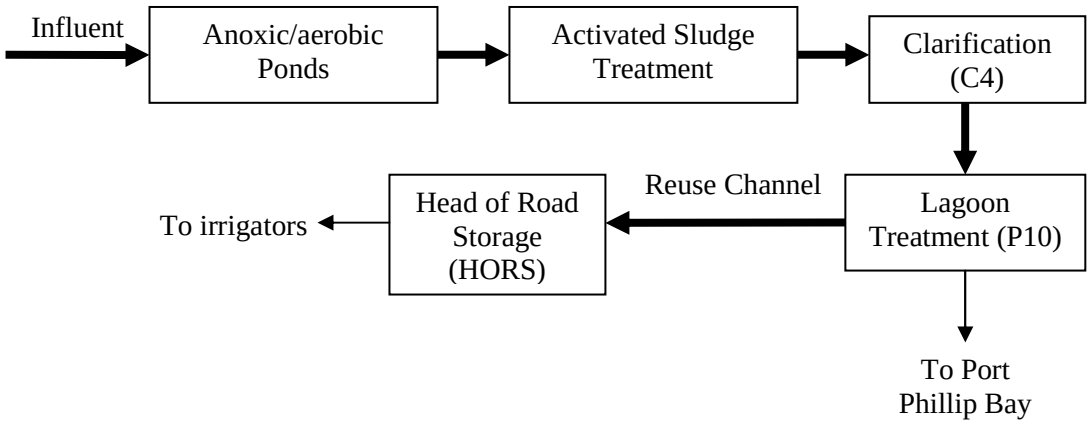


Figure 4.1: Typical schematic of WTP treatment trains

Currently the recycled water from this plant is disinfected by UV radiation and chlorine and reused by local irrigators. However, due to industrial wastewater inputs and saline aquifer intrusion, the treated water is mildly saline (~1700 $\mu S.cm^{-1}$) and so is not suitable for long term agricultural use. For this reason salt reduction by reverse osmosis (RO) has been proposed to improve the water quality. Due to high concentrations of EfOM and the presence of microbes in the treated wastewater, and the high rejection rate of dissolved components by

RO membranes, pre-treatment is required to reduce the organic fouling and prevent biofouling. Microfiltration (MF), ultrafiltration (UF) or even nanofiltration (NF) membranes are commonly used as pre-treatments to RO because they are quick and effective in removing larger to smaller organic matter and microbes (Goosen et al., 2004). The propensity for fouling, and characterisation of the organic components in the fouling layer, on MF and UF membranes were investigated and the results are reported in this chapter.

The treatment process at WTP provided an opportunity to test the fouling rate of a single feed water source with varied levels of treatment. Samples were collected from the HORS site, which receives water from the final pond in the lagoon system (P10) the reuse channel, the overflow from one of the four clarifiers (C4), and the overflow from P10. Samples were collected fortnightly and assigned batch numbers (Table 4.1). During spring and summer the lagoon systems occasionally experience algal blooms. Algal blooms have been reported to cause rapid reduction in membrane flux (Montgomery Watson, 1997; Her et al., 2004). The fouling propensity of clarified activated sludge treated effluent and lagoon treated effluent were examined. Water transportation and land use were two major considerations for any future membrane filtration plant at WTP, therefore the most suitable feed water needed to be determined.

The aims of this chapter are to investigate which source of feed water from WTP provides the greater flux rate for MF and UF treatments, and identify which water properties contribute to the fouling of these membranes.

Table 4.1: Water quality and sample dates of source waters

Batch Number	B1		B2		B3		B4		B5	
Sample date	2/10/2006		16/10/2006		30/10/2006		13/11/2006		27/11/2006	
Sample	HORS	C4	HORS	C4	HORS	C4	HORS	C4	HORS	C4
TOC (mg/L)	12	17	13	17	15	10	14	24	12	17
SS (mg/L)	18	8	8	10	4	14	16	27	10	23
Turbidity (NTU)	18	2.6	6.1	4.1	1.4	7.7	6.1	7.7	6	7.2
TDS (mg/L)	960	920	960	910	1100	960	1000	960	1000	880

4.2 Results and Discussion

4.2.1 Flux Decline

Samples of clarifier effluent (C4) and lagoon treated effluent (HORS) were tested to determine if the lagoon treatment improved the filterability of the water or if clarified effluent was more suitable for membrane filtration processes.

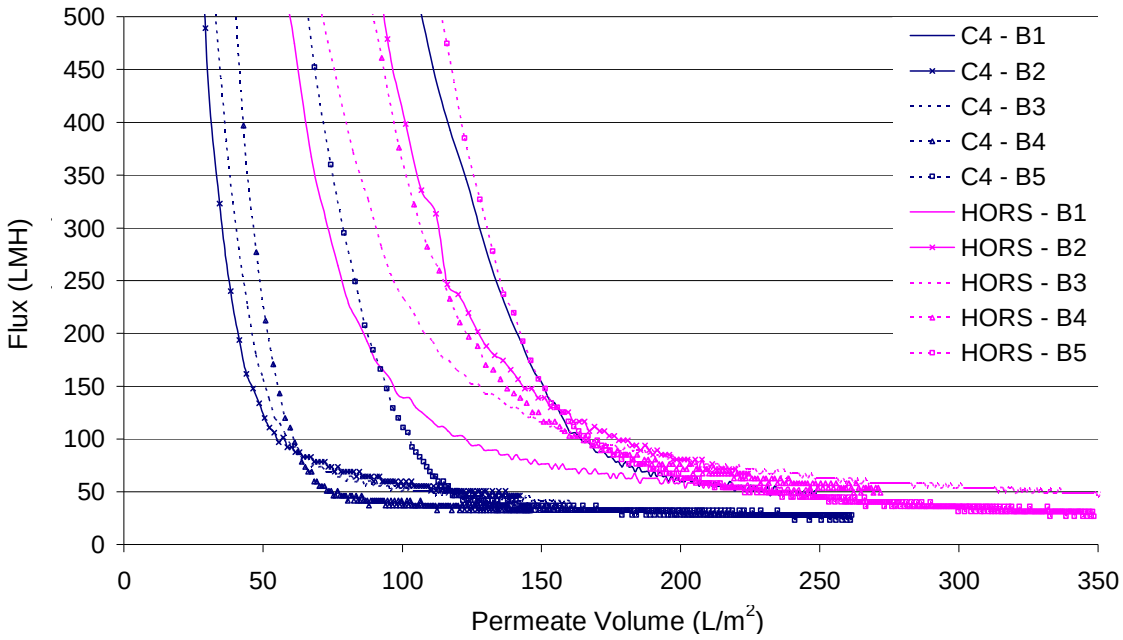


Figure 4.2: MF flux profiles of HORS and C4 samples

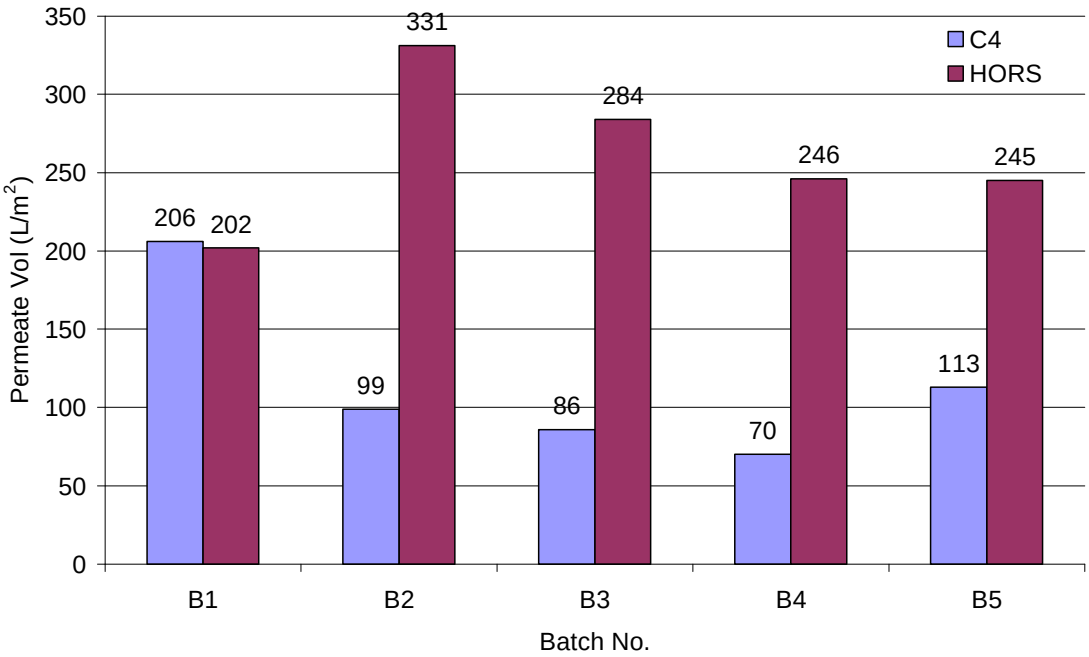


Figure 4.3: Specific volumes of MF permeate for HORS and C4 samples at a final flux of 55 LMH.

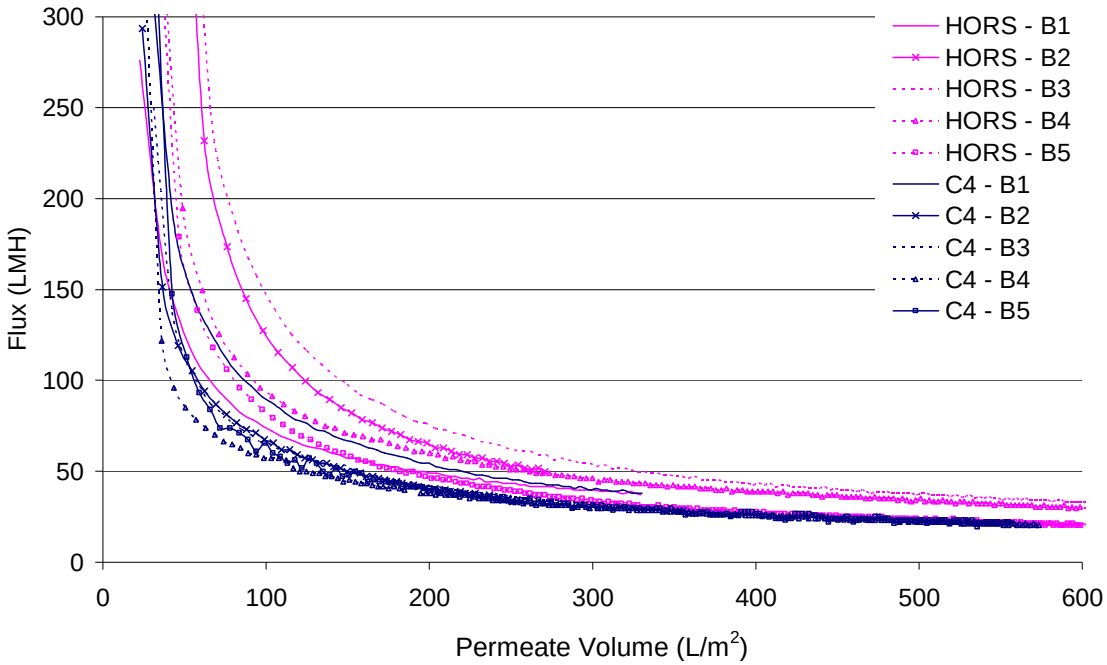


Figure 4.4: Flux profiles of HORS and C4 samples for UF membrane

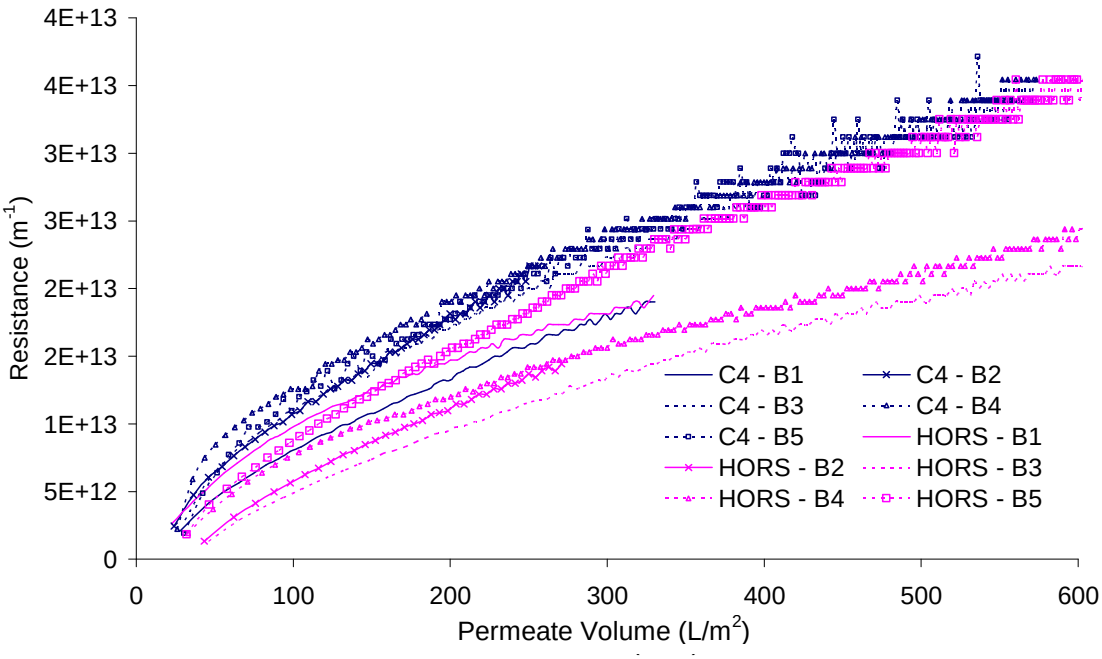


Figure 4.5: Resistance profiles of HORS and C4 samples for UF membrane

For MF the HORS sample did not foul as rapidly as the C4 sample (Figure 4.2). Samples from C4 quickly fouled the membrane causing a rapid drop in flux rate and a lower quasi-steady state flux compared with HORS samples.

A flux rate of 55 LMH was used as an arbitrary endpoint to represent significant flux decline (Section 3.1.3). HORS samples gave more than 200 L/m^2 of permeate before the flux rate reached 55 LMH, compared with C4 samples which typically gave only 100 L/m^2 of permeate (Figure 4.3). Of the five batches the HORS samples typically provided better flux profile and permeate volume compared with the C4 samples. The one exception was batch B1, for which similar results were obtained.

Similar to MF, for UF the HORS samples did not foul as rapidly as the C4 samples (Figure 4.4). Samples from C4 quickly fouled the membrane causing a rapid drop in flux rate and a lower quasi-steady state flux compared with HORS samples. The increase in membrane resistance illustrates the difference in performance between these two samples more clearly (Figure 4.5). Nearly all the HORS samples developed lower resistance than the C4 samples, thus demonstrating a lower degree of membrane fouling by HORS samples. The reduced rates of fouling resulted in an increase in permeate production (Figure 4.6). Although the variation in permeate volume between the samples was not as great for UF as it was for MF, the trend for HORS samples having higher permeate volumes than C4 samples (50 to 150 L/m^2 more) remained the same.

The general trend was that HORS samples provided slower flux decline and higher permeate volume than C4 samples, although exceptions were batch B1 where C4 and HORS samples performed similarly, and HORS sample B5, which fouled almost as rapidly as the C4 samples.

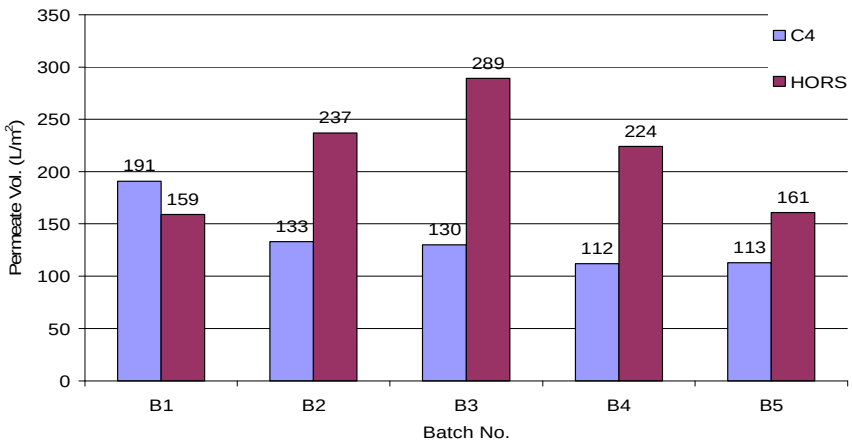


Figure 4.6: Specific permeate volumes of UF permeate for HORS and C4 samples at a final flux of 55 LMH.

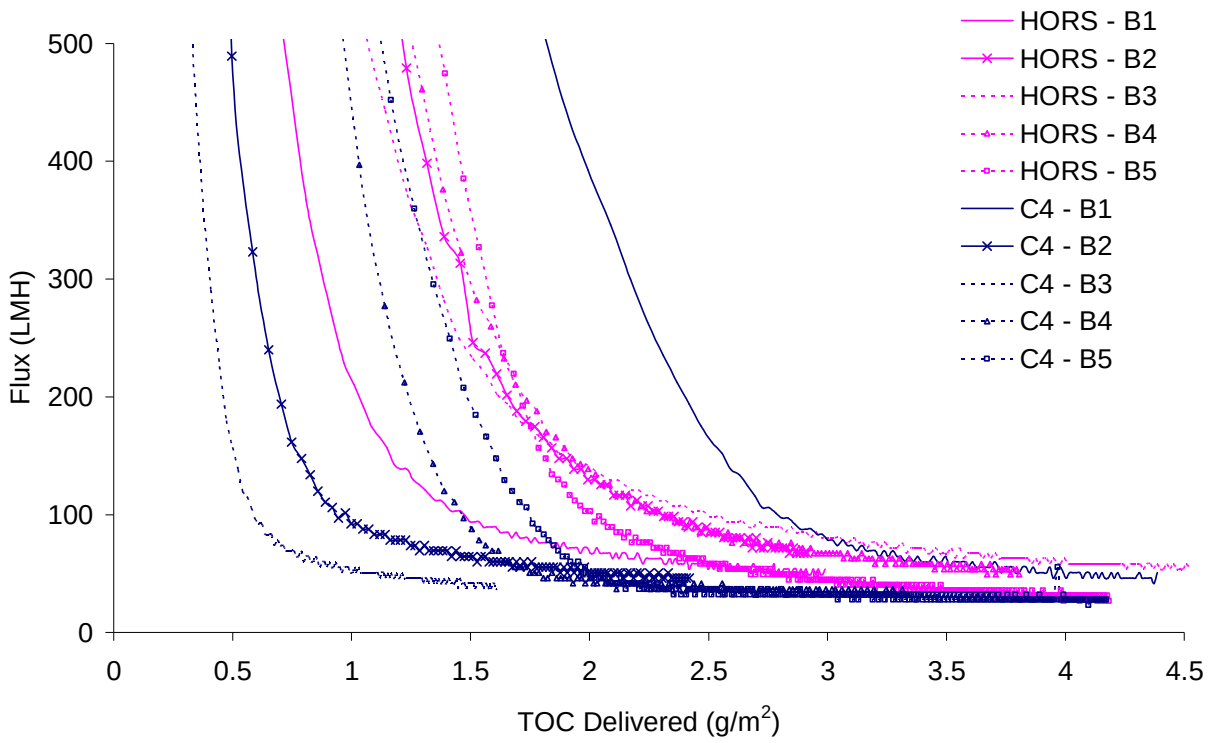


Figure 4.7: MF flux profiles of HORS and C4 samples in terms of TOC delivered

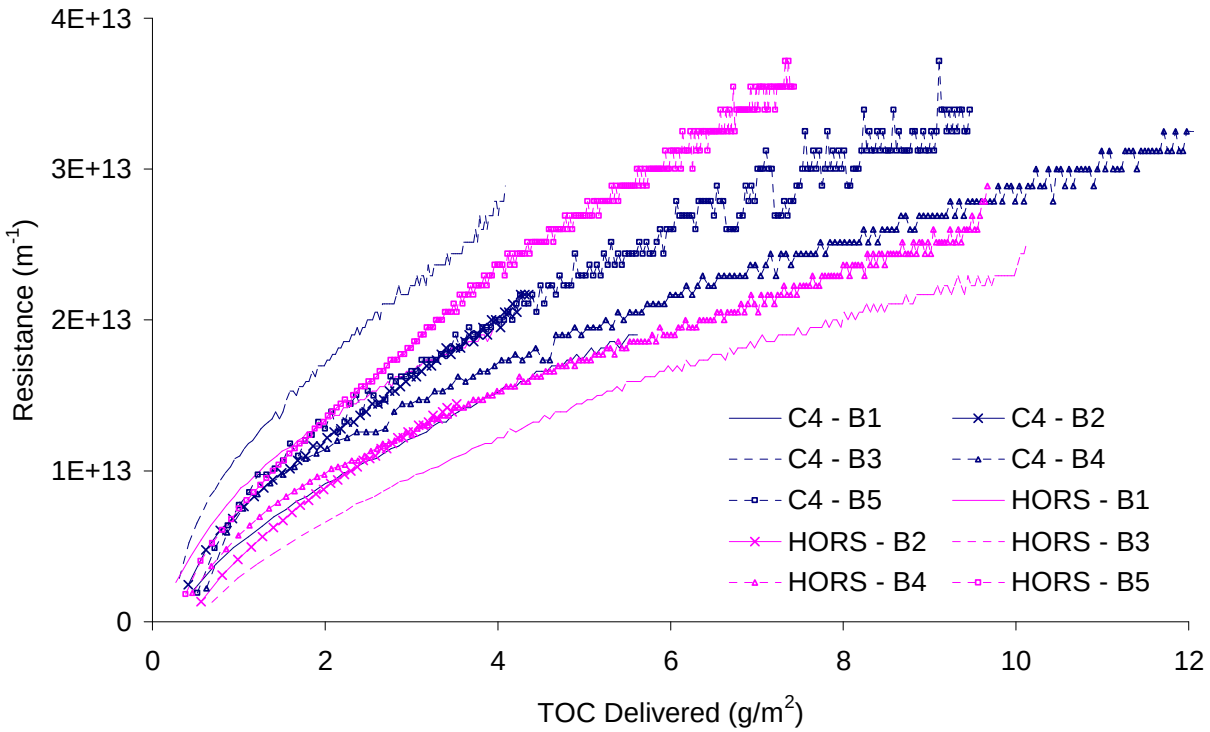


Figure 4.8: UF resistance profiles of HORS and C4 samples in terms of TOC delivered

4.2.2 Significance of TOC

The association between TOC concentration and membrane fouling is well reported in the literature (Goosen et al., 2004). Typically C4 samples contained a higher concentration of TOC compared with HORS samples (Table 4.1) and therefore a higher fouling rate was to be expected. However other factors such as organic composition and the presence and nature of particulate matter have also been associated with an increase in fouling rate.

Figure 4.7 shows the flux profiles of the HORS and C4 samples in terms of TOC delivered to the MF membrane surface. Similar to Figure 4.2, C4 samples fouled the MF membrane more rapidly compared with the HORS samples. For all but B1, C4 samples fouled the membrane more rapidly and had a lower quasi-steady state flux. This suggests that differences, other than TOC concentration, between the samples caused the C4 samples to foul MF membranes more rapidly than HORS samples.

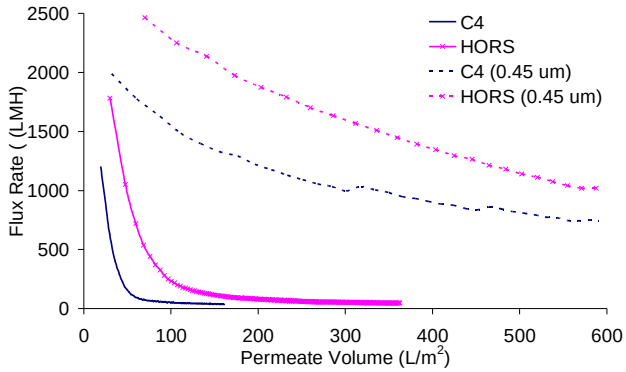
Figure 4.8 shows the resistance profiles of the HORS and C4 samples in terms of TOC delivered to the UF membrane surface. Unlike Figure 4.5 there is no clear differentiation between the HORS and C4 samples. However, for each batch, C4 samples fouled more rapidly than HORS samples with the one exception of batch B5. This trend suggests that differences in organic composition and/or other water quality characteristics caused the C4 samples to foul the UF membrane more rapidly.

4.2.3 Influence of Suspended Solids

The presence of suspended solids played a significant role in all samples in terms of MF filterability. As expected, after the removal of suspended solids by filtration (0.45 μm membrane) the rate of flux decline was not as rapid (Figure 4.9a), however the fouling propensity of C4 samples remained higher than for HORS samples, suggesting differences in the dissolved organic content. Suspended solids are likely to block pore openings as they are drawn by permeate drag forces to the membrane surface. Surface cleaning tests for early samples confirmed the reversibility of the surface fouling layer with flux rate returning to 74-85% after membranes were washed with MilliQ water. This indicates that the suspended solids played a significant role in flux decline through the fouling of the membrane surface; the non-reversible fouling was likely due to internal fouling by dissolved organic matter (< 0.45 μm). The C4 samples typically had a higher concentration of suspended solids (Table 4.1) which can explain why these samples fouled the MF membrane more rapidly than the HORS samples. B1 and B2 samples of HORS had high levels of suspended solids which may

help to explain why they performed so poorly. However there were other instances where HORS and C4 had similar suspended solid concentrations yet HORS provided better flux, suggesting fouling propensity was not due to a single factor.

The removal of suspended solids also provided a marked reduction in UF resistance of all samples (Figure 4.9b). Particulate matter is not expected to cause a significant impact on UF performance as pore plugging and blocking is less likely due the very small pore sizes. Concentration of particulate matter at the membrane surface could create a porous, secondary membrane (cake layer) as found by Kwon et al. (2005). They found that the presence of the secondary membrane caused increased flux decline, whilst the lack of the secondary membrane resulted in an increase of organic compound transmission through the filtration membrane. This suggests that particulate matter may be associated with an increase in fouling rate for UF membranes. In the present study, the removal of the suspended solids may have caused the resultant cake layer to be thinner, therefore offering less resistance.



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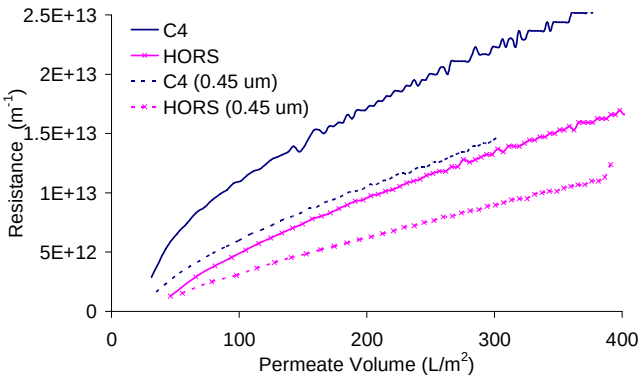


b)

Figure 4.9: Comparison of a) MF flux rate and b) UF resistance of B4 samples with and without suspended solids removed (0.45 µm filtered)

Figure 4.10 shows the relationship between total suspended solids and fouling propensity, represented by the volume of permeate before flux rate reached 55 LMH. Although it could be argued that an increase in total suspended solids resulted in an increase of fouling

propensity (albeit with very low correlation), what can be clearly stated from this graph is that parameters other than the concentration of suspended solids were responsible for increased membrane fouling. C4 samples containing similar or lower suspended solid concentrations than HORS samples fouled more rapidly, resulting in reduced permeate volume.

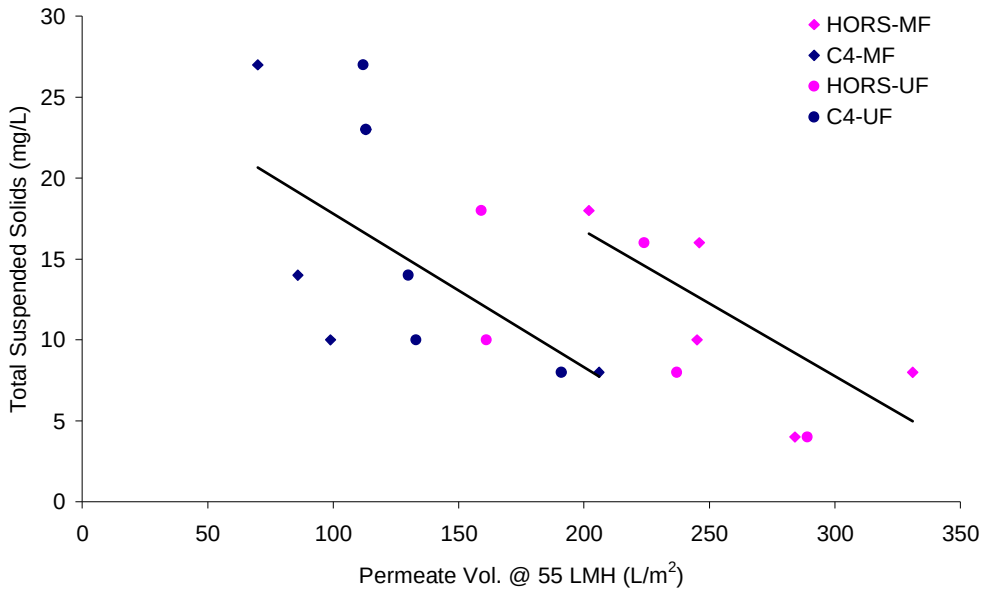


Figure 4.10: Fouling propensity of HORS and C4 on MF and UF membranes in relation to total suspended solids of samples (B1-B5)

4.2.4 Turbidity and Fouling Propensity

Suspended solids contribute to sample turbidity, it is therefore expected that the relationship between turbidity and volume of permeate produced be similar to that of suspended solids. Although it is possible to find a negative linear relationship (with poor association) between turbidity and fouling propensity (Figure 4.11) for an individual sampling point (eg., C4), that relationship cannot be used for another sampling point (eg., HORS). It can therefore be concluded that although an increase in turbidity is likely to increase the fouling rate, it is not a reliable measure of fouling propensity.

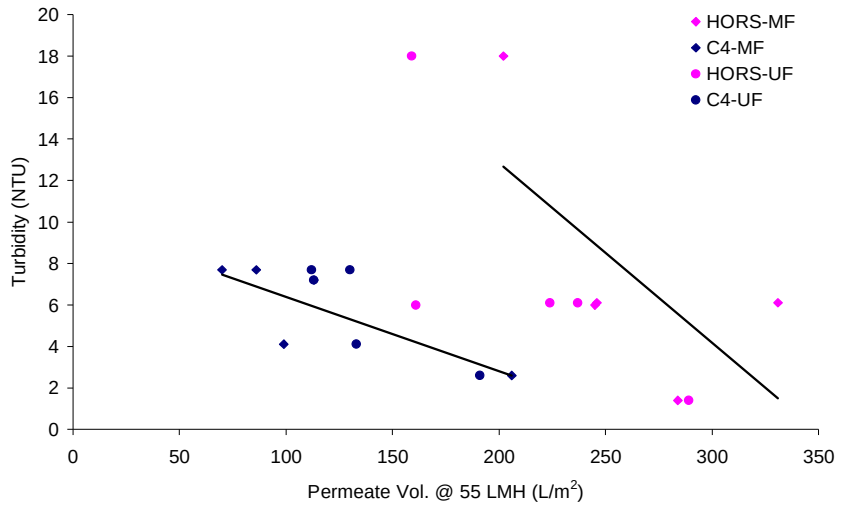
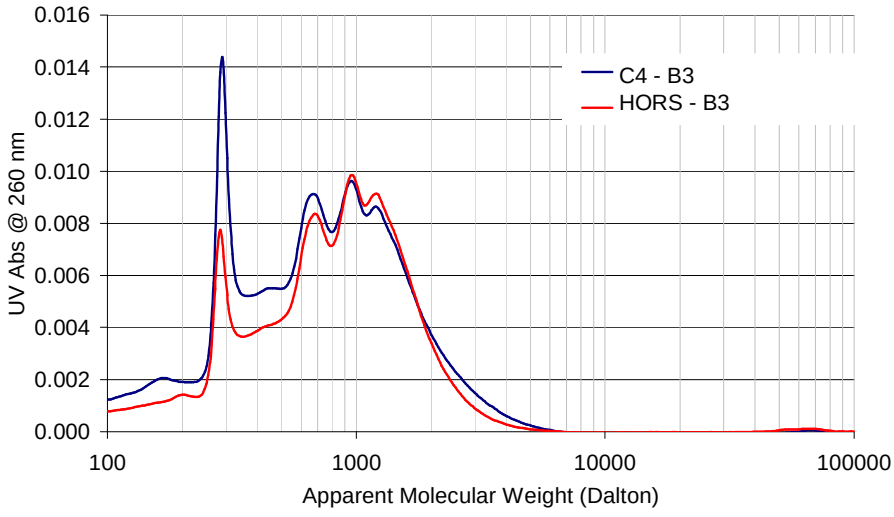


Figure 4.11: Fouling propensity of HORS and C4 on MF and UF membranes in relation to turbidity of samples (B1-B5)



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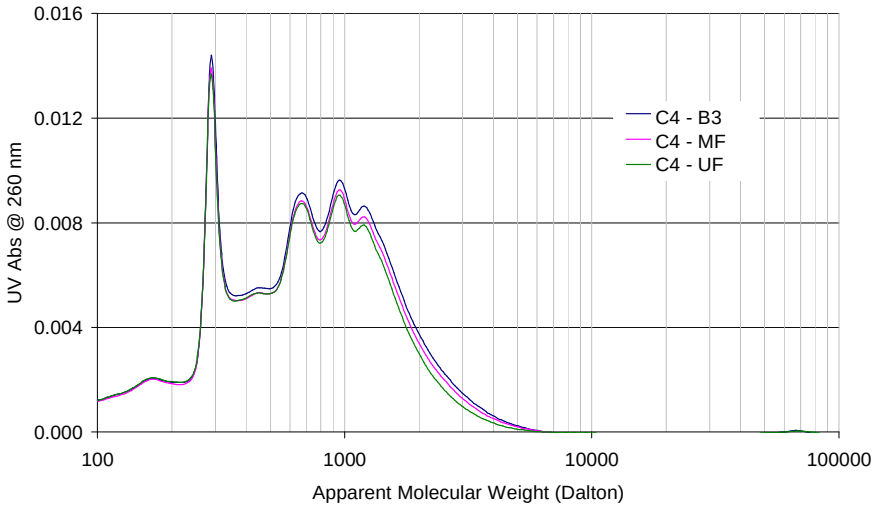


b)

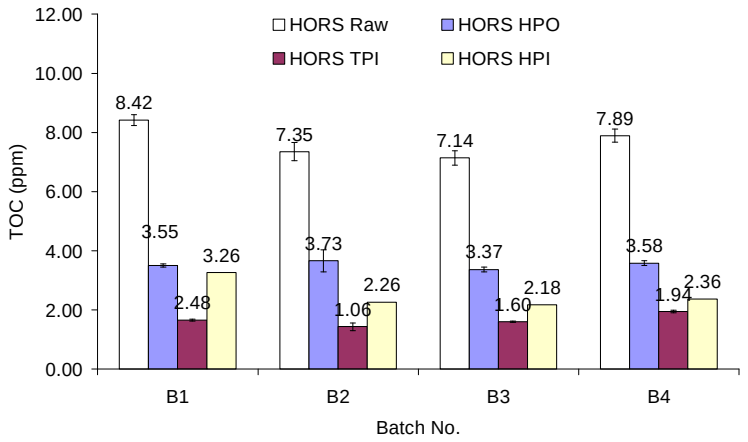
Figure 4.12: HPSEC-UV chromatograms for a) Batch 3 HORS and C4 samples and b) C4 MF and UF permeate

4.2.5 Size Exclusion Chromatography

HPSEC-UV analysis (Section 3.1.9) of HORS and C4 samples did not show any major differences in the molecular weight distribution of UV-absorbing dissolved organics (Figure 4.12a). Absorbance spectra (190-900 nm) of the samples showed they had significant absorbance at 260 nm, however not all organic compounds absorb within this range (Lee et al., 2004; Buchanan, 2005), e.g. hydrophilic macromolecules such as colloids, proteins, and polysaccharides (Her et al., 2003; 2004). Differences in peak heights from 300 and 900 Da, which are associated with humic compounds (Lee et al., 2006a; Shon et al., 2006; Lozier et al., 2007), suggest for this particular batch (B3) the HORS sample contained a lower concentration of humic compounds compared with the C4 sample. Permeates from UF and MF showed only a slight decrease in these peak heights (Figure 4.12b) indicating these compounds did not significantly contribute to fouling of the membranes. This suggests that the difference in fouling propensity between HORS and C4 samples is due to organic compounds that are not apparent in these HPSEC-UV chromatograms, eg., hydrophilic compounds such as proteins and polysaccharides that make up colloids.

4.2.6 Dissolved Organic Fractions

DOC levels for the raw (ie., untreated) HORS samples were consistently lower than the raw C4 samples (Figure 4.13). The raw DOC was separated (Section 3.1.8) into HPO (humic-like acids), TPI and HPI (charged and neutral compounds; polysaccharides and proteins) (Chen et al., 2003). There was good association between the higher DOC concentration of the HPI fraction in C4 samples and the higher fouling propensity of these samples. This is expected as the membrane materials were hydrophilic and therefore the charged compounds within the HPI fraction were likely to adhere to the membrane due to surface interactions (Goosen et al., 2004). Neutral compounds also found in the HPI fraction are reportedly a main determinant in flux decline (Fan et al., 2001). Therefore a sample with a high HPI content is likely to cause rapid flux decline (Fan et al., 2001; 2008). The C4 samples had the highest HPI level and fouled the MF and UF membranes the most rapidly. B1 had similar concentrations of HPI for HORS and C4 samples and this explains why the two samples performed similarly in MF and UF filtration tests. These observations support the view that HPI (ie., polysaccharides and proteins) content is a major contributor to membrane fouling.



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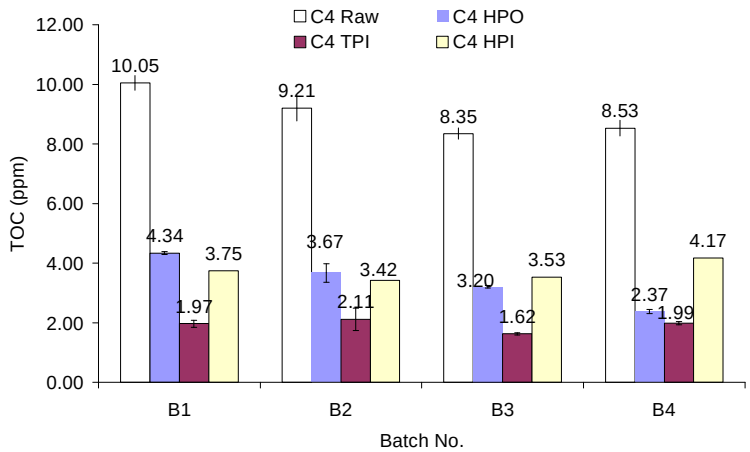


b)

Figure 4.13: DOC concentration of membrane feed solution (RAW), hydrophobic fraction (HPO), transphilic fraction (TPI), and hydrophilic fraction (HPI) of a) HORS and b) C4 samples

The higher concentration of HPI compounds in C4 samples is likely due to activated sludge treatment prior to clarification. Microbes in the activated sludge release soluble microbial products (SMP) such as polysaccharides and proteins (Jarusutthirak et al., 2002). These HPI compounds are not as prominent further down the treatment train, ie., in the effluent from the lagoons, due to UV and microbial activity in the lagoons. However, in the event of an algal bloom in the lagoons it is expected that the HPI concentration would increase significantly.

4.2.7 Fouling layer characteristics

ATR-FTIR analysis of fouled MF and UF membranes showed similar spectra for all samples, with the MF data shown in Figure 4.14. The peak near 1000-1120 cm^{-1} which is associated with alcoholic C-O absorption, and a broad OH band around 3400 cm^{-1}, indicate the presence of polysaccharide-like substances within the fouling layer. N-H peaks at 3300 and 1550 cm^{-1}, together with a peak at 1640 cm^{-1} corresponding to a stretching vibration of a C=O connected to amides, indicate the presence of peptide groups as found in proteins. Aliphatic CH_2

absorption bands are present at 226 and 2853 cm^{-1}. ATR-FTIR analysis of UF membranes fouled by 0.45 µm prefiltered samples exhibited very similar spectra to UF membranes fouled by unfiltered samples with differences only in peak height. Trends for MF membranes fouled with 0.45 µm prefiltered samples were not clear due to insufficient concentration of organic foulant on the membrane surface. Overall, irrespective of sample type or membrane, the major compounds detected in the fouling layer were proteins and polysaccharides. This finding is consistent with the results of other researchers who have investigated the impact of SMPs on filtration membranes (Jarusutthirak et al., 2002; Her et al., 2004; Shon et al., 2006).

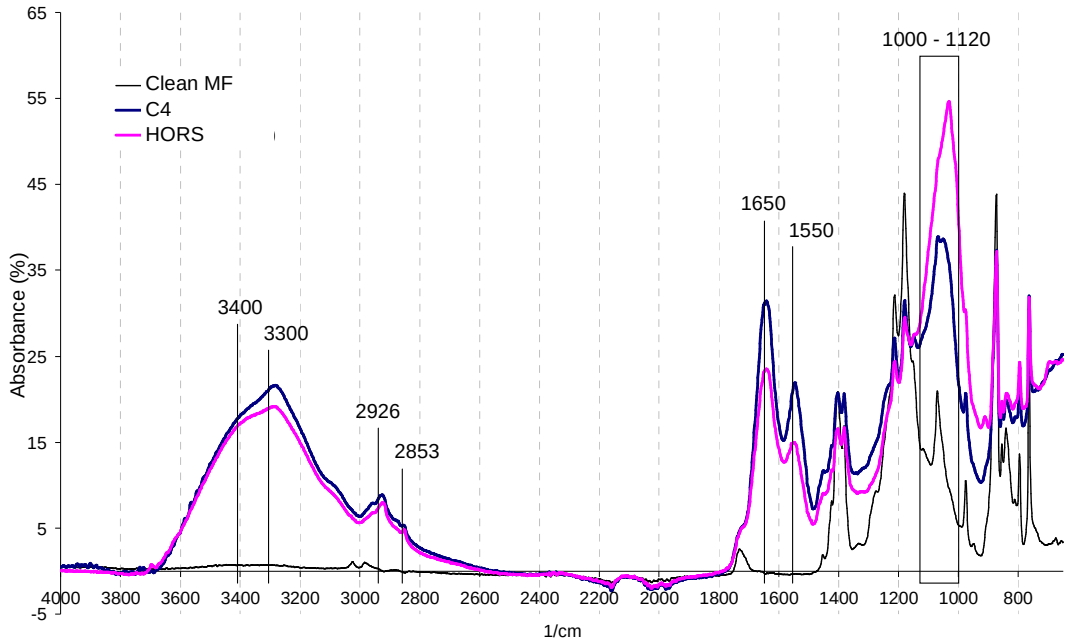
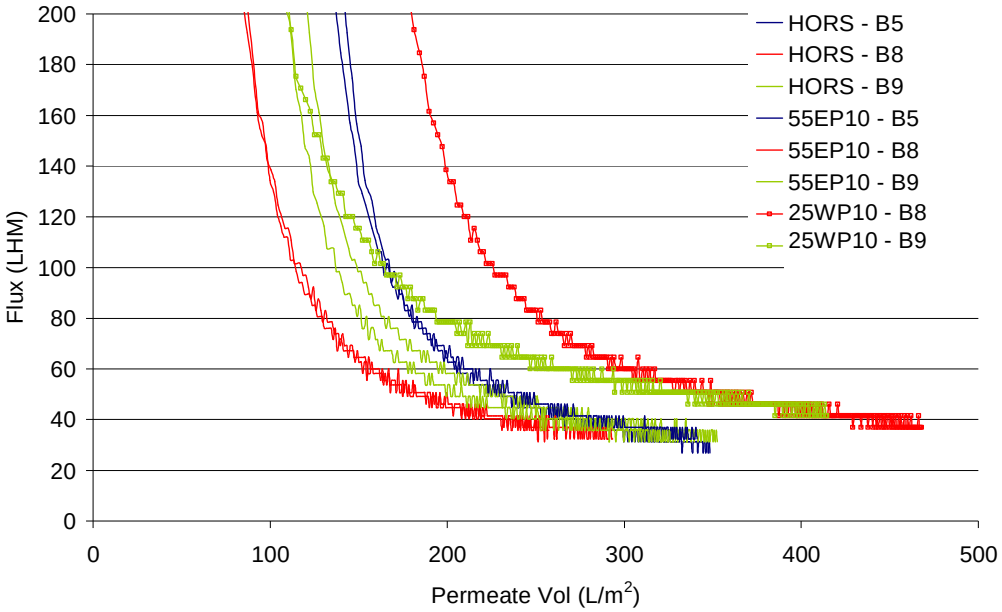


Figure 4.14: ATR-FTIR spectra of clean, and fouled MF membrane by HORS and C4 sample (B3)

4.2.8 East and West lagoons, and HORS effluent

Water from the final lagoons (P10) of the 25 West and 55 East WTP treatment trains is transported about 6 km to a 200 ML storage pond (HORS) through an open, earthen-based reuse channel and pipeline. HORS can be filled with either 25 West P10 or 55 East P10 effluent, or a combination of the two, depending on the water quality of the respective effluents. The transportation through an open channel and presence of two treatment trains raises two questions:

1) does the transportation of P10 water to HORS affect the fouling propensity, and
2) are the fouling propensities of effluents from 55 East 10 and 25 West P10 different?



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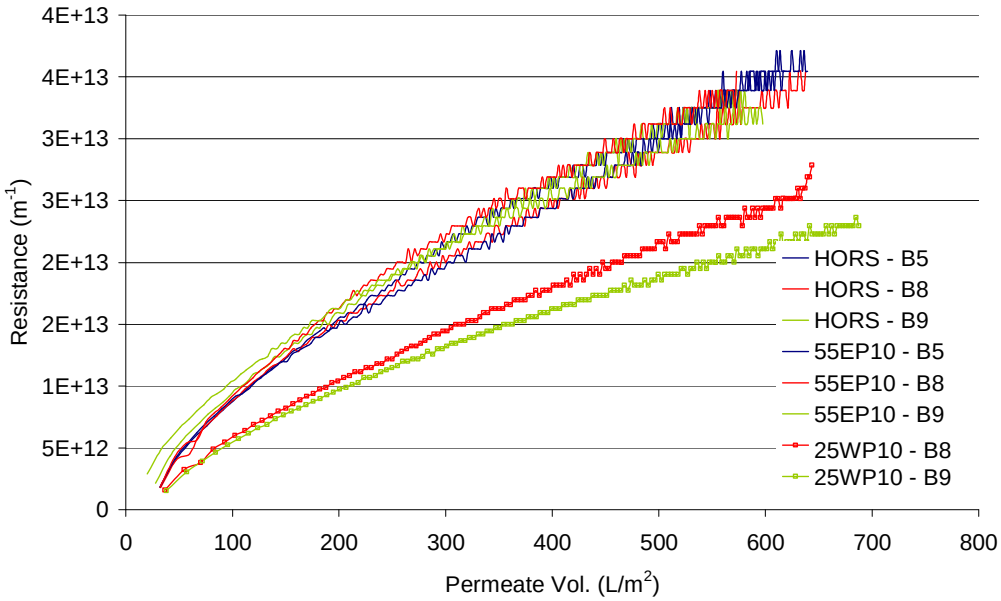


b)

Figure 4.15: a) MF flux and b) UF resistance of HORS, 25 West P10 and 55 East P10 samples when HORS was supplied by 55 East P10 effluent

Figure 4.15a shows the MF flux profiles of HORS, 25 West P10 and 55 East P10 samples when HORS was supplied solely by 55 East P10 effluent (B5, B8 and B9). It clearly shows that when 55EP10 effluent supplied the HORS site there was no discernible difference in the fouling propensity. This suggests that transportation of the effluent from the 55 East P10 site through the channel to the HORS site had no significant impact on the MF fouling rate. However, there was clear distinction between the 55 East P10 and 25 West P10 samples, the latter demonstrating a lower rate of fouling.

The UF results displayed a similar trend to MF (Figure 4.15b). The variability in fouling resistance between HORS and 55 East P10 samples was negligible compared with 25 West P10 samples. Again the 25 West P10 samples did not foul the membrane as rapidly.

4.2.8.1 Water quality

The water qualities of 25 West P10 and 55 East P10 effluents differ due to operational and structural differences between the 25 West and 55 East treatment trains (Appendix 1).

Table 4.2: Water quality of final lagoons in 25 West P10 and 55 East P10 lagoon systems

Batch No.	Sample	Turbidity (NTU)	TSS (mg/L)	TOC (ppm)
B5	*55 East P10*	3	6	14
	25 West P10	16	23	11
B8	*55 East P10*	8.1	13	18
	25 West P10	1.5	3	10
B9	*55 East P10*	5.7	10	13
	25 West P10	2.3	6	12
B11	*55 East P10*	3.6	10	32
	25 West P10	14	19	30
B12	*55 East P10*	1.3	18	14
	25 West P10	15	15	12

Table 4.2 shows the difference in turbidity, TSS and TOC of the effluent from the two treatment systems. In terms of turbidity and total suspended solids there was no consistent trend between the two. For some batches the 55 East P10 samples had better water quality, and at other times 25 West P10 samples were better. The 25 West P10 sample consistently had a lower TOC than those from 55 East P10. The disparity between the two systems is predominantly due to differences in construction and retention time. The lagoons in the 55 East treatment train are long and shallow with a retention time of about 17.5 days, compared with the lagoons in the 25 West treatment train which are shorter and deeper and have a retention time of about 28.3 days. Operational differences as well as environmental factors such as wind and rain also have an impact on the water quality of the final lagoon effluents.

For the 55 East P10 and 25 West P10 samples used for MF and UF filtration experiments (B8 and B9) (Figure 4.15) the 25 West P10 samples had lower concentrations of suspended solids and TOC than 55 East P10 (Table 4.2). This is the likely cause for the disparity in MF and UF fouling between 55 East P10 and 25 West P10 samples.

The HPI fraction of all samples (Figure 4.16) showed no appreciable divergence suggesting that this was not a main contributing factor. A lower HPO and TOC level combined with lower suspended solids are the apparent contributors to the improved flux of 25 West P10 samples with MF and UF membranes.

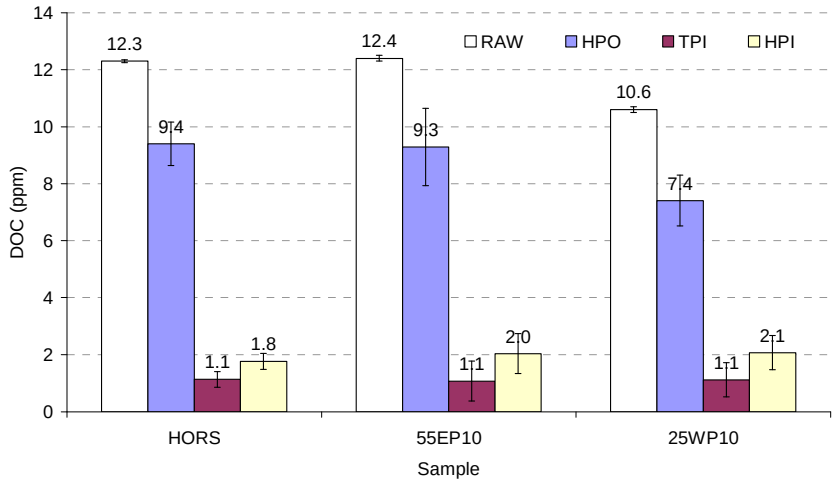


Figure 4.16: Organic fractions of B8 samples

It is therefore concluded that, based on the data obtained for these samples, 25 West P10 effluent fouled the MF and UF membranes the least and transportation of P10 effluents via the channel to the HORS site is unlikely to have an impact on the fouling propensity of these waters.

4.3 Conclusion for Chapter 4

The rate of flux decline for MF and UF membranes was typically greater for the C4 samples than HORS samples, particularly for the MF membrane. The presence of suspended solids played a significant role in the fouling rate of both C4 and HORS samples. However, this was not the only contributing factor as C4 samples still fouled MF and UF membranes more rapidly than HORS samples after the removal of suspended solids, and samples of C4 which had similar concentrations of suspended solids to HORS samples fouled the membranes more rapidly. The C4 samples generally had higher TOC levels and fractionation by DAX-8 and XAD-4 resins showed that they typically contained higher concentrations of hydrophilic organic compounds (ie., polysaccharides and proteins). HPSEC-UV analysis showed no

appreciable difference in apparent molecular weight distribution of UV-absorbing molecules (ie., aromatic compounds such as humic and fulvic) between C4 and HORS samples, nor between feed solutions and membrane permeates. ATR-FTIR analysis indicated the presence of proteins and polysaccharides in the fouling layer of both HORS and C4 samples.

It is therefore reasonable to conclude that the suspended solid content of these samples contributed to the fouling of MF and UF membranes, but was not the sole factor in determining fouling propensity. Rather, the higher concentration of TOC and of hydrophilic compounds in the C4 samples was also a prominent influence in the fouling of these membranes.

The higher concentration of hydrophilic compounds in C4 samples is likely due to SMP compounds produced during activated sludge treatment. Although the lagoon-treated samples contained lower concentrations of hydrophilic compounds, this would probably change significantly in the event of an algal bloom in the lagoons.

Taking these data into account, the water from the HORS is the most suitable feed source for MF and UF treatment.

Fouling propensity was greater for the lagoon effluent taken from the 55 East treatment train compared with the 25 West treatment train. Differences in levels of suspended solids, TOC and HPO fraction were the likely cause. This suggests 25 West P10 is the preferred water source for HORS for any future filtration plant, however more long term analysis is required due to changes in both treatment trains over time.

Chapter 5 - Investigation into MF & UF Fouling by *Anabaena circinalis*

The presence of algal cells in feed water significantly increases the fouling of filtration membranes due to deposition and concentration onto the membrane surface of algal cells, and the release of cellular soluble and particulate organic carbon (Montgomery Watson, 1997; Habarou et al., 2005; Liang et al., 2008). This chapter investigates the impact of dissolved and particulate algal organic matter, derived from a culture of the blue-green alga *Anabaena circinalis*, on the fouling of MF and UF membranes.

5.1 Growth Phase

As algal cells grow they excrete EOM into the water column. EOM comprises mostly protein- and polysaccharide–like compounds (Pivokonsky et al., 2006). As the cells lyse intracellular compounds are released into the water column (Nguyen et al., 2005; Pivokonsky et al., 2006). The mixture of extracellular and intracellular compounds due to cell lysis is hereafter referred to as algal organic matter (AOM).

The life cycle of an algal population can be monitored by TOC and chlorophyll-a measurements (Pivokonsky et al., 2006). As the cells multiply there is an increase in chlorophyll-a and gradual increase in TOC. When the cells lyse the TOC rapidly increases as the intracellular organics are released, and the concentration of chlorophyll-a decreases due to release into the water column and conversion to red catabolites (Hortensteiner, 1999).

A strain of *Anabaena circinalis* was cultured as per Section 3.1.12. TOC, DOC and chlorophyll-a measurements, recorded every second day, were used to plot the algal life cycle.

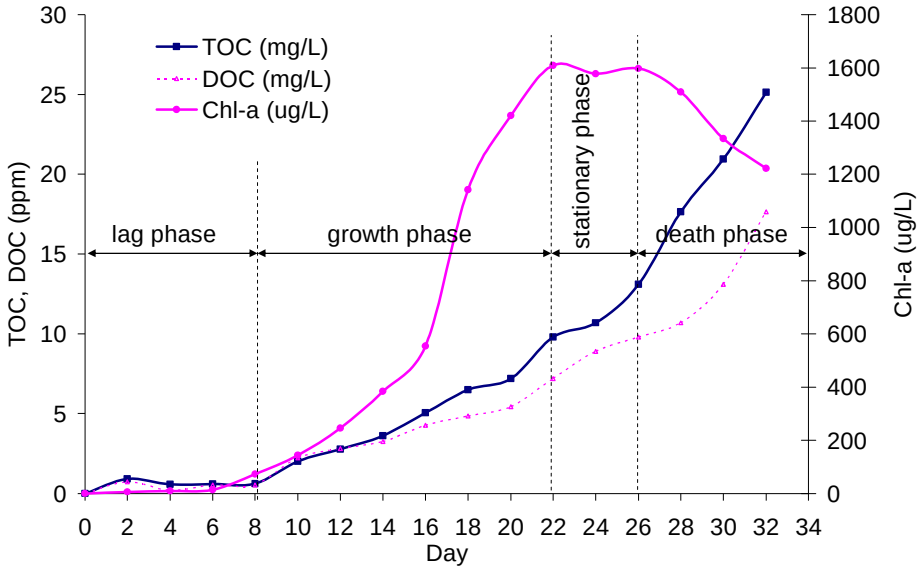


Figure 5.1: Chlorophyll-a, TOC and DOC levels for an *Anabaena circinalis* culture

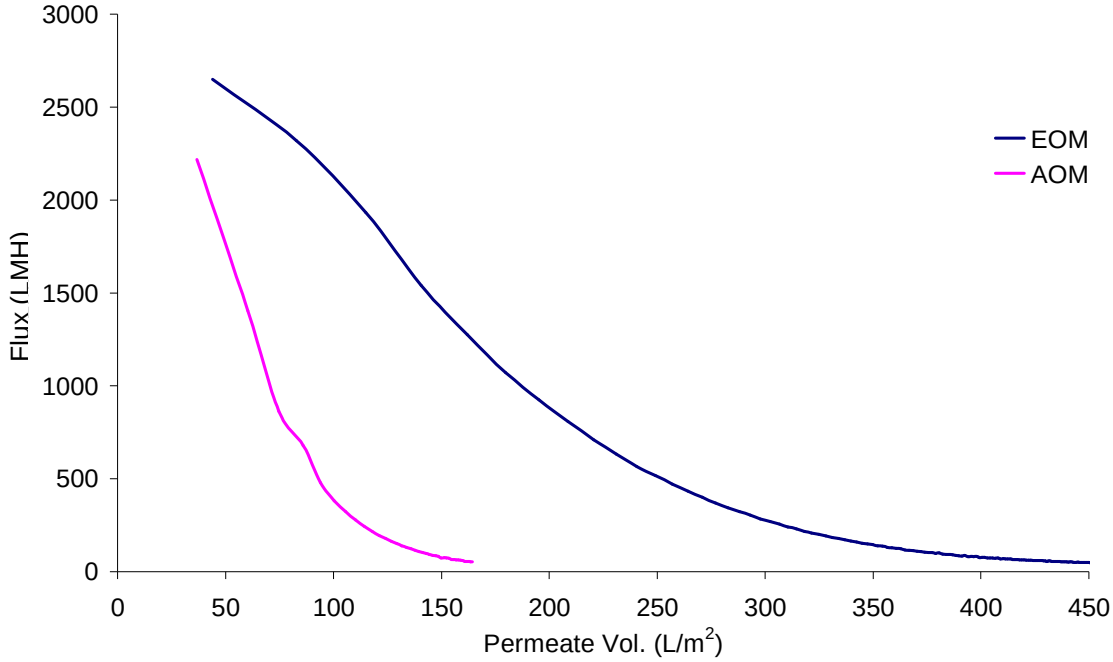
Under the experimental conditions the typical life cycle of the *Anabaena circinalis* strain was 30 days. As shown in Figure 5.1 the chlorophyll-a concentration increased until day 22, the period over which the cells grew and multiplied rapidly due to adequate levels of nutrients, light and CO_2. This is referred to as the growth phase. Between days 22 to 26 cell growth reached a stationary phase, as indicated by the plateau in the chlorophyll-a concentration. From day 26 cells entered the death phase as evidenced by the rapidly increasing TOC and fall in chlorophyll-a concentration. These changes in chlorophyll-a and TOC were consistent with similar work by Pivokonsky et al. (2006).

Representative growth phase EOM samples were collected on day 15 whilst representative AOM samples were taken on day 30 during the lysis or death phase. These samples were used to represent organic content during the beginning of an algal bloom and at the end of an algal bloom.

5.2 Filterability of EOM & AOM

The rise in TOC during and after an algal bloom is problematic for membrane filtration as it causes an increase in fouling rate and flux decline as demonstrated in Figure 5.2 a) and b). The EOM solution, which had a TOC of 5 ppm, gradually fouled the MF membrane reducing its flux rate from 3600 to 55 LMH after 450 L/m^2 of permeate production. The AOM, which had a TOC of 15 ppm, fouled the MF membrane much more rapidly and reduced its flux rate to 55 LMH after just 160 L/m^2 of permeate production. The flux profiles of EOM and AOM displayed a similar trend for UF as for MF. The EOM solution reduced the UF membrane flux rate from 1500 to 55 LMH after 120 L/m^2 of permeate production compared with 32 L/m^2 for AOM. This is consistent with the well established relationship between TOC concentration and membrane fouling (Goosen et al., 2004; Zularism et al., 2006), the higher TOC concentration of AOM solution (due to cell lysis) compared with EOM resulted in an increased rate of membrane fouling for both MF and UF.

Differences in organic composition between EOM and AOM may be a contributing factor to the rate of flux decline. Figures 5.3a and b show the relationship between TOC delivered to the membrane surface and flux decline. The initial rate of MF and UF membrane flux decline was greater for the EOM sample. However the EOM and AOM flux profiles aligned as the flux reached quasi-steady state. For MF the TOC delivered to the membrane surface for the flux rate to drop to 55 LMH was 2.2 g/m^2 and 2.4 g/m^2 for EOM and AOM, respectively. For UF the TOC delivered to the membrane was 0.6 g/m^2 for both EOM and AOM.



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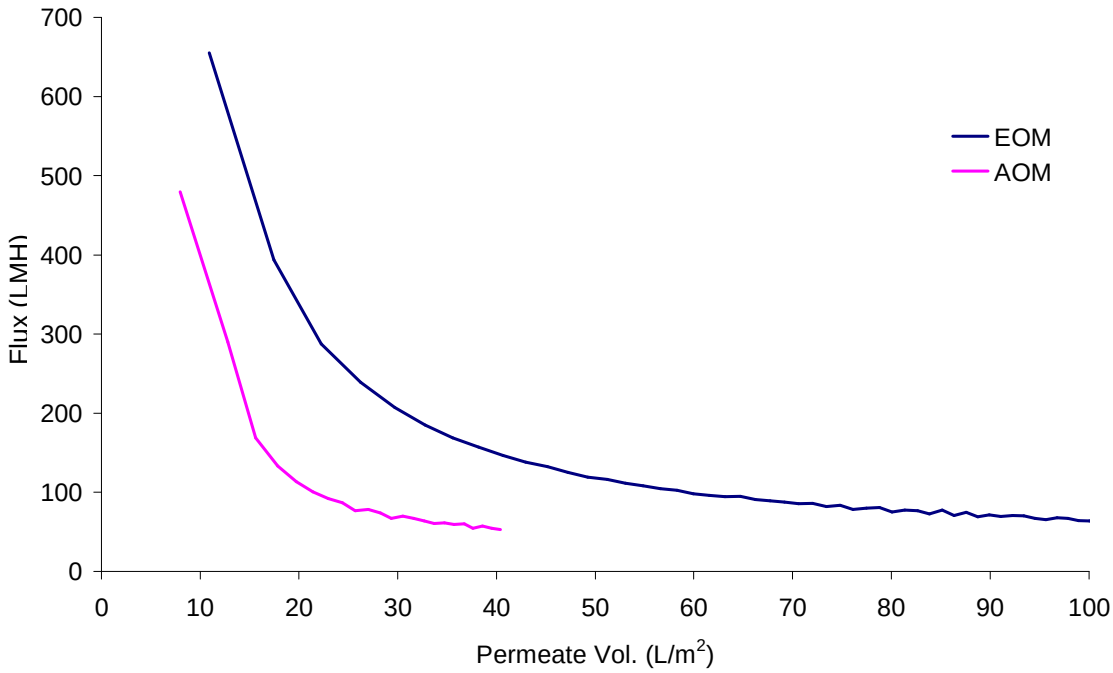
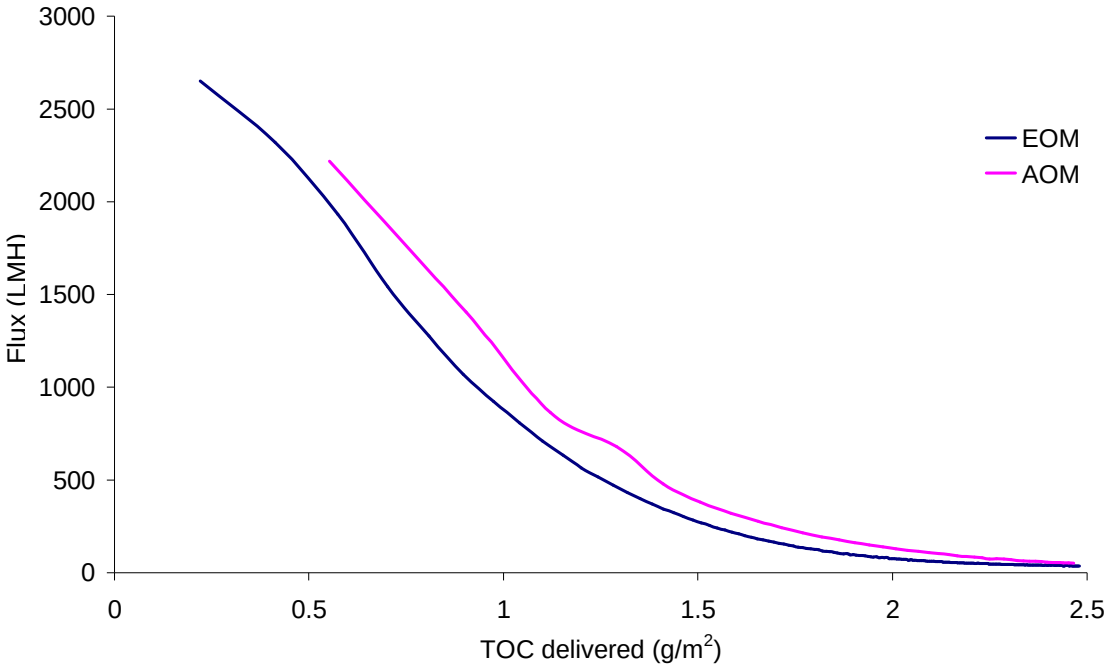
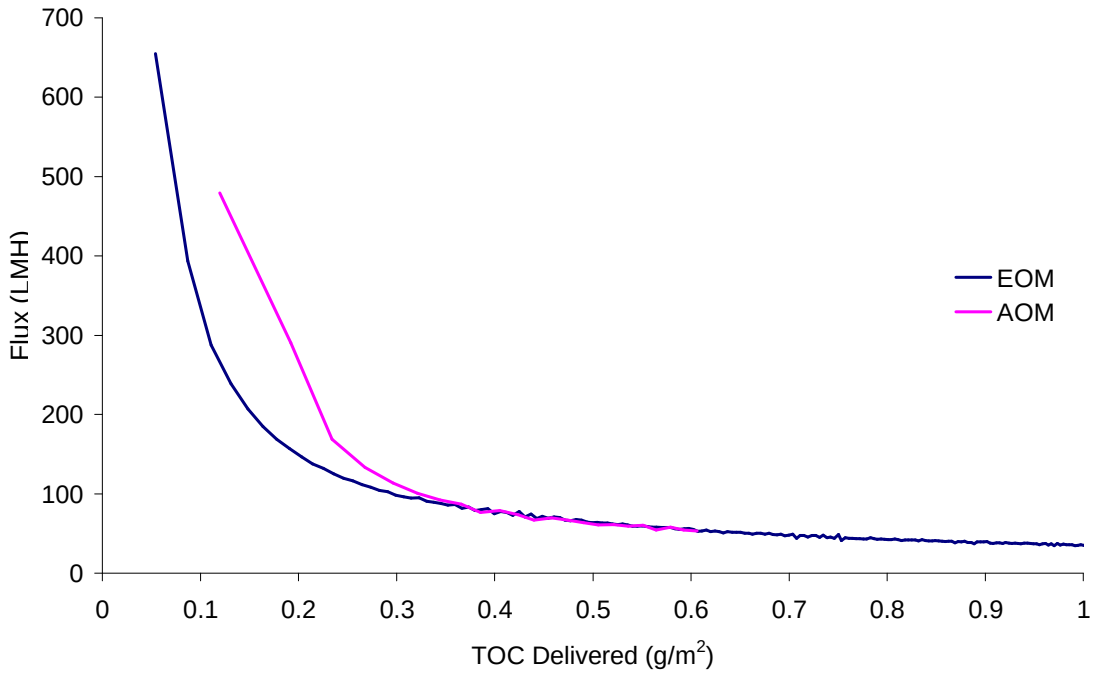


b)

Figure 5.2: Flux profiles of EOM and AOM with regard to permeate volume for a) MF and b) UF.

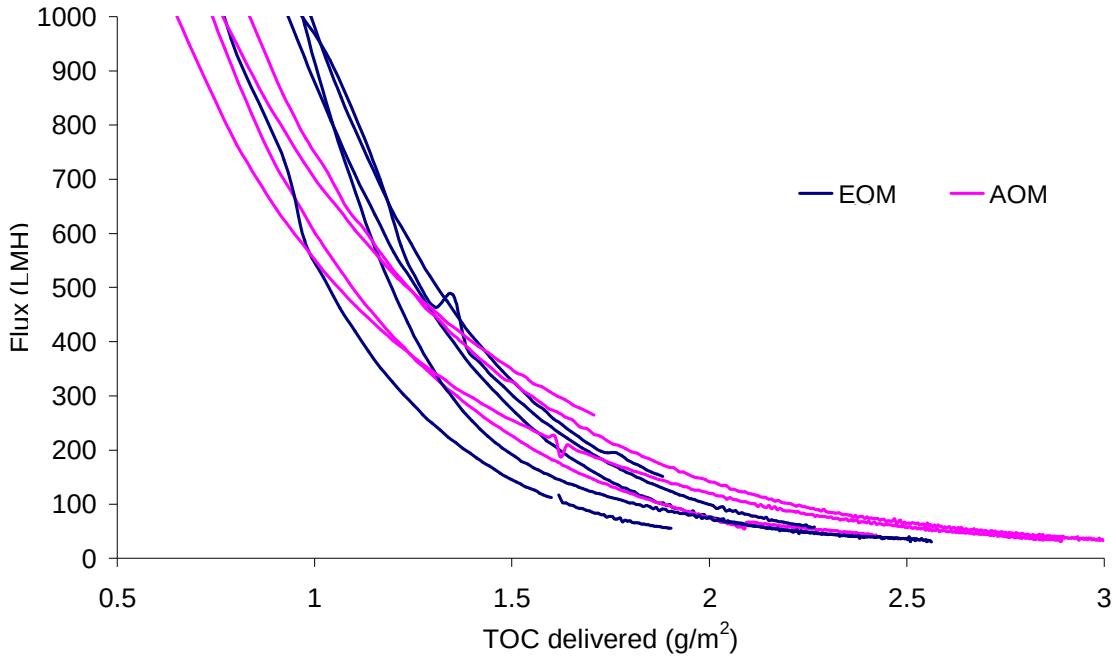


a)

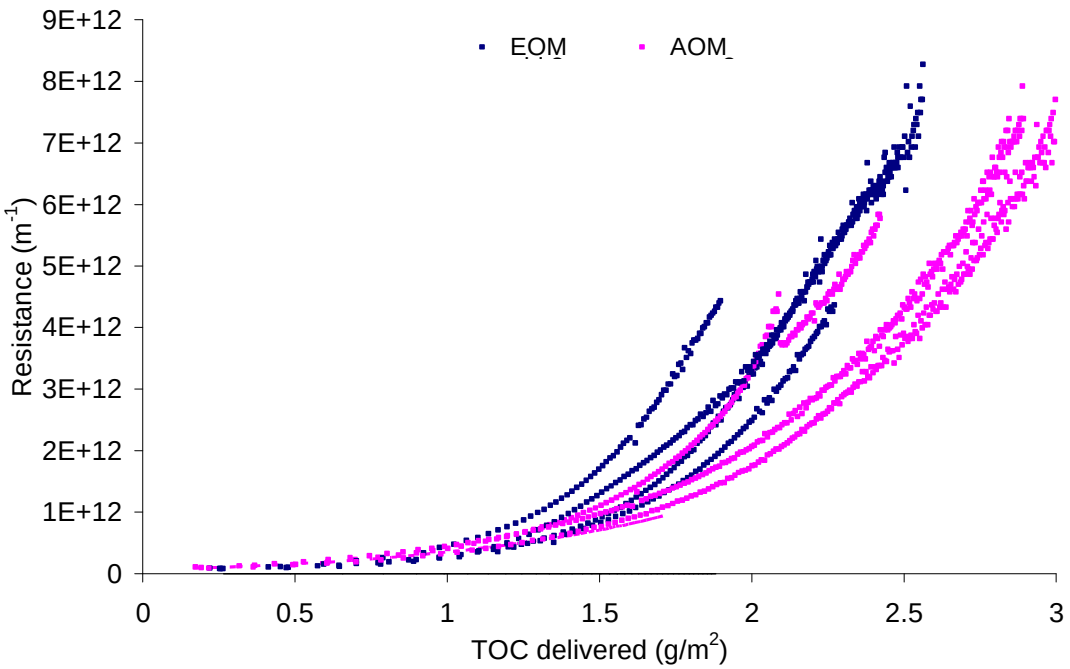


b)

Figure 5.3: Flux profiles of EOM and AOM with regard to TOC delivered for a) MF and b) UF.



a)



b)

Figure 5.4: MF a) flux profiles and b) resistance profiles for EOM and AOM with regard to TOC delivered to the membrane surface

5.3 Investigation of Comparative Filterability of EOM & AOM

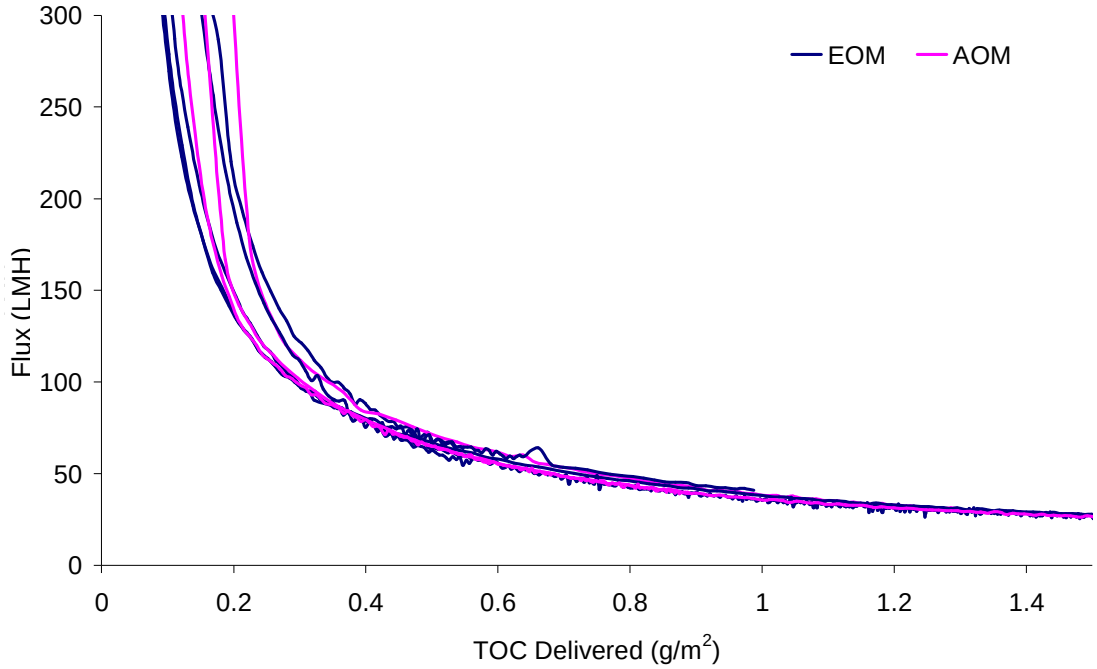
Although there was no significant difference in flux decline between EOM and AOM based on TOC delivered to the membrane surface, further investigation was undertaken to identify compositional differences and their influence on flux declines. To determine the effect of composition on MF and UF, the EOM and AOM samples were diluted with Milli-Q water to give a TOC concentration of 5 ppm and the pH was adjusted to 8.

5.3.1 Fouling Propensity of EOM & AOM

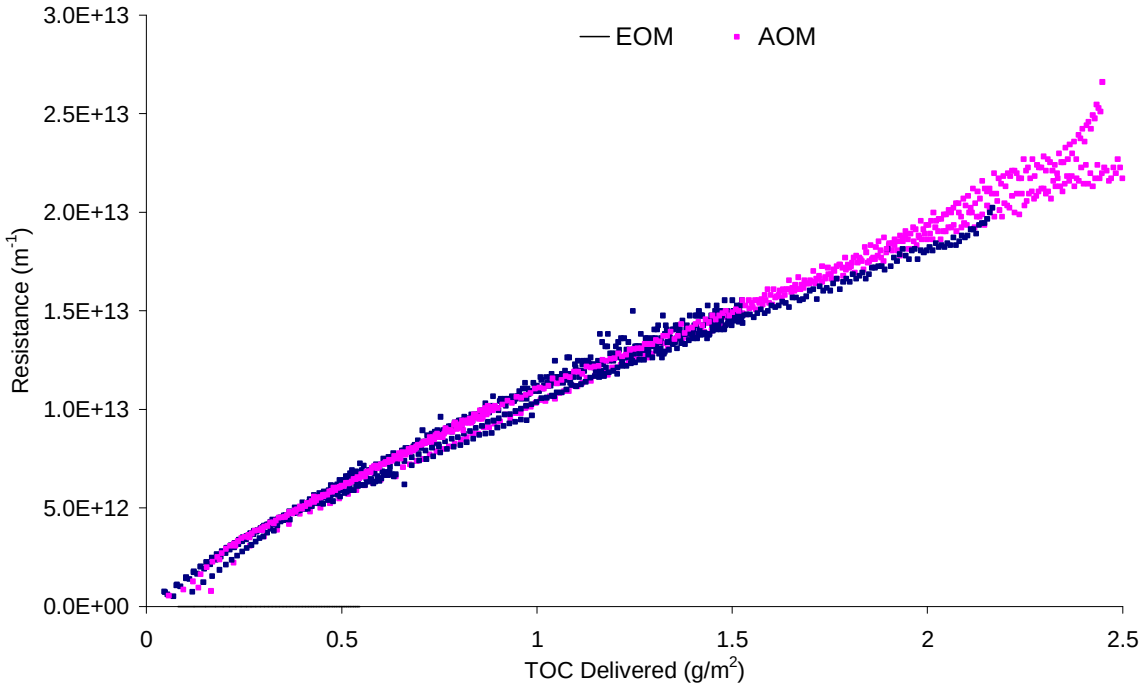
For MF, AOM was found to cause more rapid initial flux decline than EOM (Figure 5.4a). However after 1.25 g/m^2 of TOC was delivered to the membrane surface (equivalent to 240 L/m^2 of permeate production) the rate of fouling caused by AOM decreased, whilst the rate of flux decline caused by the EOM sample remained quite high. This trend was present for EOM and AOM derived from 4 different cultures of *Anabaena circinalis*, as shown in Figure 5.4a. The increase in membrane resistance illustrates the difference between these two samples more clearly (Figure 5.4b). EOM had a greater fouling effect than AOM on the MF membrane, resulting in more rapid increase in membrane resistance.

Overall, EOM was found to cause greater MF flux decline than AOM. When the flux rate had dropped to 55 LMH the EOM had produced only 424 ± 10 L/m^2 of permeate compared with 568 ± 10 L/m^2 for AOM. This difference is equivalent to 0.40 ± 0.05 g/m^2 TOC, suggesting that differences in the characteristics of the organic components are responsible for the disparity.

The fouling rates of the EOM and the AOM samples on the UF membrane were very similar (Figure 5.5a, b). There was no discernible difference in the fouling rate nor membrane resistance between the EOM solution and the AOM solution. The initial flux decline and near-steady state flux rates of the two solutions could not be clearly distinguished. Given that the TOC levels of the solutions were the same and the rate of flux decline per gram of TOC delivered to the membrane surface was also the same, it maybe concluded that the TOC concentration of the EOM and AOM samples played a more significant role than the organic composition in fouling propensity of either sample for UF.



a)



b)

Figure 5.5: Fouling of UF by EOM and AOM. Flux decline a) and resistance b) versus TOC delivered

5.3.2 MF and UF Removal of TOC

The removal of TOC by MF for EOM and AOM samples was approximately 30% compared with up to 71% removal by UF (Table 5.1). MF removed similar amounts of TOC from both EOM and AOM suggesting a similar mode of fouling, however the resultant foulant layer was different as indicated by the flux profiles. UF removed more TOC from AOM than EOM, suggesting a difference in the mode of fouling or organic composition for AOM.

Table 5.1: TOC concentration of feed and permeates for EOM and AOM

Sample	TOC (ppm) [% removal]		
	Raw	MF	UF
EOM	5.22 ± 0.06	3.54 ± 0.03 [32]	2.43 ± 0.02 [53]
AOM	4.9 ± 0.2	3.45 ± 0.05 [30]	1.40 ± 0.01 [71]

5.3.3 Suspended Solids Contents of EOM and AOM Samples

Table 5.2 lists the total suspended solids concentration and turbidity of the EOM and AOM feed samples. The AOM sample contained a much higher concentration of suspended solids than the EOM sample. As noted in Section 4.2.3 the presence of suspended solids played a significant role in the rapid flux decline of MF and UF membranes. Although the AOM sample contained a higher concentration of suspended solids it did not foul the MF faster than the EOM sample. A possible explanation for this is the suspended solids in the AOM sample aggregated to form a secondary layer on the MF membrane surface resulting in increased permeability of the fouling layer (Kwon et al., 2005).

Table 5.2: Total suspended solids, turbidity and UV absorbance in EOM and AOM feed solutions

Sample	TSS (ppm)	Turbidity (NTU)	A_{254}
EOM	40	2.38	0.033
AOM	92	2.95	0.096

5.3.4 Organic Fractions of EOM and AOM

The components of the DOC content of all feed water samples, MF and UF permeates were separated into three fractions: hydrophobic acids (HPO), transphilic acids (TPI) and hydrophilic compounds (HPI), using DAX-8 and XAD-4 resins (Figure 5.6). Prefiltering (0.45 μm) and pH adjustment of samples for analysis resulted in reduced TOC values (Table 5.3) compared with Table 5.1.

Table 5.3: DOC of feed and permeates for EOM and AOM at pH 2

Sample	DOC (ppm)		
	Raw	MF	UF
EOM	3.58 ± 0.05	3.00 ± 0.08	1.81 ± 0.11
AOM	3.76 ± 0.02	3.47 ± 0.09	1.76 ± 0.03

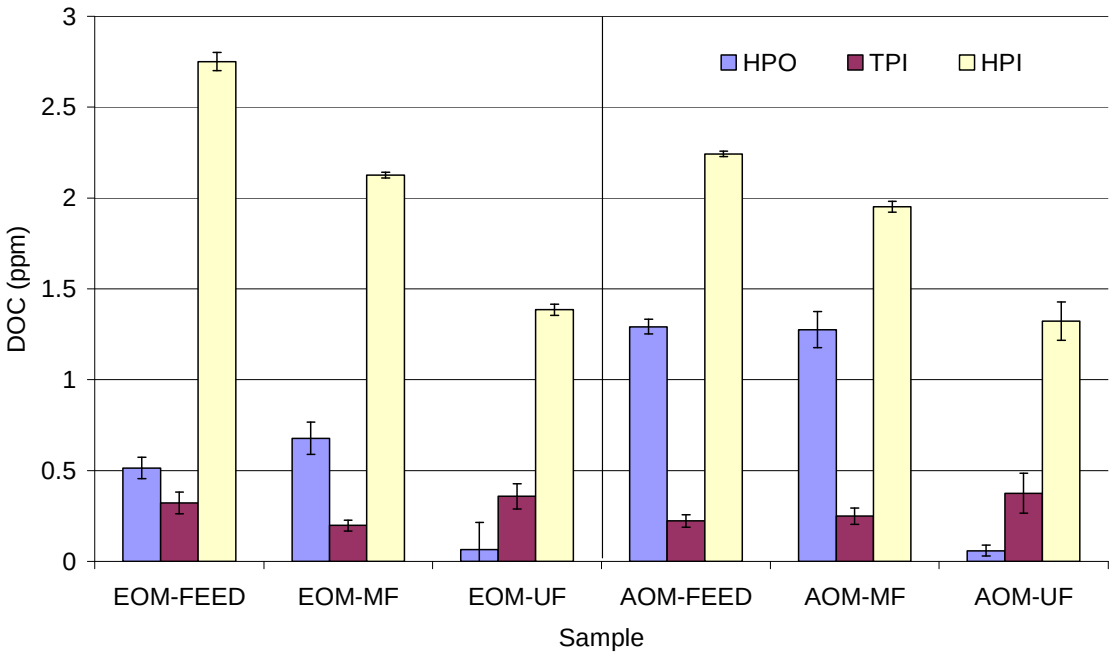


Figure 5.6: Hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) organic fractions of feed water and MF and UF permeates of EOM and AOM samples.

The EOM feed solution contained higher levels of HPI than the AOM feed solution. Proteins and polysaccharides excreted by growing algal cells (Nguyen et al., 2005; Pivokonsky et al., 2006) have been associated with HPI fractions and are therefore attributed to the higher HPI concentration (Lee et al., 2006a). The AOM feed solution contained higher levels of HPO than the EOM solution. The increase in HPO concentration, which is associated with humic acids (Nguyen et al., 2005; Pivokonsky et al., 2006; Lee et al., 2006a), is attributed to cell lysis products.

MF removed some of the HPI fraction of both EOM and AOM solutions and little, if any, of the HPO and TPI fractions. The hydrophilic property of the MF membrane means charged organics have an affinity for the membrane surface. Additionally, neutral compounds can also adhere to the membrane surface as there is no surface charge rejection (Goosen et al.,

2004). Thus the charged and neutral organics such as proteins and aliphatic compounds of the HPI fraction contributed to the fouling of the MF membrane for both the EOM and AOM feed solutions.

UF removed some of the HPI and HPO fractions, but no measurable quantity of the TPI fraction, from both EOM and AOM solutions. It is important to note that although the EOM feed solution had a much higher concentration of HPI than the AOM feed solution, the amount of HPI that passed through the membranes was almost identical. This suggests the concentration of non-retained HPI compounds is proportionately equal in the EOM and AOM solutions. The reduction in the HPO fraction was significant for the EOM solution, and even greater for the AOM solution due to its feed having a higher HPO concentration. However, like the HPI fraction, the concentration of breakthrough HPO was very similar for both EOM and AOM permeates, suggesting that the proportional concentration of non-retained HPO compounds was the same in the EOM and AOM solutions. The decrease in HPI and HPO fractions may be attributed to the hydrophilicity and tightness of the UF membrane (100 kDa). The tighter pore size means a higher rejection of organics, particularly for HPI compounds which have an affinity for the hydrophilic membrane surface.

5.3.5 3D Fluorescence Emission-excitation Matrix (EEM) Analysis of EOM & AOM

Fluorescence emission-excitation matrix (EEM) analysis provides useful information about fluorophores within a sample. The matrix can be divided into five regions based on the type of organics (Figure 2.1).

Figures 5.7a and b show the EEM spectra of EOM and AOM feed solutions, TOC concentrations as reported in Table 5.1. Both EOM and AOM samples contained two peaks in the SMP region, Region IV (Table 5.3); a prominent peak (Ex: 280 nm, Em: 342 nm) and a smaller peak (Ex: 285 nm, Em: 325 nm). The peak intensity in this region was greater in the EOM sample, suggesting a higher concentration of SMP-like compounds. In the aromatic protein region (Region II) a very intense peak was detected in the AOM sample. A similar but less intense peak was detected in the EOM sample; however the peak location was slightly different (Table 5.3) suggesting slight differences in the characteristics of these proteins. This agrees with the findings of Pivokonsky et al. (2006) that EOM contained little or no protein and protein concentration and diversity increased as the cells began to lyse. In the humic acid-like

EOM AOM

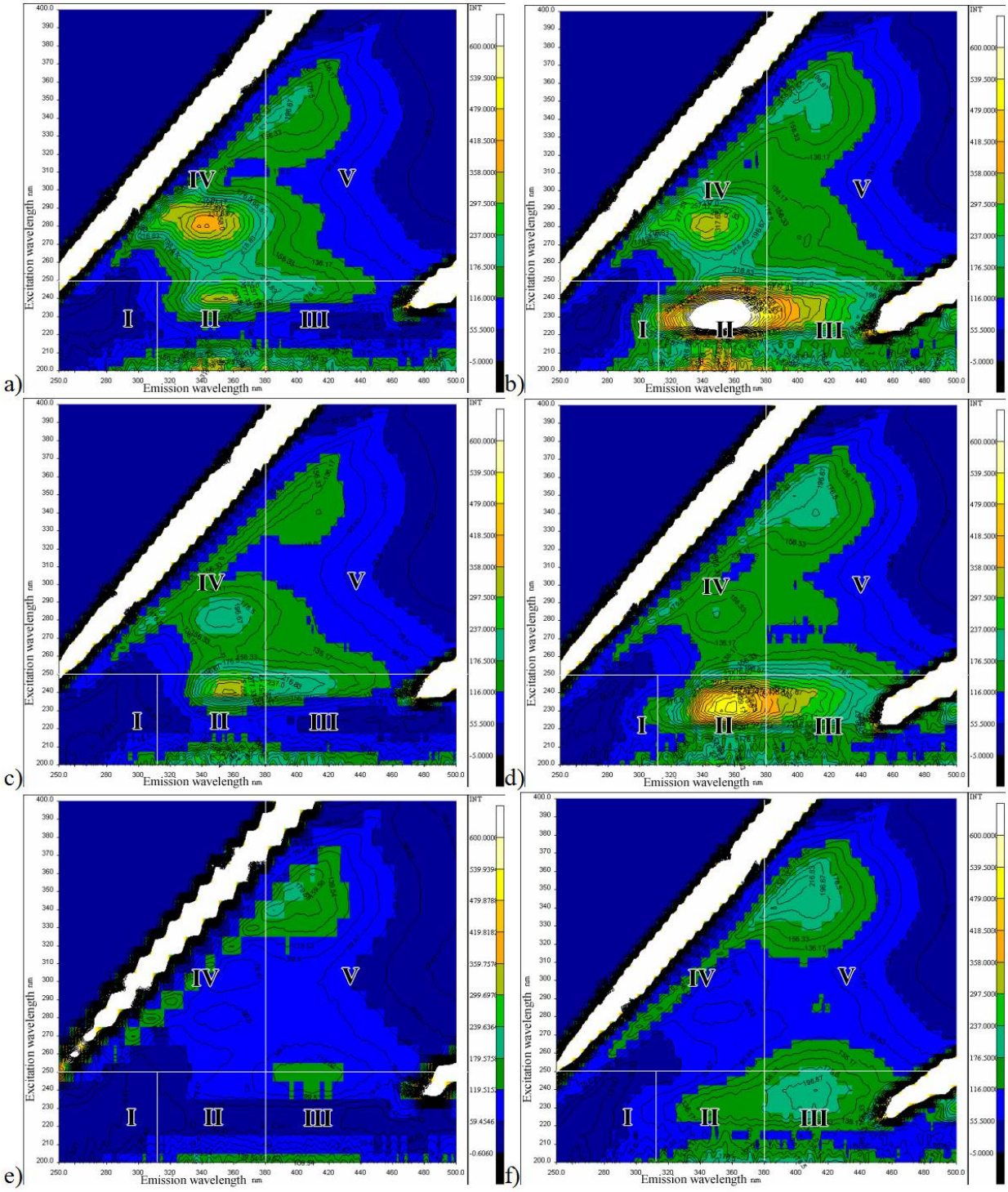


Figure 5.7: EEM of EOM a) feed solution c) EOM MF permeate and e) EOM UF permeate, and of b) AOM feed solution d) AOM MF permeate and f) AOM UF permeate

region (Region V) there is a peak which is more prominent in the AOM sample (Ex: 285 nm, Em: 410 nm). There is also an apparent peak in both EOM and AOM samples (Ex: 355 nm, Em: 405 nm), however this is most likely amplification of the adjoining peak shoulder caused by water scattering (Zepp et al., 2004). These two peaks indicate that the AOM sample contained higher concentrations and more types of humic acid-like compounds. Fulvic acid-like compounds were present in EOM and AOM samples; however the peaks were masked by the strong protein peak.

Table 5.3: Peak locations and intensities of EEM spectra for EOM and AOM solutions

Sample	Peak location (excitation λ nm, emission λ nm) [peak intensity (AU)]				
	Region I (protein-like)	Region II (protein-like)	Region III (fulvic-like)	Region IV (SMP-like)	Region V (humic-like)
EOM	-	240, 351 [325]	250, 410 [*]	285, 325 [317] 280, 343 [380]	340, 410 [167]
AOM	-	230, 350 [798]	240, 410 [*]	287, 321 [284] 280, 342 [330]	347, 413 [186] 285, 410 [*]

* value not measurable due to water scattering or peak area overlap

After MF the peak intensity of the SMP-like (Region III) compounds was reduced by more than 50% for EOM and AOM samples (Figure 5.7c & d). The peak intensity of protein-like compounds (Region II) was significantly reduced for the AOM sample but virtually unchanged for the EOM sample. The humic and fulvic acid-like peaks (Regions IV & V) remained unchanged for both samples. This corresponds with the findings of the previous section that HPI compounds (protein- and SMP-like compounds) were removed by MF and HPO (humic acid-like compounds) and TPI (fulvic acid-like compounds) passed through the membrane.

The UF membrane removed nearly all of the SMP-like and protein-like compounds from the EOM and AOM solutions. There was virtually no removal of humic acid-like compounds and the change in fulvic acid-like compounds was indeterminate due to overlapping caused by the protein peak. These findings apparently differ from those for resin fractionation, where virtually all HPO acids (associated with humic acids) were removed by UF and less than half of the HPI fraction (associated with charged and neutral proteins and aliphatic compounds) was removed. This may be due to the heterogeneity of compounds within the fractions in that not all compounds are fluorophores. Thus it is likely that the HPI compounds that passed

through the membranes were not strong fluorophores, and therefore did not provide a good peak response in Region II. Furthermore, TPI fractions have been noted to fluoresce in Regions IV and V (Lee et al., 2006). The TPI fraction was not retained by the membranes and therefore this would account for the unchanged peak in Region V.

5.3.5.1 Fluorescence Regional Integration (FRI)

FRI provides semi-quantitative data for the EEM regions by calculation of peak volumes (Chen et al., 2003). This allows for inclusion of spectral shoulders and other features that would otherwise be difficult to assess.

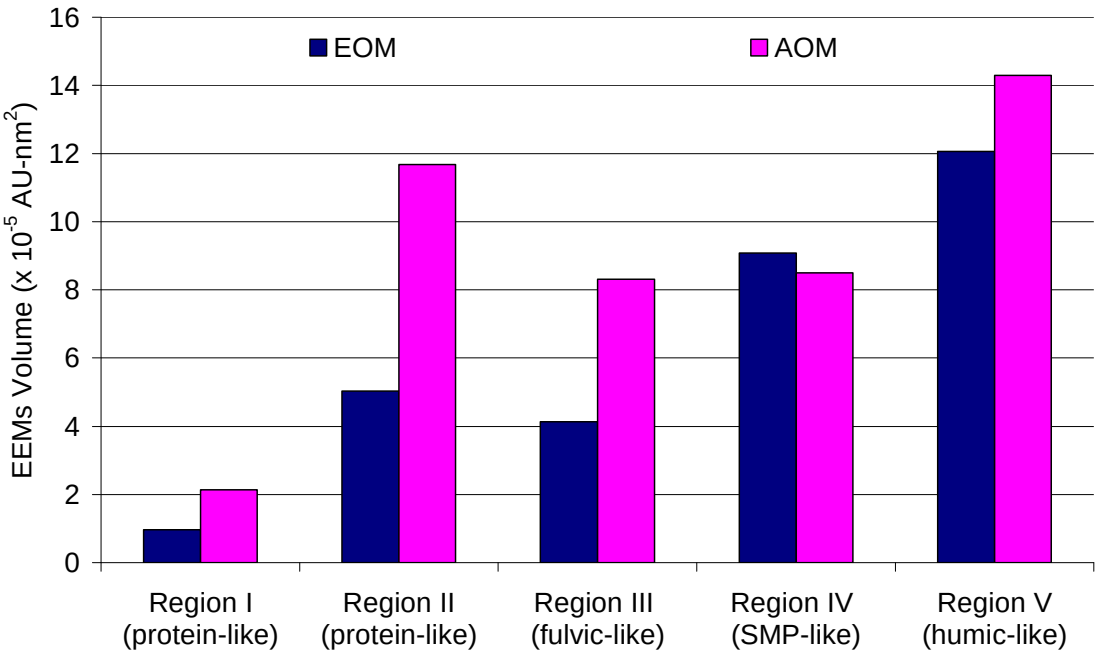


Figure 5.8: EEM volumes of EOM and AOM feed solutions

Figure 5.8 provides a graphical representation of the peak volumes in each region for the EOM and AOM samples. AOM had a larger peak volume in Regions I and II than EOM, indicating that the AOM sample contained a higher concentration of protein-like compounds. Conversely, for Region IV (SMP-like) the EOM sample contained a slightly higher concentration than AOM. According to the results in Section 5.3.4 the EOM sample contained a higher concentration of HPI compounds, however FRI analysis suggests the opposite. This is likely due to sample heterogeneity and concentration of fluorophores as discussed in the previous section. Differences in values between in Region III (fulvic-like) for EOM and AOM may be due in part to the spectral shoulders from Region II spreading into Region III (Figure 5.7a & b). Figure 5.9 shows the protein peak (350 nm) shoulder spreading into the fulvic peak region (410 nm). A slight change in the protein peak gradient at 410 nm

indicates a peak in the fulvic-like region which can be seen more clearly in the UF permeate EEM (Figure 5.7e & f). For Region V the AOM had a higher FRI value than the EOM, suggesting that the AOM contained a higher concentration of humic-like compounds. The higher concentration of SMP-like compounds in EOM and higher concentration of humic-like compounds in AOM correspond with the findings in Section 5.3.4.

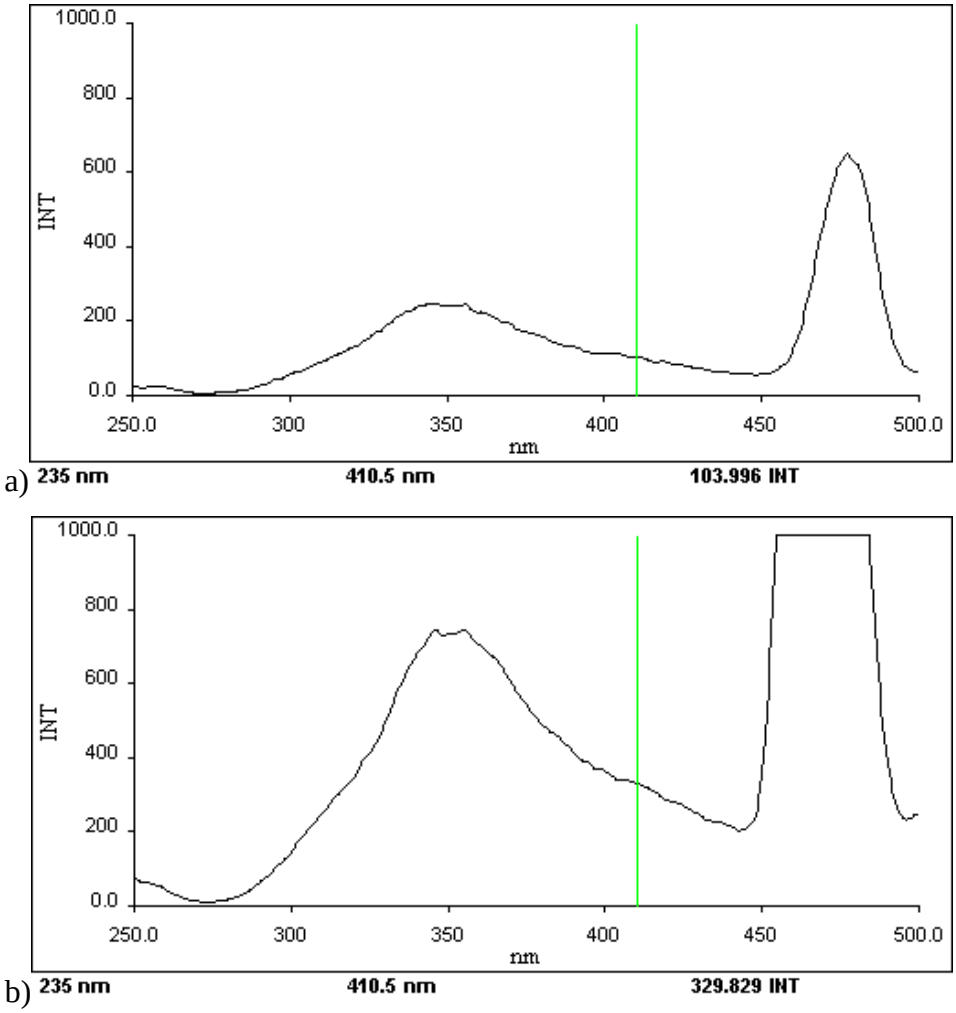


Figure 5.9: Fluorescence spectra at 235 nm excitation of a) EOM and b) AOM

5.3.6 HPSEC-UV

HPSEC with UV detection was conducted to examine the effect of MF and UF on the molecular weight distribution of UV-absorbing organic compounds of the EOM and AOM samples (Figure 5.10). The AOM sample had a larger peak at 42,300 Da compared with the EOM sample. This area is associated with macromolecules such as colloidal particles, proteins and polysaccharides, and the higher peak response suggests that the AOM sample had a higher concentration of these types of compounds, similar to the reports by Her et al. (2003; 2004) and Lee et al. (2004; 2006a). Absorbance at 254 nm (Table 5.2) was higher for AOM indicating that the sample contained a higher concentration of aromatic and conjugated

molecules. Due to the relationship between UV-absorbance and fluorescence, it is suggested that the same compounds that were attributed to the higher protein-like peak in EEM and FRI analysis for the AOM sample are associated with the 42,300 Da peak. A large peak at apparent molecular weights of 1353 Da and 1147 Da for EOM and AOM samples, respectively, which are associated with humic compounds are of similar peak height. This suggests that the concentration of these particular compounds was similar for both EOM and AOM samples. The molecular weight range between 1850 and 5820 Da is also associated with humic compounds (Her et al., 2003; 2004; Lee et al., 2004; 2006a; Lozier et al., 2007). The AOM sample displayed a larger peak area in this region compared with the EOM sample, indicating that the AOM sample had a higher concentration of larger humic compounds. Fulvic compounds have been associated with peaks around 680 Da. The peak at 620 Da was slightly greater in the AOM sample than the EOM sample, suggesting that the AOM sample had a higher concentration of fulvic compounds. These results correspond with those reported in Section 5.3.5.

The samples were analysed in order of EOM, AOM, EOM-MF, EOM-UF and AOM-UF. As observed in Figure 5.10, a contaminant peak occurred at 1100-700 Da in the EOM-MF sample and became more obvious with the succeeding samples. This appears to have caused partial saturation of the column and resulted in faster elution times, as evidenced by the shift in the humic peak (1147 Da) (Harris, 2003). Despite this, general conclusions can still be made after taking these interferences into consideration. For the EOM sample, MF removed some of the macromolecular components (42,300 Da). The humic acid peak at 1353 Da was not decreased in peak height, although it did shift slightly. After UF, the peaks for the humic acids and macromolecular compounds in EOM were further decreased in size. A similar trend occurred for the AOM sample. The UF permeate showed a marked reduction in the humic acid peak, and almost complete removal of the macromolecular compound peak for AOM. From these data it can be concluded that AOM contained a higher concentration of UV-absorbing macromolecules and humic compounds than EOM. MF appeared to remove only some of the macromolecules (proteins and polysaccharides) from the EOM. UF removed some humics and marked amounts of macromolecular compounds from EOM, and substantial amounts of humics and almost all the macromolecular organics from the AOM.

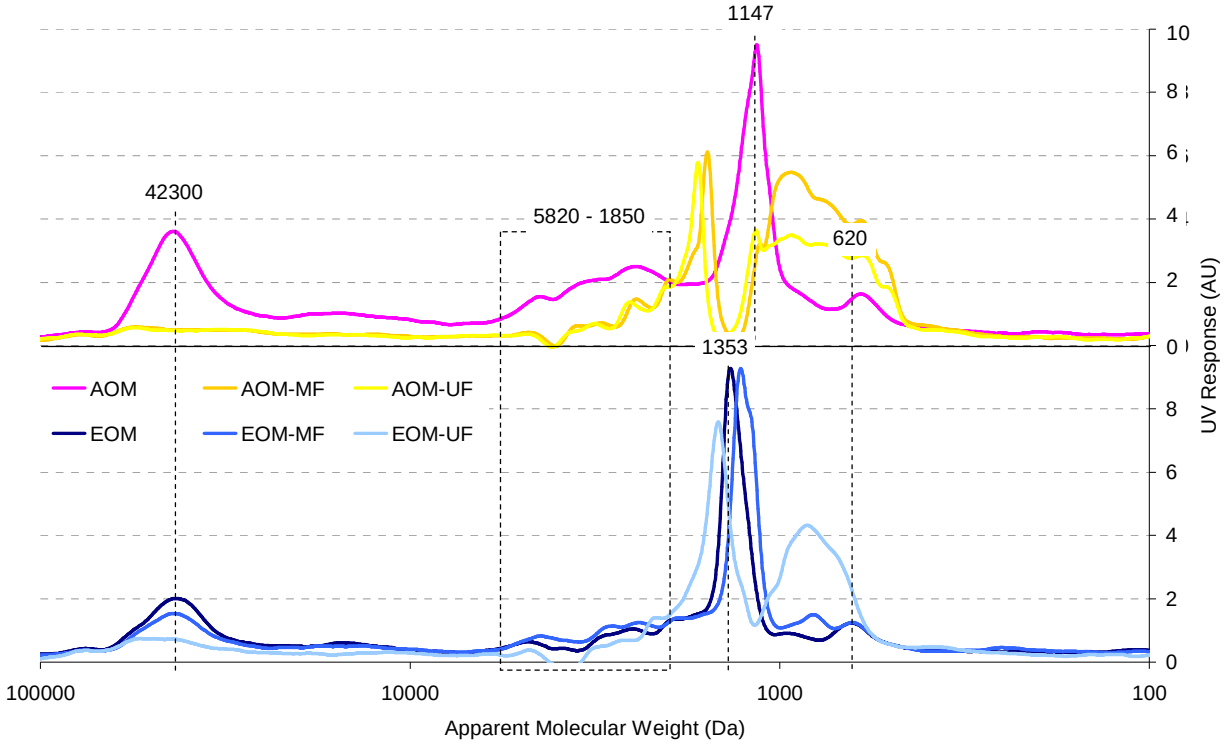


Figure 5.10: Apparent molecular weight distribution of EOM and AOM feed solutions and respective MF and UF permeates as determined by HPSEC-UV

5.3.7 Algal Fouling Layer Characteristics

5.3.7.1 ATR-FTIR Spectroscopy

ATR-FTIR analysis of fouled MF and UF membranes showed similar spectra (Figure 5.11). Similar to the functional groups identified in Section 4.2.8, EOM and AOM fouling layers displayed the presence of protein- and polysaccharide-like compounds. The broad OH band around 3400 cm^{-1} and peaks near 1000-1120 cm^{-1} suggest the presence of polysaccharide-like compounds. N-H peaks at 3278 cm^{-1} and 1550 cm^{-1}, together with amide connected C=O stretching at 1650 cm^{-1} suggest the presence of peptide groups. The presence of proteins and polysaccharides in the fouling layer is consistent with the results of the previous sections and other research (Jarusutthirak et al., 2002; Her et al., 2004; Shon et al., 2006). The presence of small peaks at 2851 cm^{-1} and 1720 cm^{-1} indicates the presence of carboxylic acids (ie., humic and fulvic acids).

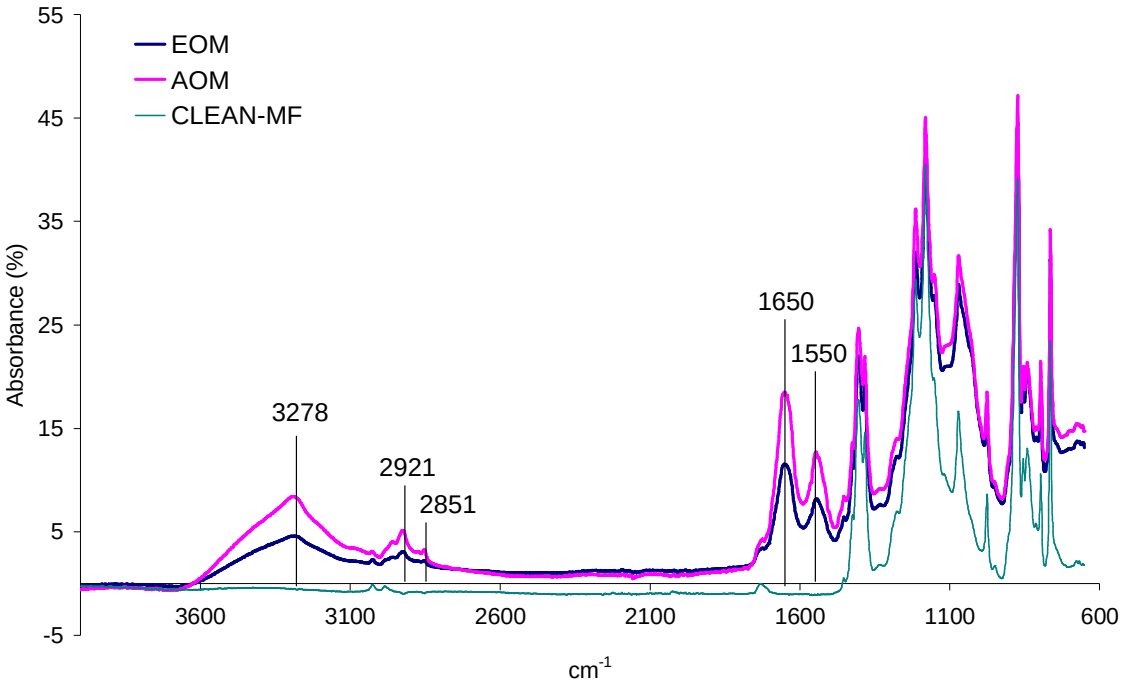


Figure 5.11: ATR-FTIR spectra of clean and fouled MF membrane by EOM and AOM

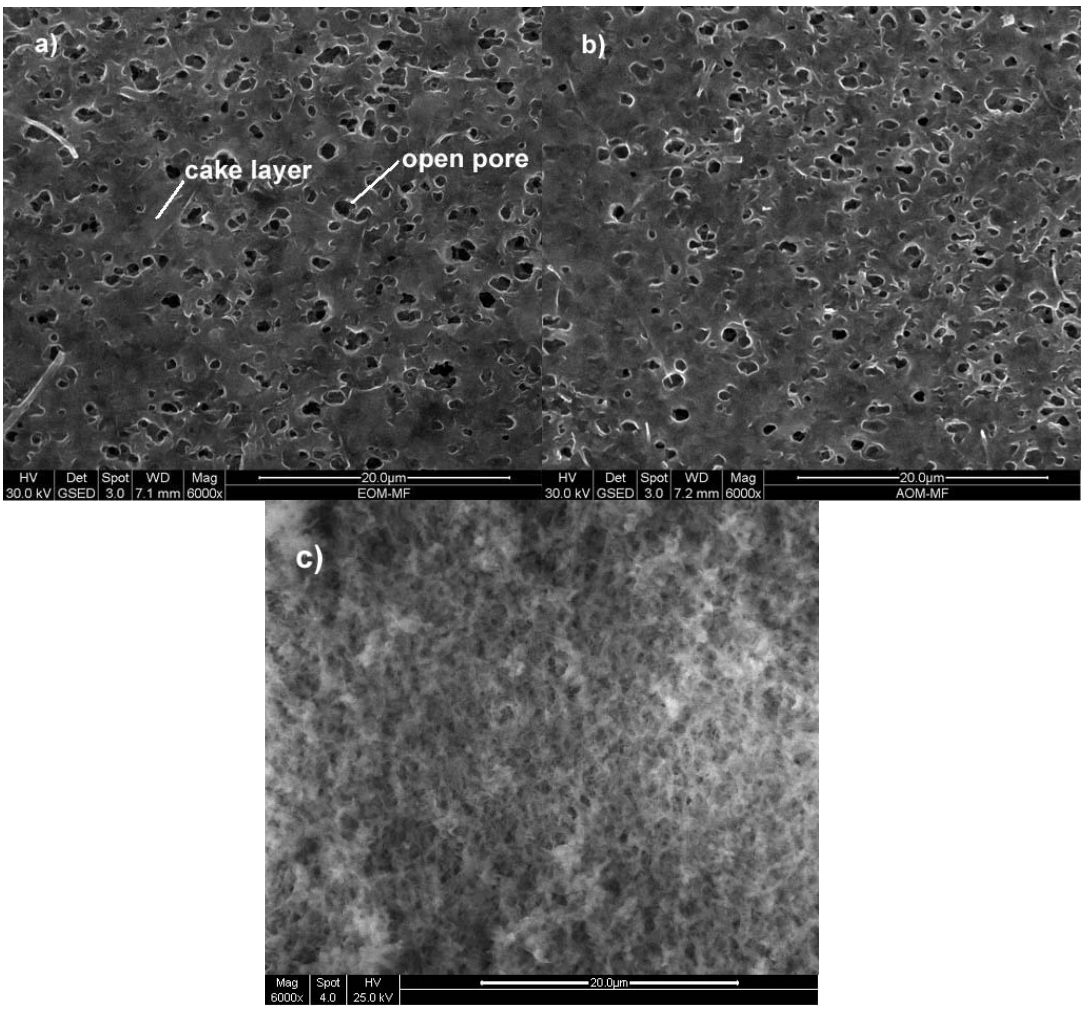


Figure 5.12: ESEM images of c) clean and a) EOM and b) AOM fouling layer on MF membrane

5.3.7.2 Scanning Electron Microscopy

Images obtained using an Environment Scanning Electron Microscope (ESEM) showed no discernible difference in the fouling layer of EOM and AOM samples on MF membranes (Figure 5.12), which had treated similar amounts of TOC (2.5 g/m^2). The similarity in cake layer formation and open channel pores suggests the mode of fouling for EOM and AOM were analogous.

The featureless, flat cake layers formed on the UF membranes did not provide much information other than the cake layer formed by the EOM and AOM appeared to be similar.

5.4 Fouling by Hydrophilic EOM & AOM

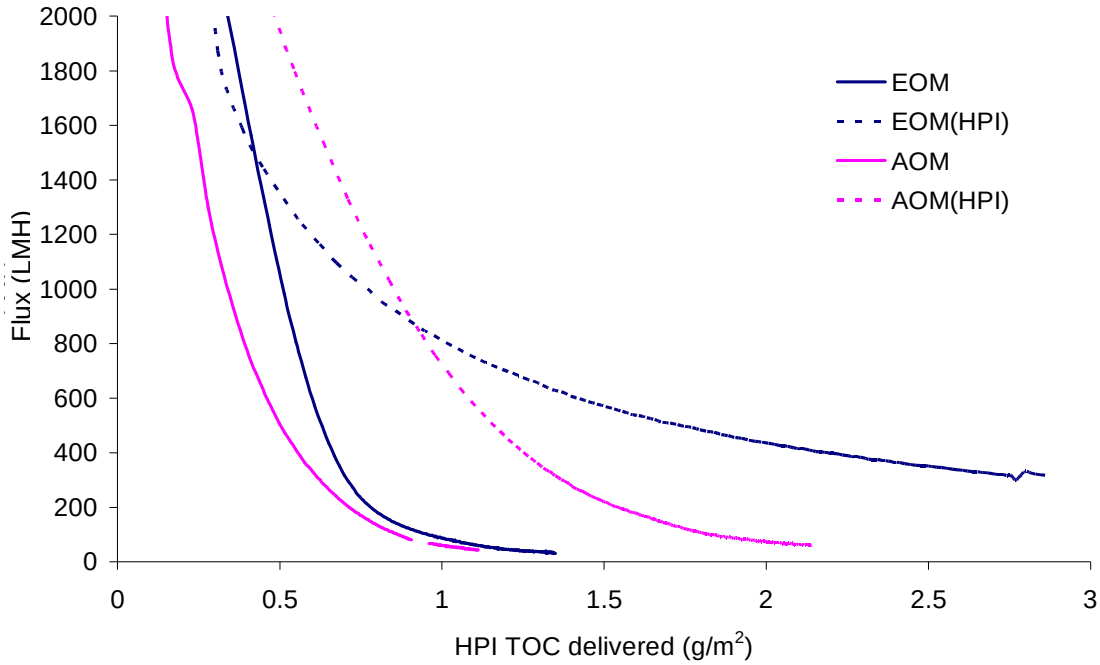
Based on the findings in the previous sections, the hydrophilic organic compounds such as SMP and proteins in EOM and AOM play a major role in the fouling of hydrophilic MF and UF membranes. This is consistent with the findings of other researchers (Fan et al., 2001; 2002; Habarou et al 2005; Lee et al., 2006).

The HPI fractions of the EOM and AOM samples were subjected to MF and UF to determine the effect of the HPI compounds on membrane flux and if there were any difference in the fouling propensity of the HPI compounds of the EOM and AOM samples. The HPI fraction was isolated by the removal of hydrophobic and transphilic organics by DAX-8 and XAD-4 resins (Section 3.1.8). The HPI solutions were adjusted to pH 8 prior to MF and UF. The DOC levels for the EOM HPI and AOM HPI solutions were 2.9 ± 0.3 ppm.

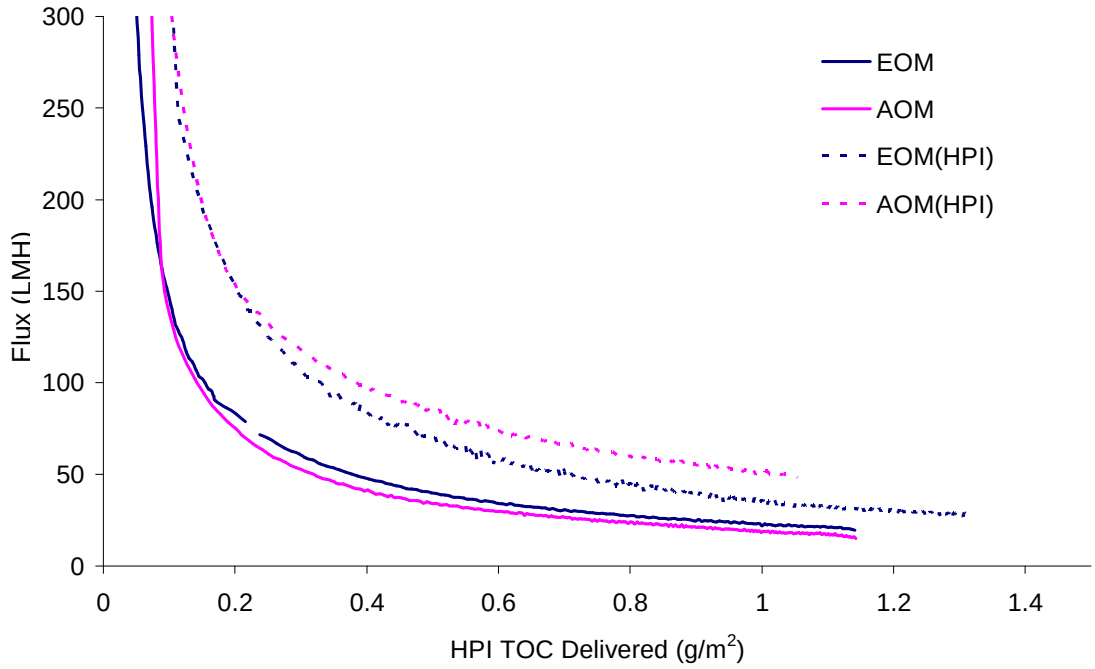
Figure 5.13a shows the MF flux profiles of the HPI fractions and the initial EOM and AOM feed samples based on the relative concentration of HPI within the solutions. For both EOM and AOM the reduction in flux was greater for the feed solutions than the HPI solutions. This indicates that the fouling on the MF membrane was not due solely to the HPI fraction within the EOM and AOM samples, but involved other fractions such as HPO acids and suspended particulates. The fouling rate of EOM(HPI) was not as rapid as of AOM(HPI) which reflects the flux profile of the feed solutions. This suggests that the composition of the HPI fraction in the EOM and AOM samples was different and that the AOM(HPI) compounds were more prone to fouling.

Similar to MF, the UF flux decline for the HPI fractions was not as great as that of the feed sample HPI (Figure 5.13b). As for MF, this indicates that the fouling on the UF membrane was not due solely to the HPI fraction within the EOM and AOM samples. Interestingly, the

propensity of fouling differed in that the EOM(HPI) fraction fouled more rapidly than the AOM(HPI) fraction. This suggests a difference in the EOM(HPI) and AOM(HPI) compounds, as found from MF flux decline, however the fouling propensity is higher for the EOM(HPI) fraction for UF.



a)



b)

Figure 5.13: a) MF and b) UF flux profiles of hydrophilic fractions of EOM and AOM

5.5 Membrane Flux Recovery

For the MF and UF filtration experiments a representative flux cut-off point of 55 LMH was deemed to be the point of significant fouling. The fouled membrane surface was hydraulically cleaned and backwashed using Milli-Q water (Section 3.1.3). The pure water flux rate was compared with the initial pure water flux rate and the difference was attributed to irreversible fouling caused by the fouling feed solution. Irreversible fouling resistance was calculated as per Section 3.1.3.

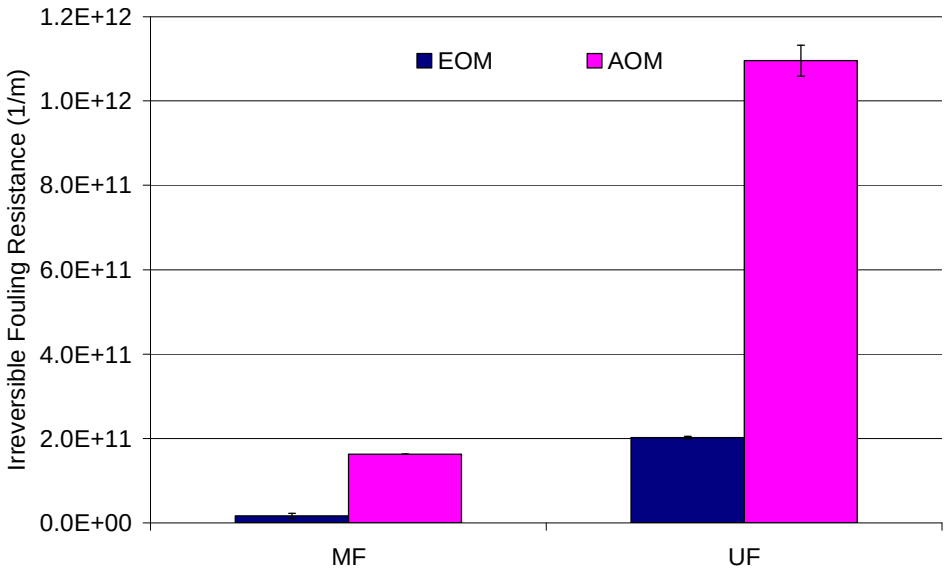


Figure 5.14: Irreversible fouling layer resistance

Figure 5.14 shows the irreversible fouling resistance of MF and UF membranes after fouling by EOM or AOM solutions, hydraulically cleaning and back flushing with Milli-Q water. Irreversible fouling was more prominent in the AOM sample. For both membrane types the irreversible fouling was an order of magnitude greater for AOM- than for EOM-fouled membranes. This suggests that although the rate of membrane fouling by EOM and AOM on MF and UF membranes is fairly similar (Section 5.3), some AOM constituents are more strongly attached to the membrane surface and cause greater irreversible fouling. This may be due to differences in the characteristics of the components of the hydrophilic fraction (proteins and polysaccharide-like materials), and the hydrophobic fraction (humic acids). The concentration of the latter was higher in AOM (as shown by resin fractionation and EEMs/FRI) and was almost completely removed by UF (as shown by resin fractionation).

5.6 Conclusions for Chapter 5

Comparison of the flux rates for EOM and AOM solutions at the same concentration (5 ppm) showed that EOM had a greater fouling effect than AOM on the MF membrane, whereas the fouling rates were very similar for both sample types for the UF membrane. Resin fractionation of the dissolved organic carbon showed that EOM contained a higher proportion of hydrophilic compounds than AOM and ATR-FTIR analysis showed the presence of proteins and polysaccharides in the EOM and AOM fouling layers. FRI and EEM analysis indicated that EOM contained a slightly higher concentration of SMP-like compounds compared with AOM, and AOM had a higher concentration of protein-like compounds. The higher concentration of proteins in AOM was attributed to lysis products, and the higher concentration of SMP compounds in EOM was attributed to the extracellular layer. From these analyses it was found that the higher concentration of hydrophilic organic compounds in EOM, and the higher concentration of SMP compounds within the EOM hydrophilic fraction, were responsible for the higher rate of MF fouling. Further investigation of the heterogeneity of EOM and AOM protein- and SMP-like fractions would ascertain more detailed differences in their compositions.

MF removed approximately 30% of the TOC, mainly hydrophilic compounds, from both the EOM and AOM solutions, indicating that the proteins and polysaccharides in this fraction were the main contributors to the fouling of the membrane. For UF, more TOC was removed from the AOM (70%) than from the EOM (53%). UF removed more hydrophilic organic compounds than MF, and gave significant removal of hydrophobic (ie., humic acid-like) material for both EOM and AOM. The presence of suspended solids most likely contributed to the fouling layers, however, EOM which had the lowest suspended solids concentration, fouled the MF membrane slightly faster than AOM. It may be possible that the higher concentration of suspended solids in AOM resulted in a more permeable cake layer, although ESEM analysis did not show evidence to substantiate this.

Given that proteins and polysaccharides, which make up the hydrophilic fraction, are typically larger than hydrophobic acids it may be expected that the EOM sample would foul the MF and UF membrane more rapidly. However, given the relatively large pore size of the membranes used it is evident that interactions due to surface chemistry also contribute greatly to the formation of the fouling layer.

The flux declines caused by EOM and AOM were similar for UF, and only slightly dissimilar for MF, however the irreversible fouling resistance was an order of magnitude greater for AOM for both membrane types. It is postulated that the higher concentration of proteins released through cell lysis, as evidenced through EEM and FRI analysis, and/or the higher humic acid content contributed to the irreversible fouling of the membranes.

Chapter 6 - Conclusions and Recommendations

6.1 Conclusions

Samples from different parts of the WTP treatment train were tested for fouling propensity. The plant uses a combined activated sludge–lagoon treatment (AS-lagoon) process. The lagoons are subject to occasional blue-green algal blooms hence filtration experiments using MF and UF membranes were conducted in a stirred cell system to determine the most suitable feed water supply for a future membrane filtration plant. Clarified activated sludge effluent (C4) was found to foul MF and UF membranes more rapidly than AS-lagoon treated effluent (HORS). The more rapid flux decline for MF and UF for C4 was attributed to the higher concentrations of suspended solids and TOC, in particular of the HPI fraction, in the C4 effluent. Examination of the fouled membranes indicated that proteins and polysaccharides, ie., components of the HPI fraction, were the major components of the fouling layer.

Effluent from the 25 West P10 lagoon had a lower fouling propensity than that of 55 East P10. Slight differences in the suspended solids, TOC and HPO fraction content were the likely cause.

Anabaena circinalis, a cyanobacterium commonly referred to as a blue-green alga, was cultured to ascertain differences in fouling propensity of organic carbon released by the cells during the growth phase (extracellular organic matter - EOM) and lytic phase (algal organic matter - AOM). Comparison of the flux rates for EOM and AOM solutions at the same concentration (5 ppm) showed that EOM had a greater fouling effect than AOM on the MF membrane, whereas the fouling rates were very similar for both sample types for the UF membrane. The EOM feed had a markedly higher proportion of hydrophilic to hydrophobic components than the AOM feed. These were attributed to proteins and polysaccharides that make up the SMP-like fraction, which are excreted by the blue-green alga during its growth phase.

MF removed approximately 30% of the TOC, mainly hydrophilic compounds, from both the EOM and AOM solutions, indicating that the proteins and polysaccharides in this fraction were the main contributors to the fouling of the membrane. For UF, more TOC was removed from the AOM (70%) than from the EOM (53%). UF removed more hydrophilic organic compounds than MF, and gave significant removal of hydrophobic (ie., humic acid-like) material for both EOM and AOM.

It is therefore postulated that the SMP compounds excreted by the blue-green alga during its growth phase had a slightly higher fouling propensity than the proteins and humic acid-like matter released during cell lysis.

Irreversible fouling of both MF and UF membranes was an order of magnitude greater for AOM. This was attributed to differences in the characteristics of the hydrophilic fraction and the hydrophobic fraction (ie., humic acid-like matter). The concentration of the latter was higher in AOM and was almost completely removed by UF.

MF and UF of the HPI fractions of the EOM and AOM showed markedly different fouling profiles than those of the non-fractionated samples. This change in fouling propensity clearly demonstrates that the HPI fraction, although contributing significantly to the formation of a fouling layer, is not the only contributing fraction.

The major finding of this project is that the organic carbon compounds released during the growth phase (EOM) of *Anabaena circinalis* have a similar fouling propensity for UF than those released during the lysis phase (AOM), and a slightly higher fouling propensity for MF. However, due to the presence of higher UV-absorbing hydrophilic compounds, higher concentration of intracellular proteins and/or humic acid-like matter in the AOM, irreversible fouling was significantly higher during the lysis phase.

6.2 Recommendations

Based on the results of this study, it is recommended that HORS effluent be used for any future membrane filtration systems at WTP. However, it should also be noted that during the sampling period of this report no algal bloom occurred in the lagoons. As shown by the results for the algal study, such an event would likely have a more significant impact on membrane fouling than C4 effluent. Filtration experiments during an algal bloom at WTP are recommended to determine the extent of such an event on the filtration membranes.

Effluent from 25 West P10 is the recommended water source for HORS based on the samples studied in this report. However, long term analysis is required to better inform this decision due to water quality changes in both treatment trains over time.

Further investigation is also required to identify which specific SMP, protein-like and hydrophobic compounds were associated with the surface fouling layer and irreversible fouling layer, and which are associated with the growth phase and lysis phase of the alga.

The methods used in this report for culturing and harvesting algal organic matter are recommended as they replicate natural processes that occur in a water body. By allowing the cells to break down naturally, instead of using liquid extraction, freeze drying, or grinding, reduces the likely occurrence of artefacts from such processes.

Investigations using the methods described in this report with different algae are recommended to further inform changes in fouling propensity during the life cycle of algae. It is also recommended that EOM and AOM samples be mixed with NOM to assess interactions between allochthonous and autochthonous organic matter and fouling propensities.

Chapter 7 - References

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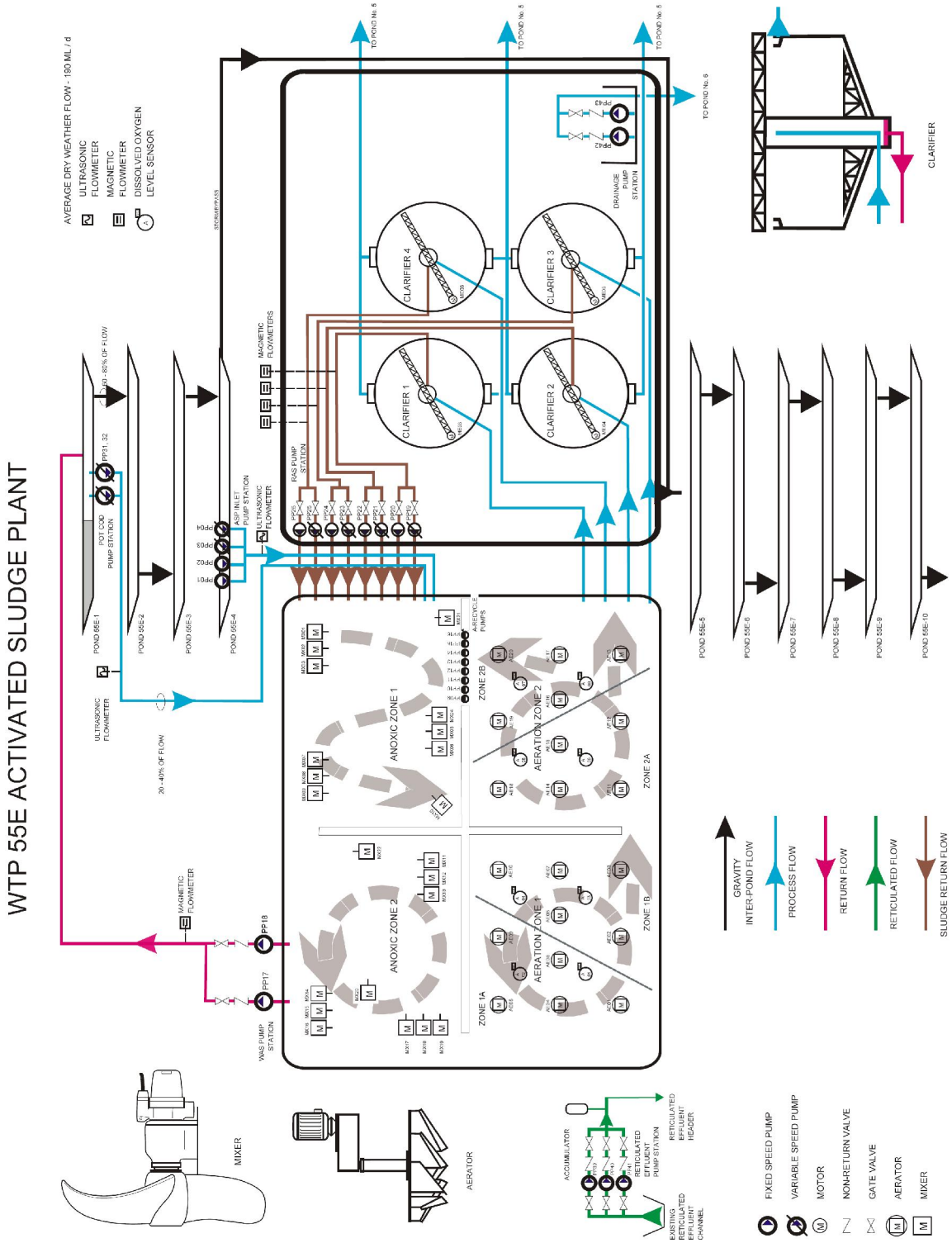
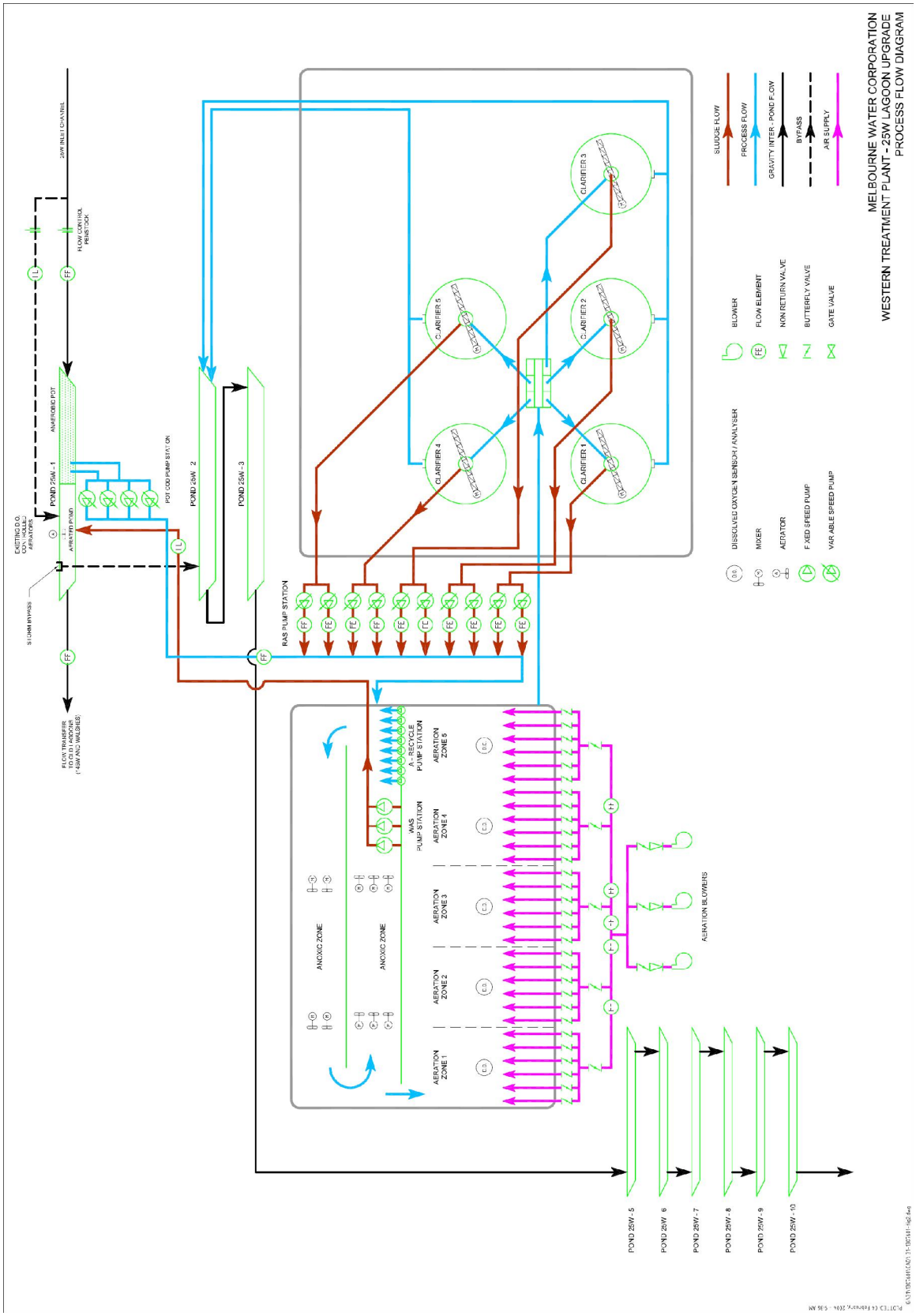
Appendix 1: Western Treatment Plant Schematics

Schematic of 55 East Treatment Train, provided by Melbourne Water Corporation, 2007.



Schematic of 25 West Treatment Train, provided by Melbourne Water Corporation, 2007.



Appendix 2: MLA Growth Medium Preparation

MLA Medium:

The following solutions were made up in individual volumetric flasks:

Stock Solutions:

1. $MgSO_4.7H_2O$ 4.94 g / 100.00 mL

2. $NaNO_3$ 8.50 g / 100.00 mL

3. K_2HPO4 1.392 g / 200.00 mL

4. H_3BO_3 0.247 g / 100.00 mL

5. Vitamins

Working Stock Solution

to 100.00 mL of distilled water, the following was added:

Biotin 0.05 mL primary stock

Vitamin B_{12} 0.05 mL primary stock

Thiamine HCl 10.0 mg

Primary Stocks

Biotin 10.0 mg / 100.00 mLH_2O

Vitamin B_{12} 10.0 mg / 100.00 mLH_2O

6. Micronutrients

Stock Solution [100.00 mL]

to 80mL of distilled water each of the following constituents was added separately, and mixed to dissolve each addition

Na_2EDTA 0.436 g (added first & stirred on low heat to fully dissolve)

$FeSO_4.7H_2O$ 0.1625 g

$NaHCO_3$ 0.060 g

$MnCl_2.4H_2O$ 0.036 g

then 1mL of the following primary stocks was added (each was made up separately):

Primary Stocks	(per 100.00 mL dH_20)
$CuCl_2.2H_2O$	0.0683 g.
$ZnCl_2$	0.1043 g.
$CoCl_2.6H_2O$	0.10 g.
$Na_2MoO_4.2H_2O$	0.06 g.

Finally, the micronutrient stock was made up to 100.00 mL with distilled water.

If precipitate formed the pH was increased up to 7.

7. $NaHCO_3$ 1.69 g / 100.00 mL

8. $CaCl_2.2H_2O$ 2.94 g / 100.00 mL

All solutions were stored at 4^oC

Nutrient Stock Preparation:

1. Preparation of MLA Medium (1000.00 mL volume)

To 520 mL distilled water the following was added

$MgSO_4.7H_2O$	40.00 mL
$NaNO_3$	80.00 mL
H_3BO_3	40.00 mL
H_2SeO_3	40.00 mL
Vitamin stock	40.00 mL
Micronutrient stock	40.00 mL

The solution was then autoclaved (121°C for 20 min) to sterilise.

After autoclaving, 200.00 mL of K_2HPO_4 was added by sterile filtration (0.22 μm)

3. To 100.00 mL of H_2O 1.69 g of $NaHCO_3$ was added and the solution autoclaved (121°C for 20 min) to sterilise.

4. To 100.00 mL of H_2O 2.94 g of $CaCl_2.2H_2O$ was added and the solution autoclaved (121°C for 20 min) to sterilise.

Sample Preparation:

To prepare 1 L sample add	
Sterile distilled water	964 mL
Sterile MLA Medium	25 mL
Sterile $NaHCO_3$	1 mL
Sterile $CaCl_2.2H_2O$	1 mL
Algae culture	10 mL