

MITIGATION OF MEMBRANE FOULING IN MICROFILTRATION & ULTRAFILTRATION OF ACTIVATED SLUDGE EFFLUENT FOR WATER REUSE

**A thesis submitted in fulfilment of the requirement for the degree of
Doctor of Philosophy (PhD)**

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DECLARATION

I hereby declare that:

- the work presented in this thesis is my own work except where due acknowledgement has been made;
- the work has not been submitted previously, in whole or in part, to qualify for any other academic award;
- the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program

Signed by

Sy T. Nguyen

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NOMENCLATURE

ACH: Poly(aluminium) chlorohydrate	HS: Humic substances
AER: Anion exchange resin	LC-OCD: Liquid chromatography with UV detection and organic carbon detection
AFM: Atomic force microscopy	MBR: Membrane bioreactor
AMWD: Apparent molecular weight distribution	MF: Microfiltration
AOC: assimilable organic carbon	MFI: Modified fouling index
AS: Activated sludge	MW: Molecular weight
ATR-FTIR: Attenuated total reflection-Fourier transform infrared spectroscopy	MWCO: Molecular weight cut-off
BAC: Biological activated carbon	NEU: Hydrophilic neutral fraction
BOD: Biological oxygen demand	NF: Nanofiltration
BV: bed volume	NOM: Natural organic matter
CDOC: Chromatographic dissolved organic carbon	OCD: Organic carbon detection/detector
CHA: Hydrophilic charged fraction	PAC: Powdered activated carbon
COD: Chemical oxygen demand	PACl: Poly(aluminium) chloride
Da: Dalton ($= \text{g mol}^{-1}$)	PAN: Polyacrylonitrile
DAX-8: Acrylic ester resin	PVDF: Polyvinylidene fluoride
DOC: Dissolved organic carbon	PS: polysulfone
DOM: Dissolved organic matter	PES: polyethersulfone
DBPs: Disinfection by-products (DBPs)	PEEK: Polyetheretherketone
EDTA: Ethylenediaminetetraacetic acid	PTFE: Polytetrafluoroethylene
EDX: Energy dispersive X-ray spectroscopy	PVP: Polyvinyl pyrrolidone
EEM: Excitation-emission matrix	RO: Reverse osmosis
EfOM: Effluent organic matter	SDS: Sodium dodecyl sulphate
EPS: Extracellular polymeric substances	SEC: Size exclusion chromatography
HFM-116: polyvinylidene fluoride membrane with a molecular weight cut-off of 100 kDa (supplied by Koch Membrane Systems)	SEM: Scanning electron microscopy
HFM-180: polyvinylidene fluoride membrane with a molecular weight cut-off of 100 kDa (Koch Membrane Systems)	SHA: Slightly hydrophobic acid fraction (= Transphilic fraction)
HFK-141: polyethersulfone membrane with a molecular weight cut-off of 30 kDa (Koch Membrane Systems)	SOC: Synthetic organic compounds
HOC: Hydrophobic organic carbon	SMP: Soluble microbial products
HPI: Hydrophilic fraction (= hydrophilic charged fraction + hydrophilic neutral fraction)	SS: Suspended solids, in this thesis SS is defined as the particulate matter retained by a 0.5 μm glass-fibre filter
HPO: Hydrophobic acid fraction (= very hydrophobic acid fraction)	SUVA: specific UV absorbance [$\text{L m}^{-1}\text{mg}^{-1}$]
	TFC: Thin-film composite
	TMP: Transmembrane pressure [Pa]
	TOC: Total organic carbon
	TPI: Transphilic fraction
	TSS: Total suspended solids

UF: Ultrafiltration
 UMFI: Unified membrane fouling index
 UV: Ultraviolet
 UVA₂₅₄: UV absorbance at the wavelength 254 nm [cm⁻¹]
 UVD: UV detection/detector
 VCF: Volume concentration factor
 VHA: Very hydrophobic acid fraction
 VVLP: Flat-sheet polyvinylidene fluoride membrane with pore size 0.1 µm (supplied by Millipore)
 XUNP-003: Hollow-fibre polyvinylidene fluoride membrane with pore size 0.1 µm (supplied by Pall Corporation)
 XAD-4: Polyaromatic resin
 IRA-958: Strong anion exchange resin

Symbols

A : Effective membrane surface area [m²]
 A_0 : Reference membrane area for the calculation of the MFI, equal to dynamic viscosity at 20°C, equal to $13.8 \times 10^{-4} \text{ m}^2$
 C_b : Particle/solute concentration in the bulk feed
 C_f : Concentration of the membrane foulant in the feed
 E_{RW} : Cleaning efficiency of the membrane cleaner [%]
 $fn(J, n)$: Function relating the permeate flux at time t and at time $t = 0$ in cross-flow filtration for the different models
 G : Constant in the cake filtration model for cross-flow filtration [s m⁻²]
 J : Permeate flux [L m⁻² h⁻¹]
 J_0 : Pure water flux of the virgin membrane [L m⁻² h⁻¹]
 J' : Permeate flux at the end of the filtration experiment [L m⁻² h⁻¹]

J_{BW} : Pure water flux of the fouled and then backwashed membrane [L m⁻² h⁻¹]
 J_c : Pure water flux of the membrane after chemical cleaning [L m⁻² h⁻¹]
 J^* : Critical flux in cross-flow filtration models [m s⁻¹]
 j_c : Critical flux for the complete blocking model in cross-flow filtration [m s⁻¹]
 j_i : Critical flux for the intermediate blocking model in cross-flow filtration [m s⁻¹]
 j_s : Critical flux for the cake filtration model in cross-flow filtration [m s⁻¹]
 K'_s : Hermia's parameter for standard blocking model filtration in cross-flow filtration
 k : Constant in dead-end filtration models
 k_{CB} : Constant for the complete blocking models in dead-end filtration [s⁻¹]
 k_{IB} : Constant for the intermediate blocking model in dead-end filtration [s⁻¹]
 k_{SB} : Constant for the standard blocking (or pore adsorption) model in dead-end filtration (s⁻¹)
 k_{CF} : Constant of the cake filtration model in dead-end filtration [s⁻¹]
 m_c : Mass of the cake
 n : Constant in dead-end and cross-flow filtration models, $n = 0, 1, 1.5$, and 2 correspond to the cake filtration, intermediate pore blocking, standard pore blocking, and complete pore blocking models, respectively
 ΔP : Transmembrane pressure [Pa]
 ΔP_0 : Reference transmembrane pressure for the calculation of the modified fouling index (MFI), equal to 2.0 bar
 R_a : Hydraulic resistance exerted by adsorptive fouling [m⁻¹]

R_c : Hydraulic resistance exerted by the cake layer
[m⁻¹]

\hat{R}_c : Specific resistance of the cake formed on the
membrane surface

R_{cp} : Hydraulic resistance exerted by concentration
polarisation [m⁻¹]

R_{if} : Hydraulic resistance exerted by hydraulically
irreversible fouling [m⁻¹]

R_m : Hydraulic resistance exerted by the virgin
membrane,

R_p : Hydraulic resistance exerted by pore blocking
[m⁻¹]

R_{res} : Hydraulic resistance exerted by residual
fouling after chemical cleaning [m⁻¹]

R_{rf} : Hydraulic resistance exerted by hydraulically
reversible fouling [m⁻¹]

R_{tf} : Hydraulic resistance exerted by total fouling
[m⁻¹]

t : Filtration time [s]

V : permeate volume [m³]

\dot{V} : Permeate volumetric flow rate at time t [m³ s⁻¹]

\dot{V}_0 : Permeate volumetric flow rate at time $t = 0$ [m³
s⁻¹]

v : Accumulated specific permeate volume, i.e., total
permeate volume per unit membrane area [L m⁻²]

WFR : Pure water flux recovery by chemical
cleaning [%]

Greek letters

ε_0 : Membrane surface porosity at time $t = 0$

μ : Dynamic viscosity [Pa s]

μ_0 : Reference dynamic viscosity for the calculation
of the MFI, equal to dynamic viscosity at 20°C [Pa s]

$\Delta\pi$: Differential osmotic pressure [Pa]

σ : Blocked area per unit volume of filtrate [m⁻¹]

SUMMARY

Membrane fouling has been a major obstacle in microfiltration (MF) and ultrafiltration (UF) of secondary effluent. Feed pre-treatment is a common practice for fouling mitigation. However, the diversity in the characteristics of effluent organic matter (EfOM) and the complexity of the fouling phenomenon make it difficult to predict the effectiveness of different pre-treatments. Therefore, this research sought to obtain a more detailed understanding of the effects of various feed pre-treatment methods on membrane fouling in MF and UF of secondary effluent, using an activated sludge (AS) effluent in Victoria (Australia) as an example. This effluent had a brownish yellow colour, which may limit customers' willingness to purchase the product water for reuse. The pre-treatments investigated included coagulation (without removal of the coagulated matter prior to MF or UF), ozonation, ozonation followed by biological activated carbon (BAC) filtration, and adsorption with an anion exchange resin (AER) and a powdered activated carbon (PAC).

The research was divided into two parts. The first part dealt with dead-end filtration using polyvinylidene fluoride (PVDF) and polyethersulfone (PES) membranes. Two PVDF MF (0.1 μm) membranes, one of which was less hydrophobic than the other, and two hydrophobic PVDF UF membranes of different molecular weight cut-offs (MWCO) (100 kDa and 50 kDa) were used. A relatively hydrophilic PES UF membrane (MWCO = 30 kDa) was also investigated. The second part was dedicated to cross-flow filtration with ceramic membranes. Single-channel tubular membranes made of α -alumina (0.1 μm) and zirconia (20 nm) were used.

The fouling behaviour of the raw (i.e., non-pre-treated) effluent was studied first. Analysis of the feed and the MF and UF permeates with liquid chromatography with organic carbon detection (LC-OCD) revealed that biopolymers, which contained proteins and polysaccharides (molecular weight (MW) $\gg 20,000$ Da), and humic substances (HS, MW=1,000–20,000 Da) were the EfOM components responsible for fouling of all the membranes investigated. The contribution of biopolymers to fouling was much greater than that of HS, as indicated by the higher rejection of the former by the membranes. HS caused hydraulically irreversible fouling, whereas biopolymers contributed to both hydraulically reversible and irreversible fouling. The roles of biopolymers and HS in causing fouling were

further confirmed by the results obtained from the study on the effects of the feed pre-treatments on the membrane fluxes and membrane cleaning experiments.

Flux data analysis showed that for dead-end MF, fouling by the raw effluent was governed by pore adsorption and pore blocking during the first 20 minutes of filtration and then followed the cake filtration model. For the PVDF UF membranes, fouling switched from pore adsorption and pore blocking to cake filtration after the first 5 minutes of filtration. Fouling of the PES UF membrane could be described by the cake filtration model over the course of filtration.

The effect of coagulation on membrane fouling in dead-end filtration with the polymeric membranes was then investigated. Coagulation with poly(aluminium) chlorohydrate (ACH) and alum at $2.5 \text{ mg Al}^{3+} \text{ L}^{-1}$ significantly improved the permeate flux and reduced hydraulically irreversible fouling. This was attributed to the coagulants removing the colloidal organic matter, including some biopolymers and HS responsible for fouling, from the raw effluent. Unlike MF fouling by the raw effluent, MF fouling by the coagulated effluent followed the cake filtration mechanism from the beginning of filtration. The MF flux improvement was greater for alum than ACH, whereas the two coagulants had a similar flux enhancing effect for UF. Flux improvement by coagulation was also observed in cross-flow MF tests with the alumina membrane.

Coagulation pre-treatment did not reduce the true colour of the effluent to the desired level (20–25 Pt-Co units) unless very high coagulant doses (approximately $40 \text{ mg Al}^{3+} \text{ L}^{-1}$) were used. Therefore, ozonation and adsorption pre-treatment with AERs and PAC were considered. It was found that the colour removal target could be achieved by

- (i) Ozonation of the raw effluent at $10 \text{ mg O}_3 \text{ L}^{-1}$ for 10 minutes,
- (ii) Pre-adsorption of the raw effluent with an AER at 10 mL L^{-1} with a 20-minute contact time (1 bed volume of the resin treated 1500 bed volumes of the raw effluent), or
- (iii) Pre-adsorption with a PAC (Acticarb PS1300) at 150 mg L^{-1} for 30 minutes.

Dead-end filtration tests with the raw and ozonated effluent (after ozone had decomposed) showed that ozonation led to significant flux improvement, which was attributed to the breakdown of some biopolymers and HS to compounds with lower MW and hydrophobicity.

However, as this pre-treatment generated some low MW compounds ($MW < 500$ Da), it may accelerate membrane biofouling. Consequently, BAC filtration of the ozonated effluent was considered. This additional pre-treatment led to further flux improvement in MF and in UF with the 100 kDa membrane, but did not affect the flux of the tighter UF (30 kDa) membrane. The hydraulically irreversible fouling was reduced after ozonation whereas BAC filtration did not affect this type of fouling. BAC filtration showed potential to reduce biofouling since the filter removed the majority of the low MW compounds generated during ozonation.

Pre-treatments with the PAC and the AER neither reduced nor worsened membrane fouling in dead-end filtration. This was due to the fact that although the AER and the PAC removed more than 50% of HS from the raw effluent, they did not remove biopolymers – the largest contributors to membrane fouling. Similarly, cross-flow filtration tests showed that while ozonation improved, pre-adsorption with the AER did not affect the flux performance of the ceramic membranes.

For cross-flow MF and UF, rapid back-flushing the ceramic membranes at 600 kPa for 1 second every 12 minutes resulted in significant flux improvement. The application of rapid membrane back-flushing in combination with coagulation or ozonation pre-treatment showed the ability to maintain high permeate fluxes in cross-flow filtration of secondary effluent.

Chemical cleaning of the 50 kDa PVDF and 30 kDa PES membranes fouled by the raw effluent was conducted. The most effective cleaners were sodium dodecyl sulphate, Terg-a-zyne, and NaOCl. The results verified that hydrophobic attraction was the major force keeping the hydraulically irreversible foulants and the membranes together and that HS played a role in causing internal adsorptive fouling.

This work showed that only the pre-treatments which led to the removal (coagulation) or breakdown in the structures (ozonation) of biopolymers reduced membrane fouling. Therefore, pre-treatment for fouling reduction in MF and UF of secondary effluent should target the biopolymers (i.e., proteins and polysaccharides). Furthermore, less hydrophobic MF membranes would likely to benefit more from feed pre-treatments for fouling reduction than more hydrophobic counterparts, as hydraulically irreversible fouling of the formers is likely to be less severe and more easily mitigated.

CHAPTER 1. INTRODUCTION

1.1. Background of the project

Australia has experienced long-term and severe droughts over the last decade and is expected to face these events more frequently in the future (Australian Government - Bureau of Meteorology 2008). As a result, water authorities are seeking alternative water sources to meet the increasing demand due to increasing population. It is recognised that reusing municipal wastewater will significantly increase Australian water availability (Victorian Government - Department of Sustainability and Environment 2004). The Australian Federal and State Governments therefore have initiated many water reuse and seawater desalination projects. One of these was the upgrade of the treatment processes at a municipal wastewater treatment plant (WWTP) in Victoria. This WWTP treats sewage via 4 stages: preliminary, primary, and secondary treatments followed by disinfection. A small amount ($< 5\%$) of the disinfected secondary effluent is used as recycled water, mainly for irrigation and cleaning, and the rest is discharged to the ocean. The purpose of this upgrade was to enable the WWTP to produce “Class A” recycled water, which is suitable for use in new housing estates, agriculture, and industry. It would also help to reduce flow to the ocean outfall and enable the WWTP to meet increasingly more stringent regulatory requirements on the quality of discharged water.

Microfiltration (MF) and ultrafiltration (UF) of the secondary effluent to remove suspended solids (SS) and pathogens were considered as tertiary treatment options for the recycled water. A major concern with this effluent was its brownish yellow colour, which may limit customer willingness to purchase and reuse the effluent. Therefore, the WWTP also aimed to reduce the true colour (i.e., colour after filtration through a $0.45\ \mu\text{m}$ membrane) of the AS effluent (which can range over 65–120 Pt-Co units) by approximately 75–80%, so that the final effluent would have a true colour of 15–25 Pt-Co units, which appears almost colourless.

1.2. Rationale

Membrane processes for the treatment of water and wastewater have been widely accepted due to their high quality product water and affordability. However, for this technology to be used efficiently, membrane fouling needs to be minimised. Fouling of filtration membranes

results in a reduction in water throughput, necessitating process downtime, membrane cleaning, and more frequent membrane replacement.

The fouling phenomenon is complex and is influenced by several factors, such as feedwater and membrane characteristics and operating conditions (Mulder 1996). Feed pre-treatment is commonly practised to reduce membrane fouling. However, the complexity of the fouling phenomenon makes it difficult to predict the effectiveness of pre-treatment methods on fouling reduction. For example, both beneficial and adverse effects of coagulation on membrane fouling have been reported (Adham *et al.* 2006). Furthermore, whereas secondary effluents at some WWTPs have a brownish yellow colour (most likely due to the high concentration of humic substances), information regarding the effectiveness of different pre-treatment methods for colour removal on fouling reduction in MF and UF of municipal secondary effluent is scarce.

To date the vast majority of the membranes used in water and wastewater treatment are made of polymeric materials. However, it has been predicted that ceramic membranes will become competitive alternatives in the next decade (Pearce 2011). Previous studies on MF and UF of water and municipal wastewater using ceramic membranes have focussed on the permeate flux and quality. The effects of feed pre-treatments on membrane fouling have received little attention. With the growing use of ceramic membranes, it is useful to have more detailed understanding of their fouling behaviour in these applications.

1.3. Research objectives

The purpose of this study was to identify the components responsible for membrane fouling and the fouling mechanisms in MF and UF of the brownish yellow secondary effluent collected from the WWTP mentioned in Section 1.1. The effectiveness of different pre-treatments on fouling reduction was also investigated. Dead-end filtration with polymeric membranes and cross-flow filtration with ceramic membranes was examined. This study focussed on the use of PVDF, PES, alumina, and zirconia membranes, which are the most widely used membranes in water and wastewater treatment. The pre-treatments under investigation included:

- (i) Coagulation
- (ii) Ozonation
- (iii) Ozonation followed by biological activated carbon (BAC) filtration

- (iv) Adsorption with a powdered activated carbon (PAC), and
- (v) Adsorption with an anion exchange resin (AER).

Coagulation was investigated as it is the most widely used pre-treatment for MF and UF of water and wastewater. The other pre-treatments were considered for their ability to remove colour-imparting compounds from the secondary effluent and their impact on the filtration process.

The research was divided into 2 parts. The first part dealt with dead-end MF and UF with the polymeric membranes. The research questions to be addressed included:

- (a) What were the components in the effluent responsible for flux reduction during MF and UF of the secondary effluent? Of these, which components were responsible for hydraulically reversible and irreversible fouling?
- (b) What were the predominant fouling mechanisms in dead-end MF and UF of the effluent, as suggested by the flux data and the identity of the foulants?
- (c) Which of the pre-treatment methods listed above reduced membrane fouling and what were the reasons for the fouling reduction? Which methods could reduce the true colour of the raw effluent to 20–25 Pt-Co units while improving the MF and UF flux?
- (d) What were the most effective cleaning agents for the fouled membranes?

The second part was dedicated to cross-flow MF and UF with the alumina and zirconia membranes with the following research questions:

- (a) Were the membrane foulants in cross-flow filtration with the ceramic membranes different or similar to those in dead-end filtration with the polymeric membranes?
- (b) Would coagulation, ozonation and adsorption pre-treatment with the AER improve the flux performance in cross-flow MF and UF?
- (c) Rapid membrane back-flushing with the back-flush device being a piston driven by air pressure has been used to improve the flux performance in cross-flow MF of water and wastewater from industrial sources (e.g., yeast suspensions and electroplating wastewater) with tubular ceramic membranes. Would this technique also be useful in cross-flow MF and UF of the secondary effluent?

It is expected that the findings will contribute to the knowledge pool in the area of membrane fouling mechanisms and fouling mitigation. They will help to explain why one feed pre-

treatment method is better than others in terms of fouling reduction and hence will assist WWTPs in the selection of the pre-treatment methods suitable for their purposes.

CHAPTER 2. LITERATURE REVIEW

2.1. Overview of conventional municipal wastewater treatment processes

The treatment of municipal wastewater is typically accomplished via 4 stages: preliminary, primary, secondary, and tertiary.

2.1.1. Preliminary treatment

The purpose of this treatment is to remove large solids and grit from the wastewater to prevent damage to the rest of the unit operations. This is usually accomplished by screening. Coarse screens with openings of 6 mm or larger are used to remove large solids and rags, whereas fine screens may be used to remove smaller particles (Rowe & Abdel-Magid 1995; Vesilind 2003; Hammer & Hammer 2008).

2.1.2. Primary treatment

Primary treatment aims to reduce the SS level of the wastewater and to remove floating materials such as fat, oil, and grease. It is usually done using settling tanks (or clarifiers), wherein suspended particles heavier than water settle by gravity under quiescent conditions and floating materials are removed by skimming. The settling of particulates can be enhanced by pre-aeration or chemical coagulation (Vesilind 2003).

2.1.3. Secondary treatment

This involves a biological treatment process in which micro-organisms consume dissolved organic matter (DOM) in wastewater to grow and reproduce, hence reducing the biological oxygen demand (BOD) of the wastewater (Vesilind 2003). Secondary treatment can be done using fixed film, suspended, or lagoon systems.

In fixed film systems, microbes grow on fixed objects (such as rock, sand, or plastic) and are exposed repeatedly to the wastewater for adsorption of organic material and to the atmosphere for oxygen (Vesilind 2003). In suspended systems (e.g. activated sludge), microbes are suspended in wastewater by agitating the wastewater for several hours after which the biomass is settled out as sludge in a secondary clarifier. Lagoons are shallow basins which

hold the wastewater for several months to allow natural degradation of sewage (Vesilind 2003).

2.1.4. Tertiary treatment

Secondary effluent may contain contaminants (e.g., nitrogen and phosphorus species, disinfection by-products, colour, pathogens, metals and salts) at levels higher than regulatory requirements and therefore require further treatment before being discharged to local waters or recycled. These treatment processes can be physical (e.g., membrane filtration and granular media filtration), biological (e.g., oxidation ponds), or chemical (e.g., precipitation of phosphorus, iron and manganese) (Rowe & Abdel-Magid 1995; Vesilind 2003).

2.2. Membrane filtration in water and wastewater treatment

Nowadays, a variety of membrane processes (MF, UF, nanofiltration (NF), and reverse osmosis (RO)) have been used to treat water and wastewater at many facilities worldwide. Examples of municipal wastewater treatment plants using membrane filtration to treat secondary effluent include West Basin Water Recycling Plant in Los Angeles, California (design flow = 45420 m³/day), Chandler Wastewater Reclamation Plant in Chandler, Arizona, Scottsdale Water Campus in Scottsdale, Arizona (design flow = 45420 m³/day), the NEWater plants in Singapore, and the three advanced wastewater treatment plants at Bundamba, Luggage Point, and Gibson Island of the Western Corridor recycled water project in Queensland, Australia. In these treatment plants, MF or UF is used as a pre-treatment for NF or RO.

There has been growing interest in the integration of membrane processes into existing water and wastewater treatment facilities for various reasons, such as to meet more stringent regulatory requirements for reuse and discharge and/or increase plant capacity (Water Environment Federation 2006). The advantages of membrane filtration over conventional filtration using granular media include superior quality of product water, small size, low energy consumption, easier maintenance and capacity extension, and the capability of handling wide fluctuations in feedwater quality (Clever *et al.* 2000).

MF and UF membranes have also been used widely in membrane bioreactors (MBRs). In MBRs, the activated sludge process and membrane filtration are used in combination to

achieve biological treatment and solids/liquid separation (Le-Clech *et al.* 2006). As the focus of this study is on membrane fouling in MF and UF of secondary effluent, membrane fouling in MBRs will be briefly discussed in this literature review.

2.2.1. Membrane classification

Membranes are usually classified according to their pore size, the molecular weight (MW) of the rejected material, the applied pressure, and their water affinity. The pore size, MW cut-off (MWCO), and operating pressure of the 4 different types of membranes are given in Table 2.1.

MF membranes are capable of removing SS, some protozoan cysts (e.g., the pathogens *Giardia* and *Cryptosporidium*), and bacteria (3–6 log removal). UF can remove some colloidal materials, dissolved macromolecules, and some viruses. NF and RO membranes are capable of removing dissolved solids (including ions); the separation capability of NF membranes lies between that of UF and RO membranes (Stephenson *et al.* 2000). MF and UF are conducted at much lower transmembrane pressure (TMP) than NF and RO and therefore are often called low pressure membrane filtration.

Table 2.1 Some characteristics of different membrane types
(Water Environment Federation 2006)

	MF	UF	NF	RO
MWCO (Da)	> 100,000	> 2,000–100,000	300–1000	100–200
Pore size (µm)	0.1–10	0.01–0.1	0.001–0.01	< 0.001
Operating pressure (psi)	1 – 30	3 – 80	70–220	800–1200
Operating pressure (kPa)	(7–207)	(20–550)	(480–1500)	(5500–8250)

Based on separation mechanism, filtration membranes can be categorised as either dense (NF and RO membranes) or microporous (MF and UF membranes) (Mulder 1996). The separation mechanism of MF and UF membranes is size exclusion (or sieving), i.e., components larger than the pore size are prevented from permeating through the membrane. For NF and RO membranes, besides size exclusion, separation also relies on the large differences in the solubility and diffusion rates of water and solutes. The much slower diffusion rate of solutes than water across the membranes allows the production of a solute-free permeate stream

(Bellona *et al.* 2004; Water Environment Federation 2006). Based on water affinity, membranes can be divided into 2 groups, namely hydrophobic membranes and hydrophilic membranes (Mulder 1996).

2.2.2. Membrane materials and structures

Membranes can have symmetric or asymmetric structures. Symmetric microporous membranes are cast from one material and their pore size can be either uniform (isotropic) or varied (anisotropic). For anisotropic membranes, the surface having the smaller pore size is used as the filtering surface. Integral asymmetric membranes (or “skinned” membranes) consist of a very thin (<1 µm) layer (skin) and a thicker (up to 100 µm) porous layer that adds support and is capable of high water flux. A more recent development is thin-film composite (TFC) membranes, made by bonding a thin layer of cellulose acetate, polyamide or other acetate-containing compounds to a thicker porous substrate (Water Environment Federation 2006).

Filtration membranes available on the market are produced from a diverse range of materials, which can be organic or inorganic. The most widely used organic materials include polyvinylidene fluoride (PVDF), polysulfone (PS), polyethersulfone (PES), polyacrylonitrile (PAN), polypropylene, cellulose acetate, polyamide, and polytetrafluoroethylene (PTFE). PS and PES have been used extensively as the base material for the majority of commercial membranes used in water treatment plants in the United States (Adham *et al.* 2006). Each membrane material has its advantages and disadvantages in terms of costs, thermal stability, chemical resistance, and biodegradability (Stephenson *et al.* 2000; Water Environment Federation 2006).

Polymeric MF membranes can be produced from PTFE, PVDF, polypropylene, polyethylene, cellulose esters, polycarbonate, PS, PES, polyimide, poly (ether imide), aliphatic polyamide, and polyetheretherketone (PEEK). The first 4 polymers are hydrophobic whilst the remainder are hydrophilic (Mulder 1996). Different from MF membranes, which can be symmetric or asymmetric, UF, NF and RO membranes generally have an asymmetric structure with a much denser top layer and consequently require a higher applied pressure to overcome their higher membrane hydraulic resistance. UF membranes are normally made from PS, PES, sulfonated PS, PVDF, PAN (and related block-copolymers), cellulotics (e.g., cellulose acetate), aliphatic

polyamide, poly (ether imide), and PEEK. Typical materials used in the production of RO membranes include cellulose esters (most commonly cellulose diacetate and cellulose triacetate), aromatic polyamide, and polybenzimidazoles (Mulder 1996).

Ceramic membranes, the majority of which are made from aluminium oxide (alumina, Al_2O_3), titanium oxide (titania, TiO_2), and zirconium oxide (zirconia, ZrO_2), are also available. Ceramic membranes generally have better thermal, chemical, and mechanical resistances, and longer service life than their polymeric counterparts (up to 15 years compared to 3-5 years) (Owen *et al.* 1995; Heijman & Bakker 2007). However, they require careful handling as the material is brittle. Unlike the polymeric membranes, the high thermal and chemical resistances of ceramic membranes make it possible to clean the fouled membranes at high temperatures and with high concentrations of cleaning agents, therefore complete flux recovery can be achieved with simple chemical cleaning (Bottino *et al.* 2001) with a lower risk of membrane degradation. The high chemical resistance also allows ceramic membranes to treat ozonated water without being damaged by high residual ozone concentrations (Schlichter *et al.* 2004). Another advantage of ceramic membranes compared with polymeric membranes is their higher operating fluxes (Heijman & Bakker 2007). Furthermore, with ceramic membranes it is possible to incorporate oxidation processes, such as UV irradiation, with filtration to remove contaminants in water and wastewater. In these applications, titanium oxide acts as a photocatalyst which initiates the oxidation of contaminants (Djafer *et al.* 2010). Ceramic membranes have been used widely in the food, beverage, and dairy industries and in the treatment of industrial wastewater (Daufin *et al.* 2001; Finley 2005). However, because they are more expensive than polymeric membranes, their use in water and municipal wastewater treatment is still rather limited. Interestingly, they have been used widely in Japan for the production of drinking water. Recently, decreasing cost has led to a growing interest in the use of ceramic membranes in the water industry (Ciora & Liu 2003; Heijman & Bakker 2007; Mueller & Witte 2008; Pearce 2011).

2.2.3. Membrane configurations

Membrane geometry (or configuration) and the way in which the individual membranes are housed to produce modules are very important factors affecting the overall process performance. Common membrane configurations in wastewater treatment include plate-and-

frame, spiral-wound cylinder, hollow-fibre, tubular, and rotating flat-plate (Stephenson *et al.* 2000).

The plate-and-frame configuration consists of a series of flat membrane sheets and support plates. Many membrane sheets are welded to a support plate on both sides, forming a membrane cartridge. These cartridges are often housed in a container (cassette) in which they are slid into grooves for support. The cartridges are typically spaced 10 mm apart. Feedwater is filtered as it flows between and parallel to the cartridges (Water Environment Federation 2006).

The spiral-wound configuration consists of several flat membrane sheets, each of which is sealed on three sides and the open side is glued to a perforated plastic collection tube. A flexible permeate spacer is placed between two successive membrane sheets. Flow through the spiral-wound configuration is outside-in (Stephenson *et al.* 2000).

In the hollow-fibre configuration, millions of fibres are looped into a U-shape and the ends are potted into a special epoxy resin which serves as a tube sheet (Vesilind 2003). The preferred direction of water flow in hollow-fibre systems is “outside in”, i.e., the feedwater enters the fibres from the fibre external wall and the permeate flows inside the fibre lumen and is collected at the fibre end. This configuration can be either immersed (as in membrane bioreactors) or contained in pressure vessels, which isolate the feedwater and the permeate. With its high packing densities and low pressure requirements, which tend to result in low life-cycle cost, this configuration has the potential to become the most common membrane configuration for large municipal wastewater treatment facilities (Water Environment Federation 2006).

In the tubular configuration, the membranes are cast on a support tube which is contained in a pressure vessel. Membranes of this configuration are usually ceramic run in cross-flow mode where the feedwater flows axially within the tube, while the permeate flows radially through the porous structure of the tube wall. The permeate is collected outside the tube while the concentrate continues to flow through it (Water Environment Federation 2006). Dead-end filtration using monolith type tubular membranes has also been practised (Heijman & Bakker 2007; Mueller & Witte 2008).

2.2.4. Operation modes of membrane processes

Membrane filters may be operated in either dead-end or cross-flow mode, as shown in Figure 2.1 (Mulder 1996). In the “dead-end” mode, the pressure driving the liquid flow is applied perpendicular the membrane surface.

In cross-flow filtration, the feedwater is forced to flow at fairly high velocity in the direction tangential to the membrane surface. A thin cake layer may form due to the deposition of the solutes in the feedwater on the membrane. High liquid velocity is used to wash away some of the rejected materials from the cake layer, preventing it from building up and therefore reducing fouling (Mulder 1996).

Filtration can be operated in either constant-pressure mode or constant-flux mode (Howell *et al.* 2002). Constant-flux operation requires changing the applied pressure to maintain a constant permeate flux.

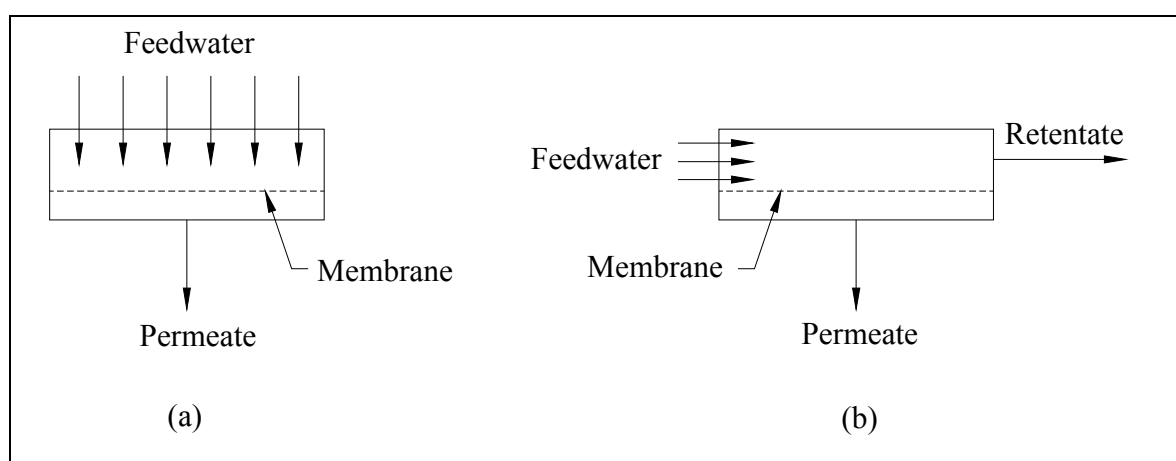


Figure 2.1. Schematic presentations of (a) dead-end mode and (b) cross-flow mode
(Mulder 1996)

2.2.5. Feedwater for membrane processes for water reuse

In WWTPs, the feedwater for membrane processes is usually secondary effluent. The organic content of this effluent is commonly known as effluent organic matter (EfOM), which contains various complex and heterogeneous compounds. EfOM can be classified into 3 different groups according to their origins (Drewes & Fox 1999):

- (i) Refractory natural organic matter (NOM) originating from drinking water,

- (ii) Synthetic organic compounds (SOC) generated during domestic use and disinfection by-products (DBPs) produced during water and wastewater treatment, and
- (iii) Soluble microbial products (SMP) derived from the biological processes of wastewater treatment. Compounds in SMP include polysaccharides, proteins, aminosugars, nucleic acids, extracellular enzymes, antibiotics, steroids, and structural components of cells (Barker & Stuckey 1999).

To reduce membrane fouling the secondary effluent is usually pre-treated to remove the foulants. The most effective pre-treatment method varies with the characteristics of the secondary effluent.

Different from MF and UF of secondary effluent, in which the feedwater contains EfOM and a relatively small amount of SS (normally less than 25 mg L⁻¹), the feed to the filtration process in MBRs is a mixed liquor containing (Jiang *et al.* 2003; Le-Clech *et al.* 2006; Meng *et al.* 2009):

- (i) The activated sludge (mixed liquor suspended solids, MLSS) with high concentrations of SS (3000–31000 mg L⁻¹ (Brindle & Stephenson 1996)),
- (ii) Bound extracellular polymeric substances (bound EPS, consists of polysaccharides, proteins, nucleic acids, lipids and humic acids which adhere to the surface of microbial cells in the sludge), and
- (iii) Colloidal and soluble organic matter, including soluble EPS (i.e., SMP, originating from substrate metabolism of micro-organisms).

2.3. Membrane fouling and factors affecting fouling

Membrane fouling can be defined as the build-up of contaminants on the membrane which causes an increase in the TMP requirement (in constant-flux filtration) or a reduction in the permeate flux through the membrane (in constant-pressure operation). It can take place at the surface (macro-fouling) or inside the pore (pore fouling or micro-fouling).

There are many ways in which a membrane is fouled, including (Barger & Carnahan 1991; Caothien *et al.* 2003):

- Deposition of particulates and suspended solids on the membrane (particulate fouling). This type of fouling can be mitigated by membrane backwashing and/or air scrubbing;
- Precipitation of DOM on the membrane surface or in membrane pores (organic fouling);
- Accumulation of biological growth in the system and/or its attachment to the membrane (biofouling). Extracellular polymeric substances (EPS) produced by the attached micro-organisms can form a viscous slimy gel, which retards the permeate flow;
- Physical or chemical reactions between some components of the feedwater and the membrane surface.

The major cause of fouling of MF and UF membranes is organic fouling, resulting from the accumulation of DOM in the feedwater in the membrane pores or on the membrane surface. Biofouling may occur in long-term operation. Membrane fouling in MBRs is more complicated than that in MF and UF of secondary effluent, due to the presence of activated sludge and bound EPS in the mixed liquor (Le-Clech *et al.* 2006).

Fouling is normally classified as reversible and irreversible fouling. Foulants in hydraulically reversible fouling generally exist as a cake layer on the membrane surface and can be removed by hydraulic cleaning such as backwashing the membrane with the permeate. Irreversible fouling is probably caused by the adsorption or pore plugging of solutes in and within the membrane pores (Zularisam *et al.* 2006). Chemically irreversible fouling is the proportion of fouling that cannot be removed by chemical cleaning of the membrane.

The nature and extent of fouling is affected by interactions of many factors, including the characteristics of the feedwater and the membranes, membrane configuration, and operating conditions.

2.3.1. Effect of feedwater content

Dissolved organic matter, inorganic materials (such as silica, alumino-silicates, iron, and aluminium), SS, and micro-organisms (bacteria and fungi) are potential foulants in membrane filtration of surface water and wastewater.

The fouling potential of DOM is governed by solution chemistry, membrane characteristics, and operational conditions. Feedwaters with higher DOM concentrations do not always cause more severe fouling, indicating that some organic fractions have a higher fouling potential than others (Water Environment Federation 2006; Her *et al.* 2008). However, there have been disagreements about which component is mainly responsible for membrane fouling.

EfOM can be separated into 3 fractions: hydrophobic, transphilic, and hydrophilic fractions. Humic substances (HS), the major component of NOM, are predominantly hydrophobic and generally divided into 3 fractions: humic acid, fulvic acid, and humin. Humic acid and fulvic acid are anionic polyelectrolytes with negatively charged carboxyl (COOH^-), methoxyl carbonyl (C=O), and phenolic hydroxyl and alcoholic hydroxyl (OH) functional groups. Humic acid is not soluble in water at pH below 2 but becomes soluble at higher pH. Fulvic acid is water soluble whereas humin is water insoluble at all pH values (MacCarthy & Suffet 1989). Humic acid contains fewer carboxylic and hydroxyl functional groups and is more hydrophobic than fulvic acid. The MW of aquatic humic acid is between 2000 Da and 5000 Da whereas MW of fulvic acid is generally less than 2000 Da (Sutzkover-Gutman *et al.* 2010). Humic acid is therefore considered to be colloidal. There are more colour centres on humic acid molecules than on fulvic acid molecules (Vik & Eikebrokk 1989).

Many researchers investigated the fouling potentials of the fractions extracted from bulk NOM and EfOM solutions (using resin fractionation) and found that the hydrophilic (non-humic) components, which contained polysaccharide-like and protein-like compounds, were the major foulants in membrane filtration (Jarusutthirak *et al.* 2002; Lee *et al.* 2004). Jarusutthirak and Amy (2006) suggested that these foulants originated from SMP generated

during the biological processes of wastewater treatment. Fan *et al.* (2001) rated the fouling potential of NOM fractions on hydrophobic PVDF MF membranes as hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged. These findings were supported by more recent studies which analysed the feeds and the permeates in dead-end UF of EfOM with size exclusion chromatography with organic carbon detection and found that the components retained by the membranes were protein-like and polysaccharide-like compounds (Laabs *et al.* 2006; Haberkamp *et al.* 2007; Henderson *et al.* 2011).

Nevertheless, other researchers found that the hydrophobic fraction of DOM (predominantly HS) was the most important component contributing to fouling (Schäfer 1999; Shon *et al.* 2006). The high aromaticity, adsorptive capacity, hydrophobicity, and high molecular weight of humic acid were believed to be responsible for its higher tendency to deposit on membrane surface (Zularisam *et al.* 2006). Aoustin and co-workers (2001) studied the fouling of UF membranes and found that the humic acid fraction was responsible for irreversible pore adsorption and plugging, whereas fulvic acid and the hydrophilic NOM caused a smaller and mostly reversible flux decline. Combe *et al.* (1999) and Yuan and Zydney (1999; 2000) also indicated that humic acid was an important foulant in MF and UF. Recently, Kim and Dempsey (2010) found that organic acids (which probably contained humic acid, as indicated by their high UVA₂₅₄), fouled MF and UF membranes more severely than any other components (including colloidal organic matter and hydrophilic bases/neutrals) in a municipal wastewater. The contradictory findings mentioned above could be attributed to differences in water sources and membrane characteristics. They also illustrate the need for identifying the foulants for a particular wastewater and membrane type.

Braghetta *et al.* (1998), on the other hand, suggested that interactions between hydrophobic and hydrophilic components might have significant influence on the foulant behaviour of the whole NOM solution. Therefore, fractionation of NOM into hydrophobic and hydrophilic fractions might not be a meaningful tool for investigation of foulant materials. This was supported by the study conducted by Jermann *et al.* (2007), which revealed that alginate (a polysaccharide) and humic acid acted synergistically, causing more severe hydraulically irreversible fouling on a relatively hydrophobic PES 100 kDa UF membrane than did the individual components. The flux decline caused by the polysaccharide was much more severe than by the humic acid. However, whereas most of the fouling by alginate was reversible (i.e., could be removed by backwashing the fouled membrane), a significant proportion of fouling

by humic acid was irreversible. The more severe irreversible fouling by humic acid than alginate was attributed to adsorption of humic acid on the membrane. The fact that most alginate retained on the membrane could be removed by backwashing, however, appears to contradict the result obtained by Kimura *et al.* (2004), who found that the polysaccharide-like compounds were responsible for irreversible fouling in UF of Chitose River water (Japan) with a 750 kDa PS membrane. Fan *et al.* (2001) also reported that the hydrophilic neutral fraction, which contained polysaccharide-like and protein-like compounds, caused more severe irreversible fouling than the hydrophobic acid (i.e., humic acid) fraction in MF of fractionated surface waters.

The presence of inorganic particles in the feedwater was found to affect the fouling behaviours of organic substances. Inorganic particles such as clay minerals competed with organic components to adsorb onto the membrane surface or in the pores. On the other hand, the high surface area of clay minerals might facilitate the adsorption of DOM on the inorganic layer. This phenomenon could have great effect on fouling characteristics. It could result in enhanced deposition of inorganic particles on the membrane and a reduction in the sorption of DOM onto the membrane, which increases membrane permeability (Zularisam *et al.* 2006). This hypothesis is supported by the studies conducted by Mallevalle *et al.* (1989) and Kaiya *et al.* (1996). In their study, Mallevalle and co-workers noticed a fouling layer consisting of an organic matrix that served as cement for inorganic constituents. Kaiya *et al.* (1996) analysed the fouling layer formed on a PP MF hollow-fibre membrane during the filtration of Lake Kasumigaura (Japan) water and found that organic matter and manganese were the predominant foulants.

The combined effect of organic and inorganic matter was also observed by many other researchers. For example, Schäfer *et al.* (2000) found that the precipitation of calcium-organic complex was the primary reason for MF membrane fouling caused by NOM extracted from a surface water. Mo and Huang (2003) investigated the foulant characteristics in a coagulation-MF combination process used for the treatment of a polluted river water and realised that fouling on the inner surface was mainly due to biofouling, whereas fouling on the exterior surface could be attributed to a combined effect of micro-organisms, organic (mainly low MW molecules), and inorganic matter (mainly calcium). It is generally understood that the presence of Ca^{2+} at sufficient concentrations in HS solutions induced more rapid fouling as the fouling layer formed was dense and had low water permeability (Al-Amoudi *et al.* 2007).

Researchers attributed this rapid fouling to Ca^{2+} binding the negatively charged HS molecules to form aggregates and/or bridging these molecules with the negatively charged membrane surface (Hong & Elimelech 1997; Cho *et al.* 2000; Ahn *et al.* 2008).

For MBRs, as the feed to the filtration process is the mixed liquor, membrane fouling is affected by the characteristics of the sludge (e.g., MLSS concentration and particle size, viscosity, and temperature) as well as the characteristics (concentration and composition) of bound EPS and soluble EPS (Meng *et al.* 2009). Contradictory findings have been reported on the effect of MLSS concentration on membrane fouling in MBRs. Many studies found that membrane fouling increased as the MLSS concentration was increased (Yamamoto *et al.* 1989; Cicek *et al.* 1999; Chang & Kim 2005; Yigit *et al.* 2008). However, others reported the opposite trend (Defrance & Jaffrin 1999; Brookes *et al.* 2006) or insignificant impact of MLSS concentration on membrane fouling (Hong *et al.* 2002; Le-Clech *et al.* 2003; Lesjean *et al.* 2005).

Bound EPS has been recognised as the major components keeping activated sludge flocs in a three-dimensional matrix. Some researchers found that bound EPS made a significant contribution to membrane fouling in MBRs (Cho *et al.* 2005; Ahmed *et al.* 2007). However, others showed that these components had no effect on membrane fouling (Rosenberger & Kraume 2003). Although different findings on the importance of bound EPS in fouling of MBRs have been reported, Meng *et al.* (2009) suggested that fouling mitigation in MBRs should focus on controlling these components (apart from SMP, as discussed in the next paragraph), since the concentration of bound EPS is closely related to many characteristics of activated sludge which have significant impacts on MBR fouling (e.g., sludge volume index, viscosity, hydrophobicity, surface charge and flocculation ability).

Several MBR studies have shown that SMP, particularly polysaccharide-like and protein-like compounds, played a much more important role than the MLSS and bound EPS in causing membrane fouling (Fawehinmi *et al.* 2004; Evenblij *et al.* 2005; Lesjean *et al.* 2005; Rosenberger *et al.* 2005; Ji & Zhou 2006; Rosenberger *et al.* 2006; Iritani *et al.* 2007). Some studies have also demonstrated that the polysaccharide-like components in SMP made a larger contribution to fouling than protein-like compounds (Rosenberger *et al.* 2006; Yigit *et al.* 2008). The role of HS in fouling in MBRs has been less well studied, as researchers have tended to focus on EPS (Le-Clech *et al.* 2006). Lyko *et al.* (2007) indicated that HS

contributed to membrane fouling by forming complexes with metal cations which deposited on the membrane surface. Hong *et al.* (2012) analysed the foulants in MBRs using fluorescence spectroscopy and liquid chromatography with organic carbon detection (LC-OCD) and found that the relative proportions of biopolymers and HS varied with the hydraulic retention time. Operating MBRs at a longer hydraulic retention time (4 hours) increased the accumulation of biopolymers in the foulant layer, whereas at shorter hydraulic retention times (1–2 hours), HS was found to be the dominant components of the foulant layer.

It is noteworthy to mention that despite significant differences in the characteristics of surface water, secondary effluent, and MBR mixed liquor, the majority of recent studies on membrane fouling have shown that polysaccharide-like and protein-like compounds are the major organic foulants in MF and UF of these feedwaters.

So far the vast majority of the investigations into the identity of the foulants have been conducted in dead-end filtration mode using polymeric membranes. Intuitively, it can be inferred that the components of the DOM responsible for fouling in dead-end filtration would also be the membrane foulants in cross-flow filtration with ceramic membranes. Previous studies, however, have not attempted to validate this inference, particularly with municipal secondary effluents. Information regarding the effectiveness of feed pre-treatments on fouling reduction in cross-flow MF and UF of municipal wastewater with ceramic membranes is also scarce.

2.3.2. Effect of solution chemistry

Solution chemistry (pH, ionic strength, concentration of multivalent cations, and water hardness) was found to contribute significantly to the nature and extent of fouling. It greatly affected the structure and hydraulic resistance of the foulant layer via controlling the charge and configuration of organic macromolecules (Seidel & Elimelech 2002). It was observed that HS tended to aggregate more at low pH and high multivalent cation (particularly Ca^{2+}) concentrations. At neutral pH and low ionic strength, the molecules tended to stretch to more linear forms (Ghosh & Schnitzer 1980).

Several studies revealed that membrane fouling by NOM was intensified in solutions of low pH, high ionic strength and high divalent cation concentration. This phenomenon could be explained as due to changes in intra- and inter-molecular electrostatic interactions between organic molecules, particularly those containing negatively charged functional groups such as carboxylic, phenolic and carbonyl. It is believed that increasing ionic concentration shielded the charges on solute molecules and facilitated their coiling and aggregation, which resulted in the accumulation of these molecules on the membrane surface (Zularisam *et al.* 2006).

Based on the UV absorbance at 254 nm (UVA₂₅₄) of surface waters at different pH values, Maartens *et al.* (1999) suggested that low pH favoured the precipitation of the humic acid and fulvic acid fractions of NOM since in such conditions the carboxyl (COOH) groups of these fractions were protonated, forming large and less soluble complexes.

Interactions among feedwater components, pH, and solution chemistry were also observed by Adham *et al.* (2006). These researchers carried out experiments on 5 different river waters and found that no single water quality parameter, such as pH, alkalinity, hardness, total organic carbon (TOC) concentration, UVA₂₅₄, specific UV absorbance (SUVA), or silica concentration could be correlated alone to the extent of fouling. They also noticed that the most important foulants were larger than 100 kDa and some were smaller than 10 kDa. There was little or no foulant material between 10 and 100 kDa. Analysing the foulants at Waikato Water Treatment Plant (New Zealand), the researchers concluded that silica at high concentrations in raw water could combine with aluminium from coagulants to form kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), a major inorganic foulant (Adham *et al.* 2006).

2.3.3. Effect of membrane characteristics

Membrane characteristics such as MWCO, pore size, surface charge and hydrophobicity/hydrophilicity are important factors affecting the rejection, types of retained solutes, rate of flux decline, and fouling mechanisms.

Electrostatic repulsion and hydrophobic attraction are the two major forces controlling the interaction between NOM/EfOM and membranes in MF and UF. Electrostatic repulsion between DOM and the membrane surface is the result of the likeness in the surface charge of these two constituents. In the pH range of typical natural water and wastewater (pH 5–8),

most membranes and DOM components carry net negative surface charges, and therefore DOM and membranes tend to electrostatically repel each other (Liu *et al.* 2001). For this reason, Cho and co-workers (2000) suggested that membranes with negatively charged surfaces should be selected to reduce fouling caused by DOM.

On the other hand, hydrophobic attraction is the attraction between molecules with similar chemical structures as a result of van der Waals force between these molecules. As a general rule, organic compounds with less than one charged functional group per every twelve carbon atoms have a great tendency to adhere to hydrophobic surfaces (such as hydrophobic membranes), since the energy of hydrophobic attraction is greater than the electrostatic repulsion energy (Liu *et al.* 2001). HS in water and wastewater is hydrophobic and therefore tends to have strong adhesion to hydrophobic membranes (Zularisam *et al.* 2006). In general, hydrophobic attraction (and therefore fouling propensity) tends to increase with increasing MW and mass to charge ratio of DOM components (Liu *et al.* 2001). Similarly, previous studies found that in MF and UF of the same DOM source, hydrophobic (e.g., unmodified PVDF, PS, and PES) membranes had a higher fouling tendency than hydrophilic (e.g., cellulose-based and hydrophilised PVDF and PES) membranes due to their higher DOM adsorption (Mulder 1996; Nakatsuka *et al.* 1996; Fan *et al.* 2001; Gray *et al.* 2008). Hydrophobic attraction between DOM and membranes has also been found to be greater at high ionic strength and high divalent cation concentrations. It is hypothesised that high ionic strength of water/wastewater causes the compression of the “double electric layer” of colloidal organic matter, which in turn reduces its repulsion from negatively charged membranes. Divalent cations (e.g., Ca^{2+}) can act as a “salt bridge” between negatively charged DOM and negatively charged membranes by charge neutralisation and therefore increase the tendency of membrane fouling (Liu *et al.* 2001).

The adsorption of DOM on the membrane surface can also alter the hydrophilicity and surface charge of membranes. The surface of hydrophilic membranes became more negatively charged as a result of rapid adsorption of HS (Childress & Elimelech 1996).

2.3.4. Effect of membrane configuration

Membrane configuration is a critical factor affecting the performance of the filtration process. Configurations that are easy to clean and create high turbulence in the water flow are better in

combating fouling. High turbulence promotes mass transfer on the feed side and therefore reduces the accumulation of matter near the membrane surface.

Other selection criteria for a good membrane configuration include (Stephenson *et al.* 2000):

- High membrane area to module bulk volume ratio,
- Easy to modularise,
- Low cost per unit membrane area, and
- Low energy consumption per unit volume of product water.

2.3.5. Effect of operating conditions

Operation in “dead-end” mode tends to result in rapid fouling due to the fast build-up of a cake layer of retained materials. In cross-flow mode, the build-up of the cake layer is slowed by the high-velocity liquid flow.

Operating conditions such as applied pressure, cross-flow velocity, and backwash frequency also greatly affect the rate and extent of fouling (Cheryan 1986; Crozes *et al.* 1997; Sheikholeslami 1999). The starting flux in MF and UF also affects the rate of flux decline. It has been found that operating at higher fluxes resulted in more rapid fouling (Field *et al.* 1995).

2.4. Resistances in membrane filtration and fouling models

The total hydraulic resistance in membrane filtration includes resistances exerted by the membrane, pore blocking, pore adsorption, the cake layer, and by concentration polarisation (Van den Berg & Smolders 1990). The membrane hydraulic resistance is a membrane constant and is independent of the feed composition and applied pressure. Pore blocking may occur in porous membranes, when solutes of the same size as the membrane pore block the pore entrance. Adsorption of solute molecules on the membrane surface or within membrane pores, if it takes place, also contributes to the total resistance (Mulder 1996). Cake formation occurs when the feed contains particles larger than the membrane pores. Pore blocking, pore adsorption, and cake formation are considered to be the 3 mechanisms of membrane fouling caused by DOM, whereas concentration polarisation, although causing flux decline, is not considered as a fouling mechanism. This will be discussed further in Section 2.4.3.

2.4.1. Fouling models for dead-end filtration

Membrane fouling during constant-pressure unstirred dead-end MF and UF is thought to proceed through successive or simultaneous steps as follows (Bowen *et al.* 1995):

- (i) Particles reaching the membrane block the smallest pores
- (ii) Particles cover the inner surfaces of bigger pores
- (iii) Some newly arrived particles attach to the particles that are already on the membrane whereas others directly obstruct some of the membrane pores
- (iv) Cake begins to form.

The general empirical equation for these steps is (Bowen *et al.* 1995):

$$\frac{d^2t}{dV^2} = k \left(\frac{dt}{dV} \right)^n \quad (2.1)$$

where

V is the total permeate volume collected at time t (m^3),

k and n are constants depending on the mechanism involved.

The following models represent the integrated form of this equation for different values of n .

2.4.1.1. Complete blocking filtration model ($k = k_{CB}$, $n = 2$)

This model is based on the assumption that particles reaching the membrane seal the pores but do not accumulate on each other. This situation often occurs when the particle size is of the same order as the pore size.

The linear form of the complete pore blocking is

$$\dot{V} = \dot{V}_0 - k_{CB}V \quad (2.2)$$

where

\dot{V} is the permeate volumetric flow rate at time t ($\text{m}^3 \text{s}^{-1}$),

\dot{V}_0 is the permeate volumetric flow rate at time $t = 0$, which can be estimated by filtration with pure (DOC-free) water, and

k_{CB} is the constant for the complete blocking models (s^{-1})

2.4.1.2. Intermediate blocking model (long-term adsorption) ($k = k_{IB}/\dot{V}_0$, $n = 1$)

This model assumes that new particles can attach to particles that have already blocked some pores or they can directly block some of the pores. It is described by the following equation:

$$\frac{1}{\dot{V}} = \frac{1}{\dot{V}_0} + \frac{k_{IB}}{\dot{V}_0} t \quad (2.3)$$

where k_{IB} is the constant for the intermediate blocking model (s^{-1})

2.4.1.3. Standard blocking model (direct adsorption) ($k = 2k_{SB}/\sqrt{\dot{V}_0}$, $n = 3/2$)

This model is also called the “pore adsorption” or “pore constriction” model. It is derived for the case in which the pore size is reduced by particles depositing on the internal pore wall. This situation is likely to occur when the particle size is much smaller than the membrane pore size.

The linear form of standard pore blocking model is

$$\frac{t}{V} = \frac{k_{SB}}{\dot{V}_0} t + \frac{1}{\dot{V}_0} \quad (2.4)$$

where k_{SB} is the constant for the standard blocking model (s^{-1}).

2.4.1.4. Cake filtration model ($k = k_{CF}/2\dot{V}_0^2$, $n = 0$)

This model accounts for the case in which particles are large and cannot enter most pores or all membrane area is already blocked. Particles are retained by sieving and form a cake on the membrane surface.

The linear form of cake filtration model is

$$\frac{t}{V} = \frac{k_{CF}}{4\dot{V}_0^2} V + \frac{1}{\dot{V}_0} \quad (2.5)$$

where k_{CF} is the constant of the cake filtration model (s^{-1})

A schematic presentation of the above fouling models is shown in Figure 2.2.

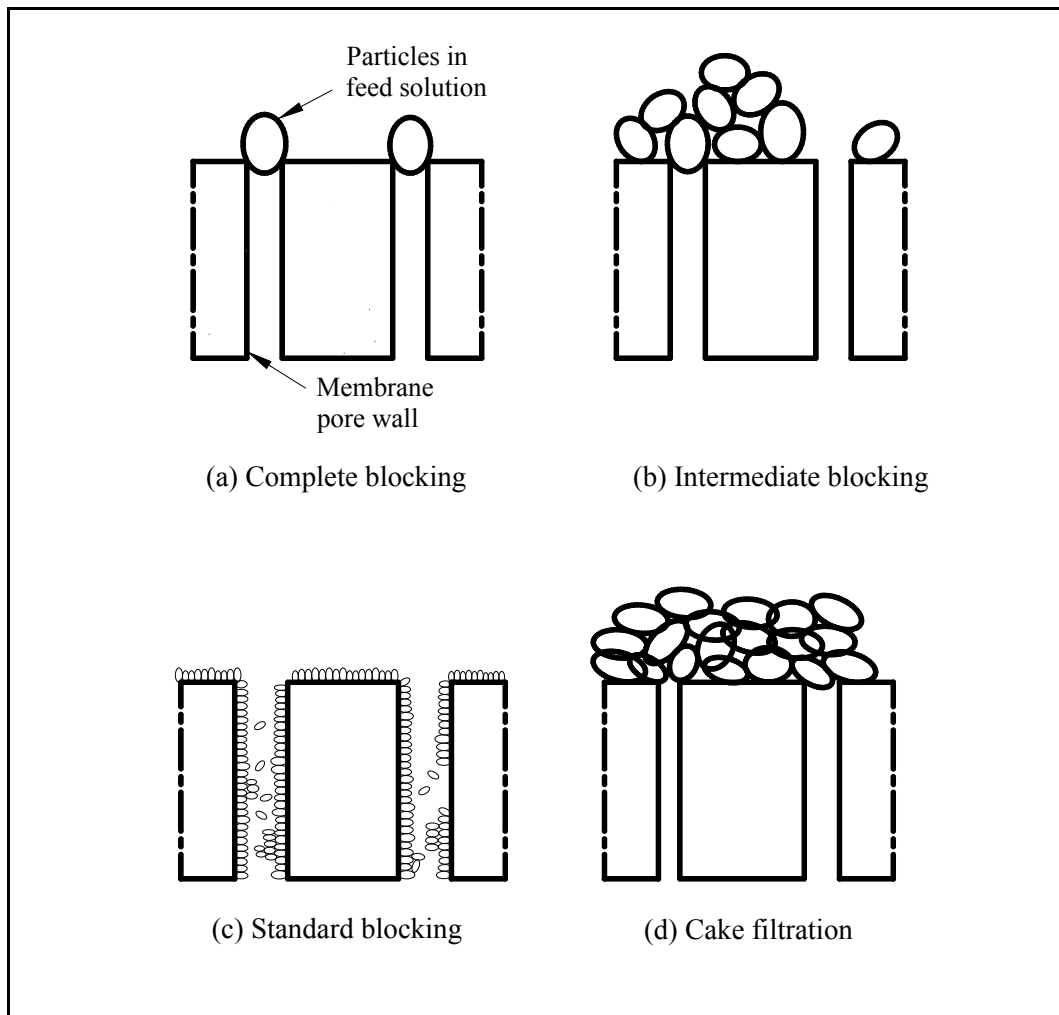


Figure 2.2. Schematic presentation of different membrane fouling models
(Bowen *et al.* 1995)

Bowen *et al.* (1995) hypothesised that where the pore size was uniform and larger than the molecules to be deposited, membrane fouling would start with a standard blocking step followed by complete blocking, intermediate blocking, and cake filtration. If the molecules were much larger than the pores, fouling would begin with complete blocking followed by intermediate blocking and then cake filtration.

Some researchers found that pore blocking, pore adsorption, and cake formation were responsible for fouling of MF membranes. For UF membranes, flux decline and enhanced rejection were attributed to internal pore adsorption of organic components in the feedwater (Zularisam *et al.* 2006). It was suggested that the initial rapid flux decline in MF and UF of biologically treated sewage effluent could be attributed to pore blocking and adsorption of

EfOM onto the membrane matrix, whereas the subsequent slow flux decline was caused by cake formation on the membrane surface (Lim & Bai 2003; Kim *et al.* 2005).

2.4.2. Fouling models for cross-flow filtration

The fouling models developed originally for dead-end filtration were modified to apply to cross-flow filtration (Field *et al.* 1995). This was done by adding terms representing the removal rate of particles from the membrane surface due to the cross-flow. The development of these models also led to the concept of critical flux, which is an important parameter in membrane filtration practice. Critical flux is the flux above which fouling starts to occur. It is reached where there is a balance between the convective force exerted on particles in the feed towards the membrane and particle back-transport. In cross-flow MF and UF, back-transport of particles is facilitated by the cross-flow (Gésan-Guizieu *et al.* 2002; Bacchin *et al.* 2006). The critical flux concept is not applicable to dead-end filtration due to the absence of particle back-transport in this filtration mode. The general form of the equations for the four fouling mechanisms in cross-flow filtration is (Field *et al.* 1995; Field & Wu 2011):

$$-\frac{dJ}{dt} = k(J - J^*)J^{2-n} \quad (2.6)$$

where J is volumetric flux at time t and J^* is the critical flux (m s^{-1}).

The equations relating the permeate flux, filtration time, and critical flux for the individual models are given below:

2.4.2.1. Complete pore blocking model ($n = 2$)

The equation describing the relationship between the flux and the filtration time for this fouling model is

$$J = (J_0 - j_c) \exp\left(\frac{-\sigma J_0 t}{\varepsilon_0}\right) + j_c \quad (2.7)$$

where

J_0 is volumetric flux at time $t = 0$ (m s^{-1}),

j_c is the critical flux for the complete blocking law (m s^{-1}),

σ is the blocked area per unit volume of filtrate (m^{-1}),

ε_0 is the membrane surface porosity at time $t = 0$

If J is lower than j_c , no flux decline is expected.

2.4.2.2. Intermediate pore blocking model ($n = 1$)

For the intermediate blocking filtration model, the relationship between the flux and the filtration time is given by

$$\sigma t = \frac{1}{j_i} \ln \left(\frac{J_0 - j_i}{J_0} \times \frac{J}{J - j_i} \right) \quad (2.8)$$

where j_i is the critical flux for the intermediate blocking law (m s^{-1})

2.4.2.3. Standard pore blocking model ($n = 1.5$)

This type of fouling is not mediated by back-diffusion of the membrane surface and the relationship between t and V is the same as in the case of dead-end filtration (equation 2.4).

In terms of flux, this relationship can be written as

$$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + \left(\frac{K'_s}{2} \sqrt{A} \right) t \quad (2.9)$$

where

K'_s is the Hermia's parameter for standard blocking model and

A is the membrane surface area (m^2)

2.4.2.4. Cake filtration model ($n = 0$)

$$Gt = \frac{1}{j_s^2} \left[\ln \left(\frac{J}{J_0} \times \frac{J_0 - j_s}{J - j_s} \right) - j_s \left(\frac{1}{J} - \frac{1}{J_0} \right) \right] \quad (2.10)$$

where

G is a constant (s m^{-2}) and

j_s is the critical flux for the cake filtration law (m s^{-1})

2.4.3. Concentration polarisation

During the operation of membrane filtration, there is always a convective flow of the solutes in the feedwater towards the membrane surface and a diffusive backflow of these components to the bulk feed solution. Before a steady state is established, the forward flow is greater than the backflow, which results in the accumulation of the solutes at the membrane-solution interface. Consequently, the concentration of the solutes at the membrane surface is higher than that in the bulk solution. This phenomenon is known as concentration polarisation (Matthiasson & Sivik 1980).

Concentration polarisation can result in a lower permeate flux and lower or higher solute retention. It causes an increase in osmotic pressure near the membrane surface, which reduces the effective TMP and consequently leads to a decrease in the permeate flux. This effect of concentration polarisation is most significant for salts and small organic molecules because these components exert a large osmotic pressure. The reduction in permeate flux caused by concentration polarisation is therefore most significant for NF and RO membranes.

The contribution of concentration polarisation to flux decline in low-pressure membrane filtration of NOM has been found to be relatively low, as MF and UF membranes are not effective in removing salts and small organic molecules. Yuan and Zydney (2000) investigated membrane fouling in MF and UF of Aldrich and Suwannee River humic acids and found that concentration polarisation contributed to less than 15% of the total flux decline for the 100 kDa membrane and less than 10% for the 300 kDa and 0.16 μm membranes. Concentration polarisation is a reversible phenomenon as its effect on flux decline can be eliminated by reducing the TMP (and hence reducing flux) (Bacchin *et al.* 2006).

2.4.4. Resistance-in-series model

The resistance-in-series model is the result of a phenomenological approach to fouling. It was based on the fact that flux decline is contributed by different factors, including pore adsorption, pore blocking, cake formation, and concentration polarisation.

According to this model, the membrane resistance and the resistances by fouling and by concentration polarisation act in series to retard the permeate flow. Consequently, the permeate flux can be written as (Barger & Carnahan 1991; Mulder 1996):

$$J = \frac{\Delta P - \Delta \pi}{\mu(R_m + R_a + R_p + R_c + R_{cp})} \quad (2.11)$$

where

$\Delta \pi$ is the osmotic pressure difference across the membrane,

R_m , R_a , R_p , R_c , and R_{cp} are the resistances exerted by the membrane, adsorption of foulants on membrane, pore blocking by foulants, cake layer formed on the membrane surface, and concentration polarisation, respectively. The membrane resistance R_m can be obtained from experiments on pure water feed.

Because in MF and UF of NOM and EfOM the rejected solutes are high MW compounds and their concentrations are low, concentration polarisation and osmotic pressure difference can usually be neglected. If the osmotic pressure difference across membrane $\Delta\pi$ is negligible, equation 2.11 is reduced to

$$J = \frac{\Delta P}{\mu(R_m + R_a + R_p + R_c + R_{cp})} \quad (2.12)$$

Many other versions of the resistance-in-series model have been used. For example, one model divides the total resistance causing flux decline (R_{tf}) into reversible resistance (R_{rf} , which includes reversible fouling and concentration polarisation effect) and irreversible resistance (R_{if} , which accounts for irreversible fouling). The permeate flux is then expressed as (Aimar & Howell 1989):

$$J = \frac{\Delta P}{\mu(R_m + R_{tf})} = \frac{\Delta P}{\mu(R_m + R_{rf} + R_{if})} \quad (2.13)$$

where R_{tf} is the resistance by total fouling

2.5. Fouling mitigation

Several approaches have been utilised to control membrane fouling. These include:

- Pre-treatment of the feedwater,
- Modification of membrane properties,
- Optimisation of module configuration and operating conditions,
- Periodic membrane cleaning,
- Evaluation of system performance using pilot plant, and
- Use of predictive models

2.5.1. Pre-treatment of the feedwater

Secondary effluent is usually pre-treated to reduce membrane fouling and/or improve the permeate quality before being introduced to MF or UF processes. Appropriate pre-treatment methods are selected based on the components to be removed and the extent of their removal. Common pre-treatment methods for MF and UF include (Water Environment Federation 2006; Huang *et al.* 2009):

- Coagulation (usually with lime, alum, or ferric salts) and flocculation

- Adsorption (most commonly used material is powdered activated carbon)
- Pre-oxidation (using ozone)
- Pre-filtration (using large pore size membranes, granular media, filter cloth, etc.)

In practice, these methods can be applied in combination, for example, coagulation followed by pre-filtration, coagulation followed by adsorption with powdered activated carbon (PAC) (Abdessemed *et al.* 2000; Guo *et al.* 2004), and ozonation followed by coagulation (Lehman & Liu 2009).

2.5.1.1. Coagulation and flocculation

For coagulation to take place the repulsive forces between like-charged particles must be overcome, i.e., the colloidal dispersion must be destabilised. In wastewater treatment, this is usually carried out by the addition of coagulants such as alum (aluminium sulphate), ferric chloride, or appropriate cationic polyelectrolytes. In flocculation, particles formed as a result of coagulation are further contacted to form larger aggregates called flocs. Polyelectrolytes that accelerate the rate of floc formation and make flocs mechanically more stable can be used as flocculant aids (Kolarik & Booker 1995).

It is thought that the removal of NOM by coagulation occurs via two major mechanisms (Gregor *et al.* 1997; Wang *et al.* 2010):

- (i) ‘Charge neutralisation’ of negatively charged NOM by cationic metal hydrolysis species which leads to the formation insoluble charge-neutral products,
- (ii) ‘Sweep coagulation’ in which NOM is removed by entrapment or adsorption on metal hydroxide precipitate (e.g., $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$).

Charge neutralisation operates at quite low metal concentrations (typically a few μM for near neutral pH conditions) where the formation of metal hydroxide precipitate is minimal. For ‘sweep coagulation’ to take place, the coagulant dose must be sufficiently high to cause rapid precipitation of insoluble metal hydroxide.

Feed coagulation is a common pre-treatment method to reduce fouling of MF and UF membranes. It is also used to enhance the removal of cysts, bacteria, viruses, algae, turbidity, silt, colour, DOM, and inorganic compounds from the feedwater. However, both beneficial and adverse effects of coagulation on membrane flux performance have been reported, reflecting the complexity of the relationships between water contents, coagulants (type and

dose), and membranes. Therefore, coagulant type and dose must be carefully selected to avoid acceleration of membrane fouling and maximise the usefulness of coagulation (Adham *et al.* 2006). Howe and Clark (2006) found that coagulation exacerbated fouling in MF of a surface water and attributed this effect to “under-dosing” of the coagulant, which led to the formation of fine flocs having sizes close to the pore sizes of MF membranes.

Previous studies on MF and UF of secondary effluent showed that coagulation led to significant improvement in the permeate flux (Kim *et al.* 2005). Haberkamp *et al.* (2007) attributed the improved flux to the removal of the high MW components (i.e., biopolymers, which contained proteins and polysaccharides, and HS) of the EfOM.

Pre-hydrolysed inorganic coagulants such as poly(aluminium) chloride (PACl) and poly(aluminium) chlorohydrate (ACH) have been used in a number of drinking water treatment plants in place of alum due to their lower alkalinity consumption and lower sludge production. The use of PACl and ACH was found to reduce breakage of coagulated flocs and reduce aluminium concentration in the treated water (Gebbie 2001). Practical experience in drinking water treatment plants indicated that ACH worked effectively over a broader pH range (5.0 – 8.0) and produced less sludge compared with alum (5.0 – 6.5), the most widely used coagulant (Jiang & Graham 1996; Gebbie 2001). These characteristics make ACH an attractive alternative for alum in coagulation of secondary effluent, particularly those with pH greater than 7.0 (such as the AS effluent being investigated in this study, pH 7.2 – 7.8).

There are two process configurations of coagulation pre-treatment for MF/UF: coagulation followed by sedimentation and in-line coagulation (Huang *et al.* 2009a). In the first configuration, the coagulated materials are allowed to settle in sedimentation basins prior to the membrane units. In-line coagulation usually uses lower coagulant doses and no removal of the coagulated matter is done before MF or UF (Choi & Dempsey 2004; Zheng *et al.* 2012). In-line coagulation is usually the preferred configuration as it reduces the process size and therefore improves process economics (Judd & Hillis 2001; Sharp & Escobar 2006).

Coagulation can be accomplished with or without prior pH adjustment of the feed water. pH adjustment is normally practised when optimal removal of DOM and contaminants (e.g., phosphorus species) is required (Water Environment Federation 2006).

2.5.1.2. Ozonation

Ozone is a strong oxidant that preferentially oxidises electron-rich compounds containing C–C double bonds and aromatic alcohols (Von Gunten 2003). Ozonation has been used widely in drinking water production to remove colour, tastes and odours. However, the application of this process in sewage treatment is quite limited (Oneby *et al.* 2010). It was found that ozonation reduced chemical oxygen demand (COD), BOD, and colour, and increased the dissolved oxygen concentration in municipal secondary effluent without causing any harmful effects on toxicity and mutagenicity (Paraskeva *et al.* 1998).

Lee *et al.* (2005) found that ozonation reduced membrane fouling in MF of a municipal secondary effluent by decomposing high MW organic materials to compounds of lower MW. Ozonation at high concentrations (~ 5.0 mg O_3 /mg SS, 15-minute contact time) also resulted in the breakdown of large SS particles and converted the particle size distribution (PSD) of the SS to a smaller and narrower range (Zhu *et al.* 2008). The SS with narrower PSD was thought to create a more porous gel layer which improved the flux performance. At lower doses (~ 0.55 mg O_3 /mg SS, 2-minute contact time), ozone was found to have a coagulation-aid effect as it enhanced particle destabilisation and consequently improved particle aggregation by coagulation. Reduced membrane fouling could also be due to the change in the SS zeta potential, which reduced the affinity between the SS and membrane surface (Zhu *et al.* 2008). On the other hand, Zhu *et al.* (2009) found that ozonation pre-treatment worsened membrane fouling in dead-end MF of a secondary effluent with a ceramic membrane (pore size = $0.1\ \mu\text{m}$). They attributed this phenomenon to the increase in the concentration of large organic molecules after ozonation and suggested this increase may have resulted from the lysis of the bacteria in the effluent.

As ozonation kills micro-organisms, it has the potential of reducing biological fouling of the downstream membrane systems. However, the treatment may lead to the release of biodegradable substances from broken bacterial cells and the breakdown of high MW DOM in water to low MW compounds (e.g., organic acids, alcohols, aldehydes, ketones). These events may facilitate bacterial regrowth (Van der Kooij *et al.* 1989; Miettinen *et al.* 1998) and therefore result in accelerated membrane biofouling. This is likely to happen when ozonation and residual ozone removal are performed continuously (Voutchkov 2008). This problem can be addressed by introducing a biological activated carbon (BAC) filtration process between the ozonation process and the membrane system.

In BAC filtration, the biodegradable materials in the ozonated water are consumed by the microbial flora attached to activated carbon (Volk *et al.* 1993; Lambert & Graham 1995; Swietlik *et al.* 2004). The operating life of the activated carbon in BAC filtration can be as long as 10 years, resulting in a low need for carbon regeneration (Wricke *et al.* 1996). Ozonation followed by BAC filtration has rarely been used in sewage treatment and therefore little research on their effects on membrane fouling has been done. The combined ozonation-BAC filtration process was trialled at the WWTP from which the samples for this study were collected.

2.5.1.3. Adsorption with ion exchange resins

Ion exchange resins are cross-linked polymers with fixed functional groups. They can be cationic or anionic ion exchangers. Anion exchange resins (AERs) have been used extensively in water and wastewater treatment (Zagorodni 2007). Typical AERs are made up of a polymer matrix (most commonly polyacrylic or polystyrene cross-linked with divinylbenzene) with fixed cationic functional groups (such as $-NH_3^+$, NH_2^+ , or $-N^+(CH_3)_3$) and exchangeable anionic groups (e.g., chloride or hydroxide ions) (Zagorodni 2007). During contact with water or wastewater, the DOM of which is predominantly in the anionic form, the negatively charged DOM molecules displace the anionic groups to attach to the cationic functional group of the AER.

AERs have been found very effective in the removal of DOM and colour in water. Many AERs have the advantage of easy regeneration. Those with higher water contents have been found to be more efficient in DOC removal due to the presence of more active sites. Strong base resins tend to be more effective for DOM removal than weak base resins (Bolto *et al.* 2002).

Water pH may greatly influence the effectiveness of the ion exchange process. Croué *et al.* (1999) suggested that at high pH, ion exchange was the dominant mechanism for the removal of DOM, whereas at neutral pH, physical adsorption also played a role. Physical adsorption is believed to be responsible for the removal of neutral organic compounds (Bolto *et al.* 2002; Cornelissen *et al.* 2008). The presence of anions and cations in water has been found to affect the ion exchange process. It has been reported that the presence of sulphate and nitrate in water reduced NOM removal by AERs, as these anions competed with NOM for active sites

on the resins (Boyer & Singer 2006). Bicarbonate and chloride may increase the NOM removal, as a result of dehydration of hydrophobic acids - a phenomenon referred to as the 'salting out' effect (Croué *et al.* 1999). The presence of iron in the water to be treated may lead to the formation of an iron dioxide coating on the resins and therefore reduce their ion exchange capacity (Hongve *et al.* 1999).

Regarding the DOM components removed by AERs, researchers have found that most AERs used for water treatment are effective for the removal of aromatic hydrophobic DOM components (humic and fulvic acids) with low to intermediate MWs (500–4000 Da) (Allpike *et al.* 2005; Boyer & Singer 2005; Zhang *et al.* 2006; Humbert *et al.* 2007). AERs are also capable of removing transphilic and hydrophilic NOM components (Croué *et al.* 1999). However, they are not effective for the removal of large molecules such as polysaccharides and proteins) (Croué *et al.* 1999; Humbert *et al.* 2007; Cornelissen *et al.* 2008).

Cornelissen *et al.* (2008) studied the removal of NOM in surface water by nine AERs and found that the resins preferentially removed HS, hydrolysates of HS (building blocks) and low MW neutral compounds with removal ranging from 1% to 60%. The resins tested showed high removals of low MW neutral compounds (approximately 50%), which was attributed to physical adsorption rather than ion exchange. The researchers also observed an increase in the concentration of biopolymers (i.e., polysaccharides and proteins) after the ion exchange treatment and attributed this increase to the washing out of polymeric compounds stemming from the manufacturing process of the AERs. The results indicate that some AERs may need appropriate treatment before being used for the removal of DOM.

Magnetic ion exchange (MIEX[®]) has been used widely in the treatment of surface water for the removal of NOM. Tests on surface water showed that MIEX was most effective in the removal of NOM with MWs between 500 and 1500 Da (Humbert *et al.* 2005). Fearing *et al.* (2004) reported that fulvic acids, due to their lower MW (800 Da), were removed more easily by MIEX[®] than humic acids (MW = 1060 Da). Similarly, Zhang *et al.* (2006) found that MIEX[®] removed the majority of low MW (500–1000 Da) components of EfOM collected from a municipal WWTP.

Although pre-treatment with AERs can remove a large proportion of DOM from water and wastewater, previous studies showed that this does not always result in fouling reduction in MF and UF. For example, fouling reduction by adsorption pre-treatment with MIEX[®] was observed by Zhang *et al.* (2006) and Kim and Dempsey (2010), while no effect on fouling was observed by Humbert *et al.* (2007). It should be noted that in their studies, Zhang *et al.* and Kim and Dempsey conducted filtration tests with secondary effluent, whereas Humbert *et al.* worked on surface water.

Zhang *et al.* (2006) attributed fouling reduction by pre-treatment with MIEX[®] to the removal of EfOM from the secondary effluent. However, the identity of the EfOM components responsible for fouling was not provided. Kim and Dempsey (2010) demonstrated that organic acids (which, according to their fractionation protocol, contained humic acids and fulvic acids) were the major membrane foulants in MF and UF of secondary effluent. Consequently, pre-treatment with ion exchange resins effective in the removal of organic acids, such as MIEX[®], IRA-958, and diethylaminoethyl cellulose, resulted in significant fouling reduction. On the other hand, Humbert *et al.* (2007) explained the ineffectiveness of pre-treatments with MIEX[®] and IRA-958 for fouling reduction as due to the poor removal of NOM components with MWs between 20 kDa and 80 kDa. The inconsistencies among the results reported in the literature suggest that further studies need to be carried out to obtain better understanding of the identity of the membrane foulants and the effect of pre-treatment with ion exchange resins on fouling.

2.5.1.4. Adsorption with activated carbon and other adsorbents

Powdered activated carbon (PAC) is used widely for the removal of taste, odour, DOM, and synthetic organic chemicals. Many water treatment plants use PAC as a pre-treatment for the feedwater to MF and UF systems. These plants utilise the membranes to separate the spent PAC, micro-organisms, and other particulate matter, from the finished water (Adham *et al.* 2006).

Previous studies have shown that adsorption of DOM on PAC is greatly influenced by the surface chemistry (particularly the surface charge) and the pore size distribution of the activated carbon (Summers & Roberts 1988a; Kilduff *et al.* 1996; Newcombe & Drikas 1997; Bjelopavlic *et al.* 1998). In general, the DOM components removed by microporous PAC

(pore size < 2 nm) are those of low MWs (< 600 Da), whereas mesoporous PAC (pore size = 2–50 nm) are capable of adsorbing DOM components with a range of MWs (from 200 Da to larger than 1000 Da) (Newcombe *et al.* 2008). It has also been reported that low MW components of NOM are adsorbed on PAC to a greater extent than larger compounds due to the size exclusion effect (Newcombe *et al.* 2008).

Many commercial PAC products have been found very effective in removing aromatic compounds, including humic and fulvic acids (Adham *et al.* 1991; Kim *et al.* 2007; Kim *et al.* 2008a; Song *et al.* 2009), and micropollutants, such as pharmaceuticals and cyanotoxins (Campos *et al.* 1998; Newcombe *et al.* 2008; Saravia & Frimmel 2008; Campinas & Rosa 2010). Regarding to studies which used PAC adsorption as a pre-treatment to MF/UF, Lin *et al.* (1999) reported that the PAC they used (C-5260, Sigma, mesoporous, average pore size = 25 nm, surface area = 730 m² g⁻¹) was effective for the removal of NOM components between 300 Da and 17,000 Da, but was not able to adsorb components outside this range. On the other hand, Haberkamp *et al.* (2007) found that other mesoporous PAC products (Norit SA Super, Norit AZO, and Donau Carbon Carbopal MB 4) were capable of adsorbing EfOM components of a wide range of MWs, including biopolymers (MW >> 20,000 Da), HS (MW = 1,000–20,000 Da), building blocks (MW = 300–500 Da) and low MW neutral compounds (MW < 350 Da).

Although PAC can be highly effective in removing DOM, using PAC as a pre-treatment for membrane systems does not guarantee a reduction in membrane fouling. For example, Carroll *et al.* (2000) observed that while PAC adsorption was able to remove nearly 70% of the DOM from Moorabool River water (Victoria, Australia), the treatment had little impact on the permeate flux in dead-end MF. However, Lin and co-workers (2001) and Mozia *et al.* (2006) found that PAC adsorption intensified fouling of UF membranes by humic acid. Lin *et al.* (2001) attributed this effect to (i) the higher fouling potential of the HS remaining after PAC adsorption than that of the untreated humic acid solution and (ii) the increased hydrodynamic resistance caused by the dense organics-PAC mixture on the membrane surface. Their second reason for the aggravated fouling was supported by Zhang *et al.* (2003), who also found that PAC particles contributed to fouling in UF of a surface water, and Dialynas and Diamadopoulos (2008), who used a municipal wastewater as the UF feed. Saravia *et al.* (2006) suggested that to avoid membrane pore plugging by PAC particles, PAC with narrow

particle size distributions and particle sizes at least 100 times larger than the membrane pore size should be used.

Improvement in MF and UF flux performance resulting from pre-treatment with PAC was observed with surface water by Konieczny and Klomfas (2002) and with municipal wastewater by Haberkamp *et al.* (2007) and Lee *et al.* (2007). Haberkamp *et al.* (2007) attributed the increased flux performance to the removal of biopolymers (which contained proteins and polysaccharides) by the PAC (SA Super, Norit). Lee *et al.* (2007), however, did not attempt to elucidate the mechanisms of the fouling reduction observed.

The differences in these findings may be due to differences in the PAC used (e.g., surface charge, pore size, particle size, and dosage) and differences in characteristics of the feeds and the membranes. They also illustrate the need to investigate the effect of this pre-treatment on membrane fouling for the AS effluent under consideration.

Pre-treating surface waters with heated iron oxide particles or heated aluminium oxide particles was found to reduce fouling of UF membranes (Chang *et al.* 1998; Zhang *et al.* 2003; Cai *et al.* 2008) by surface waters. It has been proposed that heated aluminium oxide particles can be pre-deposited on the membrane surface to form a fouling-resistant layer (Kim *et al.* 2008a) or combined with pre-coagulation to simultaneously reduce fouling and remove *ortho*-phosphorus for MF and UF in wastewater reclamation (Kim *et al.* 2008b). Koh *et al.* (2006) showed that treating natural lake water with polysulfone colloids at 5–100 mg L⁻¹ resulted in significant fouling reduction in UF and attributed this effect to the selective adsorption of the organic foulants (MW = 20–200 kDa) on the colloids. It should be noted that these novel adsorbents have only been tested with surface waters in laboratories or pilot-scale plants.

2.5.1.5. Pre-filtration

Tsujimoto *et al.* (1998) observed a reduction in irreversible fouling in UF of a surface water after pre-filtration the feed with granular activated carbon filters. However, the mechanism for the fouling reduction was unclear. Zheng *et al.* (2010) found that pre-filtration of a secondary effluent with a slow sand filter resulted in biodegradation of some biopolymers responsible for fouling of the subsequent PES UF membrane.

The use of hydrophobic low pressure membranes with coarse pore matrices to remove potential foulants has been proposed but rarely implemented since cost-effective measures need to be developed to restore their removal capacity. Other materials, e.g., filter cloth, string-wound polyester, and stainless steel, have also been used as the media for pre-filters (Huang *et al.* 2009a).

2.5.2. Selection of membrane types and surface modification

Fouling can be reduced by using membranes with narrow pore size distributions or using hydrophilic rather than hydrophobic membranes. This is particularly useful if proteins are the foulant because proteins tend to adsorb more strongly on hydrophobic surfaces (Wilf & Alt 2000). If the feed contains charged colloids, using negatively charged membranes can help to reduce fouling because most colloids are negatively charged (Mulder 1996).

Modification of the membrane surface to change its properties has been practised to reduce fouling. This can be done by various means such as low temperature plasma activation, UV irradiation, and redox radical grafting. UV irradiation can be carried out alone or with hydrophilicity-increasing agents such as dextrans (Nyström & Järvinen 1991) or N-vinyl-2-pyrrolidinone (Zhang *et al.* 2009). Redox radical grafting has been reported to increase hydrophilicity and reduce surface roughness, which in turn reduce adsorption of organic matter (Sheikholeslami 1999). Co-polymerisation of the base polymers with hydrophilic materials such as poly(ethylene glycol), poly(ethyleneimine), and ultrahigh MW poly(styrene-alt-maleic anhydride) has been reported to improve the hydrophilicity and reduce protein adsorption on the membranes (Ma *et al.* 2007; Zhu *et al.* 2007). Surface hydrophilisation of PVDF membranes has also been done by dispersing titanium dioxide nanoparticles into PVDF solutions (Oh *et al.* 2010) and surface coating with poly(vinyl alcohol) (Du *et al.* 2009).

2.5.3. Optimising module configuration and process conditions

Proper selection of module configuration and operating conditions can be very effective in reducing fouling. Concentration polarisation can be reduced by manipulating the flux and the mass transfer coefficient. The mass transfer coefficient can be increased by increasing the cross-flow velocity or changing the module configuration (decreasing module length and/or increasing the hydraulic diameter) (Mulder 1996). Turbulence promoters and pulsating flow

can be used to break the boundary layer, hence improving the mass transfer coefficient (Belfort *et al.* 1994; Mulder 1996).

In cross-flow filtration, operating at high cross-flow velocity (which consumes more energy) and low flux increases the mass transfer coefficient, hence reducing concentration polarisation and membrane fouling (Belfort *et al.* 1994; Mulder 1996). Fouling can be reduced to zero or negligible if filtration processes are operated below the critical fluxes (sub-critical flux operation) (Field *et al.* 1995; Bacchin *et al.* 2006). Compared with above-critical flux operation, this strategy requires a much larger membrane surface area for the same water productivity and hence higher capital investment. However, sub-critical flux operation has some advantages, including lower energy consumption and less usage of chemicals for membrane cleaning. Currently, in practice, to increase the water productivity, membrane filtration processes are usually operated above the critical flux and thus allow fouling. Fouling is then eliminated by frequent back-flush or back-shock, or by removing the force holding the cake to the membrane surface (Bacchin *et al.* 2006). Howell *et al.* (2002) noticed that using regular intermittent flux resulted in reduced long-term fouling.

2.5.4. Membrane cleaning

Membrane cleaning is needed to restore the permeate flux loss due to fouling. It can be accomplished by hydraulic, mechanical, or chemical means. Cleaning methods used are dependent on the foulant characteristics, membrane material, and membrane configuration.

2.5.4.1. Hydraulic and mechanical cleaning

Common hydraulic cleaning methods include backwashing and alternate pressurising and depressurising. The term “backwashing” is normally applied to dead-end filtration. During backwashing, permeate is flushed from the permeate side to the feed side to remove the fouling layer on the membrane surface. Air scouring may also be applied prior to backwashing to loosen the deposit layer (Water Environment Federation 2006). Adham *et al.* (2005) surveyed a number of drinking water treatment plants in the United Kingdom (UK) and found that backwash frequency varied from 5 to 96 per day and could last from 10 seconds to 10 minutes. In MF and UF of secondary effluents, backwashing is normally carried out every 15–30 minutes (Leslie *et al.* 1999; Decarolis *et al.* 2001; Laabs *et al.* 2006; Water Environment Federation 2006).

In cross-flow filtration, a similar technique called “back-flushing” has been used to reduce fouling (Redkar & Davis 1995). Back-flushing is normally applied for 5–10 seconds every 3–15 minutes. When back-flushing is applied for a very short duration (typically less than 1 second) and at a much higher frequency (once every few seconds), it is called “back-pulsing” (Redkar & Davis 1995; Sondhi *et al.* 2000; Gabrus & Szaniawska 2009). Back-flushing and back-pulsing are particularly useful in cross-flow filtration with tubular ceramic membranes since the membranes are able to withstand much higher pressures than polymeric membranes (Sondhi & Bhave 2001).

So far the vast majority of the studies involving back-flushing and back-pulsing in cross-flow filtration has focussed on water and wastewater from industrial sources. Matsumoto *et al.* (1988) reported significant flux improvement with back-flushing with the permeate (for 5 seconds every 3 minutes) in MF of yeast suspensions. Nipkow *et al.* (1989) observed a 42% flux improvement with back-flushing in MF of *Clostridium thermosulfurogenes* in maltose medium. Back-pulsing improved the flux performance in cross-flow MF and UF of yeast suspensions (Redkar *et al.* 1996), bacterial lysate (Parnham & Davis 1996), oil emulsions (Srijaroonrat *et al.* 1999), bovine serum albumin solutions (Kuberkar & Davis 2001), and synthetic electroplating wastewater (Sondhi *et al.* 2000). However, information regarding the effectiveness of back-flushing in reducing fouling in cross-flow MF and UF of surface water and municipal wastewater remains scant. From an economic point of view, back-pulsing is not beneficial for these applications due to the high permeate loss and energy demand.

Mechanical cleaning is normally done with oversized sponge balls and can only be used for tubular membrane configurations in the absence of turbulence promoters or other internal obstructions (Belfort *et al.* 1994; Mulder 1996).

2.5.4.2. Chemical cleaning

Chemical cleaning is used to remove contaminants which are not removed by hydraulic and mechanical cleaning methods. Chemically enhanced backwash (CEB) is used to stabilise or maintain the membrane permeability and therefore is often referred to as “maintenance” cleaning. In CEB the cleaning solution is added to the backwash water and cleaning is normally carried out at relatively low cleaner concentrations over a short time, and at ambient temperature. CEB is automatically scheduled daily to weekly. On the other hand, cleaning-in-place (CIP) is needed to recover the flux after long term operation. CIP is usually carried out with higher cleaner concentrations, longer soaking time, and possibly at elevated temperatures. It is normally applied when the membrane permeability falls below an acceptable value (Porcelli & Judd 2010). According to Adham *et al.* (2005), the frequency of CIP in the UK drinking water treatment plants varied from 0.2 to 50 per year with a median of 4 per year.

The most important consideration in the selection of cleaning agents is the compatibility of the cleaners and the membranes to avoid membrane damage. The performance of membrane cleaners needs to be evaluated based not only on their ability to restore the membrane flux, but also on the ability to maintain the product water quality. This is because although some chemicals can restore membrane flux, they may significantly reduce the rejection of viruses, bacteria, and some chemical compounds of concern (Al-Amoudi & Lovitt 2007). The mechanisms of foulant removal by different chemicals are complex and it has been realised that the chemistries of foulants, membrane cleaners, and membrane materials may not be reliable factors for the estimation of cleaning efficiency (Porcelli & Judd 2010).

Cleaning efficiency is affected by many factors, including cleaner concentration, temperature, cleaning time, and hydrodynamic conditions (Liu *et al.* 2001). Concentration of cleaning agents can affect both the equilibrium and rate of reactions. It needs to be sufficient to maintain a reasonable reaction rate as well as to overcome the mass transfer barrier imposed by the fouling layer (Liu *et al.* 2001).

According to Liu *et al.* (2001), temperature can affect the effectiveness of membrane cleaning by (a) changing the equilibrium of chemical reactions, (b) changing the reaction kinetics, and (c) changing the solubility of the foulants and/or reaction products during cleaning. In general, higher cleaning temperature improves the cleaning efficiency. Increasing temperature

increases diffusive mass transfer, foulant solubility, and reactivity of the functional groups of the foulants. High temperature also promotes swelling and mechanical destabilisation of organic foulants or biofilm layers (Liu *et al.* 2001).

Dynamic cleaning in which cleaning solutions are circulated through the system can be more effective than static cleaning such as soaking because circulation promotes contact between cleaning agents and foulants and reduces the distance of diffusion by bringing fresh chemicals close to the foulants (Liu *et al.* 2001).

In general, acids and chelating agents (e.g., ethylenediamine tetraacetic acid (EDTA) and citric acid) are effective for cleaning membranes fouled by inorganic scale. Some organic materials such as proteins and polysaccharides may be hydrolysed by inorganic acids (Liu *et al.* 2001). The “salt bridge” effect of divalent cations on HS can cause a denser and more adhesive fouling layer. Chelating agents and surfactants can form complexes with divalent cations and therefore improve the cleaning efficiency on membranes fouled by organic foulants (Al-Amoudi & Lovitt 2007). EDTA has been found very effective for cleaning membranes fouled by humic acid in the presence of Ca^{2+} (Hong & Elimelech 1997) while citric acid is effective for restoring flux of membranes fouled by iron oxides because it not only dissolves the oxides but also forms complexes with iron (Liu *et al.* 2001). Due to their low costs, hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) are widely used to clean mineral scales on fouled membranes (Porcelli & Judd 2010).

Bases, oxidants, and surfactants are used to clean membranes fouled by DOM. Alkalis clean membranes via 2 mechanisms: hydrolysis of proteins and solubilisation of HS (Liu *et al.* 2001). The hydrolysis of proteins can cause disruption in their tertiary structures and they can therefore be converted to peptides which are soluble in the bulk cleaning solutions. Alkaline conditions also increase the negative charge and solubility of HS; this increases the electrostatic repulsion between HS and the membranes and facilitates the removal of HS from the membranes (Liu *et al.* 2001). At high pH, DOM molecules tend to have a stretched, linear configuration due to the repulsion between negatively charged functional groups (Stumm & Morgan 1996; Hong & Elimelech 1997). This molecular configuration creates a looser fouling layer that allows easier access for chemicals to penetrate the inner portion of fouling layer. The increase in mass transfer leads to improvement in cleaning efficiency. The most commonly used alkali is sodium hydroxide (NaOH).

The oxidation of organic compounds in water and wastewater by oxidising agents generates oxygen-containing functional groups (e.g., ketone, aldehyde, and carboxylic acid). The presence of these functional groups generally increases the hydrophilicity of their parent compounds and therefore reduces the adhesion of fouling materials to the membranes. The disinfection effect of oxidants has also been found to reduce membrane biofouling. Sodium hypochlorite (NaOCl) is the most commonly used membrane cleaning oxidant. Hydrogen peroxide (H₂O₂) is used when the membranes (e.g., those made of polypropylene) are not chlorine tolerant or when there are concerns about health and environmental impacts of the chlorinated organic matter generated. The chlorine in NaOCl may cause swelling of membranes, which increases the mass transfer of cleaning agents to the membrane surface (Zeman & Zydney 1996). Cleaning with oxidising agents may result in degradation of membranes. Chlorination of the C-S bonds in PES membranes was observed at chlorine concentration above 150 mg L⁻¹ at low to neutral pH levels. As a result, the membrane mechanical strength was reduced significantly (Arkhangelski *et al.* 2007). Prolonged exposure to NaOCl was found to cause ageing of a PVDF membrane, leading to reductions in the membrane hydrophobicity and hydraulic resistance and changes in the pore size and pore structures (Puspitasari *et al.* 2010).

Surfactants have both hydrophilic and hydrophobic structures. They can form micelles with polysaccharides, proteins, and HS in water and help to separate these materials from the membranes. Some surfactants interfere with hydrophobic interactions between bacteria and membranes or disrupt functions of bacterial cell walls and therefore reduce fouling due to biofilm formation (Paul & Jeffrey 1984; Ridgway *et al.* 1985; Rosenberg & Doyle 1990).

Enzymes have been used to clean polypropylene membranes in some water treatment plants in the United States. However, their use in drinking water treatment is constrained by the high cost and potable water regulation (Porcelli & Judd 2010).

Mixtures of membrane cleaning agents and sequential cleaning with different chemicals have also been used (Porcelli & Judd 2010). Cleaning models developed using statistical methods have been used to optimise membrane cleaning efficiency.

2.6. Evaluating the fouling potential of feedwater

The silt density index (SDI) and the modified fouling index (MFI) have been used widely for evaluating the RO membrane fouling potential of a feedwater. As pointed out by Schippers and Verdouw (1980), SDI is not proportional to particle concentration and therefore cannot be used to predict the rate of flux decline due to particulate fouling. The MFI and the unified membrane fouling index (UMFI) can be used to evaluate the MF and UF fouling potential of surface water and wastewater, provided that fouling is governed by the cake filtration mechanism.

2.6.1. Modified fouling index (MFI)

The MFI was developed based on the cake filtration equation for constant-pressure dead-end filtration (Schippers & Verdoux 1980). It is expressed as:

$$\frac{t}{V} = \frac{\mu R_m}{A \Delta P} + \frac{\mu C_b \hat{R}_c}{2 A^2 \Delta P} V \quad (2.14)$$

where

t is the filtration time,

V is the permeate volume,

ΔP is the TMP,

μ is the dynamic viscosity of the water being tested,

A is the membrane surface area,

R_m is the flow resistance exerted by the membrane,

\hat{R}_c is the specific resistance of the cake ($\hat{R}_c = AR_c/m_c$ where R_c and m_c are the resistance and the mass of the cake, respectively), and

C_b is the particle concentration in the feed.

The slope of the straight line in equation 2.14 is defined as the MFI:

$$\text{MFI} = \frac{\mu \hat{R}_c C_b}{2 A^2 \Delta P} \quad (2.15)$$

The MFI is normalised to standard reference values $\Delta P_0 = 2.0$ bar, μ_0 = dynamic viscosity at 20°C, and $A_0 = 13.8 \times 10^{-4} \text{ m}^2$. It is determined using 0.45 μm MF membranes in constant-pressure dead-end filtration mode.

Feedwater having a higher value of MFI will have a higher fouling potential. It has been proven that MFI is proportional to particle concentration (Schipper & Verdouw 1980). The major drawback of MFI lies in the fact that it is based solely on cake filtration and does not include the contribution of other factors to fouling. Also, the MFI method does not take into account the dependence of the cake resistance on the pressure (Mulder 1996). Furthermore, the MFI does not take into account fouling by particles smaller than 0.45 μm (Schipper *et al.* 1981). To overcome this drawback, a new fouling index, called MFI-UF, was introduced. The MFI-UF is measured with a 13 kDa PAN membrane at 2.0 bar (Boerlage *et al.* 2002). More recently, Khirani *et al.* (2006a) proposed MFI-NF, which involved the use of hydrophilic PES NF membranes (500–1500 Da).

2.6.2. Unified membrane fouling index (UMFI)

The concept of UMFI was developed based on the resistance-in-series model and Darcy's law, and is written as (Huang *et al.* 2008; Lozier *et al.* 2008):

$$\frac{J_0}{J} = 1 + \left(\frac{\hat{R}_c C_f}{R_m} \right) \left(\frac{V}{A} \right) = 1 + \left(\frac{\hat{R}_c C_f}{R_m} \right) v \quad (2.16)$$

where

J_0 is permeate flux at time $t = 0$. For constant-pressure filtration, it can be determined by performing filtration with ultra-pure water (such as Milli-Q water) at the test pressure until quasi-steady state flux is reached,

J is the water flux through the membrane for the water being tested,

C_f is the foulant concentration in the feed, and

v is the accumulated permeate volume per unit membrane area

Equation 2.16 indicates that a plot of the reciprocal of the normalised flux (J_0 / J) versus v is a straight line with the y-intercept being 1. The slope of this line is defined as the UMFI:

$$\text{UMFI} = \frac{\hat{R}_c C_f}{R_m} \quad (2.17)$$

Compared with the MFI, the UMFI has the advantage of being applicable to both constant-pressure and constant-flux filtration. Furthermore, it has been found better than the MFI in predicting fouling in pilot-scale filtration using bench-scale data (Lozier *et al.* 2008). However, like MFI, UMFI is also established based on the assumption that fouling is

governed by cake formation. To extend its usability, Huang *et al.* (2009b) suggested that the index could be calculated by using only the first and the last data points of filtration tests therefore disregarding the fouling mechanisms involved.

The UMFI defined in equation 2.17 is used to evaluate the total fouling potential of a feedwater and is also called UMFI for total fouling. It is applied to a single long period of filtration or the first filtration cycle in multi-cycle filtration (interspersed by backwashing) experiments. In the latter case, it is named “UMFI_i”.

According to Lozier *et al.* (2008), there are other types of UMFI, including the UMFI for hydraulically irreversible fouling and the UMFI for chemical cleaning. The UMFI for hydraulically irreversible fouling is calculated by plotting the values of J_0 / J at the beginning of each filtration cycle against accumulated specific permeate volume (v) and taking the slope of the straight line. In another method of calculation, only values of J_0 / J for the first and the final filtration cycles are plotted against v . This latter method is intended to minimise the effect of high variability between cycles in a run (Huang *et al.* 2009b). The UMFI for chemical cleaning describes the chemically irreversible fouling for bench-scale end-of-run backwash operational mode. It is calculated by plotting J_0 / J at the beginning of the fouling filtration cycle and J_0 / J at the start of the filtration following chemical cleaning against v (Lozier *et al.* 2008).

2.7. Characterisation of filtration membranes

Surface properties, structure, and morphology of membranes have been examined by contact angle and streaming potential measurements, scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) spectroscopy, tunnelling electron microscopy, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), electron spin resonance, and Raman spectroscopy. Among these techniques, contact angle and streaming potential measurements, SEM, and AFM are the most widely used (AWWA Membrane Technology Research Committee 2005; Wyart *et al.* 2008).

2.7.1. Contact angle measurement

Contact angle has been used widely to characterise the surface energy or hydrophobicity of a membrane surface. It can be determined using techniques such as sessile drop, Wilhelmy plate, captive bubble, and solvent uptake (Washburn analysis) with manual goniometers or computerized dynamic contact angle measuring systems with digital image analysis. An ideal hydrophilic surface has a contact angle of 0° (Clark 1998). In membrane research, it is generally accepted that membranes with contact angles $> 50^\circ$ are hydrophobic membranes (Lozier *et al.* 2008).

2.7.2. Streaming potential

Measuring membrane surface charge and pore charge can give insights to fouling mechanisms because the charge determines the electrostatic interaction between the membrane and the foulant. Streaming potential has been used to estimate the zeta potential on both clean and fouled membrane surfaces (Zhu & Nyström 1998).

The zeta potential of membrane surfaces and membrane pores can be estimated using a streaming potential analyser and the Helmholtz-Smoluchowski equation, which gives the relationship between the measurable streaming potential and the zeta potential (Elimelech *et al.* 1994; Clark 1998; Soffer *et al.* 2002). Most membranes used in the water industry are negatively charged (AWWA Membrane Technology Research Committee 2005).

2.7.3. Atomic force microscopy (AFM)

AFM utilises the mechanical interactions between the membrane surface and a probe scanned parallel to the mean plane of the surface to obtain 3-D topographic images. It allows characterisation of surface roughness, pore size, and porosity in clean and fouled membranes (Clark 1998; Chennamsetty *et al.* 2006; Wyart *et al.* 2008).

2.8. Techniques for fouling characterisation

2.8.1. Characterisation of organic matter

In membrane fouling studies, DOM in the feed and the permeate has been characterised using different techniques. The analyses commonly used to investigate fouling of MF and UF membranes by surface water and municipal wastewater are listed below:

2.8.1.1. Dissolved organic carbon concentration and specific UV absorbance

Organic matter can be characterised using simple techniques such as dissolved organic carbon (DOC) concentration and UV absorbance at 254 nm. The ratio of this absorbance value (UVA_{254}) to the DOC gives the specific UV absorbance (SUVA), which is an indication of the relative amount of humic and non-humic fractions in the water (Weishaar *et al.* 2003). The percentage of DOC removal can be used as a measure of the effectiveness of the membrane in rejecting organic matter (Roddick *et al.* 2007). Nevertheless, Howe and Clark (2006) realised that the amount of DOC in the feedwater was not always a reliable indicator of its fouling potential because lower DOC concentration did not always correspond to less severe membrane fouling. This finding suggested that some specific fractions of DOC were responsible for fouling and the proportion of such fractions in the DOC varied from one water source to another.

Rapid fractionation using XAD-4 and DAX-8 resins, fluorescence excitation-emission matrix (EEM) spectroscopy, size exclusion chromatography (SEC) with UV and DOC detection, attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy, and biodegradable organic carbon (BDOC) determination can be used to obtain further information about size, structure, and functionality of dissolved organic matter in the feedwater and in the permeate.

2.8.1.2. Rapid fractionation

Rapid fractionation of organic constituents of the feed using XAD-4 and DAX-8 resins allows the separation of these components into the hydrophobic (HPO, containing mainly HS), transphilic (TPI), and hydrophilic (HPI, containing polysaccharides) fractions. The hydrophilic fraction can be further separated into the charged (CHA) and neutral (NEU)

fractions (Chow *et al.* 2004). Rapid fractionation facilitates the study of the fouling potential of organic fractions of different hydrophobicity (Roddick *et al.* 2007).

2.8.1.3. Fluorescence spectroscopy

Fluorescence excitation-emission matrices (EEMs) give information regarding fluorescent DOM in water and wastewater. They allow differentiation of fluorescent humic acid-like and fulvic acid-like materials, proteinaceous materials, and SMP in the feed, permeate, and backwashed effluent. Fluorescence spectroscopy has been proven useful for the identification of the membrane foulants which were removed by backwashing and cleaning with NaOH (Henderson *et al.* 2011). Peldszus *et al.* (2011) applied principal component analysis to the fluorescence EEMs of a biofiltered natural water and found that the concentration of the protein-like substances was highly correlated with the hydraulically irreversible fouling of the UF membrane treating this water.

2.8.1.4. High performance size exclusion chromatography

High performance size exclusion chromatography (HPSEC) with DOC and UV detection permits the determination of the apparent molecular weight distribution (AMWD) of the non-UV-absorbing and UV-absorbing molecules in water. It also gives information about the concentration of different molecular weight ranges and their chemical nature (Her *et al.* 2002; Allpike *et al.* 2005; Roddick *et al.* 2007).

2.8.1.5. Biodegradable dissolved organic carbon

Biodegradable dissolved organic carbon (BDOC) gives a measure of the biodegradability of the dissolved organic components in the feedwater and is an indication of the feedwater's biofilm formation and biofouling potential. It is determined by incubating the water sample with biologically active sand for 5–7 days under aerobic conditions and measuring DOC concentration daily. The highest DOC reduction observed during this time is taken as the BDOC concentration.

2.8.2. Characterisation of foulant materials on membranes

2.8.2.1. Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy

ATR-FTIR spectroscopy is an *in situ* technique that can be used to examine chemical structures of fouling layers. It is based on the infrared vibrational “absorption” spectra of

materials. Different peaks in the ATR-FTIR spectra correspond to compounds of different functionalities (Oldani & Schock 1989; Shon *et al.* 2004).

2.8.2.2. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy

High resolution images of clean and fouled membrane surfaces and cross sections can be obtained from SEM and electron probe microanalysis. The resolution of the images can be as high as 7Å, which is achieved with low-voltage field emission. SEM can also give information on the elemental content of the sample if used in combination with EDX spectroscopy (Clark 1998). Some researchers have used SEM/EDX to analyse foulants on the membrane surface (Al-Halbouni *et al.* 2008). The major disadvantage of SEM is the need for drying and coating of the samples because these processes are likely to introduce artefacts. This problem is resolved by environmental scanning electron microscopy (ESEM), which is conducted under low vacuum conditions (Roddick *et al.* 2007).

CHAPTER 3. MATERIALS AND METHODS

3.1. Wastewater sources

3.1.1. Raw and ozonated effluent and BAC filtrate

The WWTP from which the secondary effluent was collected utilised a conventional wastewater treatment process, which is described in Figure 3.1.

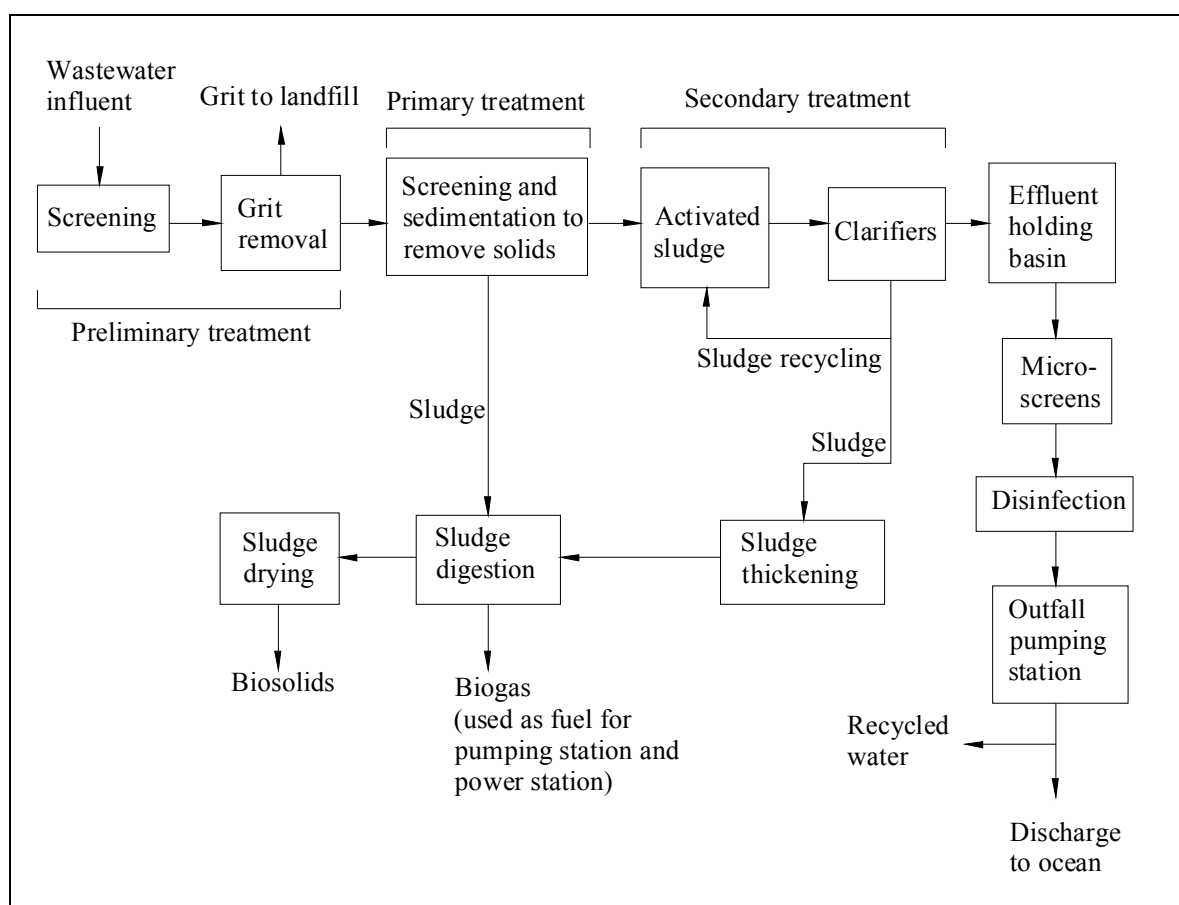


Figure 3.1. The wastewater treatment process at the WWTP

In preliminary treatment, large objects such as cotton buds, rags and other rubbish in the sewage influent were removed by screening with fine screens. The wastewater was then aerated to remove finer particles (e.g., grit and sand). It was then transferred to the primary clarifiers, where heavy objects settled and formed “sludge” at the bottom of the tanks and lighter materials (e.g., oil and fat) floated to the top of the tanks. The sludge and the floating debris were pumped to the digesters, where they were broken down by bacteria. The wastewater from the primary clarifiers was passed through the secondary treatment process,

which was an activated sludge (AS) system, for the breakdown of organic material by micro-organisms. This wastewater, after being pumped to secondary clarifiers, was passed through 3-mm micro-screens and then disinfected by chlorination. A small proportion (< 5%) of the chlorinated effluent was used as recycled water and the rest was discharged to the ocean. Because the secondary treatment at the WWTP was an AS system, in this thesis the secondary effluent being studied will also be called “AS effluent”.

The characteristics of the raw AS effluent are shown in Table 3.1 (data obtained from 36 samples collected from June 2008 to September 2011).

Table 3.1. Characteristics of the raw AS effluent used in this study

Table 3.2

Parameter	Value	Median	Mean	Standard deviation
pH	7.2 – 7.9	7.6	7.6	0.2
Total DOC (mg L ⁻¹)	10.5 – 15.9	13.8	13.5	1.4
UVA ₂₅₄ (cm ⁻¹)	0.29 – 0.44	0.39	0.37	0.04
SUVA (L m ⁻¹ mg ⁻¹)	2.1 – 3.8	2.6	2.8	0.44
True colour (mg Pt-Co L ⁻¹ or Pt-Co unit)	65 – 133*	103	101	15
Turbidity (NTU)	1.9 – 6.6	4.0	4.0	1.2
TSS (mg L ⁻¹)	2.1 – 10.9	4.2	4.5	1.9
Conductivity (µS cm ⁻¹)	900 – 1060	980	983	49
HPO (% of total DOC)	41 – 49			
TPI (% of total DOC)	21 – 27			
HPI (% of total DOC)	28 – 32			

* Values of 80–110 Pt-Co units were frequently observed

At a small trial plant within the WWTP, the raw AS effluent was ozonated at a dose of 10 mg O₃ L⁻¹ for 10 minutes and the ozone transfer efficiency was consistently greater than 96%. The ozone concentrations in the treatment process were measured (by the WWTP staff) using: (i) a process water flowmeter, (ii) a process gas (ozone/oxygen) flowmeter and an ozone concentration analyser for the process gas, (iii) a contactor off-gas flowmeter and an off-gas ozone analyser, and (iv) an ozone analyser for the concentration of residual dissolved ozone in the process water (usually zero). These measurements were used to perform a mass balance for ozone around the ozonation process and determine the ozone transfer efficiency (which was consistently greater than 96%).

The ozonated effluent was then filtered through a BAC column. The depth of the BAC bed (particle size = 8×16 mesh or 2.36×1.0 mm) was 2 m and the column was operated in downflow mode at 12 m h^{-1} and an empty bed contact time (EBCT) of 10 minutes. The growth of the microbial community in the BAC column occurred naturally, since ozonation of the raw effluent did not completely inactivate the biomass (the raw effluent contained residual biomass from the upstream activated sludge plant). The first BAC filtrate sample used in this study was collected when the BAC column had been in operation for approximately 3 months. As observed by the WWTP staff, the adsorption capacity of the activated carbon was exhausted by the time this research was conducted. Therefore, the removal of dissolved EfOM by the BAC filter observed in this study was essentially due to biodegradation.

Samples of raw and ozonated effluent and BAC filtrate were collected from the trial plant and transported to RMIT University, where they were stored at 4°C when not in use. Analyses and filtration experiments were done within 4 days of sample collection. Since ozonation of water and wastewater is known to cause breakdown of DOM structures and increase the biodegradability of water samples (Takahashi *et al.* 1995; Camel & Bermond 1998; Von Gunten 2003), the experiments with the ozonated effluent and the BAC filtrate were conducted soon after sample collection to minimise effects of biodegradation on the characteristics and fouling potentials of these samples. Monitoring the flux data of the raw effluent on day 1 and day 4 showed that the effect of sample storage on the flux data was minimal.

3.1.2. Coagulated samples

Coagulated samples were prepared in the laboratory at RMIT University. Coagulation was performed with the raw effluent in a jar test apparatus (PB-700, Phipps & Bird). The coagulants were aluminium sulphate (alum, supplied by BDH Chemicals) and (poly)aluminium chlorohydrate (ACH, supplied by Omega Chemicals as MEGAPAC 23). The tested coagulant doses were $1.0 \text{ mg Al}^{3+} \text{ L}^{-1}$ and $2.5 \text{ mg Al}^{3+} \text{ L}^{-1}$. The coagulant doses were selected based on the recommendation by the WWTP staff and common practice in municipal wastewater treatment, which tends to use in-line coagulation with low coagulant doses (normally less than $5 \text{ mg Al}^{3+} \text{ L}^{-1}$) (Decarolis *et al.* 2001; Qin *et al.* 2004; Zheng *et al.* 2012). Note that in this study, “in-line coagulation” refers to coagulation without subsequent removal of the coagulated matter by settling (Choi & Dempsey 2004; Wang *et al.* 2008). After the addition of the coagulants (without pH adjustment), the samples were mixed at 160 rpm (velocity gradient $G = 180 \text{ s}^{-1}$) for 2 minutes and then at 30 rpm ($G = 24 \text{ s}^{-1}$) for 20 minutes. In coagulation practice, the rapid mixing time may vary from 30 seconds to 2 minutes (with $G = 100\text{--}400 \text{ s}^{-1}$) whereas the slow mixing time may range from 90 seconds to 20 minutes ($G = 25\text{--}90 \text{ s}^{-1}$) (Choi & Dempsey 2004; Howe *et al.* 2006; Wang *et al.* 2008). The mixing conditions selected for this study were based on those used by Choi and Dempsey (2004) and Wang *et al.* (2008). The coagulated samples were then subjected to MF or UF without prior removal of the coagulated matter to simulate in-line coagulation (Choi & Dempsey 2004).

3.1.3. Samples pre-treated with an anion exchange resin (AER)

Attempts were made to reduce the colour of the raw AS effluent and it was found that apart from ozonation, colour reductions could be achieved by treating the raw effluent with a commercial strong base AER or a PAC. The characteristics of the AER (given by the manufacturer) are presented in Table 3.2.

Table 3.3. Characteristics of the AER used in this study

Functional group	Quaternary ammonium
Matrix	Polyacrylic
Mean pore size	45 nm
Charge capacity	0.52 meq mL^{-1}
Water content	50–60%

Initial jar tests were conducted with AER doses of 5 and 10 mL L⁻¹ to identify the resin dosage which gave a colour reduction approximately 75–80%. The AER volume was determined using a 10 mL measuring cylinder, in which the resin was allowed to settle for 1 hour. A plastic pipette was used to adjust the resin volume in the cylinder to the required doses. After adding the resin to the AS effluent, the jar contents were stirred at 100 rpm ($G = 100 \text{ s}^{-1}$) for 20 minutes. The resin was then allowed to settle for 10 minutes and the supernatant was retained for testing.

As in practice the AER is normally used to treat approximately 1500 bed volumes (BVs) of water before it is regenerated, the resin was reused without regeneration until the total volume of the AS effluent treated reached 1500 BVs. The combined treated AS effluent at each particular dose could be considered as being equivalent to that produced from plant operation. The colour removals at resin doses of 5 mL L⁻¹ and 10 mL L⁻¹ were 65% and 80%, respectively. The AS effluent sample treated with 10 mL AER L⁻¹ was used in the MF and UF tests.

3.1.4. Samples pre-treated with a powdered activated carbon (PAC)

Acticarb PS1300 (supplied by Activated Carbon Technologies) was selected for its high adsorption activity and high colour removal (as per manufacturer's information). The pore size distribution of the PAC was determined from nitrogen gas adsorption data at 77 K with a Micromeritics Accelerated Surface Area and Porosimetry (ASAP) 2000 unit. Prior to the measurement, the sample was degassed at 250°C overnight under vacuum. The total surface area of the PAC was calculated using the Brunauer-Emmett-Teller (BET) method. Volumes of micropores and mesopores were obtained from Barrett-Joyner-Halenda (BJH) pore area and pore volume analysis. The characteristics of Acticarb PS1300 are shown in Table 3.3.

Table 3.4. Characteristics of the PAC used in the study

Origin	Coal
Iodine number (mg g ⁻¹)	> 1200
Average particle size (µm)	20–30
Micropore (< 2 nm) volume (cm ³ g ⁻¹)	0.15
Mesopore (2–50 nm) volume (cm ³ g ⁻¹)	0.52
Surface area (m ² g ⁻¹)	1429

PAC adsorption of HS, the major colour-causing compounds in waters and municipal wastewaters, may take several days to reach equilibrium (Summers & Roberts 1988b). However, such a long contact time is not available in the wastewater treatment plant. Therefore, in this study, the contact time for PAC adsorption was limited to 30 minutes. The adsorption was carried out in a jar tester with a stirrer speed of 100 rpm ($G = 100 \text{ s}^{-1}$). Preliminary tests showed that for a contact time of 30 minutes, a PAC dose of 150 mg L^{-1} was needed to achieve 80% colour removal.

3.2. Analytical methods for wastewater samples

3.2.1. General characteristics

Except for the MF and UF permeates, the dissolved organic carbon (DOC) concentration, UV absorbance and true colour were obtained from samples which were vacuum-filtered through $0.45 \text{ }\mu\text{m}$ cellulose acetate membranes (C045A047A, Advantec MFS) using a procedure similar to that described by Karanfil *et al.* (2003). According to Advantec MFS (2001), this type of membrane contains little aqueous extractables and has low protein binding capacity. The vacuum flask and the filter holder were cleaned thoroughly with Milli-Q water prior to filtration with the samples. To minimise leaching of organic carbon and UV_{254} -absorbing components from the filters, the membranes were rinsed with 600 mL of Milli-Q water before use and filtrates were collected after an initial portion (approximately 10 mL) was wasted.

3.2.1.1. pH, conductivity, turbidity

The pH, conductivity, turbidity were measured using a Mettler Toledo pH meter, a Hach Sension5 conductivity meter, and a Hach 2100P Turbidimeter, respectively.

The pH meter was calibrated with standard solutions of pH 4.0, 7.0, and 10.0. Calibration of the conductivity meter was carried out with 500, 1413 and $2760 \text{ }\mu\text{S cm}^{-1}$ potassium chloride (KCl) standard solutions. Formazin standards (20, 100, and 800 NTU) were used to calibrate the turbidimeter.

3.2.1.2. UV absorbance, true colour, and residual ozone concentration

UV absorbance was measured with a Unicam UV/Vis spectrophotometer with Milli-Q water as the reference. A Hach spectrophotometer (model DR/4000) was used to determine the sample colour in Pt-Co units according to the Standard Method 2120 C (American Public Health Association 2005) and residual ozone concentration in the ozonated effluent samples

using the Indigo method (Hach Company 2003). In this method (Method 8311), the indigo reagent reacted immediately and quantitatively with ozone. The blue colour of indigo was bleached in proportion with the concentration of ozone in the sample. No residual ozone was detected in the ozonated effluent and hence did not affect the membrane flux performance.

3.2.1.3. DOC concentration

DOC concentration was measured with a Sievers 820 TOC analyser. The samples, except for the MF and UF permeates obtained from filtration tests, were filtered through 0.45 μm cellulose acetate membranes prior to this analysis. The instrument used 6.0 M phosphoric acid (H_3PO_4) to acidified the sample to pH 2 prior to analysis and aqueous ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) as the oxidiser. It operated on the ultraviolet light-persulphate oxidation method to determine the total carbon and total inorganic carbon in the sample. The total organic carbon was calculated by subtracting the latter from the former. Internal calibration was done by the manufacturer. External calibration for total organic carbon and inorganic carbon was performed using potassium hydrogen phthalate (1, 5, 10, and 25 mg C L^{-1}) and sodium carbonate (1, 5, and 25 mg C L^{-1}), respectively. The accuracy of the measurement was quoted as $\pm 3\%$ of the reading from the instrument.

3.2.1.4. Total suspended solid (TSS) concentration

TSS concentration was determined according to the Standard Method 2540 D (American Public Health Association 2005) using 0.5 μm glass fibre filter (GC50, Sterlitech Corporation, Washington, USA). For the raw and ozonated effluent, 1 L of the sample was used to determine the TSS concentration. The measurement was repeated using 1.5 L of the samples for those with TSS concentrations lower than 2.5 mg L^{-1} (to follow the Standard Method 2540 D). For the BAC filtrate, 5 L of the sample was used and therefore the amount of TSS retained by the 0.5 μm glass-fibre filter was less than 2.5 mg.

3.2.1.5. Particle size distributions and zeta potentials

The size distributions and the zeta potentials of the particles in the raw and ozonated effluent samples were measured with a Mastersizer 2000 and a Zetasizer 2000 (Malvern Instruments, UK), respectively. Mastersizer 2000 uses low angle and wide angle light scattering as well as back scattering to determine the particle properties. The particle size distribution was calculated by the Malvern software, using the intensity of the scattered light obtained from

detectors in the optical unit. The calculation was based on the Mie theory, assuming that 100% of the volume was within the measurable range. The volume median diameter, defined as the value below the 50th percentile of the particle size, was used to quantify the results. Three replicates of particle size measurement and five replicates of zeta potential measurement were performed for each sample and the average results were reported.

3.2.2. Fractionation of EfOM

Rapid fractionation following the procedure described by Lee *et al.* (2004) (Figure 3.2) was used to separate the EfOM in the samples into 3 fractions: HPO, TPI, and HPI. The fractions were recovered and used in MF and UF experiments to determine their relative fouling potentials. Fractionation was carried out using glass columns containing 25 mL of the resins. The sample flow rate passing through the resins was 3 BVs hr⁻¹.

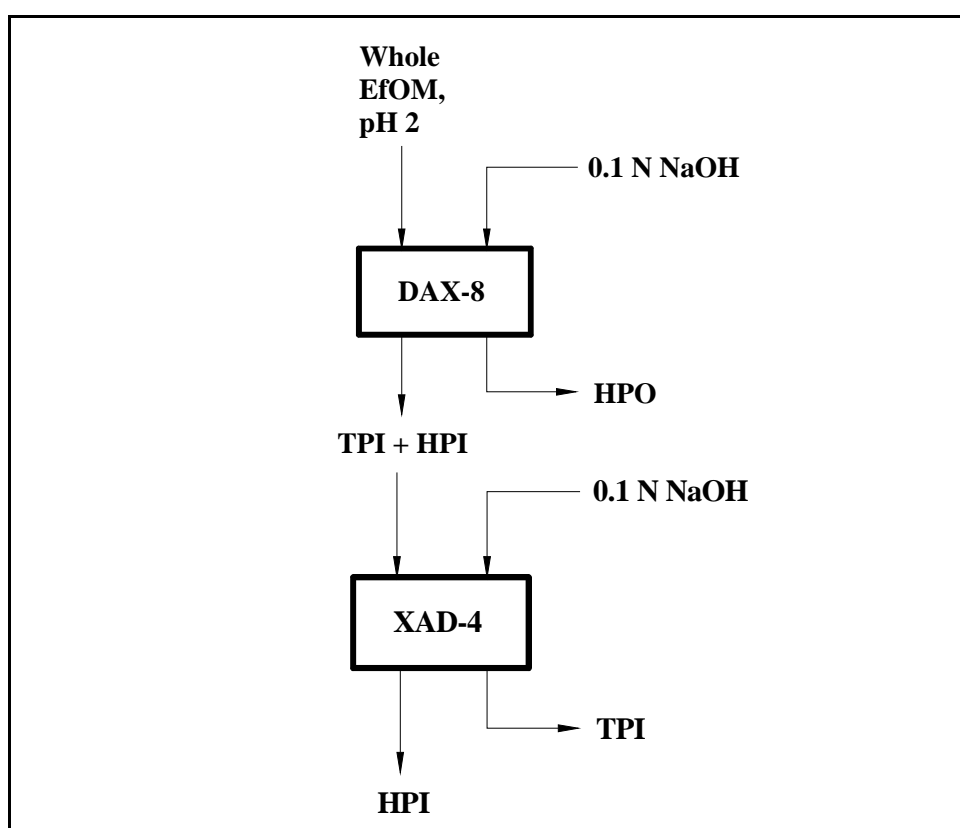


Figure 3.2. EfOM fractionation procedure (three-fraction protocol)

Samples of the raw AS effluent, ozonated effluent, and BAC filtrate were filtered through 0.45 µm cellulose acetate membranes, adjusted to pH 2 with 4.0 N HCl, and then fed onto columns of Superlite DAX-8 resin, which retained the HPO fraction. This fraction contained

mostly very hydrophobic acids (humic and fulvic acids) and some hydrophobic neutrals. EfOM not adsorbed by DAX-8 resin was fed onto Amberlite XAD-4 resin, which adsorbed the TPI fraction. This fraction was made up of weakly hydrophobic organic matter. EfOM not retained by XAD-4 resin was HPI EfOM and consisted of non-humic EfOM such as proteins, amino acids, and carbohydrates as well as organic colloids (Carroll *et al.* 2000; Shon *et al.* 2006; Lozier *et al.* 2008).

To recover the HPO and TPI fractions of the raw AS effluent to use in MF and UF experiments, these fractions were desorbed from the resins using 200 mL of 0.1 N NaOH followed by Milli-Q water so that the total volumes of HPO and TPI fractions collected were equal to the volumes of the feeds. The recoveries of the HPO and TPI fractions from the resins ranged from 90% to 97%, thus the concentrations of the collected HPO and TPI fractions were representative of the HPO and TPI fractions in the non-fractionated effluent. Before being used in the MF and UF tests, the three EfOM fractions obtained from the raw AS effluent were diluted with Milli-Q water to a DOC concentration of 1.3 mg L^{-1} , and adjusted to pH 7.6 and a conductivity of $1060 \text{ }\mu\text{S cm}^{-1}$ (same as for the non-fractionated sample) using 4.0 N HCl and 4.0 M NaCl solution. The DOC concentration of 1.3 mg L^{-1} was selected to ensure that the conductivities of the fractions could be adjusted to $1060 \text{ }\mu\text{S cm}^{-1}$.

It should be pointed out that the resin fractionation method used in this study (as well as in many previous studies (Nilson & DiGiano 1996; Jarusutthirak *et al.* 2002; Gray *et al.* 2004; Shon *et al.* 2006)) is not able to achieve 100% recovery of the fractions. The small proportion of the dissolved EfOM not recovered from the resins may have considerable contribution to membrane fouling. Furthermore, the pH adjustments may have caused some irreversible changes in the molecular structures of the EfOM. Therefore, the investigation of the fouling potentials of the three EfOM fractions was intended to serve as a complementary method for foulant identification. The identity of the EfOM components responsible for fouling was further verified using the results obtained from other analyses, including AMWDs of the feeds and the MF and UF permeates, ATR-FTIR spectra of the EfOM retained on the fouled membranes (Chapter 4), feed pre-treatment studies (Chapters 5–7), and membrane cleaning study (Chapter 8).

The four-fraction fractionation protocol (Figure 3.3) described by Chow *et al.* (2004) was used to investigate the effect of ozonation and BAC filtration on EfOM properties. In this

fractionation scheme, the very hydrophobic acid (VHA) fraction and slightly hydrophobic acid (SHA) fraction were equivalent to the HPO and TPI fractions, respectively (Carroll *et al.* 2000; Chow *et al.* 2004). The HPI fractions in the raw and ozonated effluent and the BAC filtrate were further separated into hydrophilic charged material (CHA, adsorbed on Amberlite IRA-958 ion exchange resin) and hydrophilic neutrals (NEU, not adsorbed on IRA-958 resin).

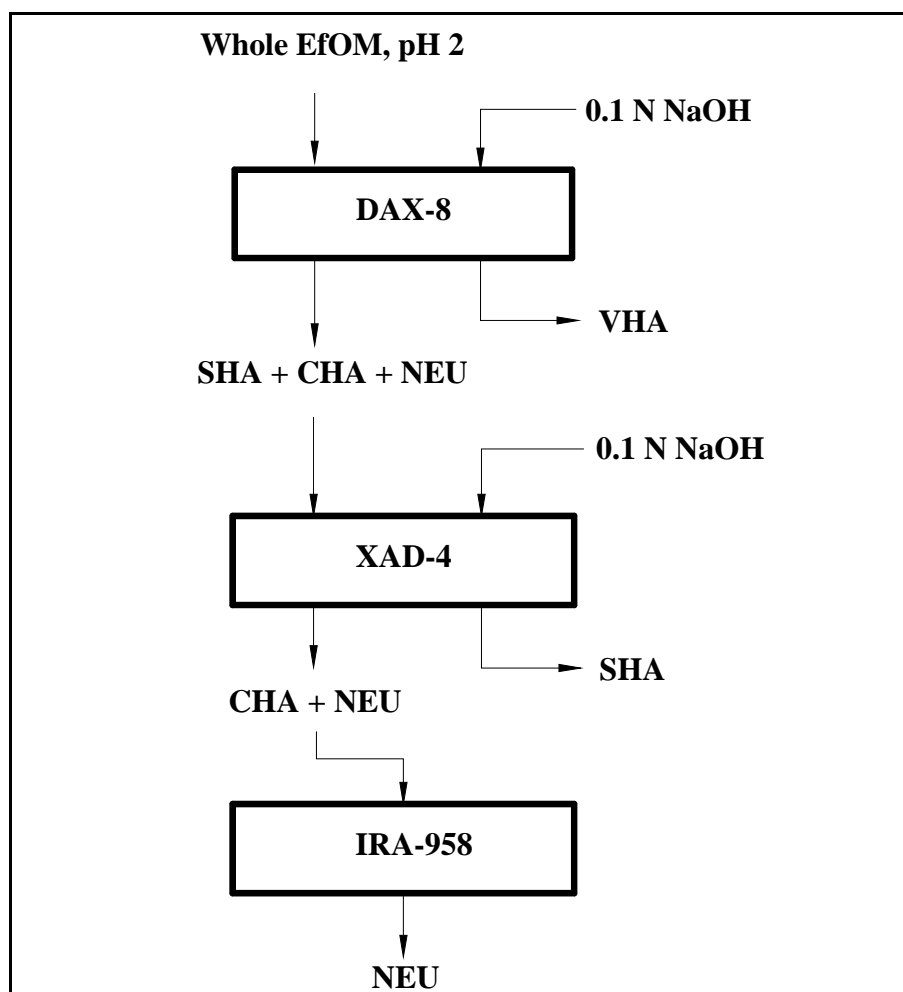


Figure 3.3. EfOM fractionation procedure (four-fraction protocol)

3.2.3. Sample AMWD

Sample AMWD was determined using liquid chromatography with organic carbon detection (LC-OCD). The instrument was an LC-OCD system (Model 8, DOC-Labor) equipped with an organic carbon detector (OCD) and a UV detector (UVD). The system design was based on the *Grüntzel* thin-film UV reactor (Huber *et al.* 2011). In this system, organic carbon in the sample was oxidised to carbon dioxide by UV irradiation at 185 nm with a persulphate

solution. The released carbon dioxide was quantified using a non-dispersive infrared detector (Ultramat 6E, supplied by Siemens, Munich, Germany).

Potassium hydrogen phthalate was used to calibrate the DOC detector. The LC column was Toyopearl TSK HW-50S (length: 250 mm, internal diameter: 20 mm) filled with 30 μm hydroxylated methacrylic resin. The mobile phase was a phosphate buffer (2.5 g L⁻¹ KH₂PO₄ and 1.5 g L⁻¹ Na₂HPO₄·2 H₂O, pH 6.4), running at an isocratic flow rate of 1.1 mL min⁻¹. Calibration of the OCD and UVD were done using potassium hydrogen phthalate. Suwannee River Humic Acids Standard II and Suwannee River Fulvic Acids Standard II from the International Humic Substances Society (IHSS) were used as reference standards for MW of HS. The sample injection volume was 1000 μL . Samples were filtered (0.45 μm cellulose acetate) and diluted with Milli-Q water to DOC concentrations below 5 mg L⁻¹ prior to analysis. The software program ChromCalc (DOC-Labor, Karlsruhe) was used for data acquisition and processing. ChromCalc divided the chromatograms into 5 different areas corresponding to biopolymers (which contained polysaccharides and proteins, MW >> 20,000 Da), humic substances (HS, MW = 1,000–20,000 Da), building blocks (breakdown product of HS, MW = 300–500 Da), low MW organic acids and low MW HS (MW < 350 Da), and low MW neutrals (mono-oligosaccharides, alcohols, aldehydes and ketones, MW < 350 Da). LC-OCD analysis gives information regarding the organic materials which are eluted from the LC column. The DOC that contributes to the chromatograms is called “chromatographic DOC (CDOC)”. For most water and wastewater samples, a small proportion of the total DOC is retained on the resin in the LC column as a result of hydrophobic interaction between the DOC and the resin (Huber *et al.* 2011). This fraction of the total DOC is called “hydrophobic organic carbon (HOC)” and usually not considered in studies which utilise LC-OCD analysis to investigate membrane fouling, as it is not useful for the interpretation of the flux data (Laabs *et al.* 2006; Haberkamp *et al.* 2007; Lozier *et al.* 2008; Zheng *et al.* 2010; Henderson *et al.* 2011). Therefore, the HOC fractions of the samples analysed with LC-OCD were not included in this thesis. For these samples, the HOC fractions accounted for 3–10% of the total DOC (i.e., the sum of CDOC and HOC).

The analysis was carried out at the University of New South Wales, Sydney, Australia. The effects of coagulation, ozonation, BAC filtration and adsorption pre-treatments with the AER and the PAC on the AMWD of the EfOM in the raw effluent were tested on two batches of samples collected on different dates and similar results for each pre-treatment were obtained.

According to Huber *et al.* (2011), LC-OCD analysis has been proven highly sensitive and reproducible.

3.3. Membrane analysis

3.3.1. ATR-FTIR spectroscopy

A Spectrum 100 FT-IR spectrometer (PerkinElmer) was used to analyse the foulant layer on the membranes. This spectrometer was equipped with a PerkinElmer® Universal ATR Accessory with a diamond ATR crystal and utilised the Atmospheric Vapour Compensation (AVC) technology to eliminate interferences from water vapour and carbon dioxide in the atmosphere. FTIR spectra of the clean and fouled membranes were collected over the wave number range of 650–4000 cm^{-1} using the ATR method. The resolution was adjusted to 4.0 cm^{-1} . The virgin membranes had Milli-Q water passed through them for 45 minutes to remove preservatives. The fouled membranes were obtained after filtration by the virgin membranes with the 0.5 μm pre-filtered effluent samples to avoid possible interferences of SS on the FTIR spectra. Prior to ATR-FTIR analysis, the membranes were dried overnight in a desiccator at room temperature. Three different areas on each membrane sample were scanned. The 3 spectra collected for each membrane sample were essentially superimposed.

3.3.2. SEM/EDX spectroscopy

SEM images and energy dispersive X-ray (EDX) spectra of dried virgin and fouled HFM-116 membrane samples were obtained with a microscope (Quanta 200, FEI) equipped with an EDAX's Si(Li) X-ray detector. The analysis was carried out at an accelerating voltage of 15 kV and a magnification of 5000 (for SEM images) and 200 (for EDX spectra). The SEM images and EDX spectra (the latter gave information on the elements present on the membranes) were collected for 3 different areas on the membrane samples and no differences between these areas were noticed.

3.3.3. Contact angle measurement

The contact angles of the virgin flat sheet membranes were measured with an OCA20 contact angle meter (DataPhysics Instruments GmbH) using the sessile drop method with Milli-Q water. The water droplet volume was 10 μL and the contact angles (computed using the Young-Laplace equation) were taken within 5 seconds. Five measurements were carried out for each membrane and the average values were reported (details are included in Appendix A). Although contact angle measurements are method- and operator-dependent, it allows

comparison of the degree of hydrophobicity of different membranes on a relative basis, provided that the protocol used is well-defined and reproducible (Lozier *et al.* 2008).

3.4. Dead-end filtration experiments

3.4.1. The membranes used in dead-end filtration

The membranes used in dead-end filtration tests are listed in Table 3.4. The primary focus of this study was PVDF membranes, as they are the most widely used membranes in MF and UF of water and wastewater. Flat-sheet and hollow-fibre MF membranes were tested to determine if membrane configuration had any significant effect on fouling, as a previous study on surface water found that flat-sheet membranes fouled more rapidly than hollow-fibre counterparts (Howe *et al.* 2007). A relatively hydrophilic UF membrane made of proprietary PES was also tested.

Table 3.5. Characteristics of the polymeric membranes used in this study

Code	Supplier	Material	Nominal pore size or MWCO	Configuration	Pure water flux (L m ⁻² h ⁻¹ bar ⁻¹) at 22°C	Contact angle (°)
VVLP	Millipore	PVDF	0.1 µm	Flat-sheet	2000 ± 150	62±2
XUNP-003	Pall	PVDF	0.1 µm	Hollow-fibre	2200 ± 100	> 90*
HFM-180	KMS**	PVDF	100 kDa	Flat-sheet	1000 ± 100	84±2
HFM-116	KMS	PVDF	50 kDa	Flat-sheet	150 ± 12	68±2
HFK-141	KMS	PES	30 kDa	Flat-sheet	220 ± 20	41±2

*Supplier information, exact value not given

**Koch Membrane Systems

The VVLP membrane was made of modified PVDF to increase the hydrophilicity (Millipore 2008). The HFM-180 and HFM-116 membranes were made of proprietary semi-permeable PVDF. Each XUNP-003 module was made of 32 PVDF membrane fibres (inner diameter = 0.8 mm, outer diameter = 1.0 mm) potted in a PES shell, giving a total filtration area (outside-in mode) of 0.0082 m². According to the manufacturer, XUNP-003 is a hydrophobic membrane with a contact angle greater than 90° (no specific value was provided).

3.4.2. Dead-end filtration system

Filtration experiments with the flat-sheet membranes were carried out using a stirred dead-end filtration cell (Amicon 8050, effective membrane area 0.00134 m²) in the arrangement shown

Figure 3.4. Tests with the MF hollow-fibre (XUNP-003) membrane used the same arrangement, except that the filtration cell was replaced with the hollow-fibre modules. The applied TMP was regulated using compressed nitrogen gas. The permeate mass was recorded every minute using a top-loading electronic balance (Explorer, Ohaus, accuracy ± 0.01 g) and logged by computer and was used to compute the permeate flux.

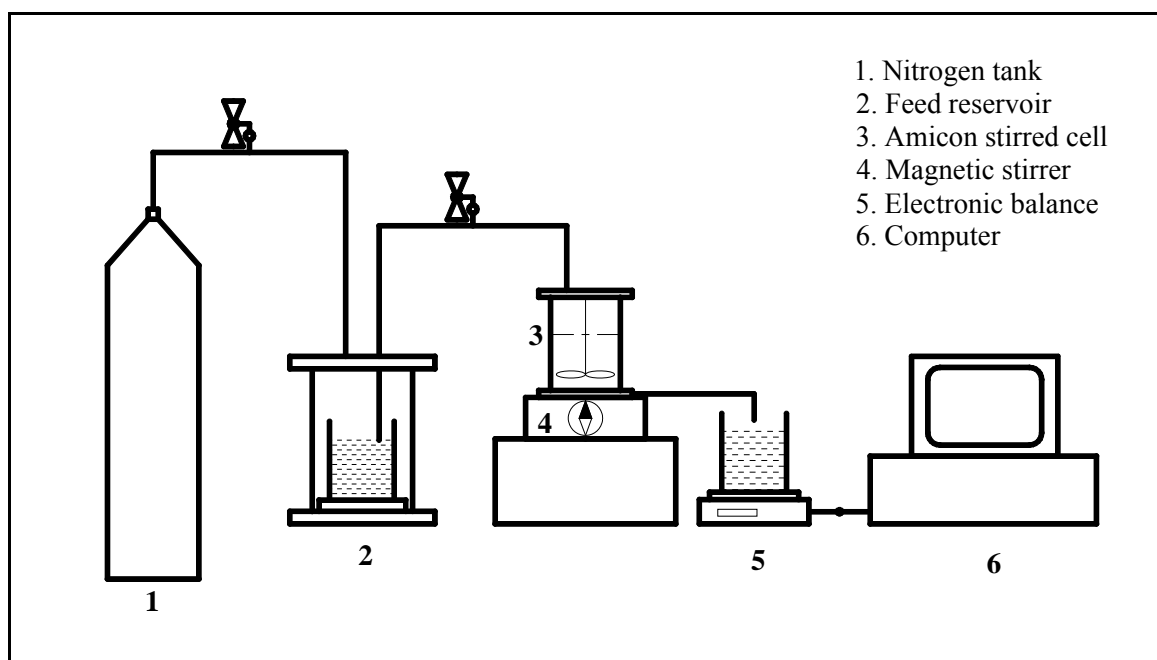


Figure 3.4. Filtration experimental set-up for the flat-sheet membranes

3.4.3. Operating conditions and general procedure

All filtration tests were carried out in the pressurised mode and at a water temperature of 22 ± 1 °C. The applied TMP was 70 kPa for MF and 110 kPa for UF, which was regulated using compressed nitrogen gas. The conditions were selected based on those used by Adham *et al.* (2006) and Howe *et al.* (2007) in bench-scale MF and UF of surface water. For the tests with the flat-sheet membranes, a stirrer speed of 60 rpm was maintained to keep the cell contents well mixed. The hollow-fibre membrane modules were run in dead-end outside-in mode.

A new flat-sheet membrane was used for each filtration run. Four hollow-fibre (XUNP-003) modules were used. The fouled XUNP-003 membranes were regenerated by soaking in a mixture of NaOH (0.025 N) and NaOCl (200 ppm available chlorine) at 35 °C for 2 hours. This chemical cleaning (recommended by the manufacturer) allowed full recovery of the membrane pure water flux. The cleaned membranes were then used in further tests. During

the experimental program, each XUNP-003 module was reused 5–6 times and no deterioration in the DOC rejection and colour rejection was observed.

Prior to filtration, each membrane was soaked in Milli-Q water for 2 hours and then had 1 L of Milli-Q water passed through them to remove membrane preservatives (or cleaning agents in the case of the XUNP-003 membrane). The pure water fluxes (J_0) of the membranes were obtained by taking the average of the Milli-Q water fluxes in the 8th, 9th, and 10th minutes, when the membranes could be considered as in quasi-steady state (Fan 2002).

3.4.4. Single-cycle filtration

Single-cycle tests are a quick method to study membrane fouling by water and wastewater. Filtration tests without intermittent backwashing were conducted with the raw and the pre-treated effluent samples until the specific permeate volume (v) reached 200 L m⁻² (MF) and 150 L m⁻² (UF). The corresponding filtration time for the raw effluent with the VVLP membrane ranged from 75 to 120 minutes, depending on the sample batch. These values for the HFM-180, HFM-116, and HFK-141 were 60–90, 150–170, and 90–110 minutes, respectively. The feeds and the permeates were collected for further analyses to identify the membrane foulants (with LC-OCD) and evaluate the rejections of UVA₂₅₄ and true colour. The flux data obtained were used to assess the effect of the pre-treatments on the flux performance. Three parameters were used for this purpose: the normalised flux, the resistance by total fouling (R_{tf}) and the UMF1 for total fouling (sample calculations for these parameters are shown in Appendix B).

The normalised flux was defined as the ratio of the permeate flux during MF or UF with the effluent samples (J) to the pure water flux of the membrane (J_0). The resistance by total fouling was calculated as

$$R_{tf} = \frac{\Delta P}{\mu J'} - R_m \quad (3.1)$$

where

J' is the permeate flux at the end of the filtration test,

ΔP is the TMP

μ is the viscosity of the wastewater (taken as 0.958×10^{-3} Pa.s, i.e., same as the viscosity of pure water at 22 °C), and

R_m is the resistance exerted by the virgin membrane,

$$R_m = \frac{\Delta P}{\mu J_0} \quad (3.2)$$

Plots of reciprocal of the normalised flux (J_0 / J) versus specific permeate volume (v) were constructed to obtain the UMFIs for total fouling, which are the slopes of the curves. The UMFI for total fouling was used to quantitatively evaluate the effect of the different feed pre-treatment methods on the flux performance. The lower the UMFI for total fouling, the better the flux performance.

Then, to investigate the effect of different feed pre-treatments on hydraulically irreversible fouling, the fouled membranes were backwashed with the permeates and their pure water fluxes were measured. The backwash procedure for the flat-sheet membranes was as follows:

- (i) Rinsing the membrane surface with Milli-Q water
- (ii) Placing the membranes upside down in the filtration cell and filtering the permeate at the operating pressure for 5 minutes
- (iii) Returning the membranes to their processing orientation and measuring the pure water flux of the backwashed membranes (J_{BW}).

Backwashing of the fouled hollow-fibre membrane was done by passing the permeate in the reverse direction (i.e., inside-out) at the operating pressure (70 kPa) for 5 minutes.

The resistances by irreversible fouling (R_{if}) were calculated using the resistance-in-series model (Kimura *et al.* 2004; Al-Amoudi & Lovitt 2007) with the following equation:

$$R_{if} = \frac{\Delta P}{\mu J_{BW}} - R_m \quad (3.3)$$

In a separate experiment, the HMF-116 and HFK-141 membranes fouled by the raw AS effluent were backwashed with Milli-Q water at 110 kPa for 5 minutes. The backwash water was then subjected to LC-OCD analysis (after being filtered through a 0.45 μm cellulose acetate membrane) to identify the EfOM components responsible for hydraulically reversible fouling.

3.4.5. Multi-cycle filtration

In real plant operation, MF and UF of secondary effluent are normally carried out in multi-cycle filtration mode (15–30 minutes filtration followed by backwashing for approximately 10 seconds to a few minutes) (Leslie *et al.* 1999; Decarolis *et al.* 2001; Laabs *et al.* 2006; Water Environment Federation 2006). Some researchers have suggested that flux data obtained with virgin membranes may not be representative for every filtration cycle (Howe *et al.* 2007). Therefore, in this study the effect of the pre-treatments on membrane fouling was also investigated with the backwashed membranes. Six filtration cycles, each of which lasted for 20 minutes and was followed by 1-minute backwashing with the permeate at the operating pressure, were conducted.

3.5. Chemical cleaning of the fouled polymeric membranes

The aim of this part of the study was to identify the best cleaning agents for the polymeric membranes fouled by the raw AS effluent and obtain more insights to the interactions between the foulants, the membranes and the cleaning agents. The 50 kDa PVDF (HFM-116) membrane was selected for its high retention of the foulants, which facilitated the tracking of these compounds on the membrane during the fouling and cleaning processes using ATR-FTIR spectroscopy and SEM/EDX spectroscopy. The three most effective cleaners for the HFM-116 membrane were also tested on the PES 30 kDa (HFK-141) membrane.

3.5.1. Membrane fouling and cleaning procedure

The virgin membranes were fouled with the raw AS effluent at 110 kPa until the accumulated specific permeate volume (v) reached 150 L m^{-2} (which took approximately 150 minutes). The fouled membranes were then backwashed with the permeate at 110 kPa for 5 minutes and their pure water flux was measured with Milli-Q water. The backwashed membranes were then soaked (with gentle shaking on an orbital shaker at 100 rpm) in 75 mL of the cleaning agent solutions at 24 °C for 45 minutes. The cleaning agents used for cleaning of the fouled HFM-116 membrane are shown in Table 3.5. These included an acid (HCl), a base (NaOH), a chelating agent (tetrasodium ethylenediaminetetraacetic acid (Na_4EDTA)), two oxidising agents (NaOCl and H_2O_2), a surfactant (sodium dodecyl sulphate or SDS), and a protease-based cleaner (Terg-a-zyme, used widely in the fermentation industry). The concentrations were selected based on common practice as well as the pH limit (pH 1.5–10.5) and chlorine

tolerance (200 ppm) of the HFM-116 membrane. Milli-Q water was used to dissolve/dilute the cleaning agents to the target concentrations.

Three fouling and cleaning cycles were also conducted with the 3 most effective cleaners on the HFM-116 membrane to determine if accumulation of residual fouling after chemical cleaning occurred. These cleaning agents were also tested on the 30 kDa PES (HFK-141) membrane (pH limit = 2.0–11.0).

Table 3.6. The membrane cleaners investigated

Chemical	Concentration	pH
Sodium hydroxide (NaOH)	0.3 mM	10.5
Hydrochloric acid (HCl)	10 mM	2.0
Na ₄ EDTA	0.4 mM	10.5
Sodium hypochlorite (NaOCl)	200 ppm as chlorine	10.5*
Hydrogen peroxide (H ₂ O ₂)	1.0 wt. %	4.5
H ₂ O ₂ /NaOH mixture pH 10.5	1.0 wt. % H ₂ O ₂	10.5
Sodium dodecyl sulphate (SDS)	10 mM	6.8
Terg-a-zyne	1.0 wt. %	9.6

*Adjusted with a small amount of HCl

3.5.2. Determination of the cleaning efficiency

Determination of the pure water flux of the chemically cleaned membranes was done after rinsing them thoroughly with Milli-Q water. The pure water flux recovery (*WFR*) was defined as the ratio of the pure water flux of the fouled membrane after hydraulic cleaning (J_{BW}) or chemical cleaning (J_c) to that of the virgin membrane (J_0). The effectiveness of chemical cleaning was evaluated using the cleaning efficiency, E_{RW} (Al-Amoudi & Lovitt 2007), with

$$E_{RW} = \frac{R_{if} - R_{res}}{R_{if}} \times 100 \quad (3.4)$$

where R_{res} is residual resistance after chemical cleaning,

$$R_{res} = \frac{\Delta P}{\mu J_c} - R_m \quad (3.5)$$

Sample calculations for *WFR* and E_{RW} are included in Appendix C.

3.5.3. Membrane analysis

Samples of the virgin, fouled, backwashed, and chemically cleaned membranes (after being dried overnight in a desiccator at room temperature) were examined with ATR-FTIR spectroscopy and SEM/EDX spectroscopy to determine if the results from these analyses could provide explanations for the differences in the cleaning efficiencies of the chemicals.

3.6. Cross-flow filtration experiments

3.6.1. The cross-flow filtration system and ceramic membranes

Cross-flow filtration tests were carried out with single-channel tubular ceramic membranes (Table 3.6) in inside-out mode. The inner diameter and outer diameter of the ceramic tubes were 7.0 mm, and 10.0 mm, respectively. The filtration surface area (based on inner diameter) was 0.005 m². The membranes were installed to be vertical in an XLAB5 pilot rig (Figure 3.5). The filtration rig and the membranes were supplied by Pall Corporation.

Table 3.7. Characteristics of the ceramic membranes used in cross-flow filtration experiments

Code	Material	Pore size	Pure water flux* (L m ⁻² h ⁻¹ bar ⁻¹)
Ceramic MF	α -alumina	0.1 μ m	1830 \pm 90
Ceramic UF	Zirconia on alumina support	20 nm	340 \pm 10

*Measured at 22°C

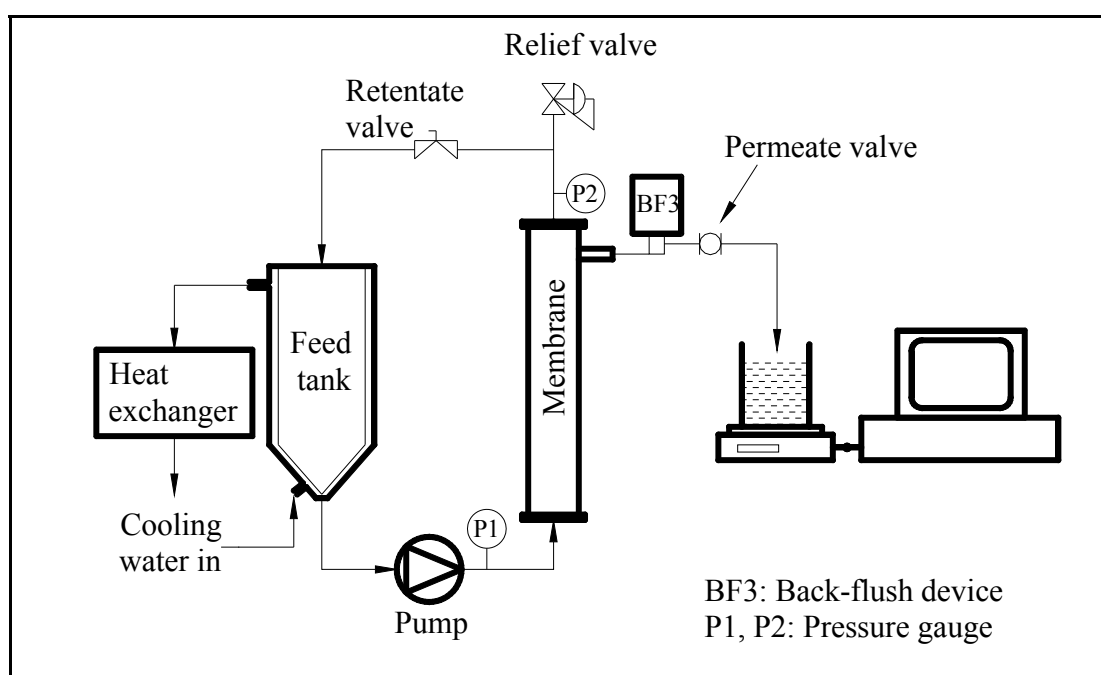


Figure 3.5. A schematic diagram of the cross-flow filtration XLAB5 pilot unit

The filtration system was equipped with a progressing cavity pump (PCM, France), a heat exchanger (for maintaining a constant feed temperature), and a back-flush device (BF3). The

cross-flow velocity could be varied by adjusting the pump speed. The filtration pressure was recorded as the average of pressures at the inlet (P1) and outlet (P2) of the membrane module. The main component of the back-flush device was a cylindrical piston, which was driven by air pressure. The permeate reservoir volume for back-flushing was 3 mL. The back-flush frequency and duration were set by a timer. Back-flushing could be applied once every 12 minutes to once every 30 seconds and the back-flush duration could be varied from 0.5 to 12 seconds. When back-flushing was activated, the piston moved rapidly to push the permeate back to the tube lumen.

3.6.2. Operating conditions for cross-flow filtration tests

All filtration tests were conducted at a water temperature of 22 ± 1 °C (which was maintained by the heat exchanger). The majority of the tests were run at a cross-flow velocity of 1.8 m s^{-1} . The corresponding Reynolds number was 12000, which was in the turbulent flow region of the regime at which most commercial membrane modules operate ($1000 < \text{Reynolds number} < 15000$) (Belfort *et al.* 1994). Progressing cavity pumps may cause pulsations in the flow due to internal leakages, which may affect the rate of membrane fouling. However, this problem was not observed with the pump used in this study, as the TMP remained steady during the filtration tests. This was probably due to the fact that the pump was new and operated at a capacity much lower than its maximum capacity (approximately 20% and 30% of the maximum pumping capacity at cross-flow velocities of 1.8 m s^{-1} and 2.7 m s^{-1} , respectively).

To align with the current pilot plant practice, tests were conducted at a starting flux (i.e., pure water flux) of $350 \text{ L m}^{-2} \text{ h}^{-1}$ (MF) and $100 \text{ L m}^{-2} \text{ h}^{-1}$ (UF). This corresponded to a TMP of 20 kPa for MF and 30 kPa for UF. For comparison, Mueller and Witte (2007) used a silicon carbide membrane ($0.5 \text{ }\mu\text{m}$) to run pilot MF tests with a highly turbid filter backwash water (turbidity = 197 NTU) at a cross-flow velocity of 3.4 m s^{-1} and the permeate flux varied from 102 to $280 \text{ L m}^{-2} \text{ h}^{-1}$. They also carried out tests in dead-end mode with an alumina UF membrane (pore size = 50 nm) at fluxes between 100 and $300 \text{ L m}^{-2} \text{ h}^{-1}$ and an alumina MF membrane ($0.2 \text{ }\mu\text{m}$) at fluxes of $100\text{--}400 \text{ L m}^{-2} \text{ h}^{-1}$. In this study, the starting fluxes of $350 \text{ L m}^{-2} \text{ h}^{-1}$ (MF) and $100 \text{ L m}^{-2} \text{ h}^{-1}$ (UF) were selected to account for the smaller pore sizes of the membranes, the much lower turbidity of the AS effluent (1.9–5.6 NTU) than the filter backwash water, and the (expected) fouling reduction by the tangential flow.

Two MF and two UF membranes were used. The fouled membranes were regenerated by soaking in NaOCl solutions (approximately 1000 ppm available chlorine) at 70°C for 45 minutes. This cleaning procedure allowed full recovery of the membrane pure water flux. The regenerated membranes were used in further experiments. Prior to the tests with the effluent samples, Milli-Q water was passed through the membranes at 70 kPa for 30 minutes to remove the membrane preservatives/cleaning agents and then at the operating pressure (20 kPa for MF and 30 kPa for UF) for 15 minutes to determine the pure water flux.

3.6.3. Determination of the membrane foulants and the effect of feed pre-treatments on the permeate flux in cross-flow filtration

Cross-flow MF and UF tests without intermittent back-flushing were conducted with the raw, coagulated, ozonated and AER-treated effluent samples to determine the effect of these pre-treatments on the flux performance. The coagulant tested was alum at 2.5 mg L⁻¹. The ozone and AER dosages were 10 mg O₃ L⁻¹ with 10-minute contact time and 10 mL AER L⁻¹ with 20-minute contact time (1 bed volume of the AER treated 1500 bed volumes of the raw effluent), respectively. Each MF and UF run lasted for 2 hours and the corresponding VCF was 1.3 for MF and 1.2 for UF. The feeds and the permeates were analysed to identify the foulants (with LC-OCD) and evaluate the rejections of DOC, UVA₂₅₄ and true colour by the membranes.

3.6.4. Effect of rapid membrane back-flushing on the flux performance

The effectiveness of rapid back-flushing on fouling reduction was investigated with the raw, coagulated, and ozonated effluent. Membrane backwashing (or back-flushing) results in additional equipment and energy costs and a loss in permeate production (Bacchin *et al.* 2006). These costs should be minimised, particularly in MF and UF of secondary effluent, where the end product has a relatively low economic value. Therefore, this study focussed on the use of rapid back-flushing (duration = 1 second) in cross-flow filtration as an analogue of backwashing in dead-end filtration (note that in dead-end filtration, backwashing normally lasts from 10 seconds to several minutes). Back-flushing was applied to MF and UF at the lowest frequency (12 min⁻¹) and the lowest feed cross-flow velocity (1.8 m s⁻¹) available to the filtration system. Some tests (without back-flushing) were also carried out at a cross-flow velocity of 2.7 m s⁻¹ to compare the effect of increased cross-flow velocity and rapid back-flushing on the flux performance.

3.7. Reproducibility of filtration experiments

The reproducibility of the flux curves was tested by performing duplicate experiments with the raw AS effluent of the same batch (Figures 3.6 and 3.7). The nearly superimposed curves indicate good reproducibility and any difference in the physical structure among the membrane samples of the same type had negligible effect on the filtration result. For the polymeric MF membranes, the deviations in the normalised flux (i.e., ratio of the pure water flux of the virgin membrane to the flux of the fouled membrane) between the duplicate runs were less than 5%. For the other membranes, these values were less than 3%.

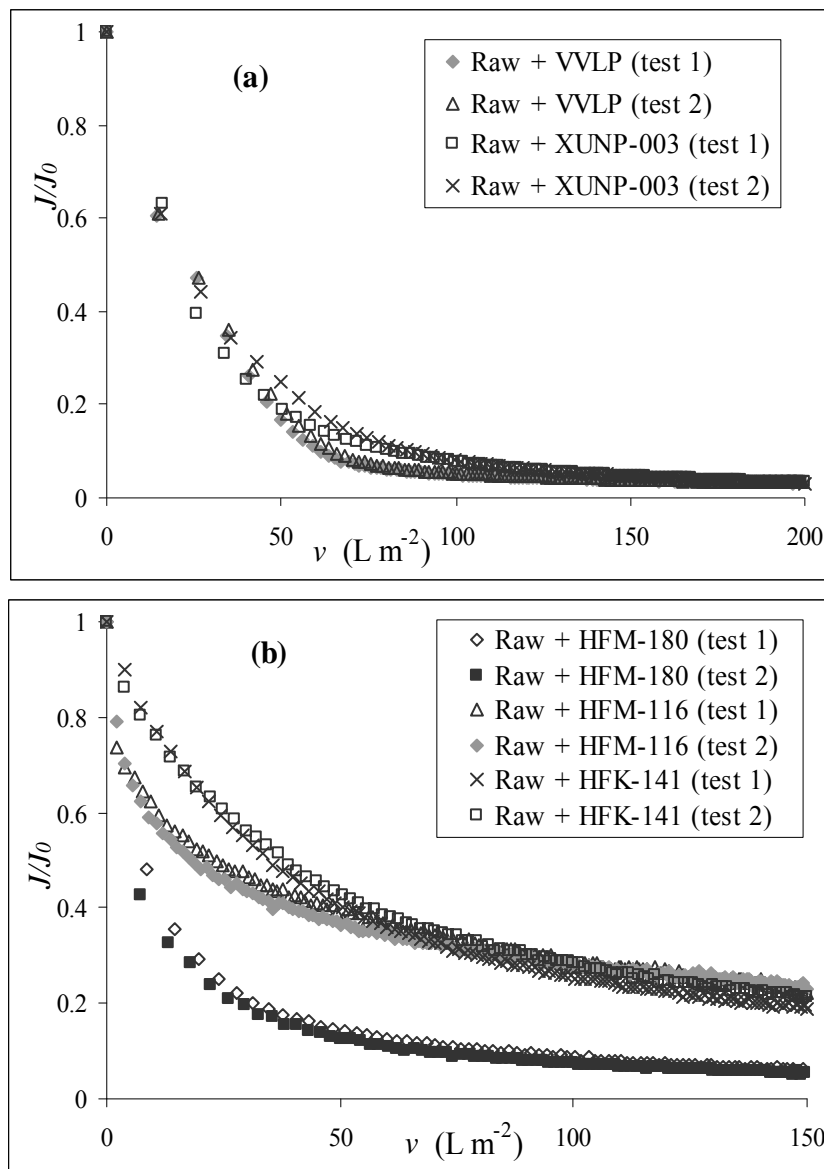


Figure 3.6. Reproducibility of (a) MF and (b) UF flux data for dead-end filtration

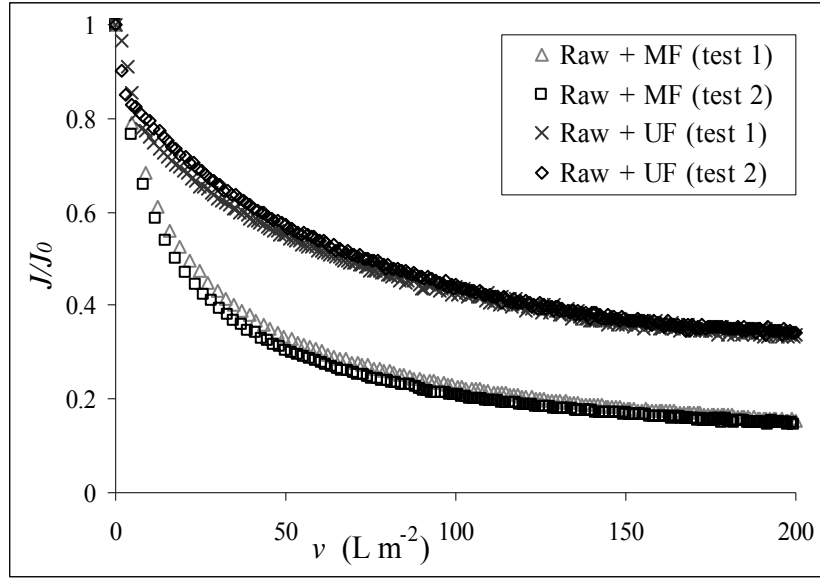


Figure 3.7. Reproducibility of flux data for cross-flow filtration
(Cross-flow velocity = 1.8 m s^{-1} , TMP = 20 kPa for MF and 30 kPa for UF)

Tests on the effects of the pre-treatments on the permeate flux (and effluent characteristics) were performed in duplicate using samples of the same batch and the results were confirmed with a minimum of one batch of samples collected on another day. The daily fluctuations in the characteristics of the raw effluent resulted in differences in the flux data for samples collected on different days. However, for each of the feed pre-treatment methods, the same effect on membrane fouling was observed for samples of different batches. On some occasions, this was further confirmed by the results obtained from multi-cycle experiments using the same samples.

3.8. Analysis of flux data for the identification of fouling mechanisms

Identification of the fouling mechanisms in dead-end MF and UF was done by fitting the flux data to equations 2.2–2.5. Attempts were also made to identify the fouling mechanisms in cross-flow filtration using the integral method for flux data analysis described by Field and Wu (2011). This method is based on equation 2.6 with the assumption that fouling is governed by complete pore blocking ($n = 2$) or pore adsorption ($n = 1.5$) in the initial period of filtration and then by intermediate pore blocking ($n = 1$) or cake filtration ($n = 0$). However, it was realised that the application of this method to the flux data obtained from the cross-flow filtration system used in this study was not theoretically robust. The reason was that the formation of a cake layer would eventually reduce the internal diameter of the membrane tube and therefore increase the cross-flow velocity of the feed. As a result, the

accuracy of the calculation of the critical fluxes using the equations derived theoretically by Field and Wu (2011) (equations 3.6 and 3.7) could not be assured. Consequently, the fouling mechanisms in cross-flow filtration of the secondary effluent were not determined in this study.

$$n = 1: \frac{\ln(J_0/J)}{t} = K_{n=1} \left(\frac{v}{t} \right) - K_{n=1} J_{n=1}^* \quad (3.6)$$

$$n = 0: \frac{1}{Jt} - \frac{1}{J_0 t} = K_{n=0} \left(\frac{v}{t} \right) - K_{n=0} J_{n=0}^* \quad (3.7)$$

where

$J_{n=1}^*$ is the critical flux for the intermediate pore blocking model,

$J_{n=0}^*$ is the critical flux for the cake filtration model, and

K_n is a constant.

CHAPTER 4. DEAD-END FILTRATION OF THE RAW ACTIVATED SLUDGE EFFLUENT

The overall objective of this study was to investigate the effects of different feed pre-treatment methods on membrane fouling in MF and UF of the effluent. To understand why one pre-treatment reduced while others worsened or did not affect fouling, knowledge of the fouling behaviour of the raw (i.e., non-pre-treated) effluent was needed. Therefore, this part of the study was dedicated to fouling in dead-end MF and UF of the raw AS effluent. The components responsible for fouling and the predominant fouling mechanisms were identified. Because the raw effluent contained SS (defined as the particulate matter retained by a 0.5 μm glass-fibre filter in this study) and EfOM, it was necessary to determine the relative contributions of these components to the flux decline. The rejections of DOC, UV-absorbing and colour-bearing compounds of the membranes were also evaluated.

Dead-end filtration experiments were conducted using PVDF (VVLP, XUNP-003, HFM-180 and HFM-116) and PES (HFK-141) membranes and the raw AS effluent with and without SS. The EfOM components responsible for fouling were identified by analysing the feed and the permeates with LC-OCD. ATR-FTIR spectroscopy was used to identify the compounds retained on the fouled membranes. The relative fouling potentials of the three fractions of the EfOM (i.e., the HPO, TPI and HPI fractions) were also determined. These fractions were obtained from the resin fractionation process described in Figure 3.2 (Chapter 3, section 3.2.2). The fractions were diluted with Milli-Q water to a DOC concentration of 1.3 mg L^{-1} , and adjusted to pH 7.6 and a conductivity of 1060 $\mu\text{S cm}^{-1}$ (same as for the non-fractionated EfOM) prior to the MF and UF tests.

The flux data obtained from MF and UF of the raw effluent samples were analysed using the dead-end filtration models to determine the predominant fouling mechanisms in MF and UF.

4.1. Effect of suspended solids (SS) on flux decline in MF and UF

The flux data for the raw AS effluent before and after the removal of SS are shown in Figure 4.1.

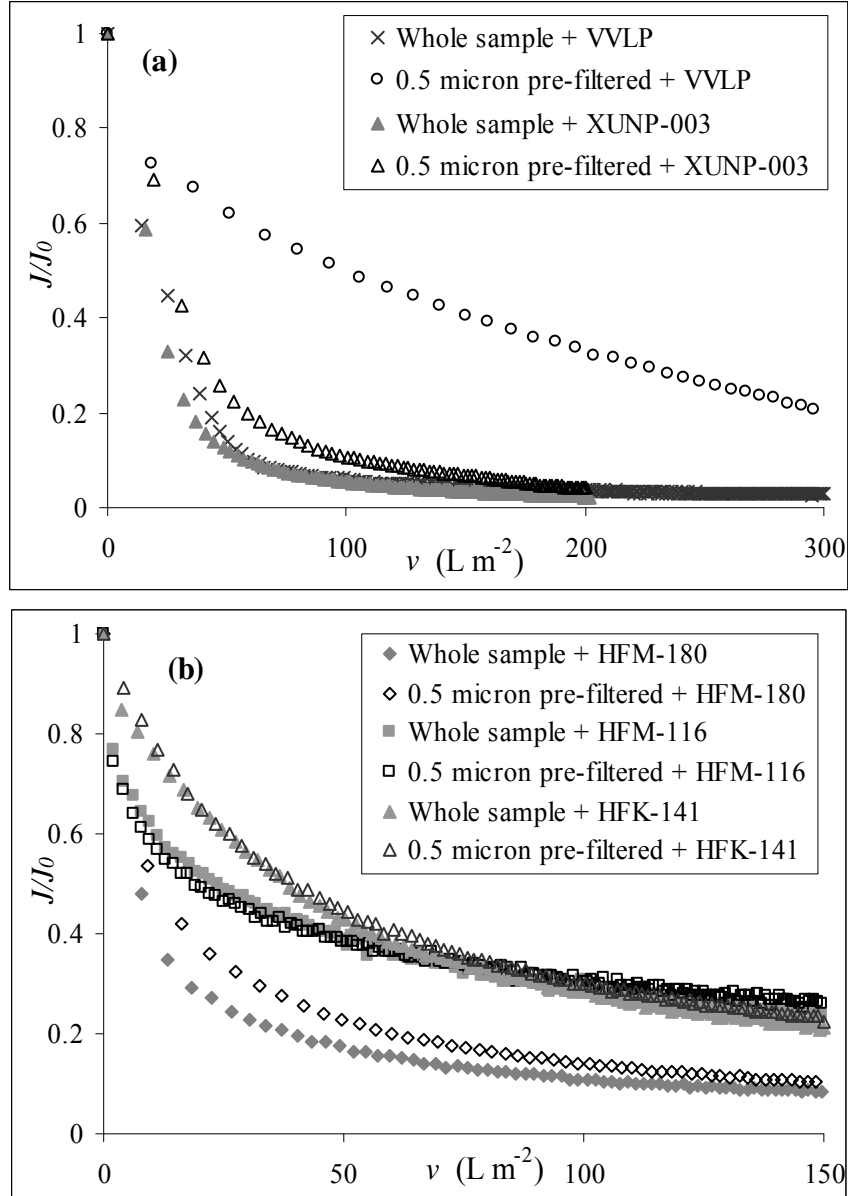


Figure 4.1. Effect of SS on (a) MF flux and (b) UF flux of the raw AS effluent
(Raw effluent collected on 26 November 2009, DOC = $14.3 mg L^{-1}$,
turbidity = 3.8 NTU, $UVA_{254} = 0.406 cm^{-1}$, true colour = 103 Pt-Co units)

The removal of SS from the raw AS effluent reduced the rate of flux decline on the MF (VVLP and XUNP-003) and the loose UF (HFM-180) membranes, but had no effect on the tighter UF membranes (HFM-116 and HFK-141). The results indicated that particles larger than $0.5 \mu m$ made some contribution to the flux reduction on the MF (VVLP and XUNP-003)

and the loose UF (HFM-180, 100 kDa) membranes. This could be attributed to the high initial permeability of these membranes (i.e., low membrane resistance, Table 4.1), which resulted in the hydraulic resistance exerted by the cake layer formed by the SS on the membrane surfaces making up a significant proportion of the total hydraulic resistance during MF and UF. On the other hand, the high hydraulic resistance of the tight UF membranes made the resistance exerted by the SS particles minor compared with the total resistance caused by these membranes and the EfOM.

Table 4.1. Hydraulic resistances for MF and UF of the raw effluent with and without SS

Case	R_m ($\times 10^{-10} \text{ m}^{-1}$)	R_{f}^* ($\times 10^{-10} \text{ m}^{-1}$)	R_{f}^* ($\times 10^{-10} \text{ m}^{-1}$)
Whole sample + VVLP	18.1	471	11.3
0.5 μm pre-filtered sample + VVLP	17.2	66.7	10.5
Whole sample + XUNP-003	15.9	673	36.0
0.5 μm pre-filtered sample + XUNP-003	15.8	373	37.7
Whole sample + HFM-180	41.0	472	55.1
0.5 μm pre-filtered sample + HFM-180	40.9	359	51.4
Whole sample + HFM-116	242	702	183
0.5 μm pre-filtered sample + HFM-116	237	677	172
Whole sample + HFK-141	173	548	87.2
0.5 μm pre-filtered sample + HFK-141	169	515	91.9

* Calculated for $v = 300 \text{ L m}^{-2}$ (VVLP), 200 L m^{-2} (XUNP-003) and 150 L m^{-2} (the other membranes)

It was noticed that for the MF and the loose UF membranes, although the total fouling (R_f) caused by the sample without SS was significantly lower than that caused by the whole raw effluent sample, the extent of hydraulically irreversible fouling caused by these two samples were fairly similar (Table 4.1). This indicated that most of the flux decline caused by the SS was hydraulically reversible, since backwashing removed the majority of the SS deposited on the membrane surfaces.

The removal of SS from the raw AS effluent resulted in a larger flux improvement in MF with the flat sheet membrane (VVLP) than with the hollow-fibre membrane (XUNP-003), suggesting that membrane configuration may have some influence on the results obtained from bench-scale experiments, although similar trends could be expected. Similar results were reported by Howe *et al.* (2007) for MF and UF of surface water. Other factors which may

contribute to this difference included differences in the degree of hydrophobicity (contact angle of the VVLP membrane = 62°, whereas that of the XUNP-003 was greater than 90°) and differences in the surface and pore morphology of the two membranes.

4.2. Identification of the EfOM components responsible for fouling

The EfOM components responsible for fouling were identified using 3 different techniques: LC-OCD analysis, fouling potentials of the HPO, TPI and HPI fractions, and ATR-FTIR spectroscopy.

4.2.1. AMWDs of dissolved EfOM in the feed and the permeates

The feed (after pre-filtration through a 0.45 µm cellulose acetate membrane) and the permeates collected from the filtration tests with the 0.5 µm pre-filtered sample were analysed with LC-OCD to determine the components retained on the MF and UF membranes. The chromatograms obtained (Figure 4.2) showed that biopolymers (MW>>20,000 Da), which included polysaccharides and proteins, and HS were the compounds most significantly retained by the membranes and therefore potentially responsible for fouling. Similar results were obtained in recent studies utilising LC-OCD for the identification of the membrane foulants in UF of secondary effluent (Zheng *et al.* 2009; Henderson *et al.* 2011). It should be noted that materials retained by membranes are not necessarily the membrane foulants. In this thesis, the role of biopolymers in causing membrane fouling was further verified by the fact that the feed pre-treatments which led to the removal of biopolymers (coagulation, Chapter 5) or breakdown in the molecular structures of biopolymers (ozonation, Chapter 6) significantly reduced membrane fouling. On the other hand, the contribution of HS to fouling was supported by the fact that cleaning the fouled membranes (after backwashing) with sodium dodecyl sulphate and Terg-a-zyme gave high pure water flux recoveries and the cleaning solutions turned yellow (an indication of the presence of HS) after use (Chapter 8).

Polysaccharides, due to their neutral charges, were likely to foul the membranes mainly by pore blocking and cake formation. Adsorption of some polysaccharides on the membranes was also possible (Jermann *et al.* 2007). Proteins are amphoteric (possessing both negatively and positively charged functional groups) and therefore can interact with the membranes through dipole interactions or by forming a cake layer on the membrane surfaces (Lozier *et al.*

2008). Some proteins can be hydrophobic in nature due to the presence of hydrophobic amino acids (e.g., proline) in their structures and can adsorb on the membranes through hydrophobic attraction. This hypothesis is supported by the presence of a small proportion of biopolymers in the HPO and TPI fractions extracted from the raw effluent (Section 4.2.3).

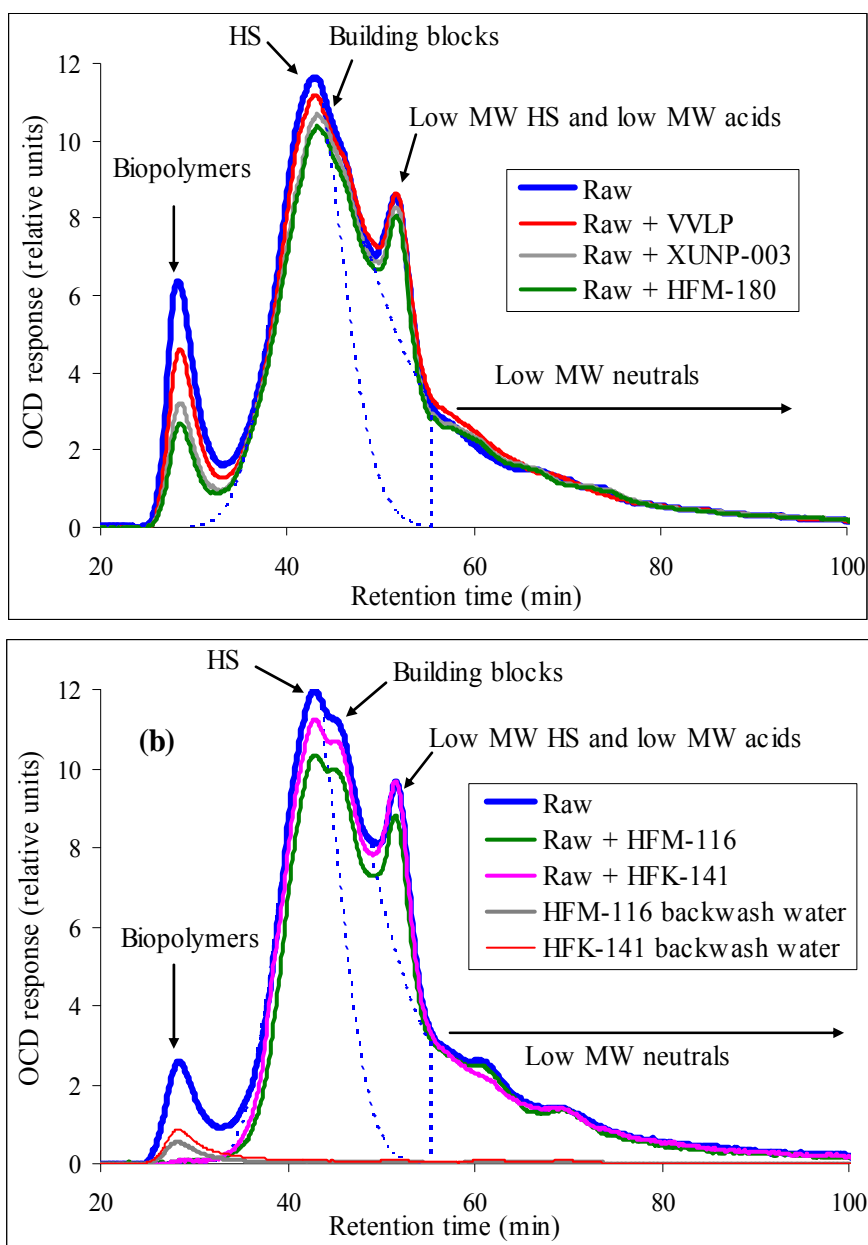


Figure 4.2. AMWDs of the EfOM in the raw effluent, the permeates and the backwash water

(a) MF and loose UF membranes (feed: $\text{DOC} = 14.2 \text{ mg L}^{-1}$, $\text{UVA}_{254} = 0.343 \text{ cm}^{-1}$) and

(b) Tight UF membranes (feed: $\text{DOC} = 13.2 \text{ mg L}^{-1}$, $\text{UVA}_{254} = 0.402 \text{ cm}^{-1}$)

(The dotted lines define the areas under the peaks, the backwash water samples were diluted with Milli-Q water to a volume same as the permeate volume)

Some HS (MW=1,000–20,000 Da) were also retained, most likely by hydrophobic interaction with the membranes (Liu *et al.* 2001; Jarusutthirak *et al.* 2002). This was supported by the higher HS retention of the XUNP-003 membrane (more hydrophobic) than the VVLP membrane, and the lower HS retention of the HFK-141 membrane (relatively hydrophilic and smaller nominal pore size) than the HFM-116 and HFM-180 membranes (hydrophobic and larger pore size). This trend in HS rejection was in agreement with the trend in colour removal, i.e., the less hydrophobic membranes gave lower colour removals (see Section 4.3). HS were found to be responsible for the colour of the raw AS effluent as the true colour of the HPO fraction accounted for approximately 80% of the true colour of the non-fractionated EfOM.

The role of HS in causing adsorptive fouling was supported by two other phenomena. First, the colour rejection by the membranes was observed from the first minute of filtration. Second, cleaning the fouled membranes with sodium dodecyl sulphate and Terg-a-zyme gave high pure water flux recoveries and the cleaning solutions turned yellow after use (Chapter 8).

The higher retention of biopolymers than HS (Figure 4.2) indicated that proteins and polysaccharides played a more important role than HS in causing fouling. Pore adsorption and pore blocking by these components were responsible for irreversible fouling, since backwashing removed a proportion of the biopolymers and essentially no HS from the fouled membrane (Figure 4.2(b), the backwash water chromatograms).

In summary, LC-OCD analysis of the feed and the permeates showed that biopolymers (i.e., proteins and polysaccharides) and HS were the EfOM components responsible for membrane fouling. HS contributed mainly to hydraulically irreversible fouling, whereas biopolymers contributed to both reversible and irreversible fouling.

4.2.2. Foulant identification by ATR-FTIR spectroscopy

To further confirm the results obtained from LC-OCD analysis, the ATR-FTIR spectra of the virgin membranes and the membranes fouled by the 0.5 µm pre-filtered effluent were collected to identify the EfOM components retained on the membranes. As seen in Figures 4.3, the foulants on the membranes showed peaks around 1069 cm⁻¹, indicating the

presence of C–O stretching of polysaccharides and/or polysaccharide-like materials (*Cho et al.* 1998, Jarusutthirak *et al.* 2002). The peaks around 1720 cm^{-1} were indications of carboxylic groups in HS. The peaks at 1540 cm^{-1} suggested the existence of N–H bonds and C=N stretching of secondary amides in the foulant layer. The peaks around 1640 cm^{-1} corresponded to stretching vibration of C=O connected to primary amides of proteins. The peaks near 2920 cm^{-1} were attributed to aliphatic C–H stretching of HS. The broad bands around $3000\text{--}3650\text{ cm}^{-1}$ were due to O–H stretching of hydroxyl groups (in polysaccharides) and N–H stretching of amides (*Cho et al.* 1998; *Howe et al.* 2002; *Jarusutthirak et al.* 2002). Consequently, it was concluded that proteins, polysaccharides and HS were the major membrane foulants in MF and UF of the raw effluent.

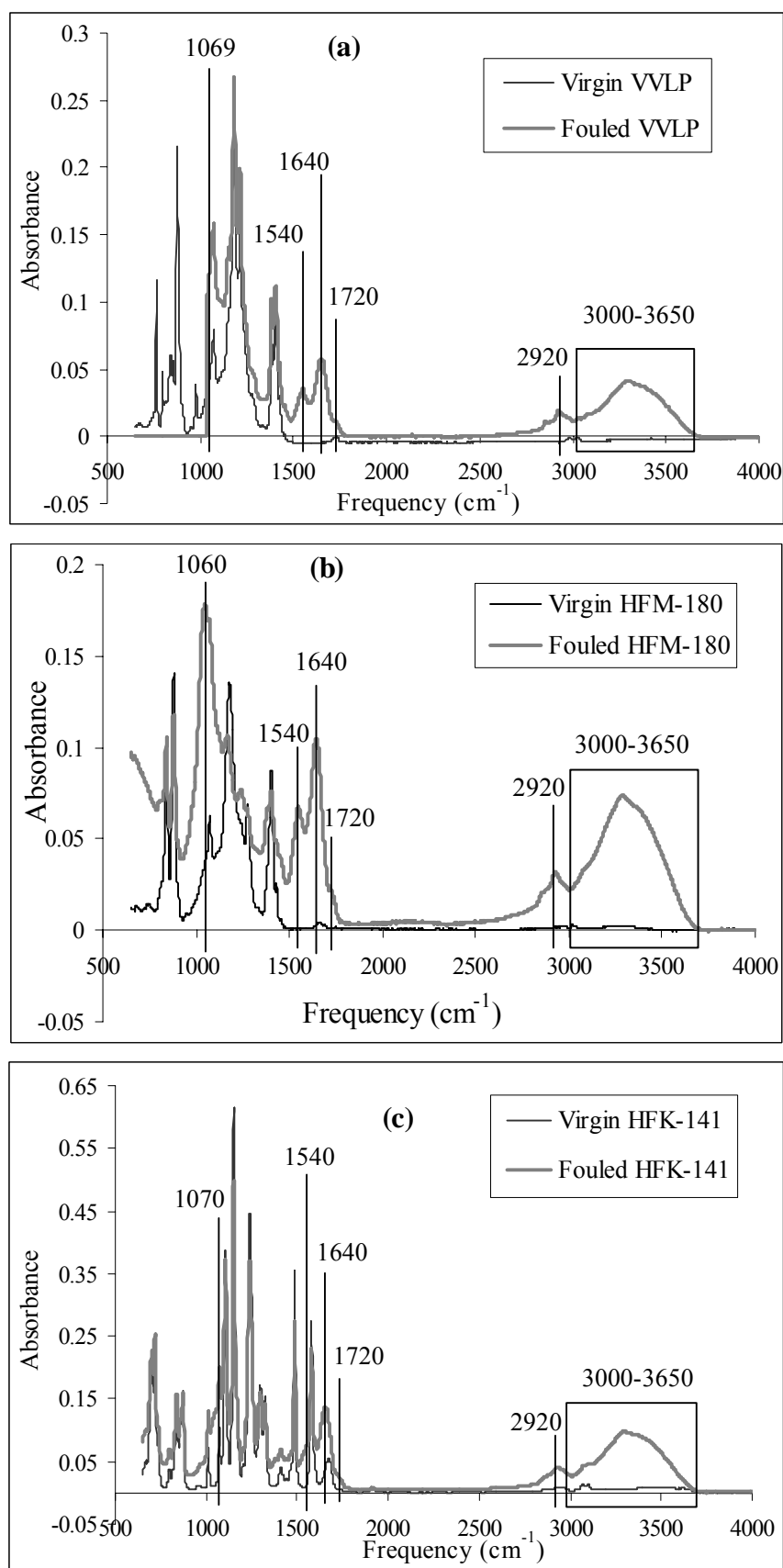


Figure 4.3. ATR-FTIR spectra of the virgin and fouled membranes (a) VVLP, (b) HFM-180, and (c) HFK-141

4.2.3. Fouling potentials of individual EfOM fractions

The EfOM fractions obtained from resin fractionation of the raw effluent (using the procedure described in Figure 3.2, Section 3.2.2) were also used in MF and UF tests to gain more insights into the characteristics of the membrane foulants. Prior to the filtration tests, the HPO, TPI and HPI fractions of the raw effluent were diluted with Milli-Q water to a DOC concentration of 1.3 mg L^{-1} , and adjusted to pH 7.6 and a conductivity of $1060 \text{ } \mu\text{S cm}^{-1}$ (same as for the non-fractionated sample). The flux data obtained are shown in Figure 4.4.

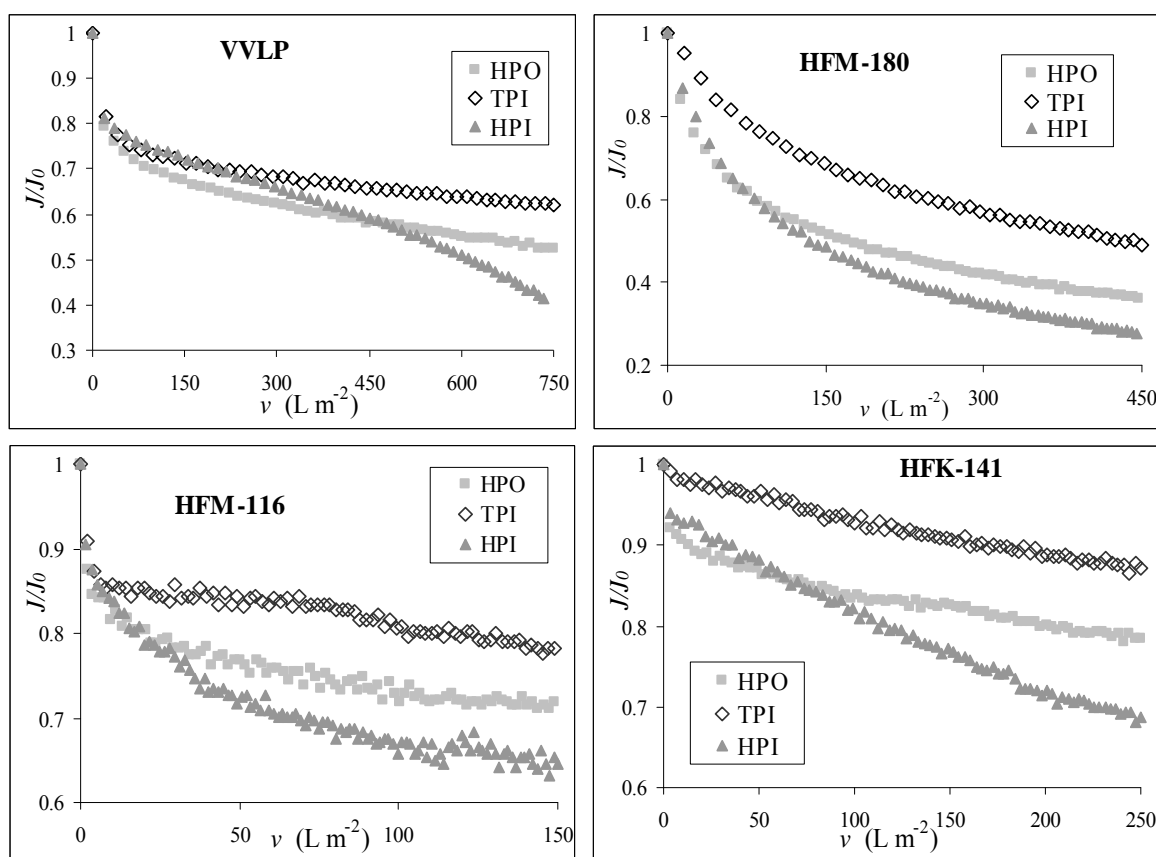


Figure 4.4. Flux data for MF and UF of different fractions in the raw AS effluent (DOC of each fraction = 1.3 mg L^{-1})

For this AS effluent, the HPI fraction had the highest fouling potential for all the membranes investigated (Figure 4.4). A similar finding for natural surface waters was reported by Carroll *et al.* (2000) and Lee *et al.* (2004). This finding, however, is different from the result obtained by Shon *et al.* (2006) who found that the HPI fraction of an AS effluent had the lowest UF fouling potential. Possible reasons for this difference include

differences in the properties of the EfOM of the two samples and the membranes (Shon and co-workers used 17,500 Da sulfonated polysulfone membranes). The higher fouling potential of the HPI fraction than the other two fractions could be attributed to the fact that the majority of polysaccharides and proteins in the raw effluent were concentrated in this fraction (Figure 4.5). The components with MW between 1,000 Da and 20,000 Da in the HPI fraction are not likely to be HS due to their very low UV response (at 254 nm) and the fact that the HPI fraction was colourless (true colour = 0). The presence of a small proportion of biopolymers in the HPO and TPI fractions indicated that some proteins and/or polysaccharides in this AS effluent were hydrophobic and therefore could contribute to adsorptive fouling of the membranes.

The HPO fraction was the most hydrophobic fraction, followed by the TPI fraction, as indicated by their UV absorbance (Figure 4.5 (a)). Adsorption on the hydrophobic membranes (via hydrophobic attraction) was therefore expected to be strongest for the HPO fraction. In addition, the fact that the HPO fraction contained some HS of higher MW than the TPI fraction (as indicated by the lower retention time of the HS peak on the HPO curve in Figure 4.5 (b)) may have contributed to the higher fouling potential of the HPO fraction, since higher MW compounds are likely to narrow the membrane pores more rapidly. Although adsorptive fouling by the HPI fraction was expected to be lower than that by the other two fractions (as indicated by the lower UVA_{254} and therefore lower hydrophobicity of the HPI fraction), the HPI fraction showed the highest fouling potential. This can be explained by the fact that pore adsorption was dominant during the initial period of filtration (as shown in Section 4.4); however, as filtration proceeded, the cake filtration mechanism, in which polysaccharides and proteins formed a cake layer on the membrane surface, became the governing fouling mechanism.

The fact each EfOM fraction contained compounds of various MWs indicated that the fractions were not “pure” in terms of molecular sizes of the constituents. This is probably one of the reasons for the different results reported in the literature regarding the relative fouling potentials of the different EfOM (and NOM) fractions isolated by resin fractionation.

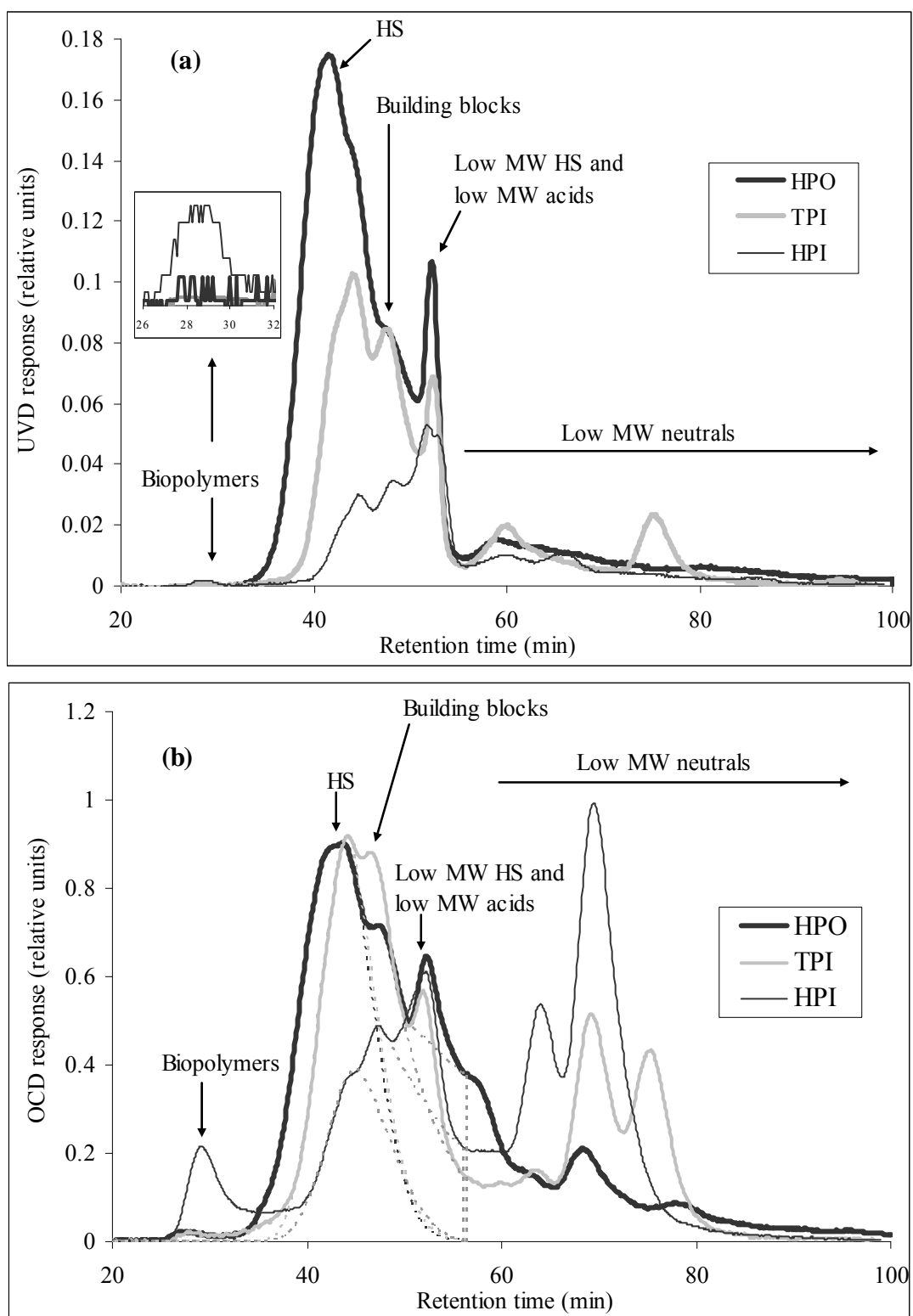


Figure 4.5. LC-OCD chromatograms of the three EfOM fractions of the raw AS effluent
 (a) UVD response and (b) OCD response (DOC of each fraction = 1.3 mg L^{-1})

4.3. DOM rejection and colour removal by the membranes

The DOM rejection and true colour removal by the membranes in MF and UF of the raw AS effluent are given in Table 4.2. The results were collected from filtration tests with 5 samples collected from June 2008 to June 2010. The turbidity of the permeates was consistently lower than 0.2 NTU, much lower than the requirement of 2.0 NTU for “Class A” recycled water.

Table 4.2. DOM rejection and colour removal by the polymeric membranes

Membrane	% DOC removal	% UVA ₂₅₄ removal	% colour removal
VVLP	4 – 9%	2 – 6%	3 – 8%
XUNP-003	8 – 16%	7 – 13%	15 – 22%
HFM-180	10 – 17%	15 – 21%	24 – 33%
HFM-116	15 – 18%	21 – 25%	35 – 43%
HFK-141	9 – 18%	8 – 12%	9 – 15%

The low DOC removals by the membranes are consistent with previous studies which used membranes of comparable pore sizes to filter surface water (Adham *et al.* 2006; Lozier *et al.* 2008; Byun *et al.* 2011) and municipal secondary effluent (Laabs *et al.* 2006; Haberkamp *et al.* 2008; Nguyen *et al.* 2009; Zheng *et al.* 2010).

4.4. Flux decline and fouling mechanisms in MF and UF of the raw effluent

4.4.1. Flux decline and fouling mechanisms in MF

As shown in Figure 4.1, rapid fouling of the membranes occurred within the first few minutes of filtration. Plots of t/V versus V were constructed to determine if fouling of the MF membranes by the raw AS effluent could be described by the cake filtration model.

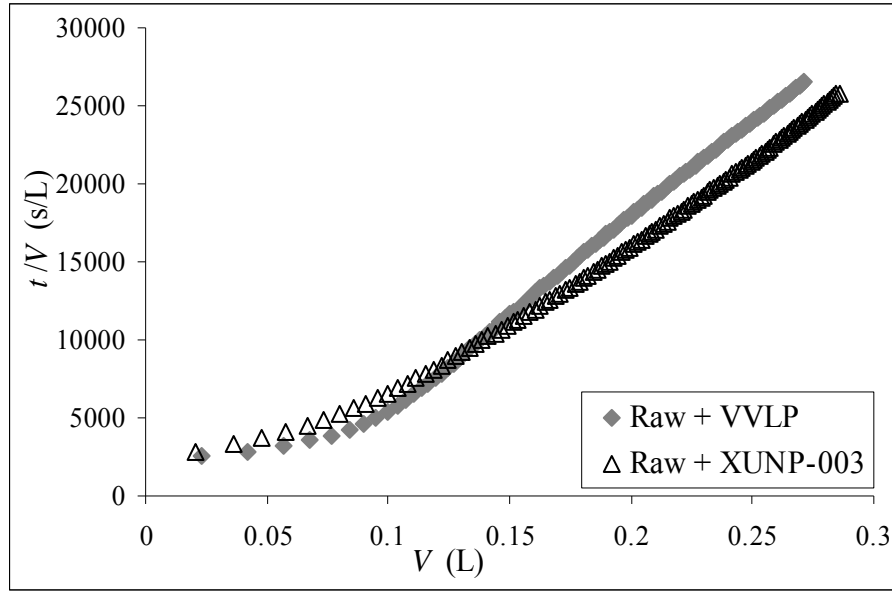


Figure 4.6. Plots of t/V versus V for MF of the raw AS effluent
(Data for XUNP-003 were normalised to a membrane area of 0.00134 m^2)
(Raw effluent: $\text{DOC} = 14.2 \text{ mg L}^{-1}$, turbidity = 3.8 NTU,
 $\text{UVA}_{254} = 0.343 \text{ cm}^{-1}$, colour = 90 Pt-Co units)

The non-linear sections of the curves in Figure 4.6 suggested that fouling in MF of the raw effluent was not governed by the cake filtration mechanism in the first 20 minutes. Because the effluent contained EfOM with various molecular sizes (from smaller than 350 Da to much larger than 20,000 Da, as shown in the LC-OCD chromatogram in Figure 4.2) as well as SS, it was highly likely that pore adsorption and pore blocking occurred simultaneously in this initial period (Bowen *et al.* 1995; Duclos-Orsello *et al.* 2006). To identify the dominant fouling mechanism in this period, the flux data were analysed using the equations 2.2–2.4 and the results are shown in Figure 4.7. The linearity of the plot of t/V versus t confirmed that pore adsorption played a significant role during the first 20 minutes of MF.

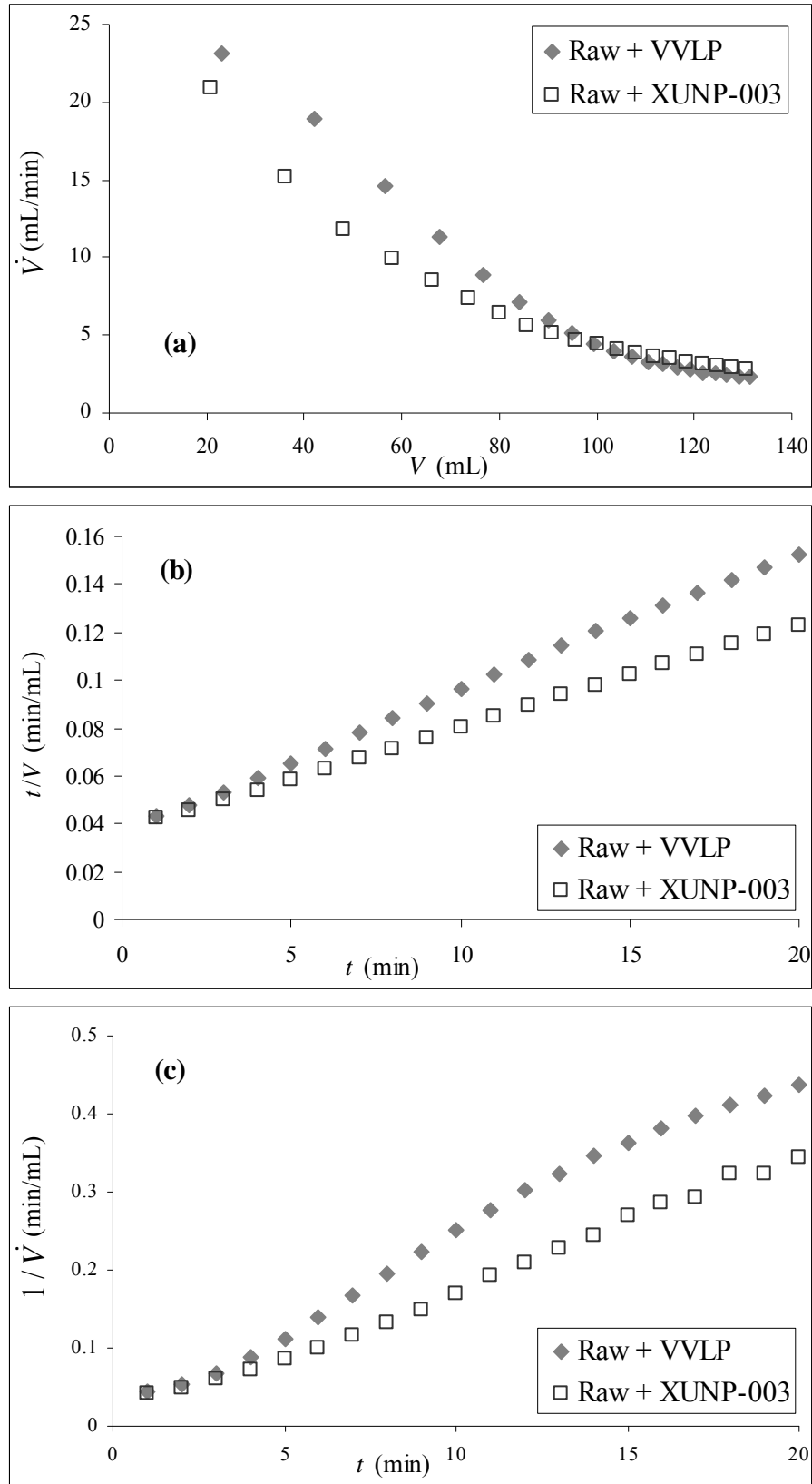


Figure 4.7. Filtration law analysis for the MF membranes

(a) Complete pore blocking, (b) standard pore blocking, and (c) intermediate pore blocking

(t : filtration time, V : permeate volume, \dot{V} : permeate volume per minute)

The best description of the sequence for MF fouling by the raw AS effluent was

- (i) Adsorption of particles smaller than the membrane pores (including polysaccharides, proteins, and HS) on the internal pore walls (standard blocking) and some contribution of intermediate pore blockage during the first 15–20 minutes, followed by
- (ii) Formation of a cake layer from particles larger than the pores, which included proteins, polysaccharides, and particles larger than 0.45 μm .
- (iii) The cake layer formed then acted as a secondary membrane for filtration of the rest of the sample

This implies that in an operation protocol similar to that used in MF plants, i.e., filtration for 15–30 minutes followed by backwashing, the governing fouling mechanism in the first filtration cycles for the virgin (or chemically cleaned) membranes would be the pore adsorption mechanism with some contribution of pore blocking. In the subsequent cycles, fouling (of the backwashed membranes) would be dominated by the cake filtration mechanism.

4.4.2. Flux decline and fouling mechanisms in UF

The UF flux data were also analysed using same approach used in MF. The plots of t/V versus V for UF of the raw AS effluent are shown in Figure 4.8. The deviation from linearity of the first few data points on the curves for the HFM-180 and HFM-116 membranes indicated fouling of these membranes was not controlled by the cake filtration mechanism in the first 5 minutes of filtration. This can be explained as during this time pore blocking and pore adsorption on these membranes were significant. The contribution of pore adsorption to the fouling of these hydrophobic membranes was supported by their relatively high HS rejection (Figure 4.2 (b)) and high colour removal (Table 4.2) observed from the beginning of filtration.

The early dominance of the cake filtration mechanism in UF was attributed to the small pore size of the UF membranes. Fouling of the hydrophilic HFK-141 membrane could be described by the cake filtration mechanism from the beginning of filtration, probably because HS adsorption on this membrane was much less significant than the deposition of polysaccharides and proteins on the membrane surface. This was supported by the lower

HS retention (as shown in Figure 4.2), lower colour removal (Table 4.2), and the higher pure water flux recovery by backwashing of the HFK-141 membrane (approximately 67%) than the HFM-116 membrane (56%).

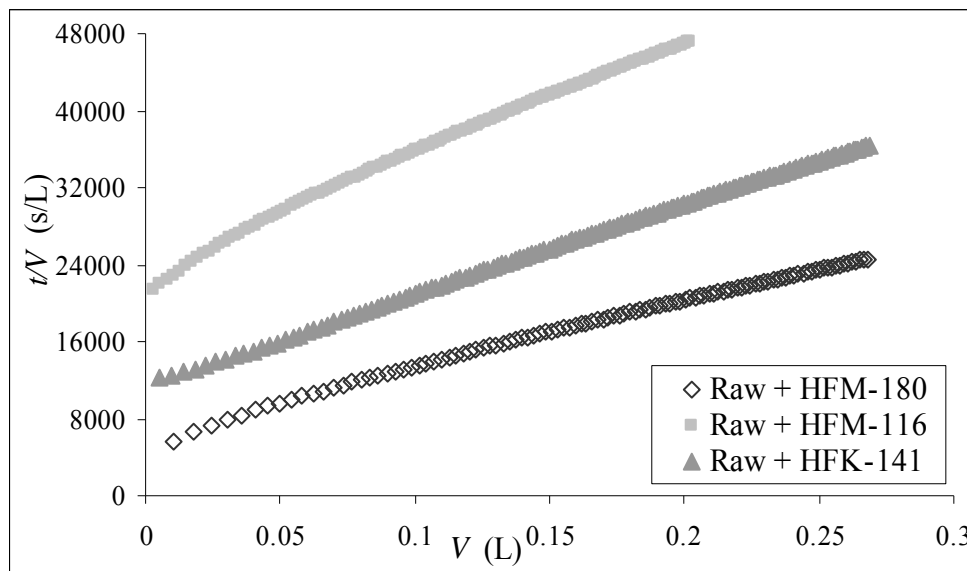


Figure 4.8. Plots of t/V versus V for UF of the raw AS effluent

Chapter 4 Summary

This part of the study investigated fouling of the PVDF and PES membranes in dead-end MF and UF of the raw AS effluent. It was found that both SS and EfOM contributed to the flux decline in filtration of the raw AS effluent with the MF and the 100 kDa UF membranes. However, SS did not contribute to flux decline of the tighter UF membranes (HFM-116 and HFK-141).

The results from LC-OCD analysis of the feed and the permeates showed that biopolymers, which contained proteins and polysaccharides, and HS were the EfOM components responsible for membrane fouling. This was supported by the ATR-FTIR spectra of the organic matter retained on the fouled membranes. As the membranes investigated retained a higher amount of biopolymers than HS, it was concluded that the contribution of biopolymers to membrane fouling was greater than that of HS. Furthermore, filtration tests with the EfOM fractions isolated from the raw effluent revealed that the HPI fraction (which contained the majority of the biopolymers of the non-fractionated EfOM) caused the most severe flux decline, followed by the HPO fraction and the TPI fraction. The role of

biopolymers in causing membrane fouling was also supported by the fact that the feed pre-treatments which led to the removal of biopolymers (coagulation, Chapter 5) or breakdown in the molecular structures of biopolymers (ozonation, Chapter 6) significantly reduced membrane fouling.

Backwashing removed a proportion of the biopolymers and essentially no HS from the fouled membranes. Therefore, it was concluded that polysaccharides and proteins contributed to both reversible and irreversible fouling, whereas fouling caused by HS was mainly irreversible. The role of HS in causing hydraulically irreversible fouling was further confirmed (in Chapter 8) by the fact that cleaning the fouled membranes with sodium dodecyl sulphate and Terg-a-zyne achieved high pure water flux recoveries and the cleaning solutions turned yellow (an indication of the presence of HS) after use.

Results from flux data analysis using the dead-end filtration models indicated that MF fouling by the raw AS effluent was controlled by the pore adsorption mechanism in the first 20 minutes of filtration and then followed the cake filtration model. Fouling of the hydrophobic UF (HFM-180 and HFM-116) membranes was dominated by the pore adsorption mechanism in the first 5 minutes of filtration, whereas fouling of the relatively hydrophilic UF (HFK-141) membrane could be described by the cake filtration model throughout the course of filtration.

CHAPTER 5. EFFECT OF COAGULATION ON MEMBRANE FOULING IN DEAD-END FILTRATION

As seen in Chapter 4, MF and UF of the raw effluent experienced rapid flux decline which needed to be mitigated to improve the water productivity. The most widely used method for fouling mitigation in MF and UF of secondary effluent is coagulation (Water Environment Federation 2006). Therefore, in this chapter the effect of this pre-treatment on membrane fouling in dead-end MF and UF of the raw AS effluent was investigated. Coagulation with alum and ACH was tested. ACH was considered for several reasons. First, practical experience in drinking water treatment plants indicates that ACH is effective in coagulation over a broader pH range (5.0 – 8.0) compared with alum (5.0 – 6.5), the most widely used coagulant. The pH of the raw AS effluent in this wastewater treatment plant varied from 7.2 to 7.8. Therefore, the use of ACH may result in better membrane flux and not necessitate preliminary pH adjustment. Second, ACH does not contain sulphate ions, which reduces the risk of odour and corrosion problems in the treatment system. These problems are more likely to occur if alum is used, since an increase in sulphate concentration of the wastewater will increase hydrogen sulphide production (Gebbie 2001). Third, ACH is known to consume much less alkalinity than alum (Duan & Gregory 2003). Coagulation with ACH will therefore result in a smaller reduction in pH of the AS effluent and may eliminate the need for pH adjustment of the MF/UF permeates. Also, coagulation with poly(aluminium) coagulants has been found to produce less sludge than coagulation with alum (Jiang & Graham 1996; Gebbie 2001). ACH is a pre-hydrolysed inorganic coagulant used in some drinking water treatment plants. However, this coagulant has rarely been used in wastewater treatment and therefore few studies on its effectiveness on reduction of membrane fouling by secondary effluents have been conducted.

Following common practice in municipal wastewater treatment, which tends to use in-line coagulation with low coagulant doses (Decarolis *et al.* 2001; Qin *et al.* 2004), and the recommendation by the operators at the wastewater treatment plant, alum and ACH were tested at relatively low doses: 1.0 and 2.5 mg Al³⁺ L⁻¹. The coagulated effluent samples were immediately subjected to MF or UF without prior removal of the coagulated flocs to simulate in-line coagulation. Filtration tests were conducted with the raw and the coagulated samples using the hydrophobic PVDF (VVLP, XUNP-003, HFM-180 and HFM-116) membranes and the PES (HFK-141) membrane. The flux data were collected

and analysed to evaluate the effect of coagulation on the flux performance. The EfOM of the raw and the coagulated effluent were analysed with LC-OCD to determine the reasons for the flux data observed.

In wastewater treatment plants, MF and UF are usually conducted in multi-cycle mode in which the membrane is backwashed with the permeate 15–30 minutes (Leslie *et al.* 1999; Decarolis *et al.* 2001; Laabs *et al.* 2006; Water Environment Federation 2006). Furthermore, some researchers have suggested that flux data obtained with virgin membranes may not be representative for every filtration cycle (Howe *et al.* 2007). Therefore, the effect of coagulation on membrane fouling was also investigated with the backwashed membranes. Six filtration cycles, each of which lasted for 20 minutes and was followed by 1-minute backwashing with the permeate at the operating pressure, were conducted.

5.1. Effect of coagulation on membrane fouling in single-cycle MF and UF

5.1.1. Single-cycle MF

Single-cycle MF and UF tests were conducted with the raw and coagulated effluent with the characteristics shown in Table 5.1. Coagulation (performed in the jar tester using the procedure described in section 3.1.2) with either alum or ACH at 2.5 mg Al³⁺ L⁻¹ removed approximately 10% of the DOC and 20% of the true colour from the raw effluent.

Table 5.1. Characteristics of the raw and the coagulated effluent samples used in single-cycle dead-end filtration tests

(Sample collected on 19 February 2009)

Parameter	Raw	Raw + 1.0 mg Al ³⁺ (ACH) L ⁻¹	Raw + 2.5 mg Al ³⁺ (ACH) L ⁻¹	Raw + 2.5 mg Al ³⁺ (alum) L ⁻¹
pH	7.8	7.8	7.6	7.2
DOC (mg L ⁻¹)	14.2	13.3	12.9	12.7
UVA ₂₅₄ (cm ⁻¹)	0.343	0.324	0.299	0.295
SUVA (L m ⁻¹ mg ⁻¹)	2.42	2.44	2.32	2.32
True colour (Pt-Co units)	90	79	72	70
Turbidity (NTU)	5.2	N/M*	N/M*	N/M*
TSS (mg L ⁻¹)	6.2	N/M*	N/M*	N/M*

* Not measured

The flux data for MF of the raw and coagulated effluent samples are shown Figures 5.1 and 5.2 for the VVLP and XUNP-003 membranes, respectively. To compare the fouling mechanisms of the different samples, plots of t/V versus V were compared. The linearity of the curves for the coagulated samples indicated that unlike MF fouling by the raw effluent, MF fouling by the coagulated samples was dominated by the cake filtration mechanism from the beginning of filtration (Figures 5.1 (a) and 5.2 (a)). This can be explained by the addition of the coagulants to the raw AS effluent destabilising the colloidal particles (including some membrane foulants) and so facilitating the aggregation of the colloids to form larger particles (or flocs) (Kolarik & Booker 1995). This reduced pore blocking and pore adsorption and allowed early dominance of the cake filtration mechanism. At the pH of this AS effluent (pH 7.8) and the low coagulant doses ($\text{mg Al}^{3+}/\text{mg DOC} = 0.18/1.0$ for $2.5 \text{ mg Al}^{3+} \text{ L}^{-1}$), coagulation was likely to proceed through a combination of ‘sweep coagulation’ mechanism (the dominant mechanism at $\text{pH} > 7$) and charge neutralisation mechanism, since there were insufficient polynuclear aluminium species and amorphous aluminium hydroxide precipitate (Wang *et al.* 2008). In the ‘sweep coagulation’ mechanism, EfOM was removed by entrapment and/or adsorption on the aluminium hydroxide precipitate, which was a hydrolysis product of alum and ACH. In the charge neutralisation mechanism, cationic aluminium species and anionic EfOM interact electrostatically to form insoluble charge-neutral particles (Gregor *et al.* 1997).

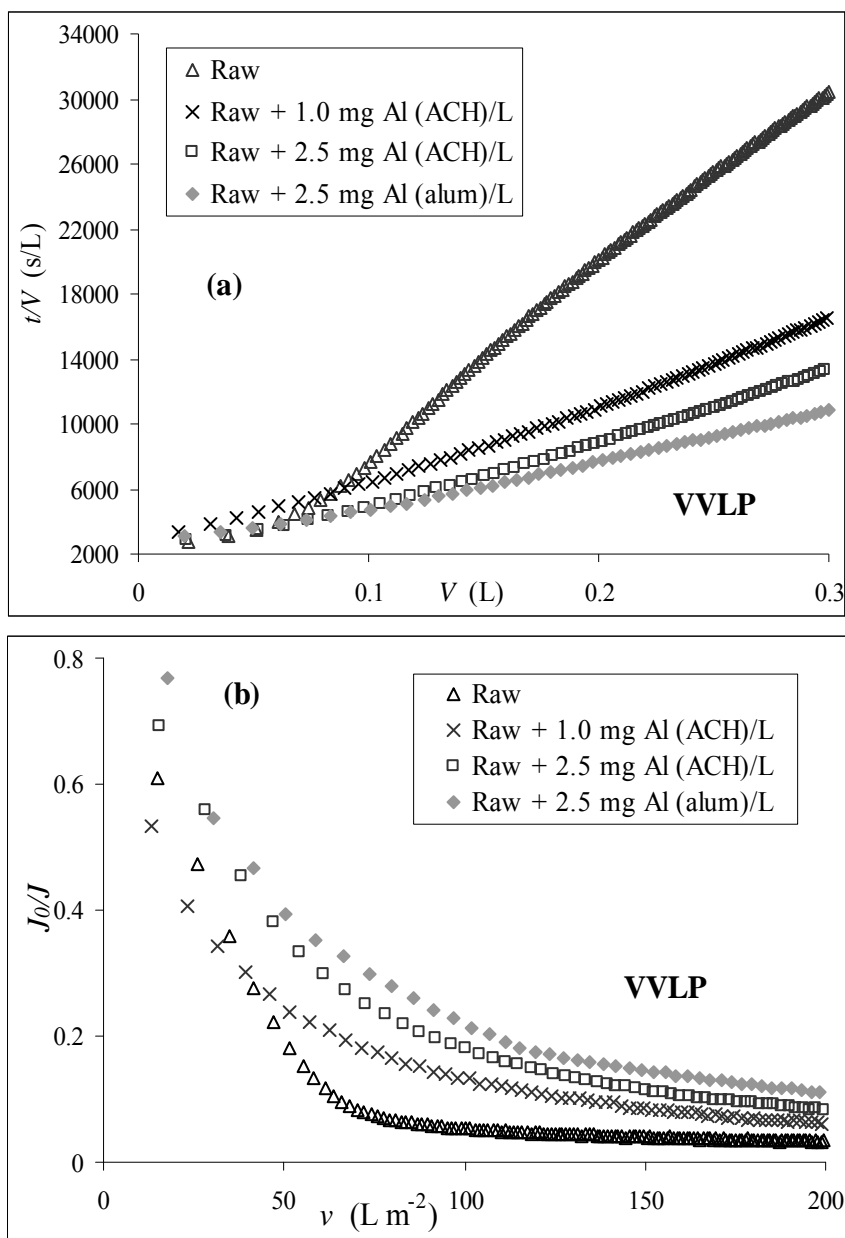


Figure 5.1. Plots of (a) t/V versus V and (b) corresponding J/J_0 versus v for MF of the raw and coagulated samples with the VVLP membrane

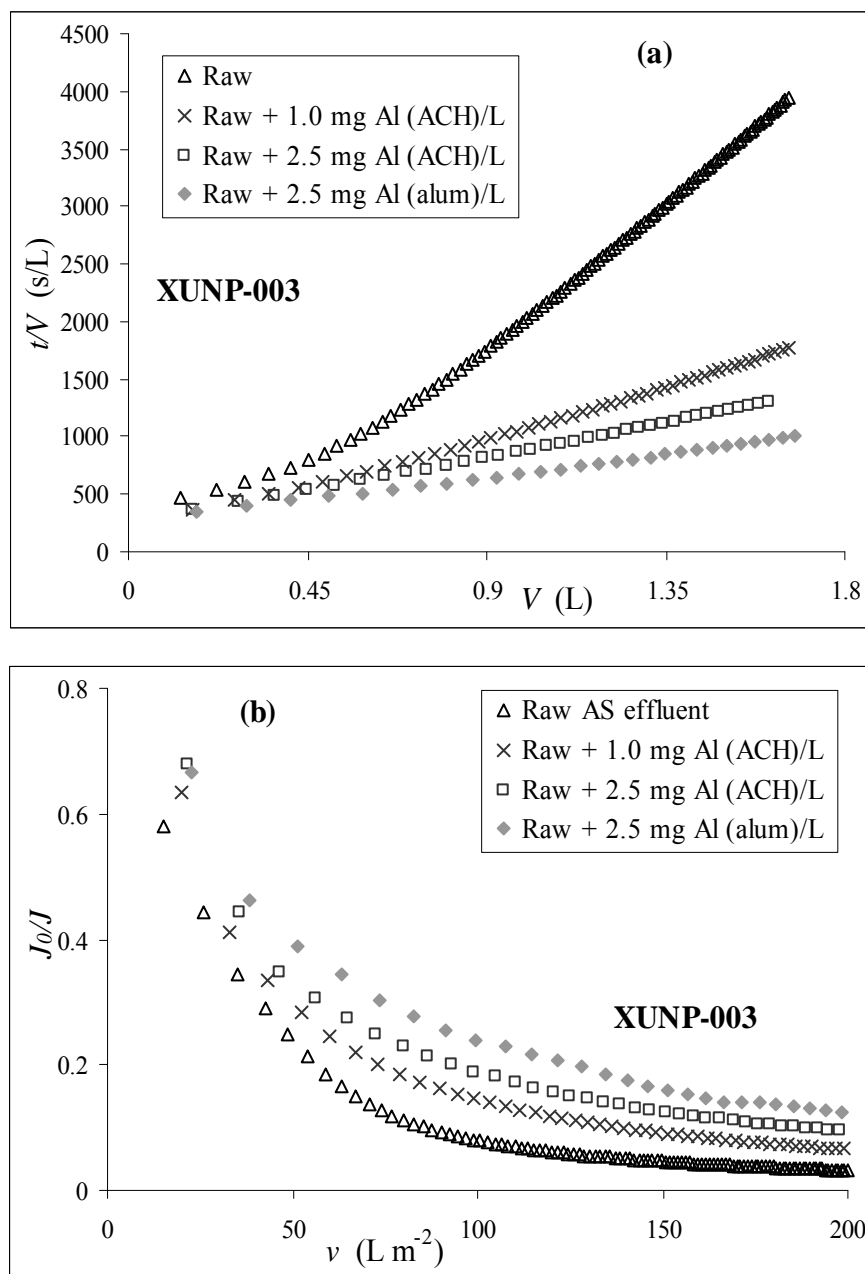


Figure 5.2. Plots of (a) t/V versus V and (b) corresponding J/J_0 versus v for MF of the raw and coagulated samples with the XUNP-003 membrane

To better understand the mechanisms of fouling reduction by coagulation, the EfOM of the raw and the coagulated samples were analysed with LC-OCD. The results obtained (Figure 5.3) showed that coagulation removed some biopolymers and HS in the raw effluent, which reduced the amount of foulants in contact with the membranes and therefore improved the flux. As can be seen in Figures 5.1 and 5.2, at the same dose (2.5 mg Al³⁺ L⁻¹), the flux improvement was slightly higher for alum than ACH. Since the removal of biopolymers and HS by the two coagulants were comparable (Figure 5.3), the higher flux improvement

by alum was probably due to the higher porosity of the cake layer formed on the membrane surface by the alum-coagulated sample (Wang *et al.* 2008). Increasing the coagulant dose from 1.0 mg Al³⁺L⁻¹ to 2.5 mg Al³⁺L⁻¹ resulted in better flux improvement (Figures 5.1 and 5.2), which was attributed to the increase in the amount of biopolymers and HS removed by coagulation (Figure 5.3).

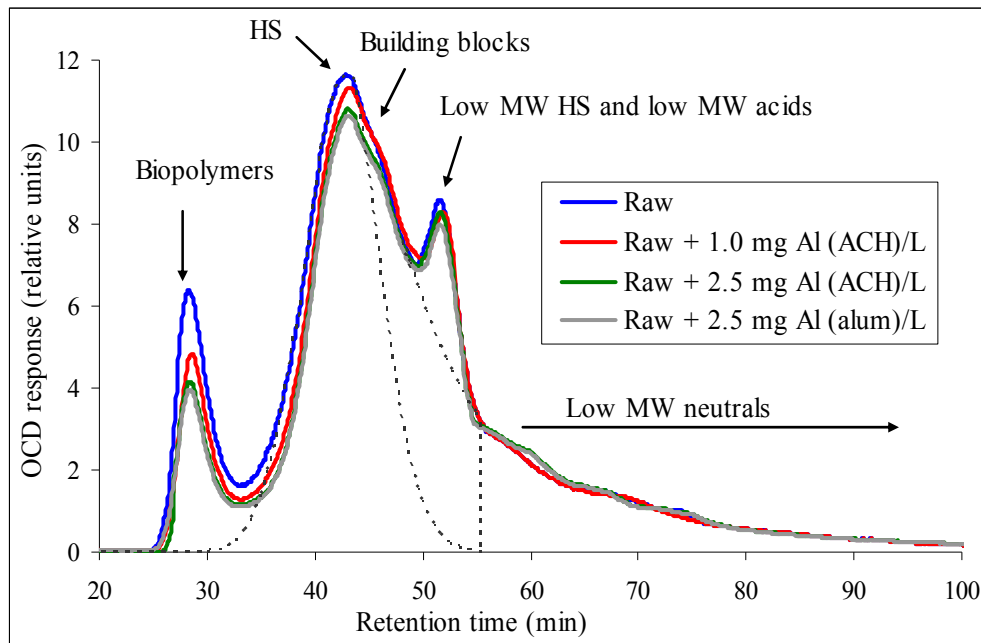


Figure 5.3. AMWDs of the raw and coagulated effluent
(Raw: DOC = 14.2 mg L⁻¹, UVA₂₄₅ = 0.343 cm⁻¹, true colour = 90 Pt-Co units)

To determine the effect of coagulation on hydraulically irreversible fouling, the fouled membranes were backwashed with the permeate at 70 kPa for 5 minutes and their pure water fluxes were measured. The calculated pure water flux recoveries (*WFR*) by backwashing and the hydraulic resistances for the different cases are shown in Table 5.2. The data showed that coagulation pre-treatment led to significant reductions in the resistance from hydraulically irreversible fouling (*R_{ir}*). This indicated a reduction in pore adsorption and pore blocking of the membranes and could be attributed to the lower concentrations of biopolymers and HS in the coagulated samples and the early formation of the cake layer which reduced the contact between these compounds and the membrane pores.

Table 5.2. Effect of coagulation on the hydraulic resistances from total fouling and irreversible fouling in MF of the effluent, and calculated pure water flux recovery by backwashing

Case	R_{tf}^* ($\times 10^{-10} \text{ m}^{-1}$)	R_{ir}^* ($\times 10^{-10} \text{ m}^{-1}$)	WFR (%)
Raw + VVLP	402	11.6	62
Raw + 1.0 mg Al^{3+} (ACH) L^{-1} + VVLP	265	2.1	89
Raw + 2.5 mg Al^{3+} (ACH) L^{-1} + VVLP	209	1.0	95
Raw + 2.5 mg Al^{3+} (alum) L^{-1} + VVLP	159	1.0	95
Raw + XUNP-003	520	35.7	31
Raw + 1.0 mg Al^{3+} (ACH) L^{-1} + XUNP-003	285	25.5	40
Raw + 2.5 mg Al^{3+} (ACH) L^{-1} + XUNP-003	186	22.0	45
Raw + 2.5 mg Al^{3+} (alum) L^{-1} + XUNP-003	134	21.8	45

* Calculated for $v = 200 \text{ L m}^{-2}$

As seen in Table 5.2, the XUNP-003 membrane experienced much more severe irreversible fouling than the VVLP membrane. Backwashing restored the pure water flux of the membrane fouled by the raw effluent to approximately 62% of the pure water flux of the virgin VVLP membrane. The corresponding value for the XUNP-003 membrane was only 31%. Factors which potentially contributed to this difference included the differences in the hydrophobicity, configuration, surface roughness and pore size distribution of the two membranes. Previous studies on surface water found that hydrophobic membranes suffered more severe irreversible fouling than hydrophilic counterparts (Fan 2002; Gray *et al.* 2008). The XUNP-003 membrane was a hydrophobic membrane with a contact angle greater than 90° , whereas the VVLP membrane was significantly less hydrophobic (contact angle approximately 62°). The greater irreversible fouling of the XUNP-003 membrane was also consistent with its higher rejection of biopolymers and HS (Figure 5.4), UV absorbance and true colour (Table 4.2, Chapter 4) than the VVLP membrane.

The fact that VVLP was a flat-sheet membrane whereas XUNP-003 was a hollow-fibre membrane likely contributed significantly to the difference in the extent of hydraulically irreversible fouling suffered by the two membranes, as membrane configuration affected the hydrodynamics of the backwash and consequently affected backwashing efficiency. During backwashing, the fouled PVDF flat-sheet was turned upside down in the filtration cell and the permeate was forced downwards through the membrane. In this case, the

permeate flow was expected to be distributed evenly across the membrane surface. Different from the flat-sheet membrane, the hollow-fibre module comprised 32 PVDF fibres (inner diameter = 0.8 mm, outer diameter = 1.0 mm, length = 102 mm) potted in a PES shell. Backwashing of the hollow-fibres involved forcing the permeate to flow axially (in the inside-out direction) in 32 individual fibres of 102-mm length. Therefore, even flow distribution of the permeate in the fibres may not have been achieved.

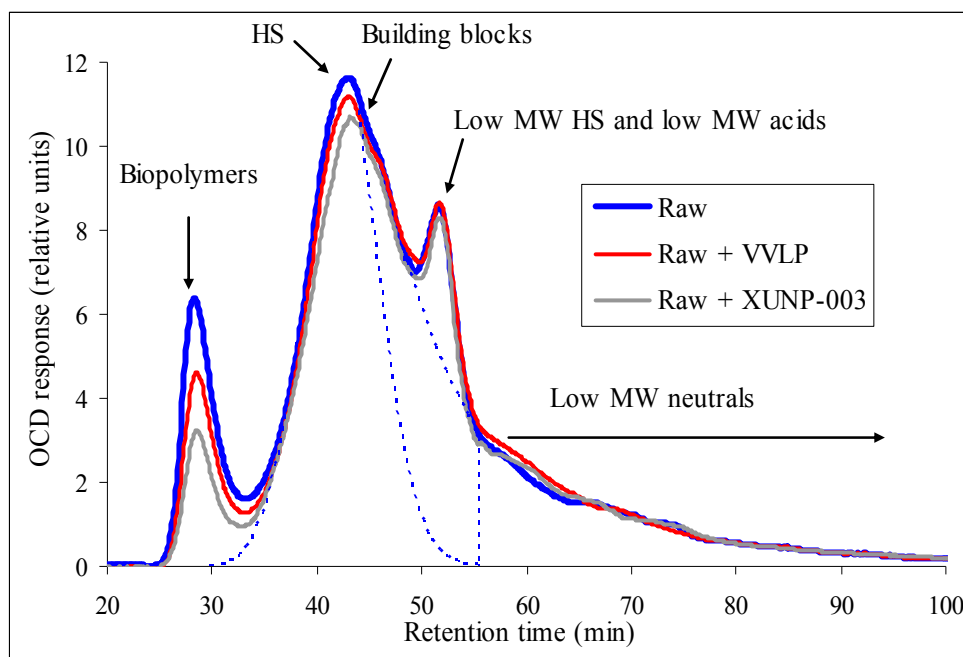


Figure 5.4. AMWDs of the feed and the permeates from MF of the raw effluent with the VVLP and XUNP-003 membranes

The reduction in the hydraulically irreversible fouling resulting from the coagulation pre-treatment was greater for the VVLP membrane than the XUNP-003 membrane (Table 5.2). For the VVLP membrane, coagulation at $2.5 \text{ mg Al}^{3+} \text{ L}^{-1}$ reduced the resistance from irreversible fouling by approximately 90%, whereas this value for the more hydrophobic membrane (XUNP-003) was only 36%. The large reduction in the irreversible fouling for the VVLP membrane indicated that coagulation removed the majority of biopolymers and HS responsible for pore adsorption and pore blocking of this membrane. However, a significant proportion of the foulants responsible for irreversible fouling of the XUNP-003 membrane still remained in the coagulated effluent. This hypothesis was supported by the fact that the XUNP-003 membrane retained more biopolymers and HS of the coagulated EfOM than the VVLP membrane (Figure 5.5).

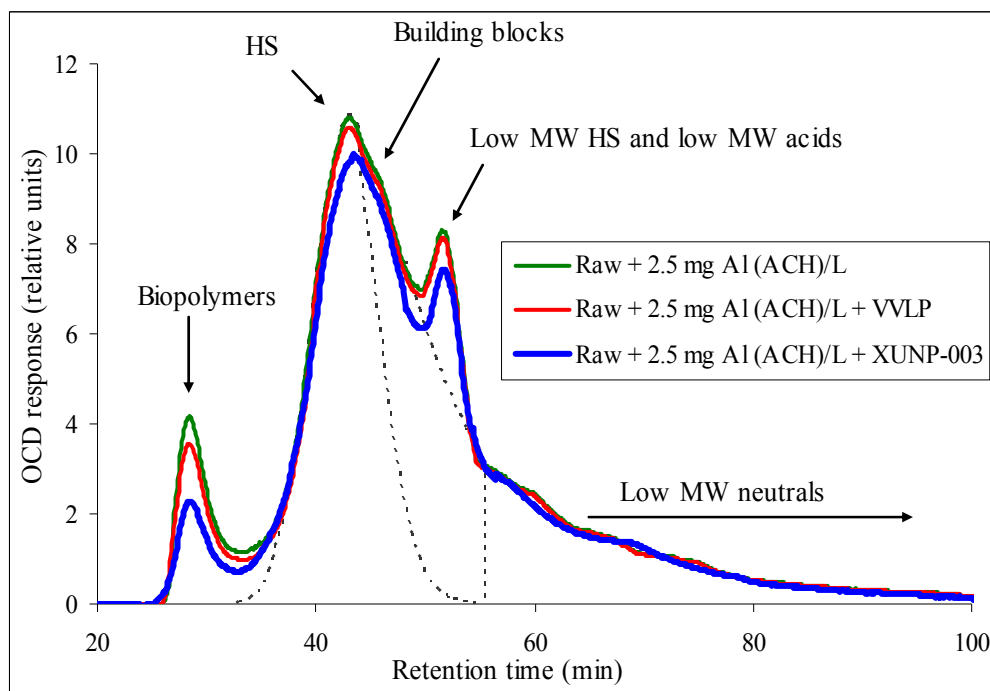


Figure 5.5. Removal of biopolymers and HS in the coagulated effluent by the VVLP and XUNP-003 membranes

The fairly similar resistances by irreversible fouling (R_{if}) of the samples coagulated with alum and ACH at $2.5 \text{ mg Al}^{3+} \text{ L}^{-1}$ indicated that the cake layers formed by the two samples on the membrane surfaces were equally easy to remove by backwashing. This observation supported the hypothesis that the difference in the MF flux of these samples was due to the difference in the cake porosity. Similar to total fouling, the reductions in hydraulically irreversible fouling were lower for the lower coagulant dose (Table 5.2) and can be attributed to the lower removal of the membrane foulants (Figure 5.3).

5.1.2. Single-cycle UF

The flux data obtained from the single-cycle UF tests with the raw and the coagulated samples are shown in Figures 5.6 and 5.7. To utilise the UMFI concept, plots of the reciprocal of the normalised flux (J_0/J) versus the accumulated specific permeate volume (v) were constructed and the slopes of the curves were taken as the UMFI for total fouling (Huang *et al.* 2009b), which are shown in Table 5.3. (The UMFI for total fouling was not computed for the MF flux data since the plot of J_0/J versus v for the raw effluent deviated significantly from linearity (due to the dominance of the pore adsorption and pore blocking mechanisms in the first 20 minutes))

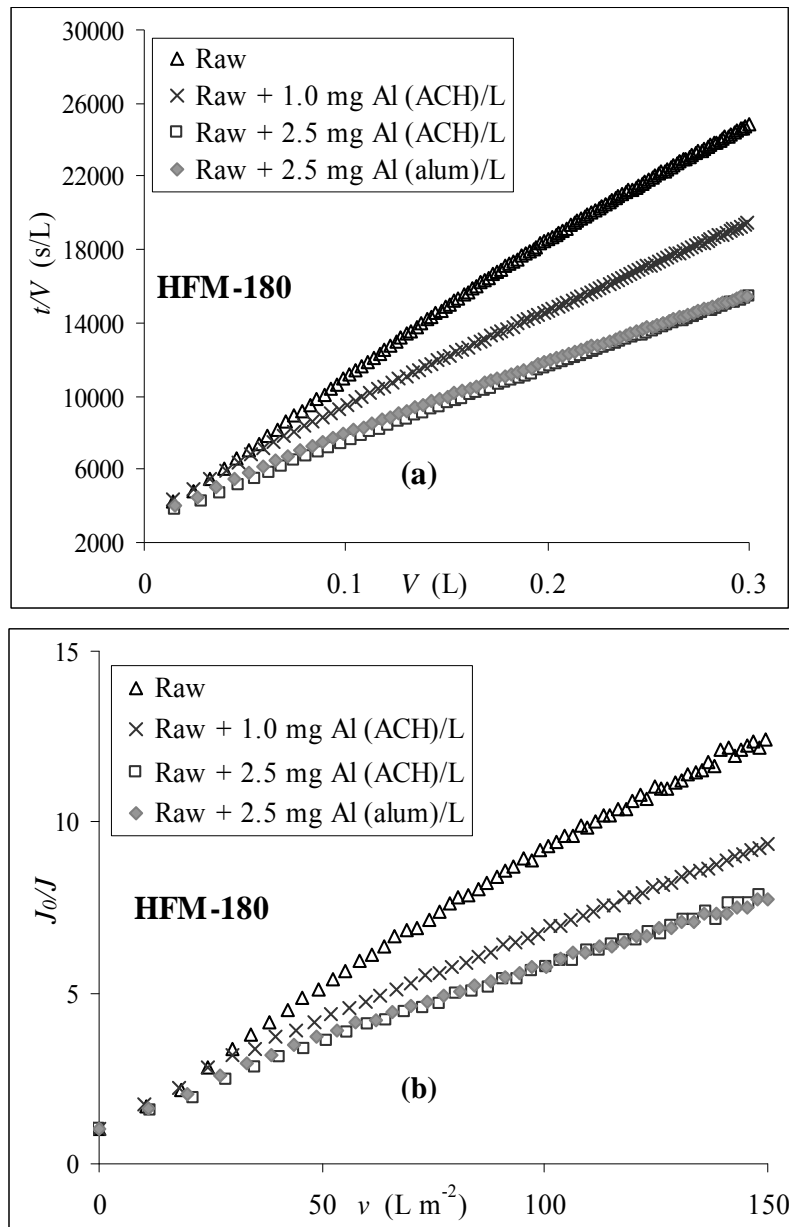


Figure 5.6. Plots of (a) t/V versus V and (b) corresponding J_0/J versus ν for UF of the raw and coagulated samples with HFM-180 membrane

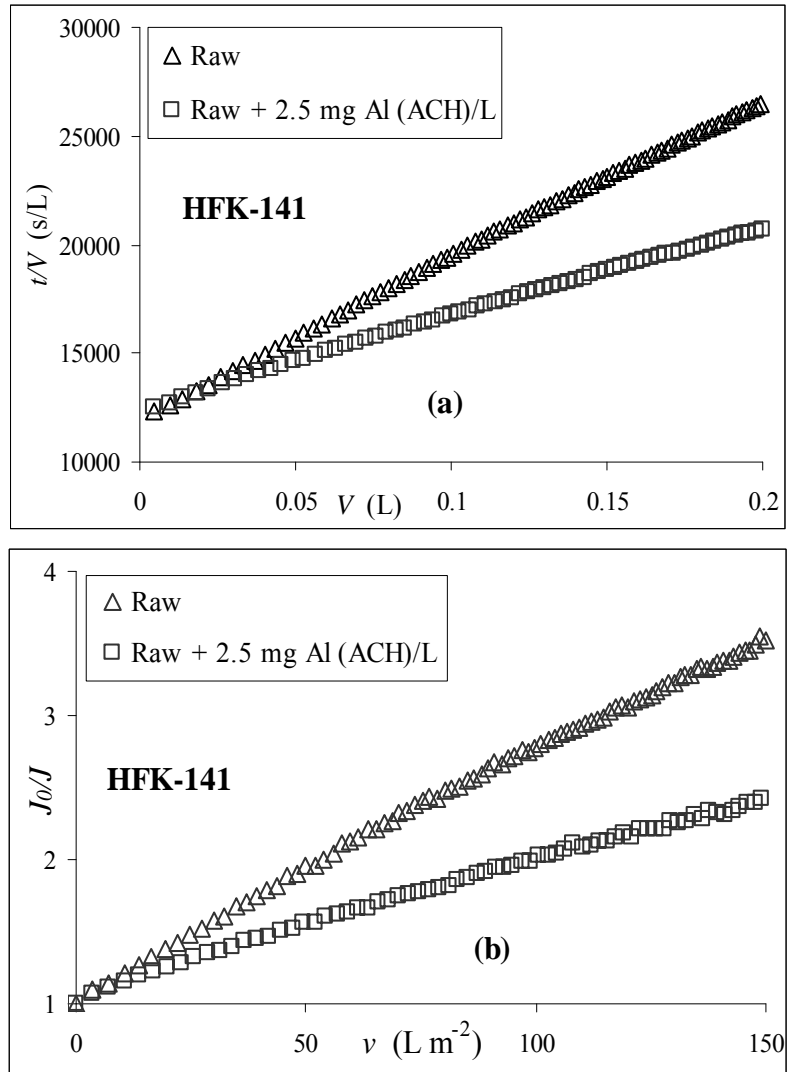


Figure 5.7. Plots of (a) t/V versus V and (b) corresponding J_0/J versus ν for UF of the raw and coagulated samples with the HFK-141 membrane

Coagulation improved the permeate flux for UF but did not change the prevailing fouling mechanism, i.e., fouling was still governed by cake filtration but with a lower UMF_I for total fouling (Figures 5.6 and 5.7 and Table 5.3). Different from MF, alum and ACH performed similarly in terms of UF flux enhancement. This was probably due to the smaller pore size of the UF membranes, which made the effect of the difference in cake layer porosities on the membrane flux insignificant.

The flux improvement by coagulation indicated that if MF and UF are conducted at a constant flux and rising TMP, as in pilot and full-scale plants, this pre-treatment would reduce not only the starting operating TMP but also the TMP rise required to sustain the

same flux as fouling occurs. This would in turn lower the energy requirement for the membrane filtration process.

Table 5.3. Values of UMFI for total fouling and resistances from total fouling and hydraulically irreversible fouling for UF of the raw and coagulated effluent

	UMFI ($\text{m}^2 \text{L}^{-1}$)	R_{if}^* ($\times 10^{-10} \text{m}^{-1}$)	R_{if}^* ($\times 10^{-10} \text{m}^{-1}$)
Raw + HFM-180	0.075	470	55.2
Raw + 1.0 mg Al^{3+} (ACH) L^{-1} + HFM-180	0.055	363	38.4
Raw + 2.5 mg Al^{3+} (ACH) L^{-1} + HFM-180	0.044	280	31.1
Raw + 2.5 mg Al^{3+} (alum) L^{-1} + HFM-180	0.042	269	32.7
Raw + HFK-141	0.017	438	67.5
Raw + 2.5 mg Al^{3+} (ACH) L^{-1} + HFK-141	0.010	250	49.2

* Calculated for $v = 150 \text{ L m}^{-2}$

Similar to MF, coagulation also reduced the hydraulically irreversible fouling of the UF membranes (Table 5.3). This indicated an opportunity for reducing the frequency of membrane chemical cleaning and would help to extend the membrane lifetime.

5.1.3. Multi-cycle filtration

Multi-cycle filtration experiments with the raw and the ACH-coagulated effluent were conducted to determine if the results obtained from single-cycle tests were applicable to a filtration protocol analogous to that used in MF and UF plants. Six filtration cycles, each of which lasted for 20 minutes and was followed by 1-minute backwashing with the permeate, were carried out. The flux data from these tests are presented in Figures 5.8 and 5.9. As seen in these figures, the highest irreversible fouling occurred in the first filtration cycle, indicating that pore adsorption and pore blocking were most severe for the virgin membranes. The increase in the hydraulically irreversible fouling with successive cycles (as indicated by the increase in the value of J_0/J) resulted from the accumulation of residual fouling which was not removed by backwashing.

Although the experimental arrangements had some limitations in simulating the membrane modules used in practice, most notably in the backwashing procedure, the results obtained

indicated that fouling reduction by coagulation observed in single-cycle tests was also achieved in multi-cycle runs. It is important to clarify this point because in practice filtration with backwashed membranes occupies the majority of the filtration time. Virgin membranes are only available at the time of purchase and chemical cleaning is done once every day (chemically enhanced backwash) or every few months (cleaning-in-place).

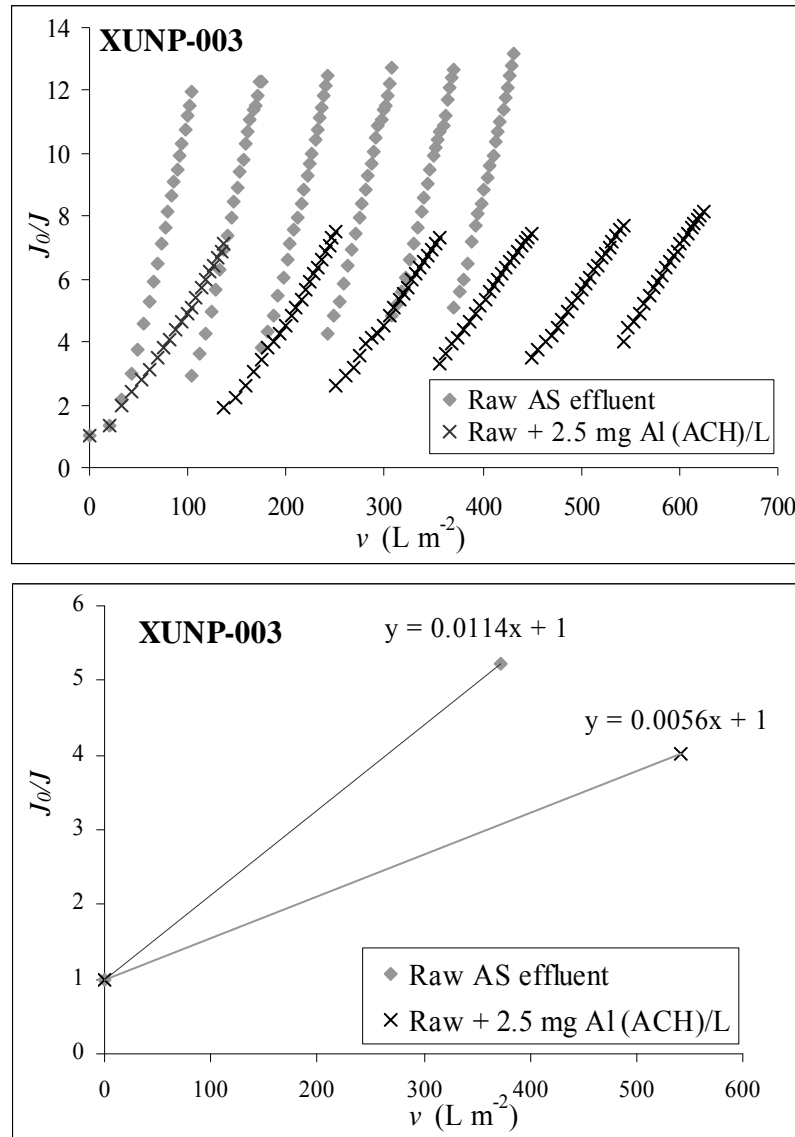


Figure 5.8. Flux data for multi-cycle MF (top) and calculation of UMFI for hydraulically irreversible fouling (bottom) for the XUNP-003 membrane

(UMFI for hydraulically irreversible fouling was calculated using the first data points of the first cycle ($v = 0$, $J_0/J = 1$) and the last cycle of filtration)

(Samples collected on 27 March 2009, Raw: DOC = 12.0 mg L⁻¹, UVA₂₅₄ = 0.400 cm⁻¹, true colour = 112 Pt-Co units, turbidity = 3.9 NTU)

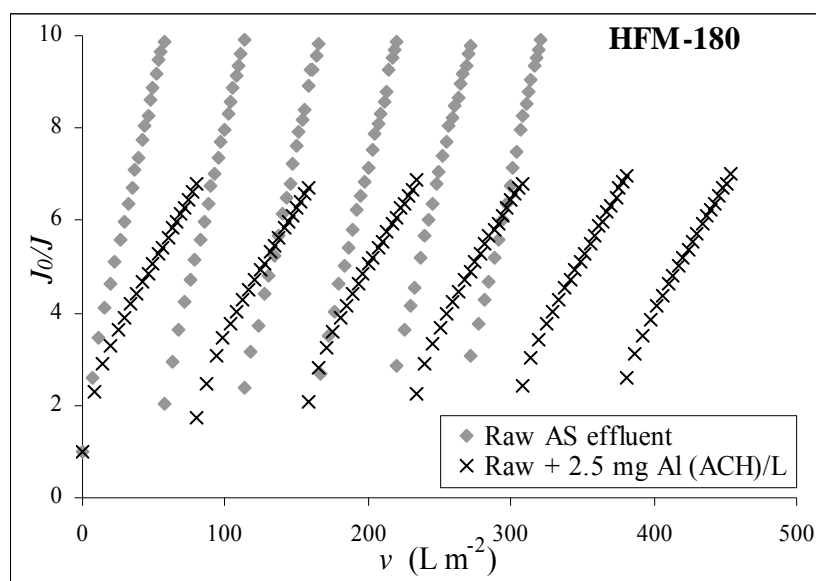


Figure 5.9. Flux data for multi-cycle UF with the raw and the coagulated effluent for the HFM-180 membrane

(Samples collected on 27 March 2009, Raw: DOC = 12.0 mg L⁻¹, UVA₂₅₄ = 0.400 cm⁻¹, true colour = 112 Pt-Co units, turbidity = 3.9 NTU)

To quantitatively evaluate the effect of coagulation on the hydraulically irreversible fouling, the UMFI for hydraulically irreversible fouling was calculated using the two-point method (Huang *et al.* 2009b) and the results are included in Table 5.4. Feed coagulation with ACH at 2.5 mg Al³⁺L⁻¹ reduced the UMFI for hydraulically irreversible fouling by approximately 50% for the XUNP-003 membrane and 45% for the HFM-180 membrane.

Table 5.4. Effect of coagulation on the UMFI for hydraulically irreversible fouling

Membrane	UMFI for hydraulically irreversible fouling (m ² L ⁻¹)	
	Raw	Raw + 2.5 mg Al ³⁺ (ACH) L ⁻¹
XUNP-003	11 × 10 ⁻³	5.6 × 10 ⁻³
HFM-180	7.1 × 10 ⁻³	3.9 × 10 ⁻³

5.2. Removal of DOC and true colour by coagulation-MF/UF hybrid

Coagulation with alum or ACH at 2.5 mg Al³⁺ L⁻¹ removed approximately 20% of the true colour and 10% of the DOC from the raw AS effluent. Alum was slightly better than ACH in removing colour-imparting compounds. The alum-treated effluent usually had a true

colour 1–3 Pt-Co units lower than the ACH-treated effluent. Compared with the permeates from MF or UF treatment, the permeates from the coagulation-MF/UF processes typically had a lower DOC concentration (0.2–1.2 mg DOC L⁻¹) and lower colour (7–20 Pt-Co units lower). However, they still had an unpleasant yellow colour (60–85 Pt-Co units for a raw effluent of 90–110 Pt-Co units). Coagulation pre-treatment of the raw effluent at 2.5 mg Al³⁺ L⁻¹ therefore was not able to address the high colour issue. It was found that a very high coagulant dose of 40 mg Al³⁺ L⁻¹ was needed to achieve the 75–80% colour removal target desired by the WWTP. The use of such a high coagulant dose is impractical due to the low economic value of the product water and additional problems such as high aluminium concentrations in the permeate and high sludge volume.

Although changes in the pH of the raw effluent by coagulation were small due to the low coagulant doses, it was seen that the pH reduction by coagulation with alum was larger than that by ACH. At a dose of 2.5 mg Al³⁺ L⁻¹, the pH of the alum-coagulated sample was 7.2 whereas the pH of the ACH-coagulated sample was 7.6, indicating lower alkalinity consumption by ACH.

Chapter 5 Summary

The effect of coagulation with ACH and alum on fouling mechanisms and flux performance for MF and UF of the AS effluent was investigated. Coagulation was found to modify the MF fouling mechanism to fit the cake filtration model from the beginning of filtration. It did not change the governing fouling mechanism of UF, but lowered the UMF_I for total fouling. The flux improvement by coagulation was attributed to the ability of the coagulants to remove some biopolymers and HS from the raw effluent. The MF flux improvement was higher for alum than ACH, whereas the two coagulants had a similar flux enhancing effect in UF. Coagulation also reduced irreversible fouling (i.e., pore adsorption and pore blocking) of the membranes and this effect was greater for the VVLP membrane than the more hydrophobic XUNP-003 membrane. Results from multi-cycle filtration tests showed that coagulation reduced fouling of the virgin as well as the hydraulically backwashed membranes. Coagulation pre-treatment, however, did not reduce the true colour of the MF and UF permeates to the desired level (20–25 Pt-Co units) unless very high coagulant doses (approximately 40 mg Al³⁺ L⁻¹) were used.

CHAPTER 6. EFFECT OF OZONATION & BIOLOGICAL ACTIVATED CARBON FILTRATION ON MEMBRANE FOULING IN DEAD-END FILTRATION

Although colour is not a criterion for “Class A” recycled water in Victoria, Australia, reducing the colour intensity of the treated AS effluent will improve customers’ willingness to purchase and reuse the product water. As mentioned in Chapters 4 and 5, neither MF and UF nor coagulation-MF/UF was able to reduce the colour of the raw AS effluent to the desired level (i.e., approximately 20–25 Pt-Co units). Ozonation was therefore trialled at the WWTP for this target. Preliminary tests showed that an ozone dose of 10 mg L^{-1} with a 10-minute contact time was sufficient to achieve the colour removal target. As ozone oxidised a proportion of the dissolved EfOM in the raw AS effluent to low MW compounds ($<500 \text{ Da}$) which may be a source of assimilable organic carbon (AOC), a BAC filter was installed downstream of the ozonation process to remove the AOC as well as suspended solids in the ozonated effluent. The WWTP also considered the use of a low-pressure membrane filtration process to remove the particulate matter and pathogens from the BAC filtrate. Therefore, this part of the study investigated the effect of ozonation (at a dose of $10 \text{ mg O}_3 \text{ L}^{-1}$ with a 10-minute contact time) and ozonation followed by BAC filtration on the characteristics and MF and UF filterability of the raw effluent.

6.1. Effect of ozonation and BAC filtration on characteristics of the raw effluent

6.1.1. Effect on general characteristics

The effects of ozonation and BAC filtration on the DOC concentration, UVA₂₅₄, true colour and turbidity were investigated on 6 different sample batches and similar trends were observed. Table 6.1 shows the characteristics of the raw and ozonated effluent and the BAC filtrate for the samples collected on 10 August 2009. The characteristics of the other sample batches used in the experiments in this chapter are included in Appendix D.

Table 6.1. Effects of ozonation and BAC filtration on the characteristics of the raw effluent (Samples collected on 10 August 2009)

Parameter	Raw AS effluent	Ozonated AS effluent	BAC filtrate
pH	7.6	7.5	6.8
DOC (mg L ⁻¹)	14.0	15.4	13.7
UVA ₂₅₄ (cm ⁻¹)	0.379	0.247	0.210
SUVA (L m ⁻¹ mg ⁻¹)	2.71	1.60	1.53
True colour (Pt-Co units)	109	28	25
Turbidity (NTU)	3.8	3.2	0.79
TSS (mg L ⁻¹)	3.7	3.6	0.2

Ozonation at a dose of 10 mg O₃ L⁻¹ for 10 minutes resulted in 75–80% reduction in the true colour of the raw AS effluent, which greatly improved its visual appearance (Table 6.1). The colour removal was attributed to the oxidation of colour-imparting compounds (i.e., compounds with conjugated C–C double bonds or aromatic rings, particularly HS) in the raw AS effluent to form colourless materials, as shown by a 34–47% reduction in the UVA₂₅₄ of the raw AS effluent. The lower SUVA of the ozonated effluent indicated a significant reduction in the hydrophobicity of the dissolved EfOM after ozonation. Ozonation increased the DOC level in the raw AS effluent by 0.5–1.7 mg C L⁻¹. This was attributed to DOC released from the breakdown of colloidal organic matter to lower MW compounds (Wang & Pai 2001; Lehman & Liu 2009) and/or breakdown of micro-organisms (e.g., bacteria, algae, protozoa). BAC filtration removed a proportion of the dissolved EfOM in the ozonated effluent yielding a filtrate with DOC level slightly lower than the DOC level of the raw effluent. Since the adsorption capacity of the activated carbon was exhausted before this study was conducted (see section 3.1.1), the removal of

DOC by the BAC filter was due to biodegradation of the EfOM by the micro-organisms growing on the filter. The small decrease in the true colour (1–3 Pt-Co units) of the ozonated effluent after BAC filtration indicated that a small proportion of HS in the ozonated effluent was consumed by the microbes on the BAC. This was further confirmed in section 6.1.3. As identified by the WWTP staff, the reduction in pH after BAC filtration (0.3–0.7 pH unit) was due to nitrification taking place in the BAC column. The BAC filter also retained the particulate matter producing a filtrate with low turbidity and TSS. Overall, the combination of ozonation and BAC filtration was very effective for removing true colour and turbidity from the raw AS effluent.

6.1.2. Effect on EfOM fractions

Previous research has investigated the effect of ozonation on the characteristics of different NOM fractions. In these studies, ozone was applied to the fractions isolated from the NOM (Marhaba *et al.* 2000; Swietlik & Sikorska 2004) and EfOM (Zhu *et al.* 2010). However, the effect of ozonation (and ozonation followed by BAC filtration) of the bulk EfOM on the relative concentrations of the fractions has not been studied. It is therefore interesting to determine this effect for the AS effluent under consideration. The result of this analysis provided an explanation for the effect of ozonation on the MF and UF flux, which is discussed in Section 6.2. Furthermore, it can be regarded as a contribution to the general knowledge of wastewater treatment.

As seen in Figure 6.1 (the results obtained from another sample set, which showed similar trends, are included in Appendix E), ozonation resulted in a reduction in the VHA fraction and increases in the other EfOM fractions. The majority of the additional DOC resulting from ozonation was SHA and CHA in nature. Some of these additions could be products of the oxidation of VHA (mainly humic and fulvic) material. A proportion of the VHA fraction in the raw AS effluent was oxidised to less hydrophobic compounds, which led to a reduction in the concentration of the VHA fraction and an increase in the SHA fraction after ozonation.

Although resin fractionation procedures involved large changes in the pH of the samples which may affect the structures and so properties of NOM and EfOM, the fractions extracted from the resins (after neutralisation) have been used in several studies to obtain insights to the effects of different water treatment processes on NOM and EfOM (Marhaba

et al. 2000; Wong *et al.* 2002; Gray *et al.* 2004; Swietlik *et al.* 2004; Shon *et al.* 2006; Zhu *et al.* 2010).

In this study, the VHA and SHA fractions of the raw and ozonated effluent were recovered from the resins by extraction with 0.1N NaOH and then adjusted to the original pH of the samples (pH 7.6) with 4.0 N HCl (as described in section 3.2.2) to investigate the effect of ozonation on their hydrophobicity. The recovery for the VHA and SHA fractions was 92–96%. The DOC concentration, UVA₂₅₄ and SUVA of the extracted fractions are shown in Table 6.2. For comparison purposes, it was assumed that the changes (if there were any) in the UV absorbance of these fractions caused by the changes in the pH during the fractionation and extraction process were similar for the raw and the ozonated effluent. The reductions in the SUVA of the VHA and SHA fractions after ozonation indicated that the VHA and SHA fractions of the ozonated effluent were significantly less hydrophobic than those of the raw effluent. The reductions in the SUVA of these fractions were also consistent with the colour removal by ozonation since VHA and SHA accounted for approximately 90% of the true colour of the raw AS effluent.

Table 6.2. Effect of ozonation and BAC filtration on the characteristics of the VHA and SHA fractions in the raw effluent

(Samples collected on 10 August 2009)

Fraction	VHA				SHA			
	DOC (mg L ⁻¹)	UVA ₂₅₄ (cm ⁻¹)	SUVA (L m ⁻¹ mg ⁻¹)	True colour (Pt-Co units)	DOC (mg L ⁻¹)	UVA ₂₅₄ (cm ⁻¹)	SUVA (L m ⁻¹ mg ⁻¹)	True colour (Pt-Co units)
Raw effluent	6.4	0.229	3.57	82	2.7	0.065	2.38	12
Ozonated effluent	5.0	0.145	2.9	N/M*	3.9	0.059	1.52	N/M*

*Not measured

It is known that ozone decomposes humic acid to give low MW substances, such as carboxylic acids (formic, acetic, oxalic, and glyoxylic acids, etc.) and aldehydes, and so increases the biodegradability of the treated water (Takahashi *et al.* 1995; Camel & Bermond 1998; Von Gunten 2003). In the ozonated effluent, the low MW acids may have been isolated in the CHA fraction due to their charge. The increase in the NEU fraction was

attributed to the breakdown of colloidal organic matter and VHA and SHA fractions. The soluble microbial products released from broken microbial cells may also contribute to this increase.

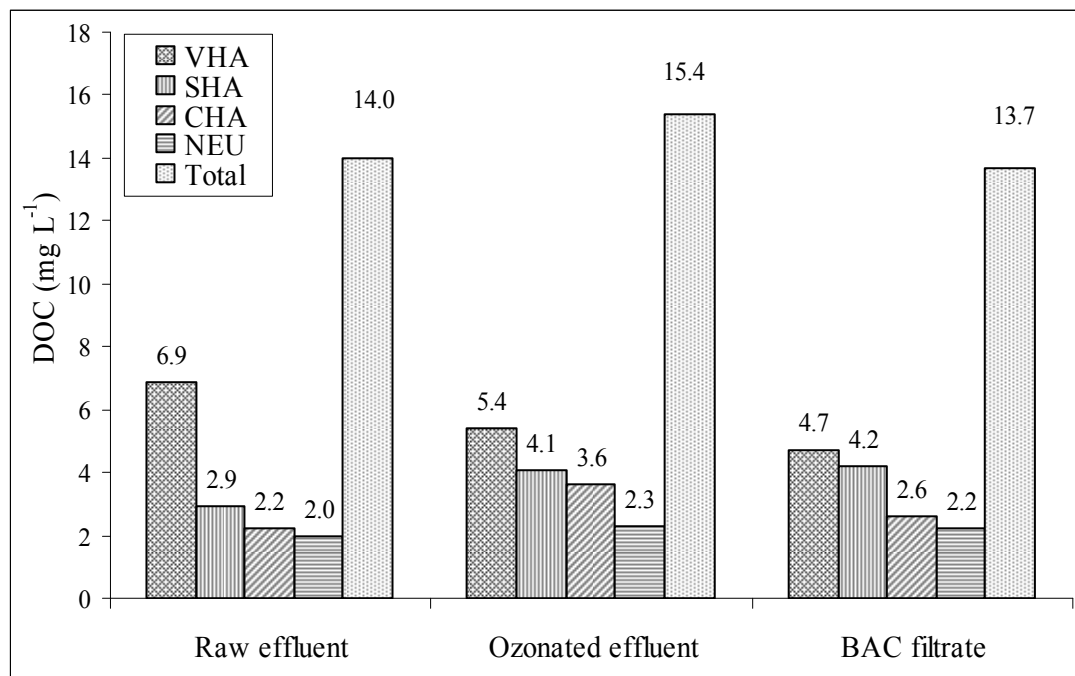


Figure 6.1. EfOM fractions in raw and ozonated AS effluents and in BAC filtrate (Samples collected on 10 August 2009)

The removal of DOC from the ozonated effluent by the BAC filter was attributed to its consumption by the microbial flora on the activated carbon. Fractionation showed reductions in the VHA and CHA components of the ozonated effluent after BAC filtration. Since the concentration of the SHA and the NEU fractions remained unchanged after BAC filtration, it was deduced that the consumption by micro-organisms and/or adsorption on BAC of these compounds was probably counterbalanced by SHA and NEU materials released by micro-organisms.

6.1.3. Effect on AMWD of dissolved EfOM

LC-OCD analysis allowed better understanding of the effects of ozonation and BAC filtration on the raw AS effluent. Figure 6.2 (a) shows the chromatograms obtained with UV detection (at 254 nm). The reductions in the UV absorbance of biopolymers, HS, and building blocks after ozonation indicated the breakdown in the molecular structures of these

compounds. HS showed the largest reduction in the UV absorbance, which can be explained by the large number of C–C double bonds and electron-rich aromatic rings in these molecules, which makes them very reactive to ozone (Von Gunten 2003). The reduction in the UV absorbance of biopolymers was small and likely to originate from the breakdown in the structures of some proteins, particularly those containing aromatic amino acids such as tryptophan and tyrosine (Cataldo 2003). BAC filtration of the ozonated effluent led to small reductions in the UV absorbance of the biopolymers and HS in the ozonated effluent, which can be attributed to adsorption and/or biodegradation taking place on the BAC filter.

The chromatograms obtained with organic carbon detection (OCD) are shown in Figure 6.2 (b). The DOC levels of different compound groups were calculated by integrating the areas under the peaks using DOC-Labor ChromCalc software (Huber *et al.* 2011) and the results are shown in Table 6.3. The chromatograms of the samples listed in Table 6.3 but not shown in Figure 6.2 are included in Appendix F.

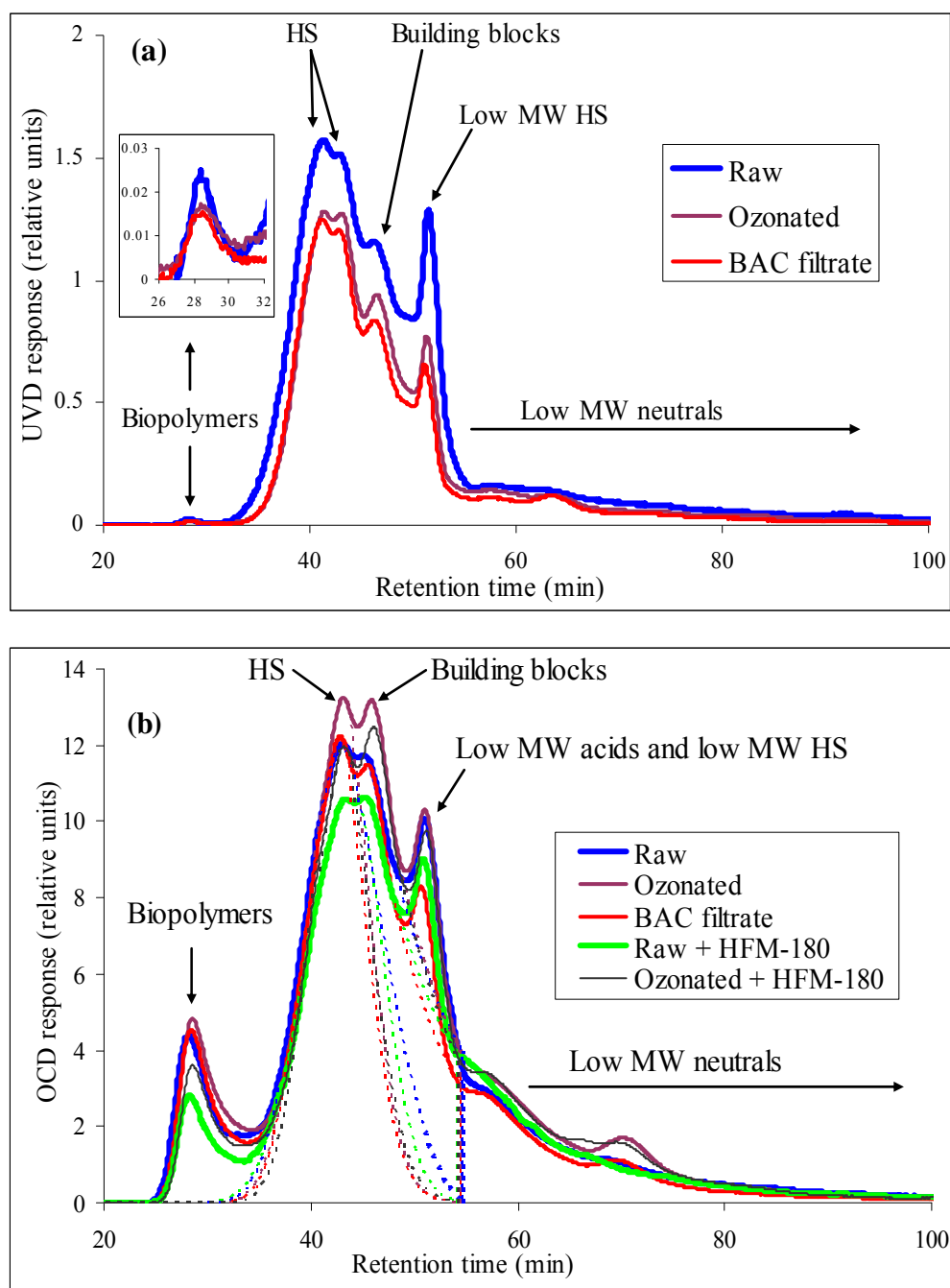


Figure 6.2. Effects of ozonation, BAC filtration, and UF on AMWD of the raw AS effluent
 (a) UV response and (b) DOC response
 (The dotted lines define the areas under the peaks)
 (Samples collected on 10 August 2009)

Table 6.3. Effects of ozonation, BAC filtration, MF with the VVLP membrane and UF with the HFM-180 membrane on the concentrations of EfOM components (in mg C L⁻¹) as determined by LC-OCD

Sample	Biopolymers ^a	HS ^b	Building blocks ^c	Low MW acids ^d	Low MW neutrals ^e
Raw	2.4	6.7	2.1	0.0	2.6
Ozonated	2.5	5.8	3.4	0.1	2.9
BAC filtrate	2.3	5.5	2.9	0.0	2.3
Raw + VVLP	1.9	6.4	2.0	0.0	2.5
Ozonated + VVLP	2.2	5.6	3.2	0.1	3.0
Raw + HFM-180	1.6	5.5	2.0	0.0	2.5
Ozonated + HFM-180	2.1	5.4	3.3	0.1	2.9
BAC filtrate + HFM-180	2.0	5.3	2.8	0.0	2.2

^aProteins, protein-like material, polysaccharides, polysaccharide-like material, amino sugars, MW >> 20,000 Da

^bMW = 1,000–20,000 Da

^cBreakdown products of HS, MW = 300–500 Da

^dMonoprotic organic acids, MW < 350 Da

^eInclude mono-oligosaccharides, alcohols, aldehydes, ketones, MW < 350 Da

Integrating the data in Figure 6.2 and Table 6.3, ozonation resulted in

- (i) a small increase in the concentration of biopolymers, which probably came from the breakdown of colloidal organic matter and/or release of intracellular matter from micro-organisms,
- (ii) partial breakdown of biopolymers, as can be seen in Figure 6.2 (a),
- (iii) a small reduction in the amount of HS due to the breakdown of HS to lower MW compounds, and
- (iv) an increase in biodegradable materials, i.e., building blocks, low MW acids and low MW neutrals, which were breakdown products of HS and possibly ozonolysis of micro-organisms.

During BAC filtration, some of the biopolymers, HS, building blocks, low MW acids, and low MW neutrals in the ozonated AS effluent were consumed by the micro-organisms on the BAC. Although HS are generally regarded as non-biodegradable, the breakdown of C–C double bonds by ozonation may have improved their biodegradability (Buls 2000), making them amenable to consumption by the microbes on the BAC.

6.2. Effect of ozonation and BAC filtration on MF flux

Figures 6.3 and 6.4 show that ozonation improved the flux through the MF membranes. As fouling of the MF membranes in the initial period of filtration was governed by the pore adsorption mechanism (Chapter 4), the higher permeate flux of the ozonated effluent than the raw AS effluent from the beginning of filtration indicated a reduction in the adsorption of the foulants on the membranes. This was supported by the fact that the membranes retained a lower amount of biopolymers and HS in the ozonated effluent than in the raw effluent (Table 6.3, results for the XUNP-003 membrane with another batch of samples is presented in section 7.2, Chapter 7). The lower adsorption capacity of the ozonated biopolymers and HS on the membranes can be attributed to the reduction in their hydrophobicity (as shown by the reductions in their UV responses in Figure 6.2 (a) and the conversion of some VHA material to SHA (section 6.1.2)), which reduced hydrophobic interactions with the membranes. It was also possible that ozonation caused changes in the secondary and tertiary structures of some proteins (Cataldo 2003), allowing them to pass through the membranes thus reducing the rate of pore blocking and cake formation. Ozone may also react with β -D-glycosidic linkages on polysaccharides and depolymerise the molecules (Wang *et al.* 1999). The fact that the concentration of biopolymers did not decrease after ozonation indicated that the breakdown products of these compounds were larger than 20 kDa and therefore remained in the biopolymers peak on the LC-OCD chromatogram of the ozonated effluent.

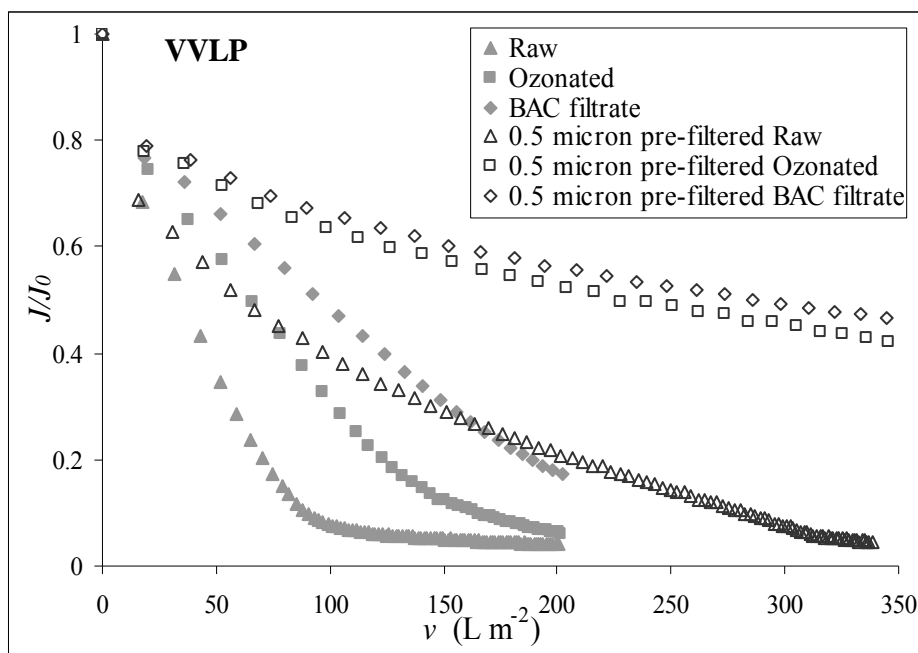


Figure 6.3. Effect of ozonation and BAC filtration on flux of the VVLP membrane
(Samples collected on 10 August 2009)

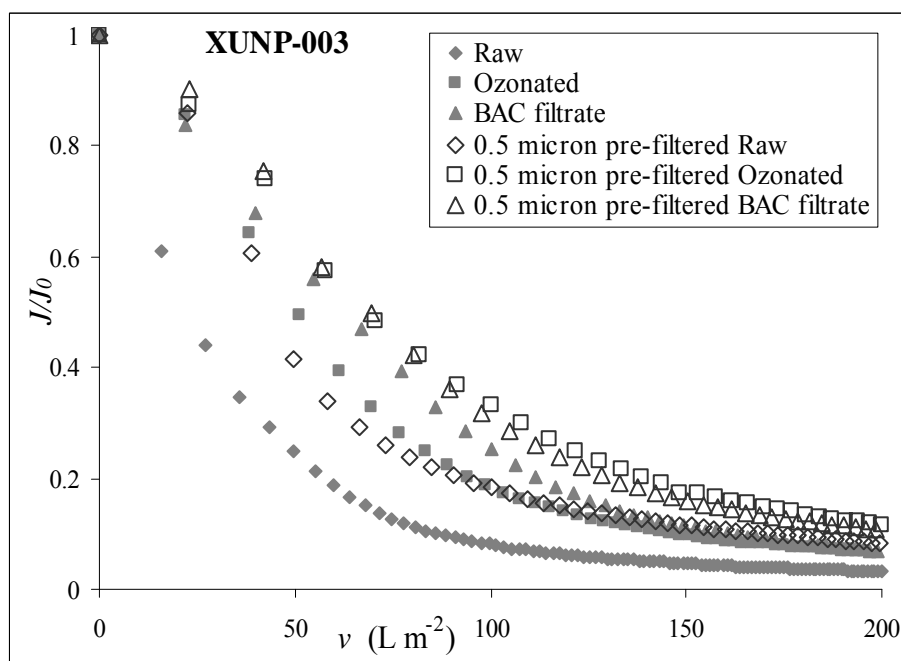


Figure 6.4. Effect of ozonation and BAC filtration on flux of the XUNP-003 membrane
(Samples collected on 10 August 2009)

BAC filtration of the ozonated effluent further reduced the rate of fouling. Since the ozonated AS effluent and the BAC filtrate had fairly similar fouling potentials after the removal of particles larger than 0.5 μm (Figures 6.3 and 6.4, open symbols), the reduction

in fouling by BAC filtration was due mainly to the decrease in the TSS level (Table 6.1). This was consistent with the small reductions in the amounts of membrane foulants after BAC filtration (Table 6.3).

Previous studies show that ozonation could change the size distribution (Zhu *et al.* 2008) and surface charge (or zeta potential) (Chandrakanth & Amy 1996; Zhu *et al.* 2008) of organic particles in water and wastewater. These changes may affect the cake permeability in membrane filtration and therefore affect the flux (Fu & Dempsey 1998). Figure 6.5 shows the particle size distributions of the raw and the ozonated effluent samples (results of the three replicates are included in Appendix G). Ozonation resulted in the breakdown of particles larger than 300 μm in the raw AS effluent. However, the flux data for the samples before and after the removal of particles larger than 0.5 μm (Figures 6.3 and 6.4) indicated that for this AS effluent this change had little influence on the membrane flux compared with the breakdown of dissolved EfOM. The zeta potentials of the raw effluent and the ozonated effluent were -13.2 ± 1.4 mV and -14.3 ± 1.5 mV, respectively, indicating that ozonation did not cause significant changes in the electric charges of the colloidal particles in the raw effluent.

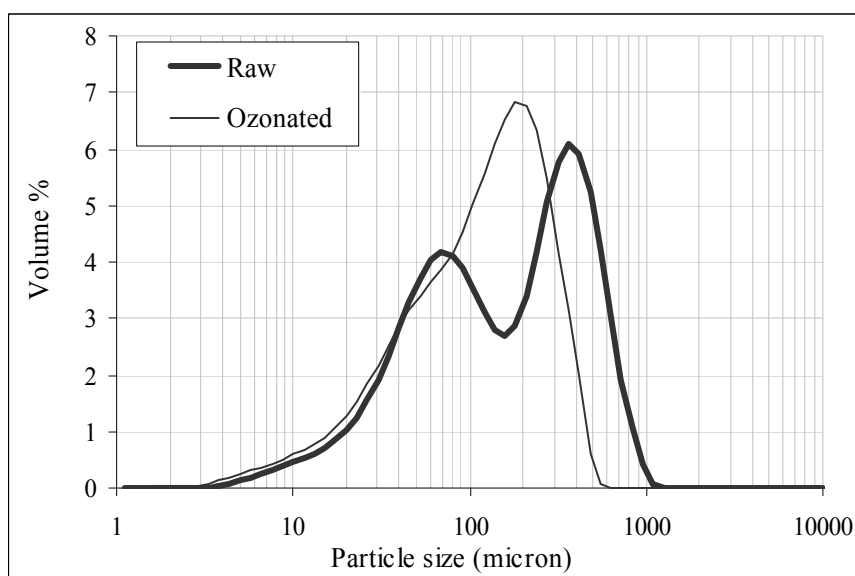


Figure 6.5. Particle size distributions of the raw and ozonated AS effluent
(Samples collected on 10 August 2009)

Ozonation of water/wastewater is known to produce compounds containing carboxylic and phenolic groups which may have a higher tendency to form aggregates with divalent cations (e.g., Ca^{2+} and Mg^{2+}) than the parent compounds and therefore may worsen membrane fouling (Zhu *et al.* 2010). However, although ozonation of this AS effluent produced some low MW organic acids (Table 6.3), the results from the MF and UF tests showed that any such negative effect on the membrane flux was either absent or compensated by the breakdown in the structures of the membrane foulants (i.e., polysaccharides, proteins and HS).

6.3. Effect of ozonation and BAC filtration on UF flux

6.3.1. UF with the HFM-180 membrane

Similar to MF, ozonation and BAC filtration also reduced fouling on the HFM-180 membrane. The UMFIs for total fouling of the HFM-180 membrane were computed for the raw AS effluent, ozonated AS effluent, and BAC filtrate using forced linear regression (y-intercept was set at 1.0 to follow equation 2.16 and facilitate flux comparison). The results were the slopes of the fitted lines (Figure 6.6) in $\text{m}^2 \text{L}^{-1}$.

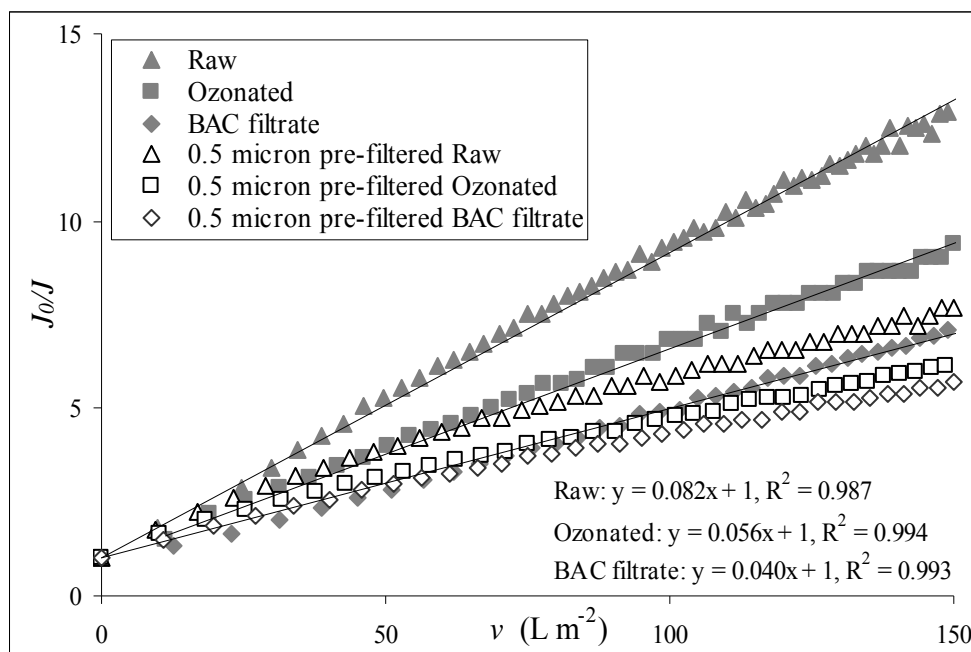


Figure 6.6. Flux data for UF of the raw and ozonated effluent and the BAC filtrate with the HFM-180 membrane (Samples collected on 10 August 2009)

Ozonation reduced the UMFI of the raw AS effluent by approximately 30%, which can be explained by the breakdown of biopolymers and HS to lower MW compounds (Figure 6.2 and Table 6.3). The lower amounts of biopolymers and HS retained by the membrane indicate that the fouling by these compounds was reduced after ozonation.

BAC filtration resulted in a 30% reduction in the UMFI of the ozonated AS effluent. Similar to MF, the flux improvement by BAC filtration was attributed to the removal of particles larger than 0.5 μm by the filter.

For the samples presented in Table 6.1 and Figure 6.6, the overall reduction in the fouling rate by the ozonation/BAC filtration pre-treatment was approximately 50% as measured by the UMFI. The flux improvement implies that if UF is conducted at a constant flux and rising TMP, as in pilot and full-scale plants, the combined pre-treatment would significantly reduce the increasing rate of TMP and therefore lower the energy requirement for the membrane filtration process.

For the 6 sample batches collected from March 2009 to August 2009, ozonation reduced the UMFI for total fouling of the HFM-180 membrane by the raw AS effluent by 22–40%. BAC filtration further reduced the UMFI for the ozonated effluent by 17–29%. Overall, the combination of ozonation and BAC filtration reduced the UMFI for total fouling by the raw AS effluent by 35–50%. The characteristics and UMFI for total fouling for these samples are included in Appendix D.

6.3.2. UF with the HFK-141 membrane

Ozonation also reduced fouling of the tighter UF (HFK-141, 30 kDa) membrane (Figure 6.7). However, different from the loose UF (HFM-180) membrane, BAC filtration did not further improve the permeate flux of the HFK-141 membrane. This was consistent with the fact that the removal of particles larger than 0.5 μm did not have any significant effect on the flux decline for this membrane (Chapter 4, Section 4.1).

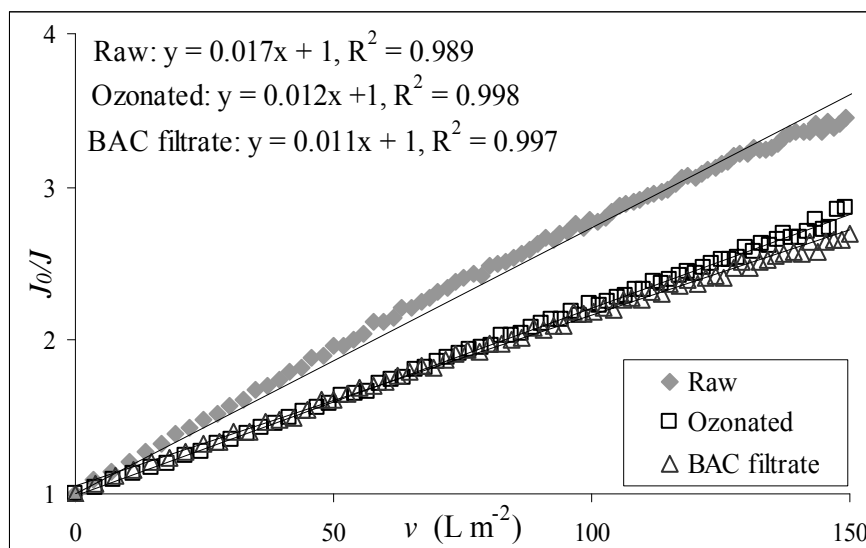


Figure 6.7. Flux data for UF of the raw and ozonated effluent and the BAC filtrate with the HFK-141 membrane
(Samples collected on 16 June 2009,
their characteristics are shown in Appendix D)

6.4. Effect of ozonation and BAC filtration on hydraulically irreversible fouling

6.4.1. Results from single-cycle filtration tests

The hydraulic resistances exerted by total fouling (R_{tf}) and hydraulically irreversible fouling (R_{if}) were calculated for the flux data in Figures 6.3, 6.4, 6.6 and 6.7, and the results are shown in Table 6.4.

Ozonation led to significant reductions in the hydraulically irreversible fouling of the membranes. This was attributed to the smaller amount of biopolymers and HS retained on the membranes (as suggested by the data in Table 6.1 for the VVLP and HFM-180 membranes). Because the amounts of biopolymers and HS removed by the BAC filter were small, this treatment did not further reduce the proportion of internal fouling. Similar to coagulation pre-treatment (Chapter 5), the reduction in hydraulically irreversible fouling by ozonation was greater for the less hydrophobic MF membrane (VVLP, 75% reduction in R_{if}) than the more hydrophobic counterpart (XUNP-003, 35% reduction in R_{if}). The results indicate that mitigation of hydraulically irreversible fouling is more difficult to achieve with more hydrophobic membranes.

Table 6.4. Effect of ozonation and BAC filtration on resistances from total fouling and hydraulically irreversible fouling (for the flux data shown in Figures 6.3, 6.4, 6.6, and 6.7)

Case	R_m ($\times 10^{-10} \text{ m}^{-1}$)	R_{if} ($\times 10^{-10} \text{ m}^{-1}$)	R_{if} ($\times 10^{-10} \text{ m}^{-1}$)
Raw + VVLP	18.2	471	11.2
Ozonated + VVLP	17.8	247	2.80
BAC filtrate + VVLP	17.5	94.0	3.11
Raw + XUNP-003	16.9	515	37.6
Ozonated + XUNP-003	17.0	248	24.7
BAC filtrate + XUNP-003	17.3	228	24.2
Raw + HFM-180	38.0	486	52.4
Ozonated + HFM-180	41.0	369	34.9
BAC filtrate + HFM-180	40.5	289	31.8
Raw + HFK-141	174	607	67.5
Ozonated + HFK-141	173	468	43.2
BAC filtrate + HFK-141	170	443	45.2

6.4.2. Results from multi-cycle filtration tests

To investigate the effect of ozonation on membrane flux in a filtration protocol similar to that used in pilot and full-scale plants, multi-cycle filtration tests (20-min filtration followed by 1-min backwashing) were conducted with the raw and ozonated effluent using the XUNP-003, HFM-180 and HFK-141 membranes. Data from these tests (Figures 6.8 and 6.9) show that fouling reduction by ozonation was also achieved in multi-cycle filtration (Data for the XUNP-003 membrane are shown in Figure 7.2, Chapter 7, where ozonation and adsorption with the AER and the PAC are compared).

The UMFI for hydraulically irreversible fouling was calculated using the two-point method (Figure 6.8 (b)) and the results (Table 6.5) show a reduction in this value after ozonation. Ozonation therefore improved water productivity and reduced the accumulation rate of residual fouling that cannot be removed by backwashing. The reduction in the hydraulically irreversible fouling achieved with the ozonation/BAC filtration pre-treatment indicated an opportunity for reducing the frequency of membrane chemical cleaning and this would help to extend the membrane lifetime.

Table 6.5. Effect of ozonation on UMFI for hydraulically irreversible fouling

Membrane	UMFI for hydraulically irreversible fouling ($\text{m}^2 \text{L}^{-1}$)	
	Raw	Ozonated
XUNP-003	11×10^{-3}	6.4×10^{-3}
HFM-180	7.6×10^{-3}	4.4×10^{-3}
HFK-141	4.1×10^{-3}	2.0×10^{-3}

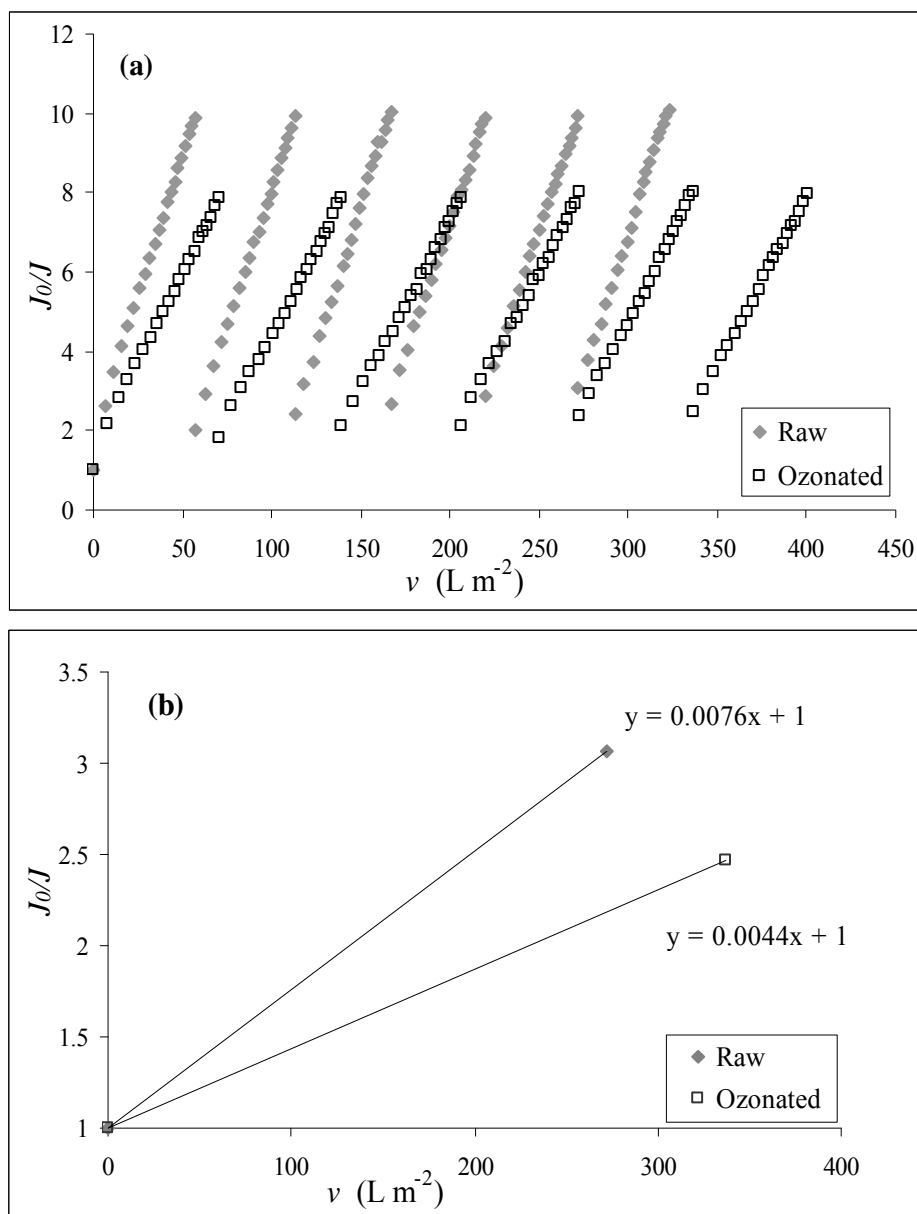


Figure 6.8. Effect of ozonation on permeate flux of the HFM-180 membrane in multi-cycle filtration

- (a) Specific permeate volume versus the reciprocal of normalised flux and
 (b) Calculation of the UMF for hydraulically irreversible fouling using the first data points of the first cycle ($v = 0$, $J_0/J = 1$) and the last cycle of filtration
 (Samples collected on 24 April 2009, their characteristics are shown in Appendix D)

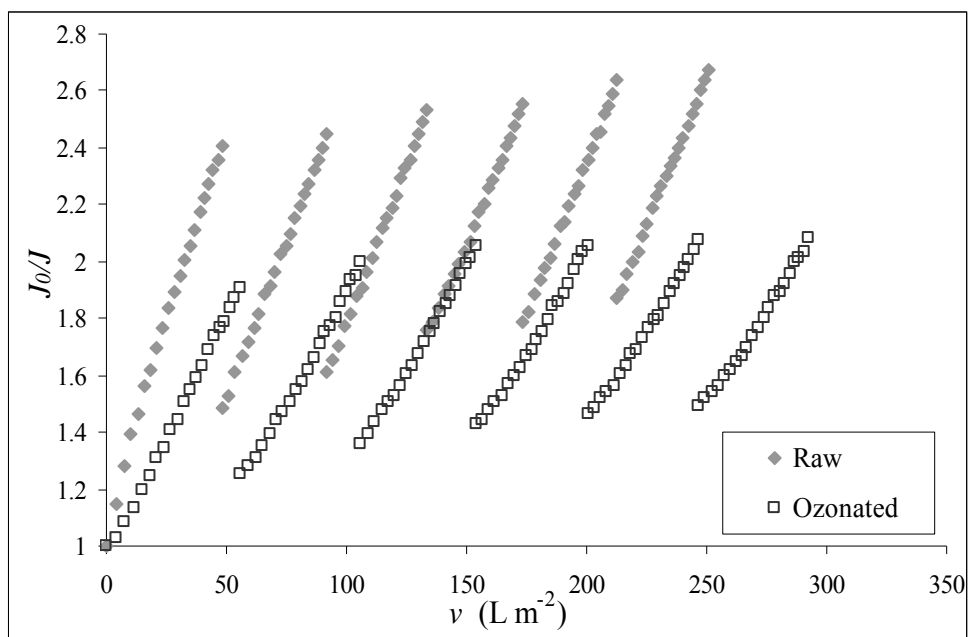


Figure 6.9. Effect of ozonation on permeate flux of the HFK-141 membrane in multi-cycle filtration

(Samples collected on 24 April 2009, their characteristics are shown in Appendix D)

6.5. Potential effect of ozonation and BAC filtration on biofouling propensity of downstream membranes

Ozonation of the raw AS effluent increased the concentrations of low MW organics (building blocks, low MW acids, and low MW neutrals) (Table 6.3). If MF or UF is used to directly treat the ozonated effluent, this could facilitate bacterial growth in the membrane unit and accelerate membrane biofouling, particularly when complete disinfection by ozonation is not achieved (Miettinen *et al.* 1998). Furthermore, the membranes retained a lower amount of biopolymers in the ozonated effluent than in the raw effluent and were not able to retain the low MW compounds (Table 6.3). Thus, ozonation caused increases in the concentrations of potentially biodegradable organic materials in the permeate, which would increase the risk of biofouling of downstream RO membranes if RO is used to further treat this permeate. The addition of the BAC filter downstream of the ozonation process potentially reduced the risk of biofouling since the filter removed the majority of the low MW organic compounds generated during ozonation (Table 6.3). However, the concentrations of biopolymers and building blocks in the permeate from the BAC filtrate were still higher than those in the permeate from the raw AS effluent (Table 6.3). Overall,

ozonation of the raw AS effluent improved the MF and UF flux but increased the risk of biofouling of these membranes and further membranes downstream. BAC filtration of the ozonated effluent reduced but did not completely eliminate this risk.

Chapter 6 Summary

The effect of ozonation and ozonation followed by BAC filtration on the characteristics and MF and UF filterability of the raw AS effluent was investigated. Ozonation at a dose of 10 mg O₃ L⁻¹ led to a 75–80% reduction in the true colour of the raw AS effluent, which was attributed to the oxidation of HS, the main chromophores. Rapid fractionation showed that after ozonation some of the VHA material in the raw effluent was converted to SHA, CHA, and possibly NEU compounds. Some additional NEU material in the ozonated AS effluent probably originated from the breakdown of high MW colloidal organic matter and micro-organisms. BAC filtration removed some of the VHA and CHA fractions from the ozonated effluent, and lowered the turbidity of the effluent to less than 1.0 NTU.

LC-OCD analysis showed that ozonation caused the oxidation of a small proportion of HS in the raw effluent to building blocks, low MW acids, and low MW neutrals. Some of these oxidation products and a small amount of the oxidised HS were then utilised by the micro-organisms on the filter media during BAC filtration.

Similar to the raw AS effluent, biopolymers and HS were the major membrane foulants in MF and UF of the ozonated effluent and the BAC filtrate. Ozonation improved the MF and UF permeate flux by breaking down a proportion of the membrane foulants to compounds with lower MW and hydrophobicity. BAC filtration of the ozonated effluent removed the majority of the particles larger than 0.5 µm and therefore led to further flux improvement in MF and in UF with the 100 kDa membrane (HFM-180). However, BAC filtration did not further improve the flux through the tighter UF membrane (HFK-141, 30 kDa). The UMFI for total fouling was used to quantitatively evaluate the effectiveness of ozonation and BMF on UF flux. The hydraulically irreversible fouling of the membranes was reduced after ozonation while subsequent BAC filtration did not affect this type of fouling. The reduction in hydraulically irreversible fouling by ozonation was significantly greater for the less hydrophobic MF (VVLP) membrane than the more hydrophobic counterpart (XUNP-003).

As ozonation of the raw AS effluent generated low MW organic components (i.e., building blocks, low MW acids and low MW neutrals), this pre-treatment may accelerate biofouling of the MF and UF membranes and further downstream membranes. The addition of the BAC filter downstream of the ozonation process showed potential to reduce the risk of biofouling since the filter removed a significant proportion of the low MW organic compounds generated during ozonation.

CHAPTER 7. EFFECT OF ADSORPTION PRE-TREATMENTS WITH A POWDERED ACTIVATED CARBON AND AN ANION EXCHANGE RESIN ON MEMBRANE FOULING

As mentioned in Chapter 2, the yellow colour of the raw AS effluent is an ongoing issue which potentially limits customers' willingness to purchase the treated effluent for reuse purposes. The fact that the colour-bearing compounds in the raw effluent were isolated in the VHA and SHA fractions (Chapter 6), which is known to contain mainly HS (Croué 1999), indicated that adsorption pre-treatment with appropriate AERs or PAC may help to address this problem. PAC adsorption has long been used for the removal of HS (Summers & Roberts 1988b). HS molecules are aromatic compounds carrying negative charges at neutral pH and were therefore expected to undergo anion exchange with AERs (Bolto *et al.* 2002).

A commercial AER and a PAC product capable of achieving the colour removal target (75–80%) were found. They were selected for their ready availability in Victoria (Australia) and the fact that they have been used for water and wastewater treatment for many years. The effect of adsorption pre-treatment with the PAC (Acticarb PS1300, Activated Carbon Technologies) and the AER (at the doses which gave 75–80% colour reduction) on membrane fouling was investigated and the results are presented in this chapter. The hydrophobic PVDF MF (XUNP-003, 0.1 μm) and UF (HFM-180, 100 kDa) membranes and the slightly hydrophilic PES UF (HFK-141, 30 kDa) membrane were used in this study. A direct comparison between ozonation and these adsorption pre-treatments is provided which may be useful for other WWTPs which are facing similar colour issues.

7.1. Effect of adsorption pre-treatments on raw effluent characteristics

As seen in Table 7.1, the 80% colour removal target was achieved by treating the raw AS effluent with ozone at 10 mg L⁻¹, the AER at 10 mL L⁻¹ or the PAC at 150 mg L⁻¹. However, different from ozonation, which caused a small increase in the DOC concentration of the effluent, adsorption with the PAC and the AER removed approximately 57% and 37%, respectively, of the DOC from the raw AS effluent, respectively. Also, the reduction in the UVA₂₅₄ after ozonation (42%) was significantly lower than after adsorption with the PAC (74%) and the AER (63%).

Table 7.1. Effect of ozonation and adsorption pre-treatment with the AER and the PAC on the characteristics of the raw effluent

(Samples collected on 08 July 2011)

Parameter	Raw	Raw + 10 mL AER L ⁻¹	Raw + 150 mg PAC L ⁻¹	Ozonated (Raw + 10 mg O ₃ L ⁻¹)
pH	7.8	7.7	7.8	7.7
DOC (mg L ⁻¹)	15.1	9.5	6.5	15.6
UVA ₂₅₄ (cm ⁻¹)	0.389	0.144	0.10	0.227
SUVA (m ⁻¹ mg ⁻¹ L)	2.58	1.52	1.54	1.46
True colour (Pt-Co units)	100	22	21	22
Turbidity (NTU)	1.9	N/M*	N/M*	1.8

* Not measured

7.2. Effect of adsorption pre-treatments on AMWD of the raw effluent

The LC-OCD chromatograms of the raw and pre-treated AS effluent samples (Figure 7.1) provided insights into the effects of the pre-treatments on the dissolved EfOM. The DOC concentrations of the different organic components, calculated by integrating the areas under the peaks, are shown in Table 7.2.

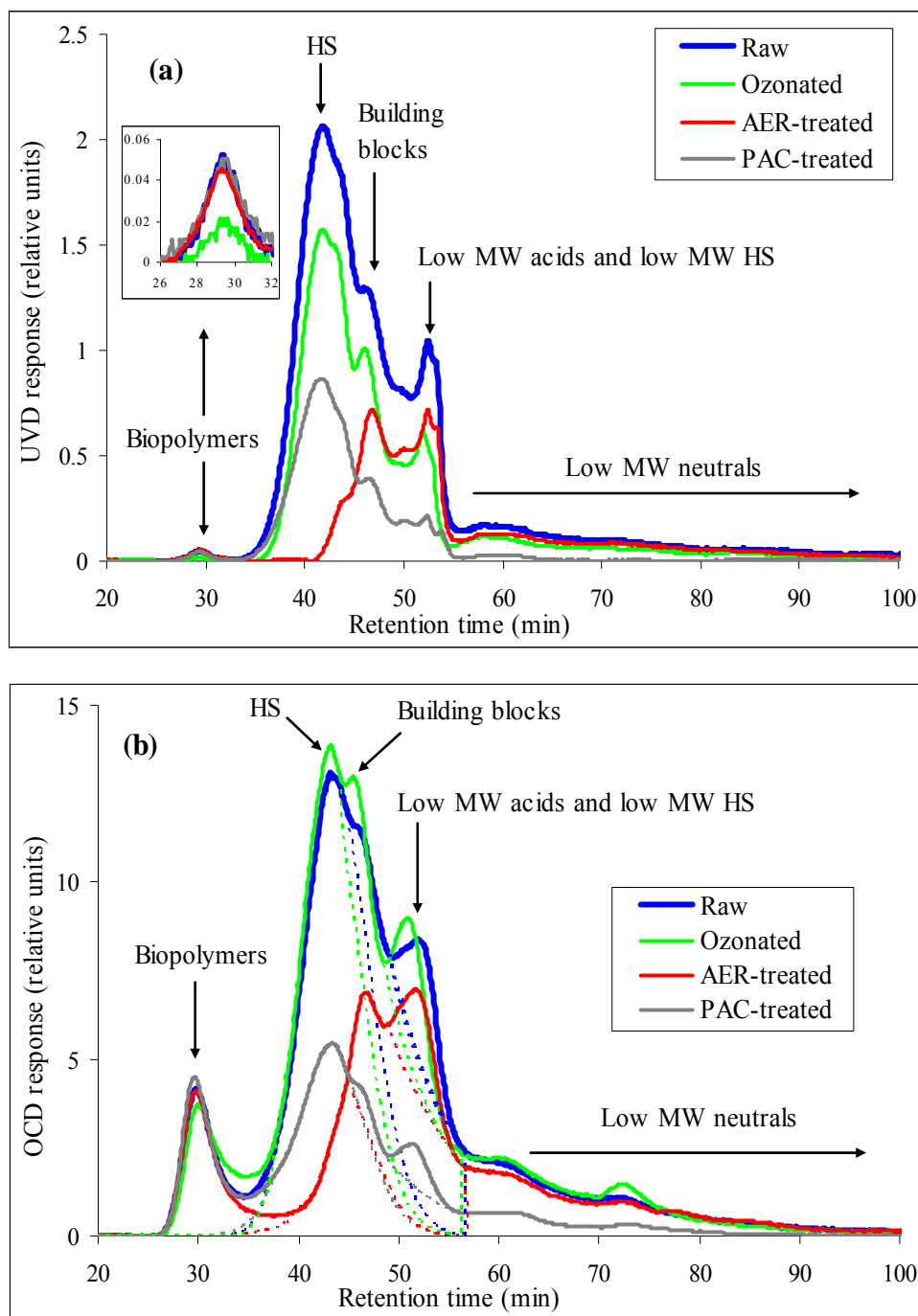


Figure 7.1. AMWDs of the raw, ozonated, AER-treated, and PAC-treated effluents

(a) UVD response, (b) OCD response

(The dotted lines define the areas under the peaks)

(Samples collected on 08 July 2011)

Table 7.2. Effect of ozonation and the adsorption pre-treatments with and without MF on the concentrations of dissolved EfOM components (in mg C L⁻¹) as determined by LC-OCD

Sample	Biopolymers	HS	Building blocks	Low MW acids	Low MW neutrals
Raw	1.3	8.0	2.4	0.0	2.2
Ozonated	1.4	7.6	2.7	0.2	2.4
AER-treated	1.3	2.5	2.4	0.0	2.2
PAC-treated	1.3	3.6	0.7	0.0	0.8
Raw + XUNP-003	0.2	7.0	2.2	0.0	2.2
Ozonated + XUNP-003	0.7	7.2	2.7	0.2	2.3
AER-treated + XUNP-003	0.3	2.0	2.3	0.0	2.2
PAC-treated + XUNP-003	0.2	2.8	0.7	0.0	0.8

The data in Figure 7.1 and Table 7.2 showed that the EfOM components adsorbed on the PAC included HS, building blocks, and low MW neutrals. The forces keeping the EfOM molecules attached to the PAC may include (Newcombe *et al.* 2008) (i) electrostatic attraction between PAC surface and EfOM, (ii) hydrophobic attraction between graphitic carbon surface and hydrophobic portions of EfOM molecules, (iii) hydrogen bonding between functional groups on EfOM and those on the carbon surface, and (iv) π -interactions between the carbon surface and the aromatic EfOM. The simultaneous operation of these mechanisms, and more importantly, the presence of both mesopores and micropores could be the reasons for the PAC removing not only building blocks and low MW neutrals but also HS. Mesopores (2–50 nm) probably provided adsorption sites for the HS molecules (aquatic fulvic acids generally have an average diameter of 2 nm whereas humic acids are larger molecules (Sutskover-Gutman *et al.* 2010)). This was supported by the fact that at the same dosage and contact time, another PAC product (provided by Tiwest Sales Australia) having a similar surface area (1427 m² g⁻¹), a lower mesopore volume (0.33 cm³ g⁻¹) and a higher micropore volume (0.25 cm³ g⁻¹) than the PAC used in this study (Acticarb PS1300, surface area = 1429 m² g⁻¹, mesopore volume = 0.52 cm³ g⁻¹, micropore volume = 0.15 cm³ g⁻¹) gave only 48% colour removal. Building blocks and low MW neutrals were likely to adsorb in both mesopores and micropores (< 2 nm). Approximately 75% of the building blocks and 65% of low MW neutral compounds in the raw AS effluent were removed by the PAC treatment.

The AER adsorbed a larger proportion of HS than the PAC. However, it was not as effective as the PAC in removing building blocks and low MW neutrals (Figure 7.1 and Table 7.2). The higher selectivity of the AER than the PAC for HS was attributed to the electrostatic attraction between the resin and the negatively charged HS molecules. During the adsorption test, it was noticed that the colour removal of the AER reduced with the passage of increasing volume of the treated sample. The colour of the effluent after the first 100 bed volumes was 8 Pt-Co units whereas after treatment of 1500 bed volumes, the colour of the combined treated effluent was 22 Pt-Co units due to increasing saturation of the adsorption sites with increasing volume.

7.3. Effect of adsorption pre-treatments on membrane fouling

7.3.1. Effect on total fouling

Whole samples and samples pre-filtered through 1.0 μm glass-fibre filters (GF/B, Whatman®) were used in MF and UF experiments to determine if the PAC particles and residual AER particles influenced the membrane flux.

The flux data for the XUNP-003 membrane are shown in Figure 7.2. MF of the whole samples and the 1.0 μm pre-filtered samples gave similar results (Figure 7.2 (b)), indicating that the PAC particles and residual AER particles had little effect on the flux. This was further confirmed by MF of a suspension containing 150 mg PAC per litre of Milli-Q water, which showed no fouling by the PAC particles. Therefore, it can be concluded that the changes in the dissolved EfOM contents resulting from the adsorption pre-treatments did not affect fouling of the membrane.

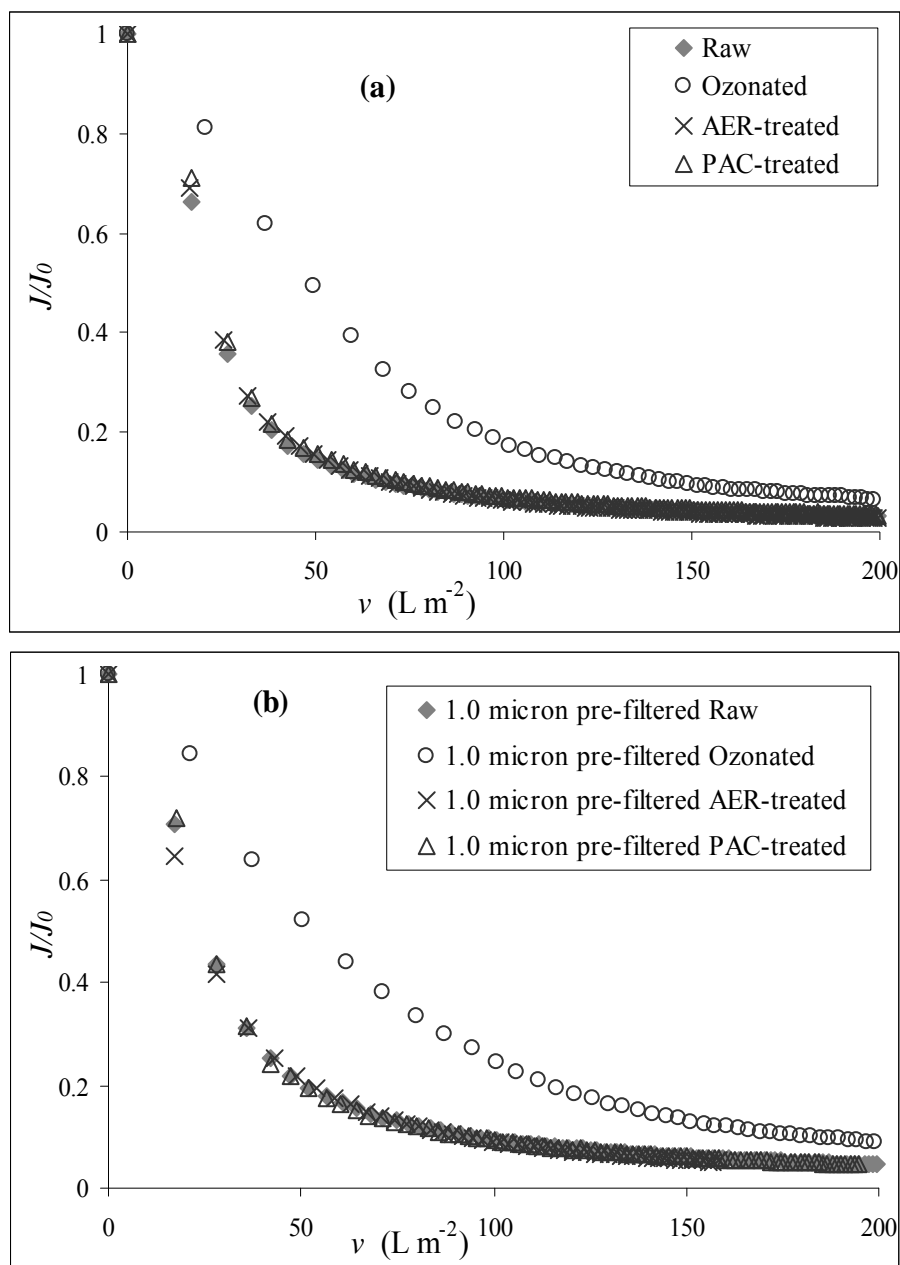


Figure 7.2. Effect of ozonation and adsorption pre-treatments on permeate flux of the XUNP-003 membrane
(a) MF of whole samples and (b) MF of pre-filtered samples
(Samples collected on 08 July 2011)

As seen in Figure 7.2, ozonation significantly improved the membrane flux, whereas pre-treatments with the PAC and the AER neither reduced nor worsened membrane fouling. The flux improvement by ozonation was attributed to the breakdown of proteins, polysaccharides and HS to less hydrophobic and lower MW compounds (as discussed in Chapter 6). The ineffectiveness of the adsorption pre-treatments in fouling mitigation can

be explained by the PAC and AER not removing biopolymers and the HS which contributed to membrane fouling from the raw AS effluent. The reasons for the inability of the PAC to remove biopolymers may include: (i) the preferential adsorption of the HS and the low MW compounds on the PAC led to the saturation of the PAC with these molecules and therefore no adsorption sites were available for the biopolymers and/or (ii) the larger size of the biopolymers molecules than the pores of the PAC. The ineffectiveness of the AER for removing biopolymers was very likely due to their lack of negatively charged functional groups at the sample pH (Humbert *et al.* 2007; Huber *et al.* 2011) as well as the larger size of the biopolymers than the AER pore size (45 nm). Different from this study, a previous study found that some PAC products (used at 50–1000 mg L⁻¹) removed both biopolymers and HS from a secondary effluent (Haberkamp *et al.* 2007).

The biopolymers in the raw, AER-treated, and PAC-treated effluents had similar fouling potentials, as shown by the similar rejections by the membrane (Figure 7.3 and Table 7.2). The membrane retained a lower amount of HS in the AER-treated (0.5 mg C L⁻¹) and PAC-treated (0.8 mg C L⁻¹) effluents than in the raw effluent (1.0 mg C L⁻¹) (Table 7.2), indicating that the HS in the pre-treated effluents probably had a lower fouling potential than the HS in the raw effluent. However, this did not result in any improvement in the MF flux.

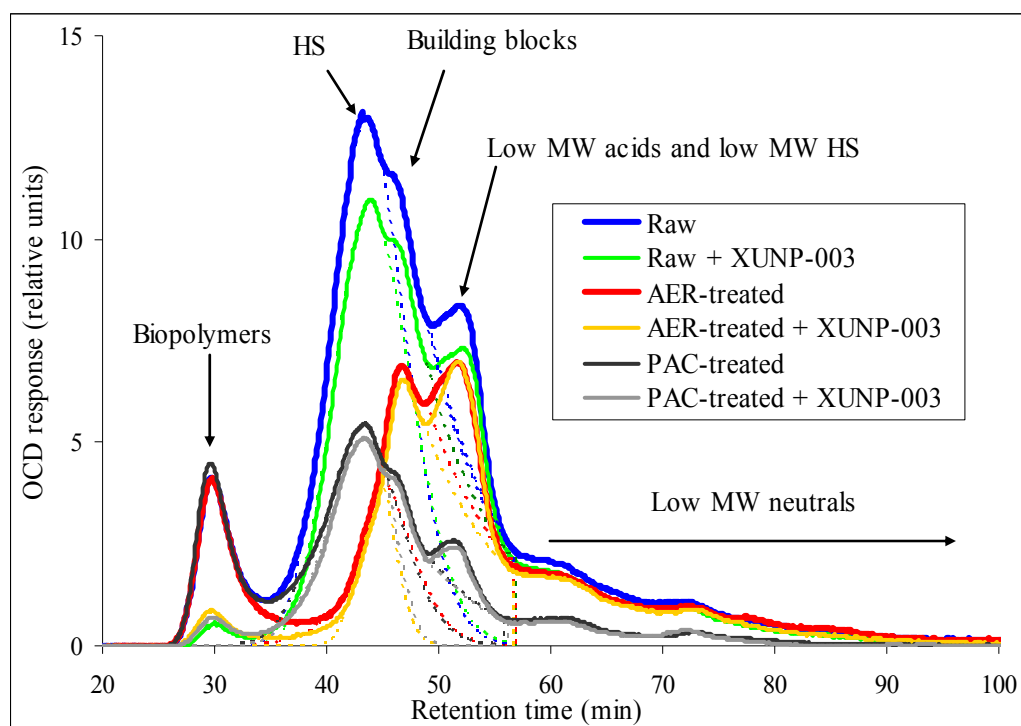


Figure 7.3. Effect of adsorption pre-treatments on the rejection of EfOM components by the XUNP-003 membrane
(Samples collected on 08 July 2011)

On the other hand, although ozonation led to a small increase in the biopolymers concentration (most likely due to the breakdown of microbial cells in the raw effluent), the oxidation of biopolymers and HS led to significant fouling reduction. As seen in Table 7.2, after ozonation the rejection of these compounds by the MF membrane reduced significantly. (For clarity of Figure 7.3, the LC-OCD chromatogram of the permeate from MF of the ozonated effluent, i.e., the sample “Ozonated + XUNP-003” in Table 7.2, is included in Appendix H). Since the removal of a large proportion of the HS (70% by the AER and 55% by the PAC) did not reduce membrane fouling, it can be concluded that although biopolymers comprised a small proportion of the total DOC in the AS effluent, they made a much larger contribution to fouling than did HS. Therefore, pre-treatments for fouling reduction should target the removal of polysaccharides and proteins rather than HS.

Experiments with the HFM-180 and HFK-141 UF membranes gave similar flux results, i.e., the adsorption pre-treatments did not affect the permeate flux (Figures 7.4 and 7.5).

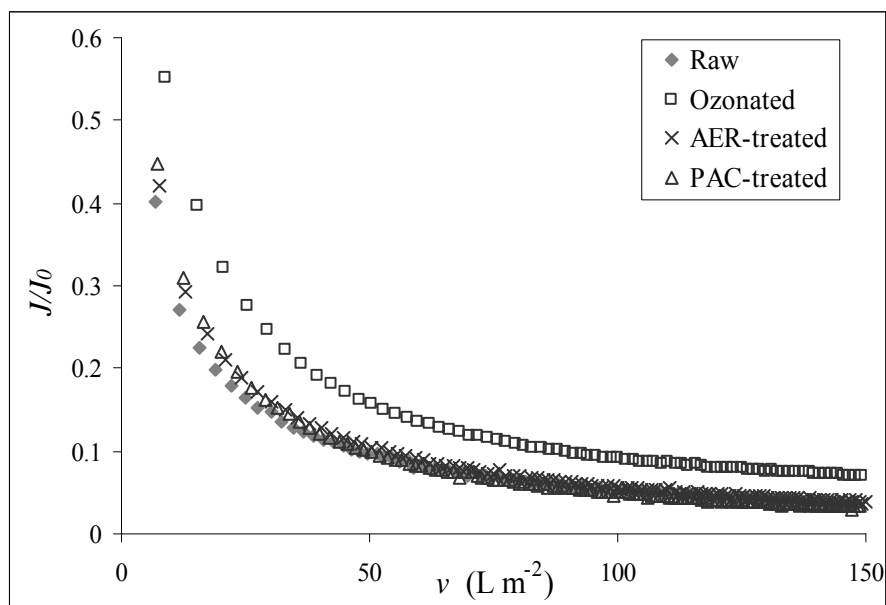


Figure 7.4. Flux data for UF of the raw, ozonated, AER-treated, and PAC-treated effluent samples with the HFM-180 membrane (Samples collected on 01 April 2011, their characteristics are shown in Appendix I)

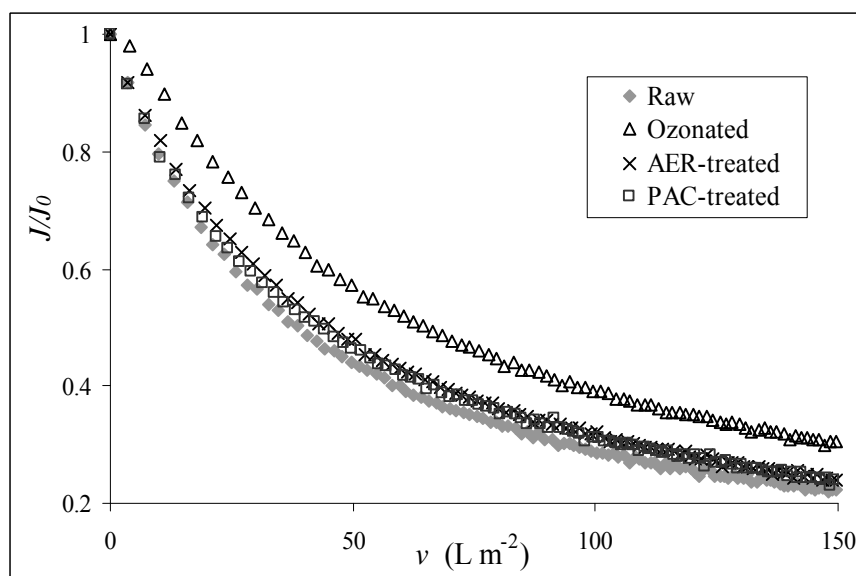


Figure 7.5. Flux data for UF of the raw, ozonated, AER-treated, and PAC-treated effluent samples with the HFK-141 membrane (Samples collected on 08 July 2011)

7.3.2. Effect on hydraulically irreversible fouling

The resistances by total fouling (R_{tf}) and hydraulically irreversible fouling (R_{if}) were calculated for the samples in Figures 7.2, 7.3 and 7.5 and the results are presented in Table 7.3. As expected, the adsorption pre-treatments did not affect the irreversible fouling of the membranes.

Table 7.3. Effect of adsorption pre-treatments and ozonation on resistance by total fouling and resistance by hydraulically irreversible fouling

Case	R_{tf}^* ($\times 10^{-10} \text{ m}^{-1}$)	R_{if}^* ($\times 10^{-10} \text{ m}^{-1}$)
Raw + XUNP-003	516	36.0
AER-treated + XUNP-003	510	36.9
PAC-treated + XUNP-003	543	37.4
Ozonated + XUNP-003	342	27.1
Raw + HFM-180	664	54.5
PAC-treated + HFM-180	641	52.8
AER-treated + HFM-180	646	55.1
Ozonated + HFM-180	534	35.9
Raw + HFK-141	576	89.8
AER-treated + HFK-141	558	83.5
PAC-treated + HFK-141	562	86.9
Ozonated + HFK-141	391	66.9

*Calculated for $v = 200 \text{ L m}^{-2}$ (MF) and $v = 150 \text{ L m}^{-2}$ (UF)

The flux data obtained from multi-cycle MF of the raw, PAC-treated, and AER-treated samples with the XUNP-003 membrane are shown in Figure 7.6. The results show that the pre-treatments did not affect the permeate flux of the virgin membrane or the hydraulically backwashed membrane.

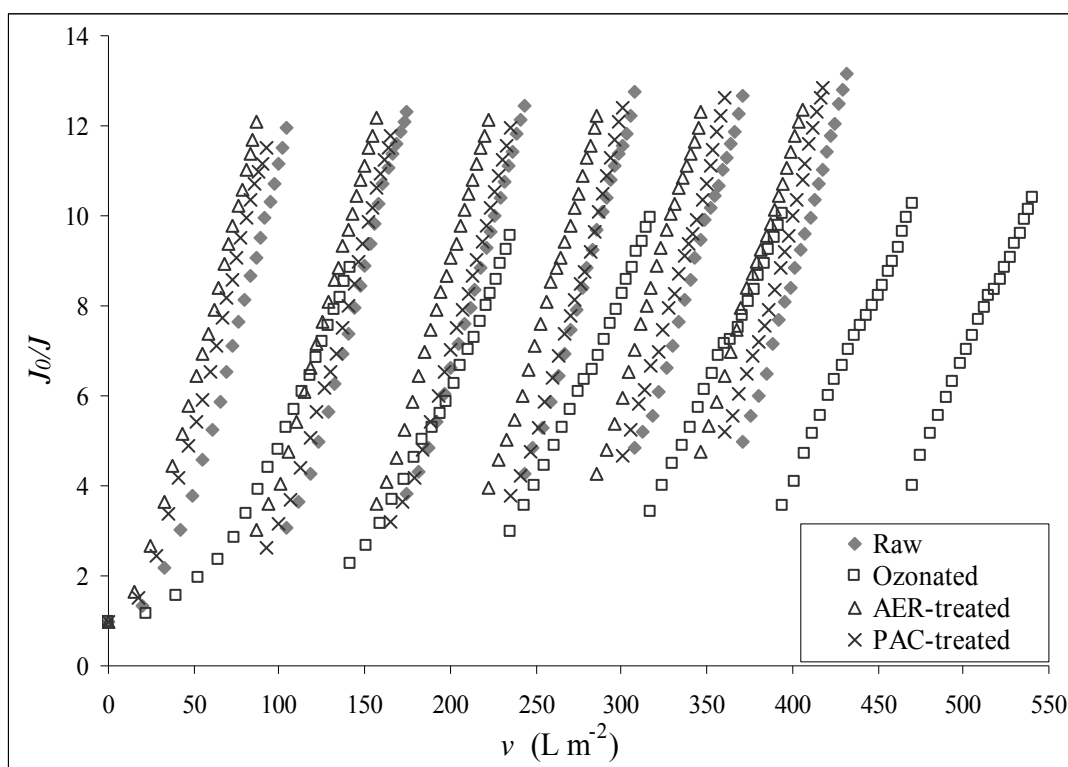


Figure 7.6. Flux data for multi-cycle MF of the raw, PAC-treated and AER-treated effluents with the XUNP-003 membrane
(Samples collected on 08 July 2011)

In terms of biofouling, since PAC adsorption removed a significant proportion of building blocks and low MW neutrals from the raw AS effluent (Table 7.2), this pre-treatment may reduce membrane biofouling. The pre-treatment with the AER probably would not affect membrane biofouling propensity as it was ineffective in removing these low MW compounds.

7.4. Practicability considerations of the adsorption pre-treatments in comparison with ozonation

Of the three pre-treatments investigated for colour removal, ozonation is the only method that produces no waste stream. Although this method involves the use of the toxic gas ozone, it is a safe and practical method with the current technologies. The adsorption methods, while utilising non-toxic materials, have the disadvantage of producing waste streams, which need further treatments before disposal.

For the AER, the spent resin needs to be regenerated, normally with brine. This process produces a waste stream with very high salinity, DOC concentration, and true colour (Bolto *et al.* 2002). NF or RO can be used to separate the brine from the EfOM and the brine can be reused for resin regeneration. The NF or RO retentate, which would contain the concentrated EfOM and probably elevated concentrations of toxic and/or bioaccumulative organic substances (such as pharmaceuticals and personal care products), would need further treatment before it can be disposed of to the environment. These further treatments add to the technical complexity, and therefore the cost may be greater.

For PAC adsorption, the PAC particles in the treated effluent may be allowed to settle in the adsorption tank prior to MF/UF. It is also possible to run MF or UF of the pre-treated effluent without prior removal of the PAC, most likely in the submerged membrane configuration (Khirani *et al.* 2006b). The spent PAC will need to be collected for reuse, regeneration or disposal. However, because its colour removal capacity will decrease after successive cycles, fresh PAC must be added to maintain the colour removal target. In addition, PAC can be a health and safety concern (although problems in handling PAC can be avoided by using the granular version of the same activated carbon). It should be pointed out that the PAC dose required for the colour removal target in this study was very high compared with typical dosages for the removal of micropollutants from water (less than 30 mg PAC L⁻¹ (Newcombe *et al.* 2008)).

The main advantage of the adsorption pre-treatments was their high DOC removals and therefore production MF and UF permeates with low DOC concentrations. Prior to being discharged for reuse, the permeates would be disinfected, normally by chlorination, and a low EfOM concentration would likely result in low concentrations of disinfection by-products (DBPs) in the product water (Reckhow *et al.* 1990; Singer 1999; Liang & Singer 2003). Ozonation pre-treatment may have both beneficial and adverse effects on the formation of DBPs. Ozonation has been found to reduce the total organic halide formation potential during the chlorination of municipal wastewater (Wert *et al.* 2007). However, this pre-treatment may lead to the formation of bromate (a suspected carcinogen), N-nitrosodimethylamine (NDMA, a carcinogenic, mutagenic and clastogenic chemical) (Hollender *et al.* 2009), and other potentially toxic oxidation by-products (Wert *et al.* 2007). Despite of this complication, the advantage (if there is any) of the adsorption pre-treatments over the ozonation pre-treatment in terms of reducing DBPs formation is of

minor significance in the current context, as the DBPs formation during chlorination of municipal wastewater has been found very low and the parameter is currently not a requirement for “Class A” recycled water, which is only used non-potable purposes (EPA Victoria 2002).

AERs have been used widely in surface water treatment for the removal of NOM (Ødegaard *et al.* 1999). The installation cost for adsorption pre-treatment with AERs is relatively low and operation is simple (Hongve *et al.* 1999). Similarly, PAC adsorption systems are relatively inexpensive to build. However, prolonged use of PAC at high doses can be very uneconomical due to the need for replacing the spent PAC (Newcombe *et al.* 2008). The capital investment for ozonation systems is probably higher than that for the adsorption processes (Oneby *et al.* 2010). However, the elimination of the need for replacing the spent PAC or treating the AER concentrate makes it a more attractive and probably a less expensive pre-treatment option. Furthermore, ozonation also provides the disinfection effect which cannot be achieved with the adsorption pre-treatments.

Overall, for the AS effluent investigated, ozonation is the best pre-treatment for colour removal, as it keeps the whole treatment process simple while reducing membrane fouling.

Chapter 7 Summary

The effect of adsorption pre-treatments for colour removal on membrane fouling in MF and UF of the AS effluent was investigated in comparison with ozonation. It was found that like ozonation (10 mg O₃ L⁻¹, 10-minute contact time), a colour removal of 75–80% was also achieved with adsorption pre-treatment with the AER (10 mL L⁻¹, 20-minute contact time, 1 BV of the AER treated 1500 BVs of the raw effluent) or the PAC (Acticarb PS1300, 150 mg L⁻¹, 30-minute contact time). Of these, ozonation was the only method which reduced membrane fouling. The reduction in fouling resulted from the breakdown in the molecular structures of the membrane foulants (i.e., biopolymers and HS). Pre-treatments with the PAC and the AER neither reduced nor increased fouling, as the components of the EfOM removed by the PAC and the AER did not make significant contributions to membrane fouling. As ozonation generated some building blocks, low MW acids and low MW neutrals, it may increase the risk of membrane biofouling. As mentioned in Chapter 6, BAC filtration of the ozonated effluent showed potential to alleviate this problem. Adsorption

pre-treatment with the PAC may reduce biofouling as the PAC removed a significant proportion of the building blocks and low MW neutrals from the raw effluent. Advantages and disadvantages of the three pre-treatments in terms of practicability were also discussed.

CHAPTER 8. CHEMICAL CLEANING OF FOULED UF POLYMERIC MEMBRANES

Although feed pre-treatments can reduce fouling and periodic membrane backwashing can significantly recover the flux by displacing some foulants, the accumulation of hydraulically irreversible foulants over long-term runs requires chemical cleaning of membranes to maintain their flux performance. This chapter investigates the ability of different cleaning agents to restore the performance of the 50 kDa PVDF membrane (HFM-116) fouled by the raw AS effluent. Analyses of the fouled, backwashed, and chemically cleaned membranes with FTIR spectroscopy and SEM/EDX spectroscopy provided insights to the differences in the cleaning efficiency of the chemicals. The HFM-116 membrane was selected for this study for its high retention of biopolymers and HS, which facilitated the tracking of these compounds on the membrane during the fouling and cleaning processes using FTIR spectroscopy and SEM/EDX spectroscopy. The membrane cleaners investigated included an acid (HCl), a base (NaOH), a chelating agent (Na₄EDTA), two oxidising agents (NaOCl and H₂O₂), a surfactant (sodium dodecyl sulphate), and a protease-based cleaner (Terg-a-zyme). The three most effective cleaners for the HFM-116 membrane were also tested on the 30 kDa PES membrane (HFK-141).

8.1. Removal of foulants by backwashing

As shown in Chapter 4, backwashing removed some proteins and polysaccharides retained by the fouled membranes, which could be attributed to these high MW compounds being larger than the membrane pores and forming a cake layer on the membrane surface. However, backwashing was not effective in displacing HS from the membranes, suggesting that HS adhered to the membrane surface and/or pore walls through strong hydrophobic attraction.

8.2. Cleaning efficiencies of different chemicals

The membrane fouling and cleaning procedures are described in Chapter 3 (section 3.6). Briefly, filtration of the raw AS effluent (collected on 19 February 2010, its characteristics are shown in Table 8.1) was conducted at 110 kPa using samples of the virgin HMF-116 membrane. The filtration was stopped when the accumulated specific permeate volume (v) reached 150 L m⁻² (which took approximately 150 minutes). The fouled membranes were

backwashed with the permeate at 110 kPa for 5 minutes and their pure water flux was measured with Milli-Q water. The backwashed membranes were then soaked in solutions of the cleaning agents (with gentle shaking in an orbital shaker at 100 rpm) at 24 °C for 45 minutes. The pure water flux of the chemically cleaned membrane was determined after rinsing them thoroughly with Milli-Q water.

Table 8.1. Characteristics of the raw effluent sample used in the membrane cleaning experiments

Parameter	Value
pH	7.8
DOC (mg L ⁻¹)	13.2
UVA ₂₅₄ (cm ⁻¹)	0.402
SUVA (m ⁻¹ mg ⁻¹ L)	3.04
True colour (Pt-Co units)	113
Turbidity (NTU)	3.5

The cleaning efficiencies (E_{RW}) of the chemicals for the fouled HFM-116 membrane are shown in Figure 8.1 (sample calculations of E_{RW} are given in Appendix C). The E_{RW} of NaOH was low, indicating that its hydrolytic effect (on polysaccharides and proteins) and solubilisation effect (on HS) (Liu *et al.* 2001) was not sufficient for effective foulant removal. HCl gave an E_{RW} of 9% for the HFM-116 membrane, which was attributed to the mild oxidation of some proteins and polysaccharides (Liu *et al.* 2001).

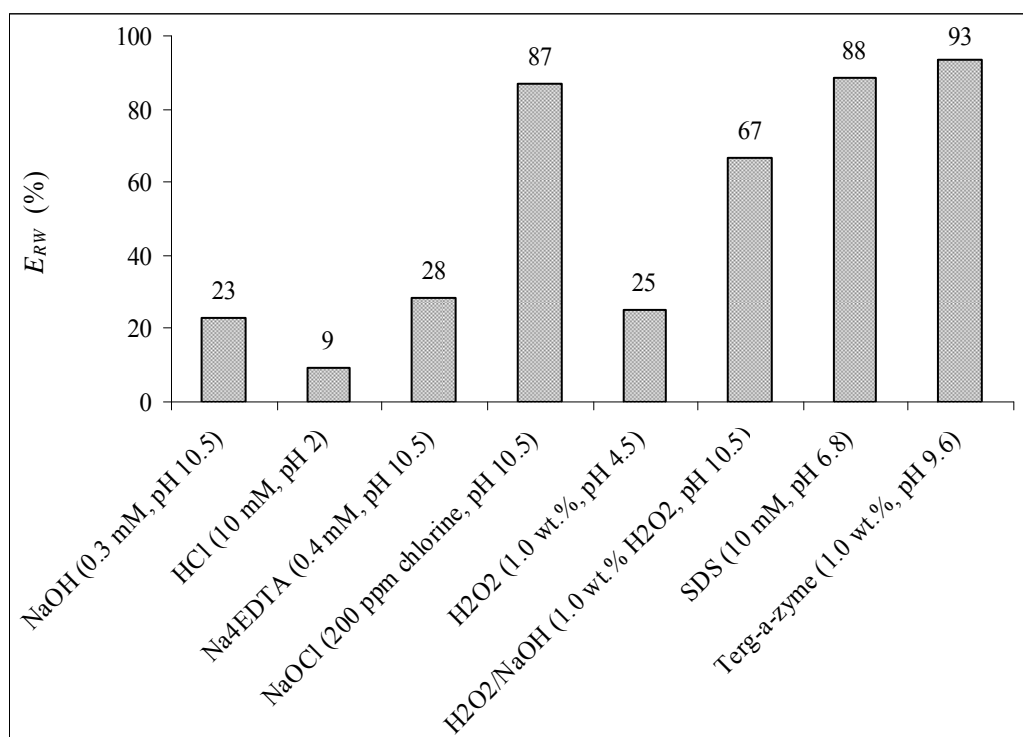


Figure 8.1. Cleaning efficiencies (E_{RW}) of different cleaners on the fouled HFM-116 membrane

The higher cleaning efficiency of the chelating agent Na₄EDTA than NaOH (both at pH 10.5) indicated that some of the HS remaining on the membrane after backwashing was probably in the form of humic-calcium complexes and Na₄EDTA recovered the membrane flux by simultaneously removing calcium from these complexes (through ligand exchange) (Hong & Elimelech 1997) and dissolving the foulants.

NaOCl and H₂O₂ are both oxidising agents which are believed to remove membrane foulants by oxidation reactions (Liu *et al.* 2001; Laabs *et al.* 2006; Porcelli & Judd 2010). Oxidation breaks down functional groups of organic foulants to carboxyl, ketonic, and aldehyde groups, making the foulants more susceptible to hydrolysis at high pH. As a result of these reactions, the foulants become water soluble and detach from the membrane. In this study H₂O₂ gave a much lower E_{RW} than NaOCl, although its concentration (10,000 ppm or 294 mM) was much higher than that of NaOCl (200 ppm chlorine or 5.6 mM). Since the E_{RW} of the H₂O₂/NaOH mixture (pH 10.5) was higher than the E_{RW} of H₂O₂ and NaOH (Figure 8.1), the low efficacy of H₂O₂ may be attributed to the acidic nature of this chemical. Chlorine may also have caused swelling of membranes, which increased the mass

transfer of the cleaning agent to the membrane surface (Zeman & Zydney 1996), resulting in a higher E_{RW} for NaOCl. Membrane cleaning with NaOCl and H_2O_2 was also conducted at 40°C and the E_{RW} of NaOCl and H_2O_2 at this temperature was 98% and 77%, respectively. Thus the higher temperature improved cleaning efficiency and NaOCl was a better cleaning agent overall. On the other hand, Arnal *et al.* (2009) found that NaOCl performed better than H_2O_2 at 25°C, but the reverse happened at 40°C when cleaning a polysulfone UF membrane fouled by a surface water. It should be noted that although the oxidative power of H_2O_2 is typically greater than that of OCI^- , exceptions have been observed, depending on the characteristics of the solution and the compounds to be oxidised (Crittenden *et al.* 2006).

SDS and Terg-a-zyme were the two most effective cleaning agents. The high E_{RW} of SDS confirmed that hydrophobic attraction was the major force keeping the hydraulically irreversible foulants and the membrane together. It is generally understood that during membrane cleaning with SDS that the hydrophobic tails of the surfactant molecules adsorb to the foulant molecules and their hydrophilic heads are orientated towards the aqueous phase (Gecol 2006). This reduces the hydrophobicity of the foulants and they are solubilised into the aqueous phase. At SDS concentrations higher than the critical micelle concentration (8.36 mM in deionised water at 20°C (Li & Elimelech 2004)), as in this study, micelles also form in the cleaning solution. These micelles diffuse into the fouling layer, dissociate and adsorb as monomers on the foulant molecules and enhance foulant solubilisation (Li & Elimelech 2004). The fact that the SDS solution and Terg-a-zyme solution turned yellow during the membrane cleaning experiment confirmed that HS played a role in causing hydraulically irreversible fouling.

Terg-a-zyme is a blend of the anionic surfactant sodium dodecyl benzene sulphonate (SDBS, 10–20 wt.%) and a protease enzyme (*Bacillus licheniformis* Subtilisin Carlsberg) (Alconox 2006, 2011). At the Terg-a-zyme concentration used in this study (1.0 wt.%), the SDBS concentration was between 2.9 and 5.7 mM, much higher than the critical micelle concentration of SDBS (approximately 0.5 mM in deionised water at 24 °C (Weiss *et al.* 2007)). Therefore, the mechanism of foulant removal by SDBS was expected to be similar to that of SDS (as described above). The higher E_{RW} of Terg-a-zyme than SDS may be due to the higher pH (which facilitated the dissolution of the foulants (Liu *et al.* 2001)) and/or

the surfactant and the enzyme acting together to solubilise the foulants. The enzyme may have broken down some of the protein foulants, making them soluble in the cleaning solution and/or more readily solubilised by the surfactant.

NaOCl, SDS, and Terg-a-zyme also showed high cleaning efficiencies for the fouled HFK-141 membrane. The values of E_{RW} of these cleaners were 96%, 103%, and 108%, respectively. The increases in the pure water flux of the membrane after cleaning with SDS and Terg-a-zyme can be attributed to these chemicals clearing the pores of materials that were left from the membrane manufacturing process and were not removed by cleaning with Milli-Q water (Nyström & Zhu 1997). The material was probably polyvinyl pyrrolidone (PVP), which has been used widely in the initial casting of PES membranes as a pore forming agent and a hydrophilising agent (Arkhangelski *et al.* 2007). It is very likely that PVP was used in manufacturing the HFK-141 membrane, as the membrane was more hydrophilic (contact angle = $41 \pm 2^\circ$ (Table 3.4)) than non-modified PES (contact angle $\approx 60^\circ$ (Cheryan 1986)). It was also possible that the adsorption of the surfactants made the membrane become more hydrophilic and therefore had a slightly higher pure water flux compared with the virgin membrane (Nyström & Zhu 1997). These hypotheses were supported by the fact that cleaning the virgin HFK-141 membrane with SDS and Terg-a-zyme increased the pure water flux of the membrane by approximately 5%. The possibility of SDS or Terg-a-zyme causing damage of the membrane was low, since the pHs of these cleaners (pH 6.8 for SDS and pH 9.6 for Terg-a-zyme) were within the pH limit of the membrane (pH 2.0–11.0), and virgin membranes were used in the tests. Furthermore, the concentrations of the cleaners investigated (10 mM SDS and 1.0 wt.% Terg-a-zyme) were those commonly used in practice (Alconox 2006; Al-Amoudi & Lovitt 2007).

From economic and practical viewpoints, NaOCl is superior to SDS and Terg-a-zyme since it is less expensive and does not create foams like the other two. However, the use of SDS or Terg-a-zyme may reduce the risk of membrane degradation caused by NaOCl in long-term use.

Three fouling and cleaning cycles were also conducted on the HFM-116 membrane with the three most effective cleaners and accumulation of residual fouling was observed (Figure 8.2).

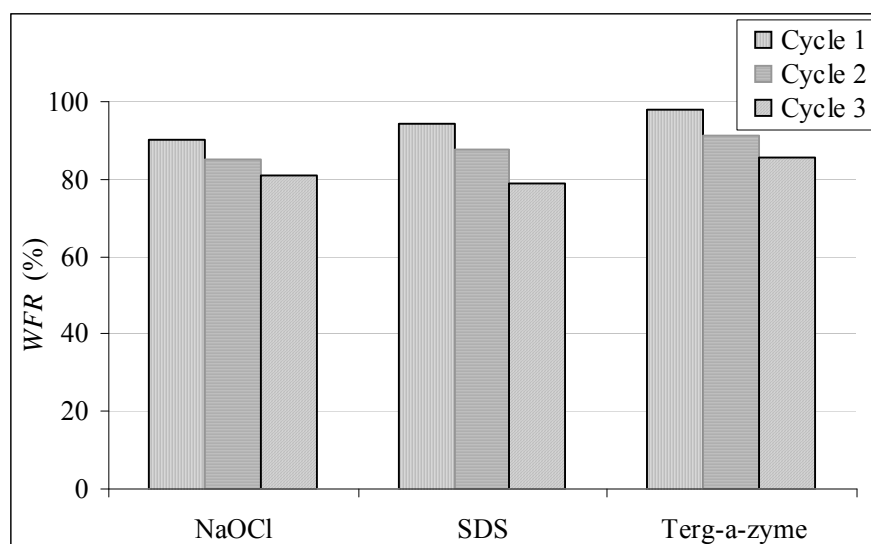


Figure 8.2. Changes in *WFR* of NaOCl, SDS, and Terg-a-zyme over three UF cycles with the HFM-116 membrane

Although this did not appear to affect the permeate flux in UF of the AS effluent in the first three filtration cycles (Figure 8.3, data for SDS and Terg-a-zyme are included in Appendix J), it can be inferred that such a reduction in the permeate flux would occur in long-term operation and therefore cleaning-in-place (CIP) with longer soaking time and/or higher cleaning agent concentrations would be needed. Elevated temperature (within manufacturer's specifications) may also be used to increase the cleaning efficiency and reduce the cleaning time. The rejections of DOC and UV-absorbance (UVA_{254}) of the virgin membranes and the chemically cleaned membranes were comparable (Table 8.2), indicating that high flux recoveries were not associated with degradation of the membranes over the 3 chemical cleaning cycles.

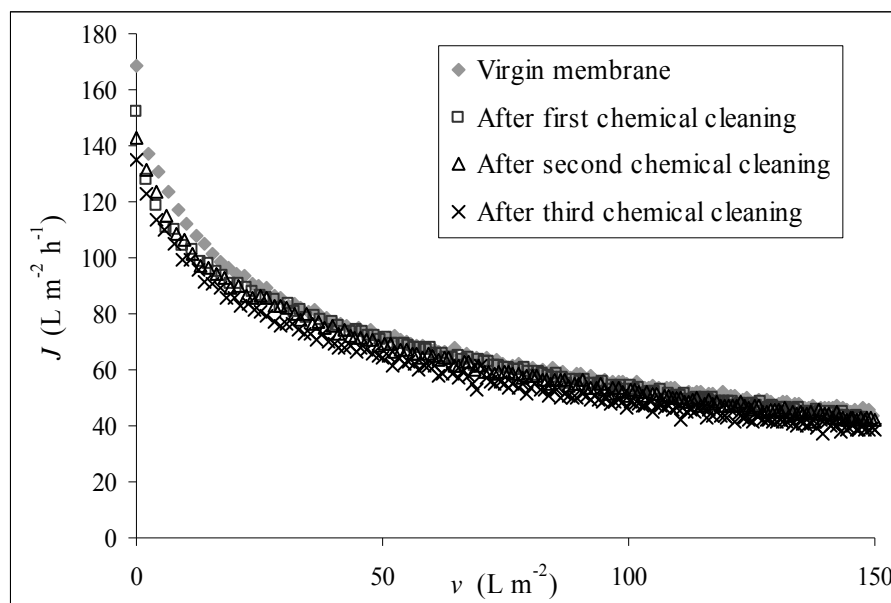


Figure 8.3. Effect of cyclic cleaning with Terg-a-zyne on the permeate flux in UF of the raw effluent with the HFM-116 membrane

Table 8.2. Effect of chemical cleaning with NaOCl, SDS, and Terg-a-zyne on the rejection of DOC and UV-absorbance of the HFM-116 membrane
(Feed: DOC = 13.2 mg L⁻¹ and UVA₂₅₄ = 0.402 cm⁻¹)

Permeate from UF with	Virgin membrane		Membrane after first chemical cleaning		Membrane after second chemical cleaning		Membrane after third chemical cleaning	
	DOC (mg L ⁻¹)	UVA ₂₅₄ (cm ⁻¹)	DOC (mg L ⁻¹)	UVA ₂₅₄ (cm ⁻¹)	DOC (mg L ⁻¹)	UVA ₂₅₄ (cm ⁻¹)	DOC (mg L ⁻¹)	UVA ₂₅₄ (cm ⁻¹)
NaOCl	10.7	0.317	10.9	0.322	10.8	0.320	10.7	0.319
SDS	10.7	0.314	10.5	0.311	10.5	0.312	10.5	0.310
Terg-a-zyne	10.8	0.321	10.9	0.325	10.8	0.324	10.9	0.327

8.3. Membrane cleanliness shown by ATR-FTIR spectroscopy and EDX spectroscopy

Backwashing removed most of the foulants on the surface of the HFM-116 membrane, leaving only traces of polysaccharides and proteins (Figure 8.4, peaks at 1640 cm⁻¹ and 3000–3650 cm⁻¹). Although the cleaning efficiencies of the chemicals investigated covered a wide range (from 9% for HCl to more than 85% for NaOCl, SDS and Terg-a-zyne), the FTIR spectra of the chemically cleaned membranes were very similar to the spectrum of the virgin membrane. The results showed that FTIR spectroscopy was a useful tool for the

identification of organic foulants on the membrane surface but could not be used to differentiate between the virgin and the cleaned membranes.

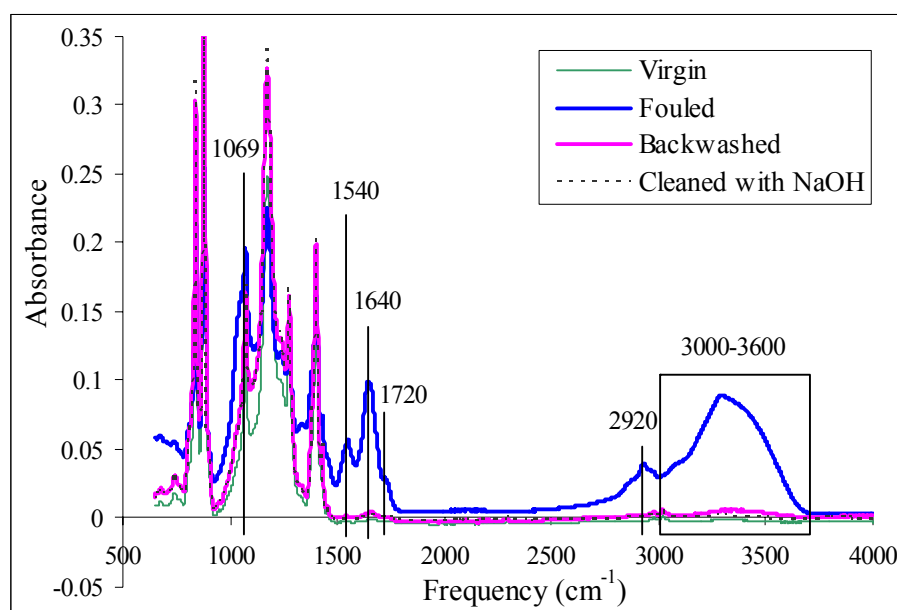


Figure 8.4. ATR-FTIR spectra of the virgin, fouled, and cleaned HFM-116 membranes

SEM images of the virgin, fouled and cleaned membranes were collected. The surface of the fouled membrane was covered with the foulant layer, which made the pores invisible. After backwashing, the pores on the membrane surface became visible, together with some remaining trace foulants. The SEM images of the chemically cleaned membranes were very similar to that of the virgin membrane (see Appendix K). SEM therefore did not allow differentiation of the membranes treated with the different cleaning agents.

The EDX spectrum of the virgin membrane (Figure 8.5) indicated the presence of carbon, oxygen, and fluorine. The presence of the foulants on the membrane resulted in an increase in the oxygen peak, a large reduction in the fluorine peak, and the appearance of the nitrogen, phosphorus, and sulphur peaks. These changes were attributed to the presence of polysaccharides, proteins and HS in the fouling layer. A trace amount of calcium was also detected, indicating that calcium may have played a role in causing membrane fouling. Calcium ion has been found to contribute to membrane fouling in UF by promoting the aggregation of organic molecules in solution via the formation of calcium bridges between the carboxylic groups of HS (Ahn *et al.* 2008). This has been discussed in section 8.2.

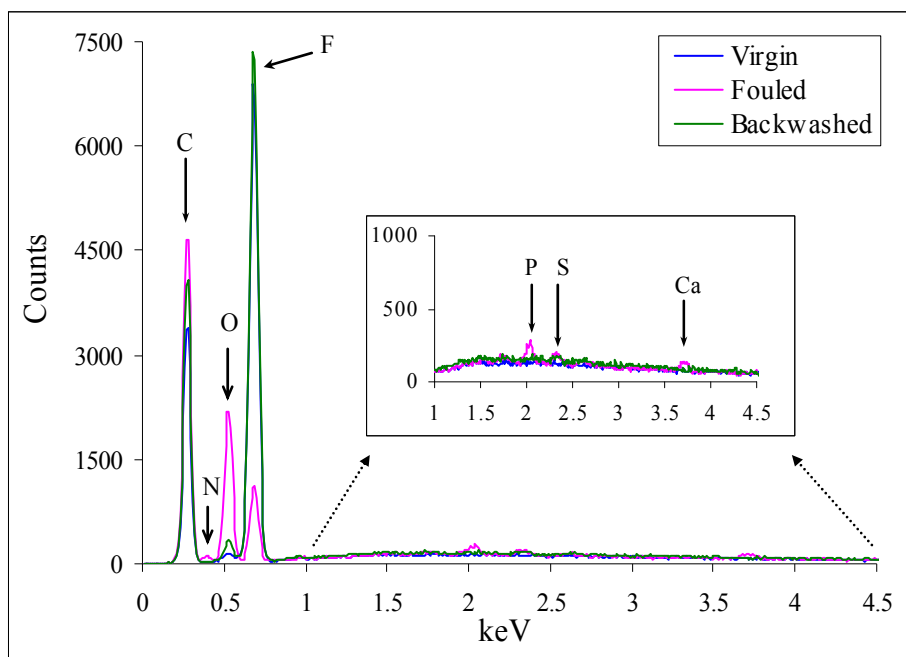


Figure 8.5. EDX spectra of the virgin, fouled, and backwashed HFM-116 membranes

The EDX spectrum of the backwashed membrane had a higher oxygen peak compared with the virgin membrane (Figure 8.5) due to the presence of organic foulants remaining after backwashing. The EDX spectra of the chemically cleaned membranes were very similar to the spectrum of the virgin membrane and therefore the technique was not able to differentiate the degree of cleanliness of these membranes.

Chapter 8 Summary

Backwashing and chemical cleaning of the PVDF (50 kDa) and PES (30 kDa) membranes used for UF of AS effluent were investigated to gain insights to the interactions between the foulants and the membranes. Hydraulic backwashing removed some of the polysaccharides and proteins retained on the membranes, but was not effective for removing HS. The alkaline cleaners were much more efficient than the acidic cleaners for removing the hydraulically irreversible foulants. The most effective cleaning agents were NaOCl, SDS, and Terg-a-zyne, with cleaning efficiencies greater than 85%. The high cleaning efficiencies of the SDS (a surfactant) and Terg-a-zyne (a blend of an anionic surfactant and a protease) indicated that hydrophobic attraction was the major force keeping the hydraulically irreversible foulants and the membranes together. The contribution of HS to hydraulically irreversible fouling was verified by the fact that these solutions turned

yellow during the cleaning experiments. Accumulation of residual fouling after chemical cleaning was observed. Membrane cleanliness was assessed using a combination of flux measurement (cleaning efficiency) and surface analyses (ATR-FTIR spectroscopy, SEM/EDX), the former being a more reliable indicator.

CHAPTER 9. MEMBRANE FOULING IN CROSS-FLOW FILTRATION

Previous chapters investigated fouling mechanisms and the effect of different feed pre-treatments on membrane fouling by the AS effluent using PVDF and PES membranes in dead-end mode. This aligned with current practice which favoured the use of polymeric membranes and the dead-end filtration mode. Although membranes made from ceramic have been used widely in the food, beverage, and dairy industries and in the treatment of industrial wastewater, the high membrane costs have limited their use in water and municipal wastewater treatment. Recently, decreasing membrane cost and improvements in module design have made them promising alternatives for polymeric membranes. As a result, research into fouling of ceramic membranes by surface water has increased in the past 5 years. However, the number of studies on the fouling of ceramic membranes in MF and UF of secondary effluent is still limited, particularly in cross-flow filtration mode.

In this chapter the fouling of single-channel tubular ceramic membranes in cross-flow MF and UF of the raw AS effluent was investigated. The MF membrane was made of α -alumina and its pore size was 0.1 μm . The UF membrane had a pore size of 20 nm and comprised a zirconia layer coated on an alumina support. The membrane foulants were determined. The effects of rapid back-flushing of the membrane and feed pre-treatments with ozone, the AER, and alum on the permeate flux were also studied. To align with current pilot plant practice, the vast majority of the MF and UF tests were conducted at a cross-flow velocity of 1.8 m s^{-1} and at a starting flux of 350 $\text{L m}^{-2} \text{h}^{-1}$ (MF, TMP = 20 kPa) and 100 $\text{L m}^{-2} \text{h}^{-1}$ (UF, TMP = 30 kPa). The corresponding Reynolds number was 12000, within the regime (1000–15000) in which most commercial membrane modules operate (Belfort *et al.* 1994).

The characteristics of the raw AS effluent used in cross-flow MF and UF tests are shown in Table 9.1. To avoid the influence of sample aging on the results, different sets of samples were used throughout the study. The characteristics of the samples collected on particular dates are included in Appendix L.

Table 9.1. Characteristics of the raw effluent samples used in cross-flow MF and UF tests

Parameter	Value
pH	7.3 – 7.8
DOC (mg L ⁻¹)	12.1 – 15.1
UVA ₂₅₄ (cm ⁻¹)	0.37 – 0.40
SUVA (L m ⁻¹ mg ⁻¹)	2.6 – 3.2
True colour (Pt-Co units)	81 – 108
Turbidity (NTU)	1.9 – 3.5

9.1. Flux decline and membrane foulants in cross-flow MF and UF of the raw effluent

9.1.1. Effect of SS on flux decline

MF and UF of the raw AS effluent with and without pre-filtration through 0.5 µm glass-fibre filters were conducted to determine the effect of SS on the flux decline. The results (Figure 9.1) showed that different from dead-end MF and UF with the HFM-180 membrane (Chapter 4), the permeate flux in cross-flow MF and UF was not affected by the SS. This can be attributed to the cross-flow preventing the deposition of SS on the membrane surface, and therefore dissolved EfOM was solely responsible for the flux decline.

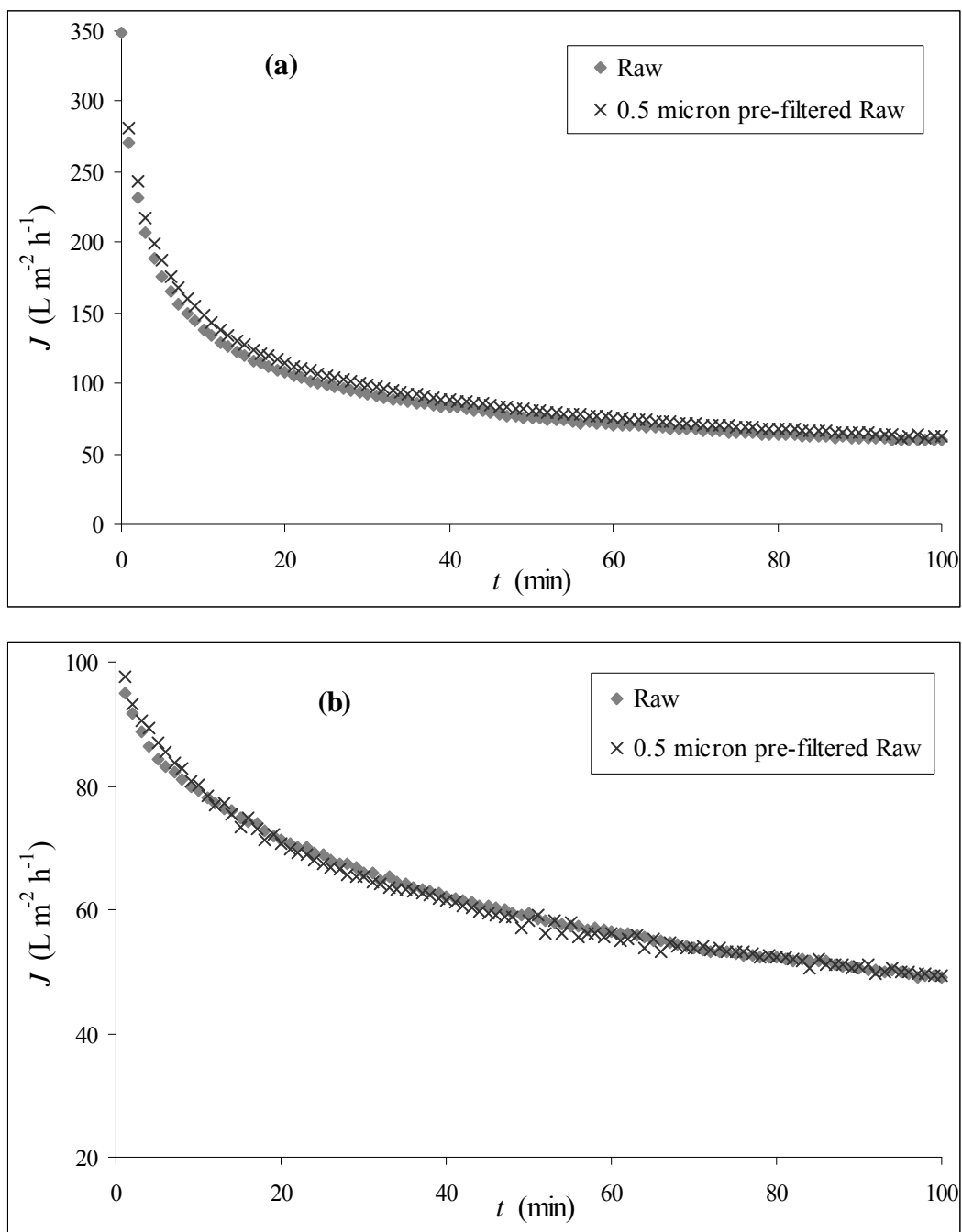


Figure 9.1. Flux data for (a) MF (TMP = 20 kPa) and (b) UF (TMP = 30 kPa) of the raw AS effluent with and without SS at cross-flow velocity 1.8 m s^{-1} (Sample collected on 01 April 2011, DOC = 14.3 mg L^{-1} , $\text{UVA}_{254} = 0.371 \text{ cm}^{-1}$, true colour = 110 Pt-Co units, turbidity = 6.6 NTU)

9.1.2. Membrane foulants in cross-flow MF and UF

To identify the EfOM components responsible for fouling of the membranes, the feed and the permeates collected after 1 hour of MF and UF of the raw AS effluent were subjected to LC-OCD analysis. The filtration conditions were: cross-flow velocity = 1.8 m s^{-1} , TMP = 20 kPa (MF) and 30 kPa (UF), and volume concentration factor (VCF) = 1.3 (MF) and 1.2 (UF).

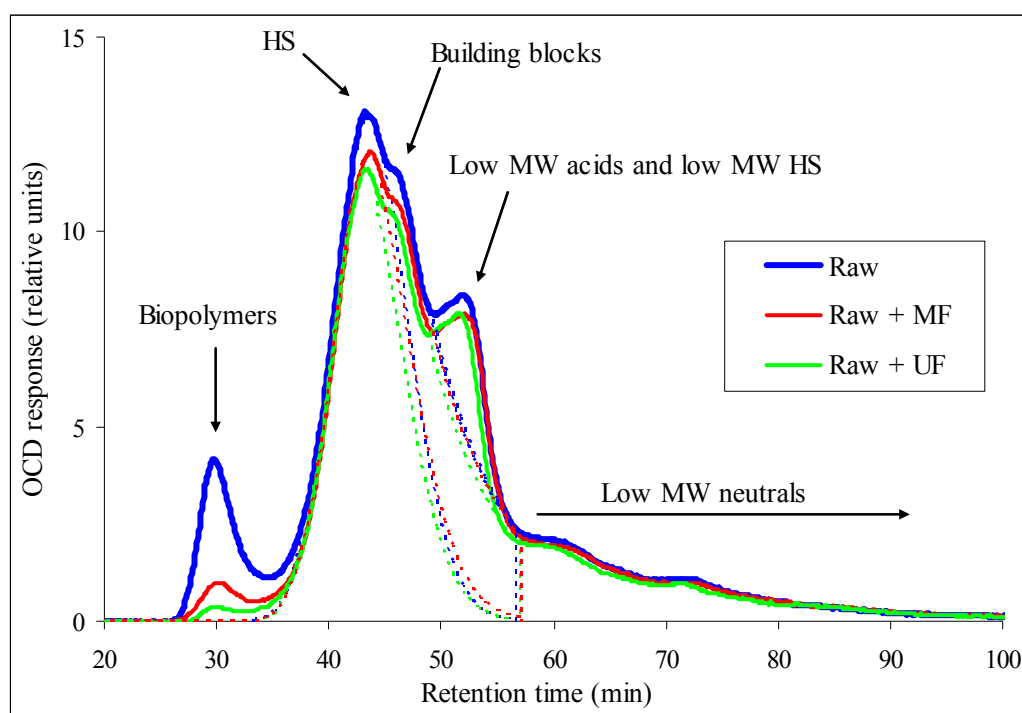


Figure 9.2. AMWDs of the raw AS effluent and the permeates in cross-flow filtration

(Raw effluent was collected on 08 July 2011, $\text{DOC} = 15.1 \text{ mg L}^{-1}$,
 $\text{UVA}_{254} = 0.389 \text{ cm}^{-1}$, true colour = 100 Pt-Co units, turbidity = 1.9 NTU)

The chromatograms (Figure 9.2) showed that similar to dead-end MF and UF, biopolymers (which contained proteins and polysaccharides) and HS were the compounds retained most significantly on the membranes and were therefore the potential foulants. The role of biopolymers in causing fouling of the ceramic membranes was further confirmed by the fact that the pre-treatment which did not affect the biopolymers in the raw effluent (i.e. pre-treatment with the AER) did not affect the permeate flux, whereas those leading to the removal of biopolymers (coagulation) or breakdown in the molecular structures of these components (ozonation) reduced membrane fouling (sections 9.3 and 9.4). Similar results

regarding the identity of the foulants were obtained by Mueller and co-workers (Mueller *et al.* 2008; 2009) for UF of surface water using a titania membrane (pore size = 50 nm). In their study, cleaning-in-place (CIP) of the fouled membrane was performed with NaOCl and the CIP waste was examined with LC-OCD and fluorescence spectroscopy which showed the dominance of biopolymers and HS in the CIP waste.

Biopolymers, with their large molecular sizes, were likely to foul the membranes mainly by pore blocking and cake formation. Some proteins can be hydrophobic in nature (e.g., those with high proline content) and therefore may adsorb on the membrane pore walls. The retention of HS by the membranes was attributed to their hydrophobic interactions with the membranes (Liu *et al.* 2001; Jarusutthirak *et al.* 2002). This was supported by the small molecular sizes of HS (1,000–20,000 Da) and the fact that colour removal by the membranes was observed from the beginning of filtration. Although the contact angles of the membranes used in this study were not measured, the literature suggests that alumina and zirconia membrane can be hydrophobic (contact angle $>50^\circ$). For example, Redón *et al.* (2005) and Koonaphapdeelert & Li (2007) reported contact angles of $55\text{--}80^\circ$ for alumina membranes. A contact angle of 75° for a zirconia membrane was reported by Dobrak *et al.* (2010).

9.1.3. DOC and colour rejection by the ceramic membranes

The rejection by the MF membrane was 6–10% for DOC (approximately $0.8\text{--}1.5\text{ mg C L}^{-1}$) and 8–10% (about 8 Pt-Co units) for true colour, which were comparable with the rejections of the polymeric membranes of the same pore size (VVLTP and XUNP-003 membranes). These values for the ceramic UF membrane were slightly higher: 12–15% for DOC ($1.6\text{--}2.4\text{ mg C L}^{-1}$) and 12–16% for colour (about 12 Pt-Co units). The turbidity of the MF and UF permeates was between 0.1 and 0.2 NTU, much lower than the requirement of 2.0 NTU for “Class A” recycled water.

9.2. Effect of rapid back-flushing on flux performance in cross-flow filtration

In the previous sections of this chapter fouling of the ceramic membranes without intermittent removal of the cake formed on the membrane surface was studied. In practice, to improve the flux performance, the cake layer is normally removed by backwashing the membrane at a predetermined time interval or when the TMP exceeds a preset value (the

latter is applied to constant-flux operation). In typical membrane filtration plants, the backwash duration may last from 10 seconds to 10 minutes (Adham *et al.* 2005). The backwash pressure is limited by the physical properties of the membrane. This value can be much higher for ceramic than polymeric membranes due to the greater strength of the former. In cross-flow filtration with tubular ceramic membranes, a technique called “rapid back-flushing” has been used to improve flux performance in MF of water and wastewater from industrial sources (e.g., electroplating wastewater) (Redkar & Davis 1995; Sondhi *et al.* 2000). In this method, the permeate is pushed back to the feed side at high pressure for a very short duration (typically less than 1 second) (Sondhi *et al.* 2000). However, its application to secondary effluent has been limited, probably due to the limited use of ceramic membranes for the treatment of municipal wastewater. In this section, the effectiveness of rapid back-flushing on fouling reduction in cross-flow MF and UF with the ceramic membrane was investigated. Back-flushing was accomplished by a piston which rapidly pushed the permeate back to the feed side when activated. The back-flush pressure, frequency, and duration were 600 kPa, 12 min⁻¹, and 1 second, respectively.

The flux data for MF of the raw AS effluent at a cross-flow velocity of 1.8 m s⁻¹ and a TMP of 20 kPa with and without membrane back-flushing are shown in Figure 9.3. It can be seen that back-flushing the membrane with the permeate every 12 minutes resulted in significant flux improvement and this effect was sustained during 7 hours of operation. The average permeate flux at the end of the test with back-flushing (84 L m⁻² h⁻¹) was more than twice that obtained without back-flushing (38 L m⁻² h⁻¹) (Table 9.2). Furthermore, the accumulated specific permeate volume increased by nearly 90% with the application of rapid back-flush. Comparable improvements in the end flux and accumulated specific permeate volume were also achieved in UF (Figure 9.4 and Table 9.2). At the end of the 7-hour UF tests, the flux without back-flushing was 33 L m⁻² h⁻¹, whereas the average flux with back-flushing was approximately 60 L m⁻² h⁻¹. The accumulated specific permeate volume was also increased by 80% with the use of rapid back-flushing.

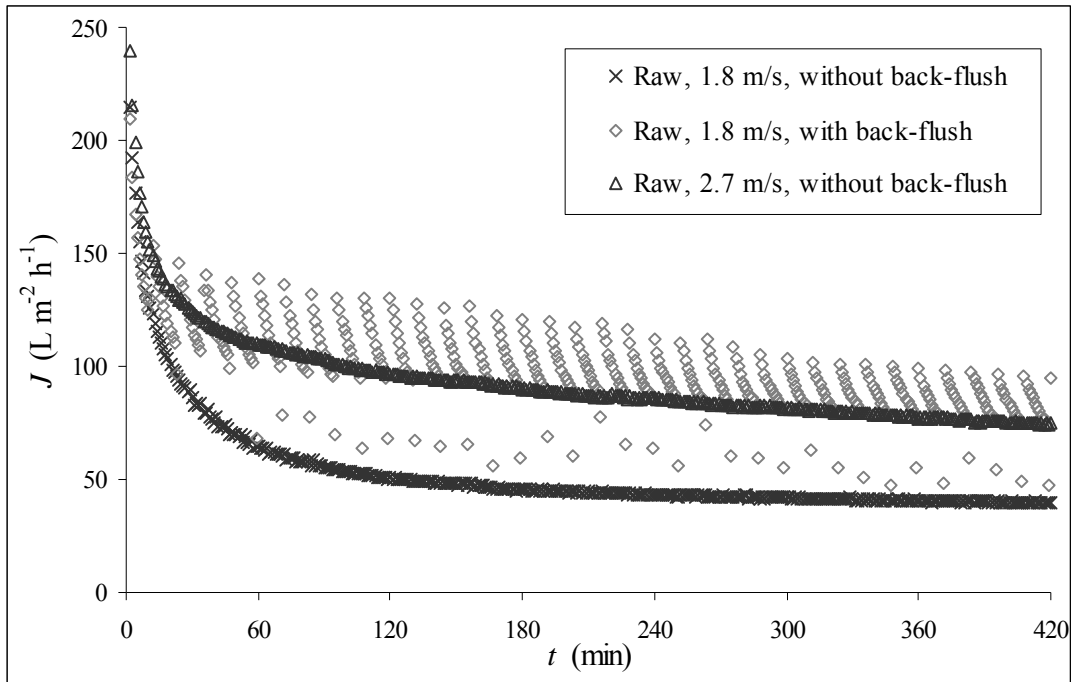


Figure 9.3. Effect of rapid back-flushing and increasing cross-flow velocity on flux performance in MF of the raw AS effluent

(TMP = 20 kPa, back-flush pressure, frequency and duration were 600 kPa, 12 min⁻¹ and 1 second, respectively, sample collected on 23 May 2011)

(The lowest data points on the flux curve for the case “with back-flush” corresponded to the permeate loss to back-flushing)

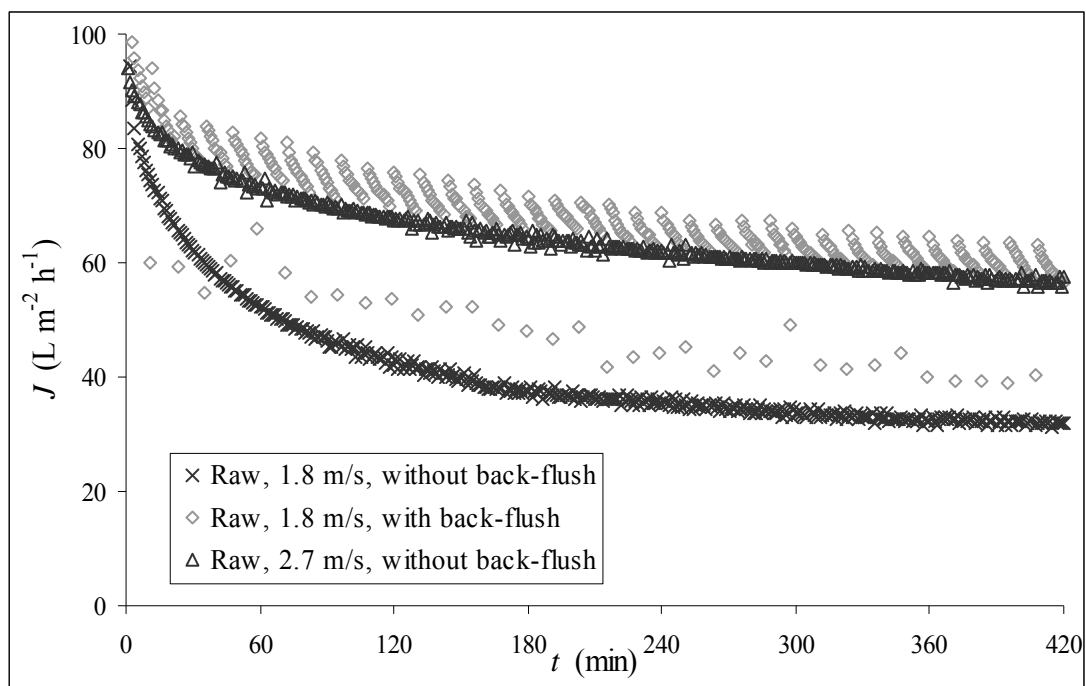


Figure 9.4. Effect of rapid back-flushing and increasing cross-flow velocity on flux performance in UF of the raw AS effluent
(TMP = 30 kPa, back-flush pressure, frequency and duration were 600 kPa, 12 min⁻¹, and 1 second, respectively
(Sample collected on 15 April 2011)

Examination of the flux data in Figures 9.3 and 9.4 revealed that back-flushing was least effective in restoring the permeate flux in the first 3–4 cycles (i.e., the first 36–48 minutes). This could be explained by the limited ability of back-flushing to remove the foulants adsorbed on the membrane pore walls or blocking the membrane pores. As filtration proceeded, the sites on the membranes available for pore adsorption and pore blocking became saturated and cake formation became the dominant mechanism causing the flux decline. It was from this point that back-flushing was most effective in dislodging the cake layer from the membrane surface.

In cross-flow filtration, flux improvement can also be achieved by operating at higher feed cross-flow velocities. The flux data obtained at a cross-flow velocity of 2.7 m s⁻¹ and the same TMP (20 kPa for MF and 30 kPa for UF) showed that the flux improvement by back-flushing was slightly higher than that achieved by increasing the cross-flow velocity by 50% (Figures 9.3 and 9.4 and Table 9.2).

Table 9.2. Average flux and accumulated specific permeate volume at the end of 7-hour MF and UF tests with the raw AS effluent at various operating conditions

Case	Average flux at the end of 7- hour run	Specific permeate volume (v) after 7- hour run
MF, 1.8 m s ⁻¹ , 20 kPa, without back-flush	38 L m ⁻² h ⁻¹	370
MF, 1.8 m s ⁻¹ , 20 kPa, with back-flush	84 L m ⁻² h ⁻¹	698
MF, 2.7 m s ⁻¹ , 20 kPa, without back-flush	75 L m ⁻² h ⁻¹	657
UF, 1.8 m s ⁻¹ , 30 kPa, without back-flush	32 L m ⁻² h ⁻¹	287
UF, 1.8 m s ⁻¹ , 30 kPa, with back-flush	60 L m ⁻² h ⁻¹	522
UF, 2.7 m s ⁻¹ , 30 kPa, without back-flush	57 L m ⁻² h ⁻¹	456

For the filtration conditions investigated, rapid back-flushing was probably more energy-efficient than increasing cross-flow velocity. The energy requirements of the back-flush device and the back-flush timer were small and the device only worked intermittently, whereas the feed pump consumed a 3.37 (= 1.5³) times higher amount of energy to increase the feed cross-flow velocity by 50%. However, it should be pointed out that as rapid back-flushing has not been practised widely in the filtration of water and municipal wastewater, it may be difficult to scale up the back-flush device, which was basically a piston driven by air pressure, for use in full-scale filtration plants.

9.3. Effect of feed pre-treatments with ozone and the AER on permeate flux

As mentioned in Chapter 6, ozonation was the preferred pre-treatment for its ability to remove colour and improve the flux performance in dead-end MF and UF with the polymeric membranes. Pre-adsorption with the AER was able to reduce the true colour of the effluent to 20–25 Pt-Co units at a practical dose (10 mL L⁻¹), whereas a high (and probably uneconomical) PAC dose (150 mg L⁻¹) was needed to achieve this colour removal target. In this section, the effect of ozonation and adsorption pre-treatment with the AER on the flux performance of the ceramic membranes in cross-flow filtration mode was

investigated. Relatively short (2-hour) MF and UF tests with the raw, ozonated, and AER-treated effluents were conducted at a cross-flow velocity of 1.8 m s^{-1} and a TMP of 20 kPa (MF) and 30 kPa (UF) without the application of back-flushing. The ozone dose was 10 mg L^{-1} with a contact time of 10 minutes. The AER dose was $10 \text{ mL resin L}^{-1}$ with a contact time of 20 minutes and stirring at 100 rpm. One bed volume (BV) of the AER was used to treat 1500 BVs of the raw AS effluent. The characteristics of the samples used are shown in Table 9.3.

Table 9.3. Characteristics of the raw, ozonated, and AER-treated effluent samples used in cross-flow MF and UF tests

(Samples collected on 08 July 2011)

Parameter	Raw	Ozonated	AER-treated
pH	7.8	7.7	7.7
DOC (mg L^{-1})	15.1	15.6	9.5
UVA ₂₅₄ (cm^{-1})	0.389	0.227	0.144
SUVA ($\text{m}^{-1}\text{mg}^{-1} \text{ L}$)	2.58	1.46	1.52
True colour (Pt-Co units)	100	22	22
Turbidity (NTU)	1.9	1.8	Not measured

The flux data obtained (Figures 9.5 and 9.6) showed that similar to dead-end MF and UF with the polymeric membranes (Chapter 7), ozonation of the raw AS effluent significantly improved the flux performance of the membranes, whereas pre-treatment with the AER neither reduced nor worsened membrane fouling.

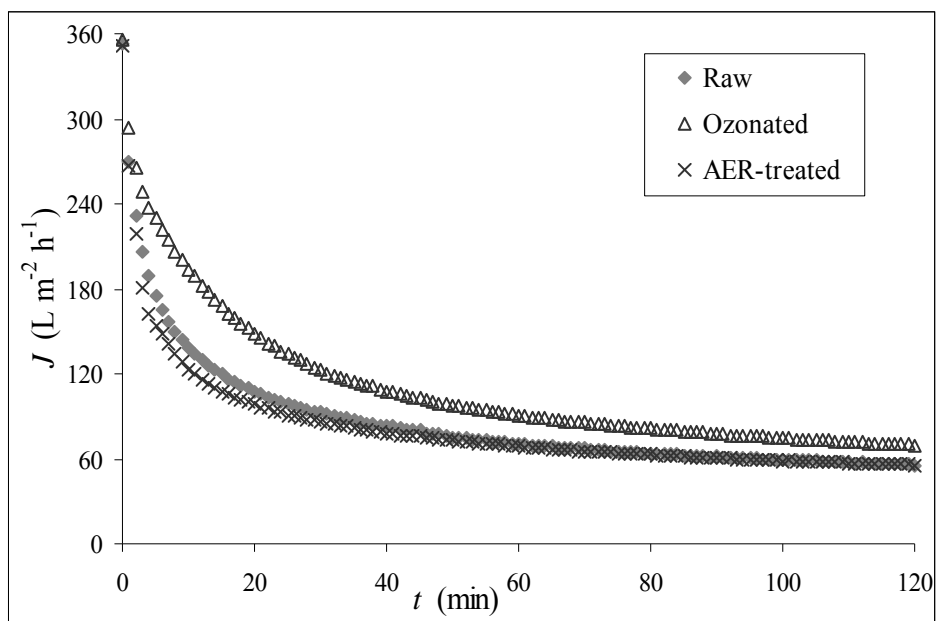


Figure 9.5. Effect of pre-treatments for colour removal with ozone and the AER on permeate flux in cross-flow MF (Samples collected on 08 July 2011)

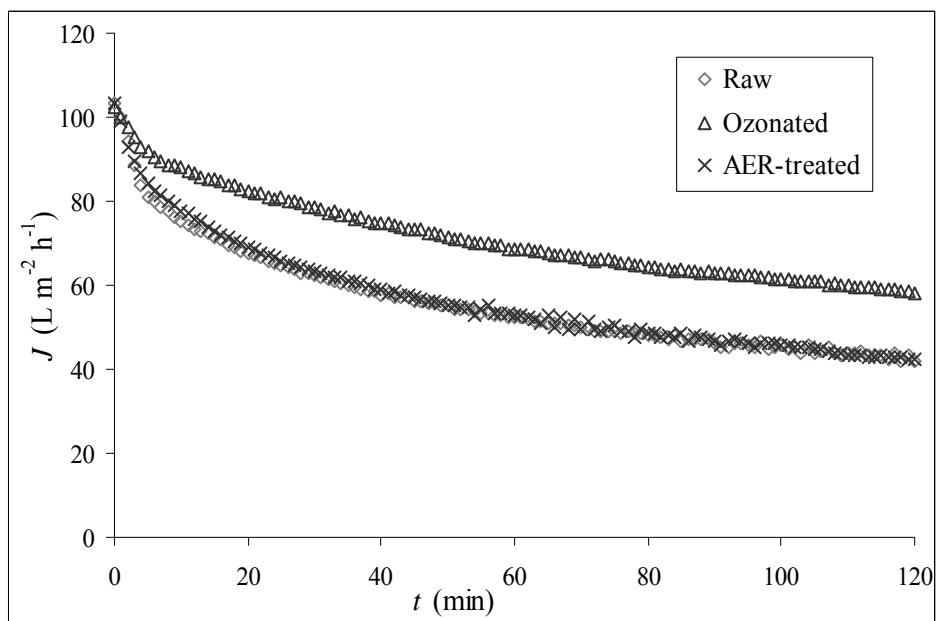


Figure 9.6. Effect of pre-treatments for colour removal with ozone and the AER on permeate flux in cross-flow UF (Samples collected on 08 July 2011)

The permeates from the raw, ozonated and AER-treated effluents collected after 1 hour of filtration were subjected to LC-OCD analysis. The results (Figures 9.7 and 9.8 and Table

9.4) showed that more biopolymers and HS in the ozonated effluent were able to permeate through the membranes than in the raw and the AER-treated effluents. Therefore, similar to the case of the polymeric membranes (Chapters 6 and 7), the flux improvement by ozonation in cross-flow filtration with ceramic membranes can be attributed the breakdown of polysaccharides, proteins, and HS to less hydrophobic and lower MW compounds. The AER removed nearly 70% of HS and essentially no biopolymers from the raw effluent. The UF membrane retained a lower amount of HS in the AER-treated effluent than in the raw effluent. However, this reduction in HS rejection was not adequate for flux improvement, indicating that polysaccharides and proteins played a much more important role in causing flux decline.

Table 9.4. Effect of ozonation and pre-treatment with the AER on the rejection of biopolymers and HS (measured in mg C L⁻¹) by the MF and UF ceramic membranes

Sample	Biopolymers	HS	Biopolymers rejection	HS rejection
Raw	1.3	8.0	-	-
Raw + MF	0.4	7.5	0.9	0.5
Raw + UF	0.2	7.0	1.1	1.0
Ozonated	1.4	7.6	-	-
Ozonated + MF	0.8	7.3	0.6	0.3
Ozonated + UF	0.6	7.0	0.8	0.6
AER-treated	1.3	2.5	-	-
AER-treated + MF	0.4	2.1	0.9	0.4
AER-treated + UF	0.2	1.9	1.1	0.6

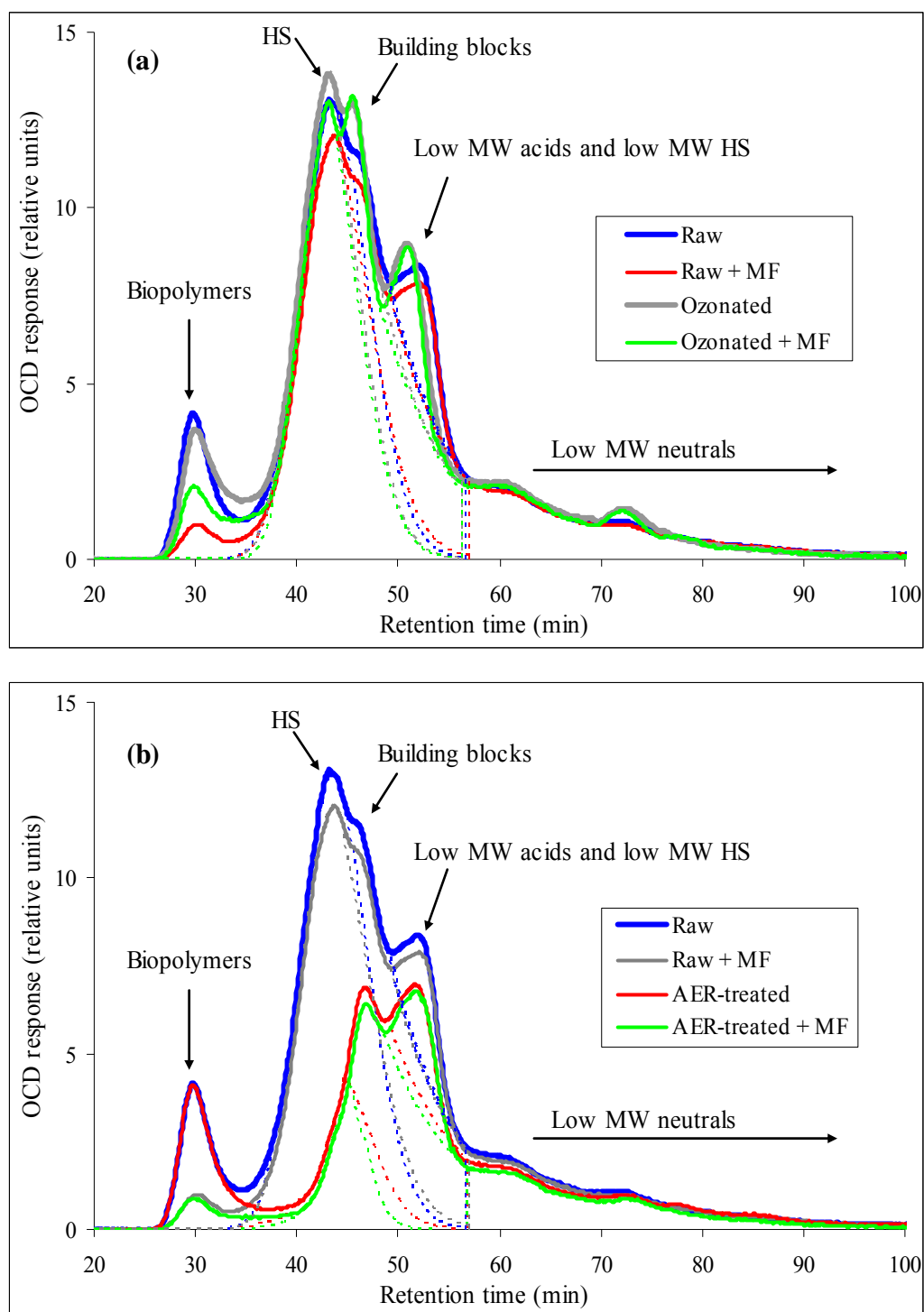


Figure 9.7. Effect of (a) ozonation and (b) adsorption pre-treatment with the AER on the rejection of proteins and polysaccharides of the ceramic MF membrane (Cross-flow velocity = 1.8 m s^{-1} , TMP = 20 kPa, without back-flushing, VCF ≈ 1.3) (Samples collected on 08 July 2011)

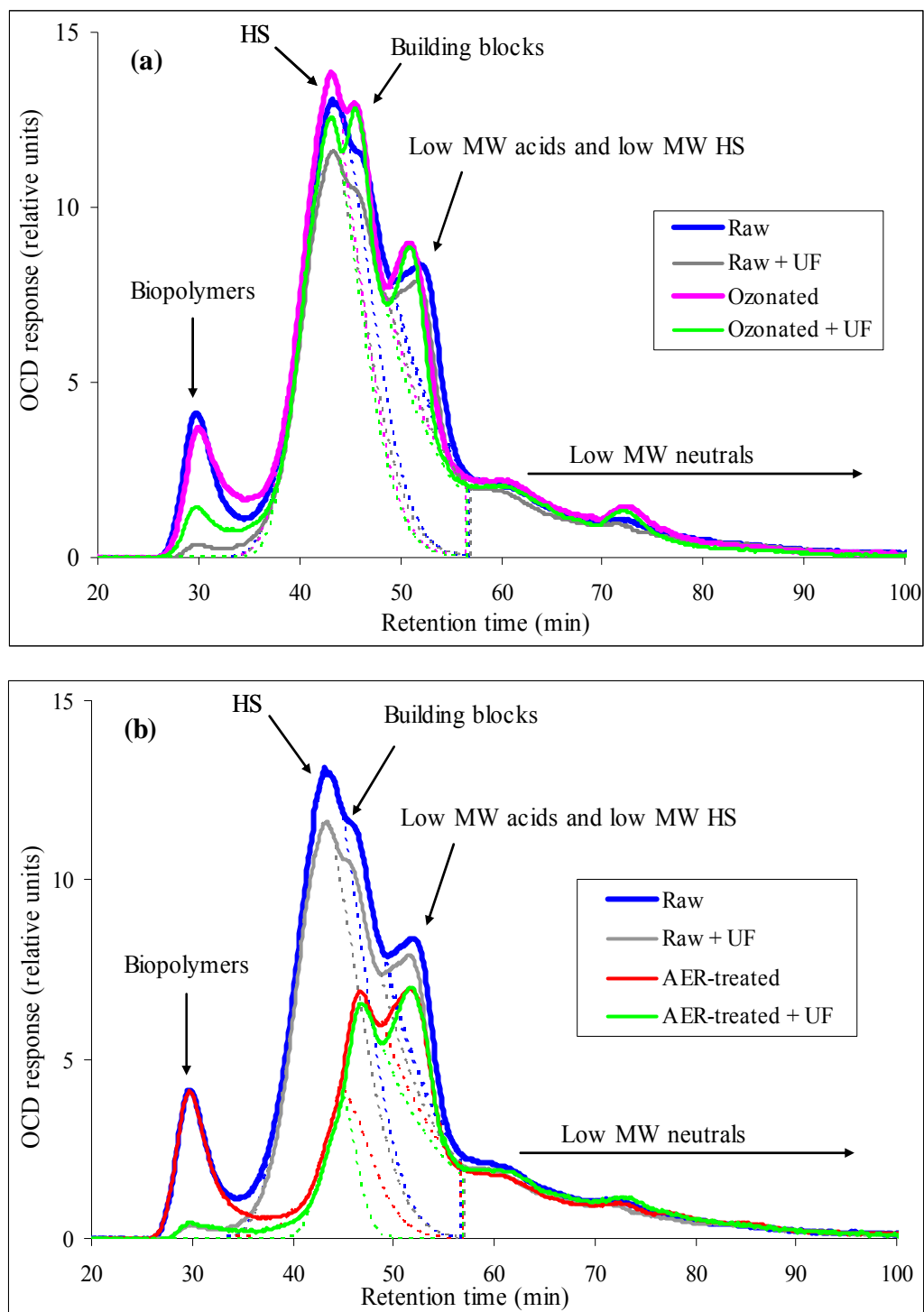


Figure 9.8. Effect of (a) ozonation and (b) adsorption pre-treatment with the AER on the rejection of different EfOM components of the ceramic UF membrane (Cross-flow velocity = 1.8 m s^{-1} , TMP = 30 kPa, without back-flushing, VCF ≈ 1.2) (Samples collected on 08 July 2011)

The effectiveness of ozonation in fouling reduction was also tested in the back-flushing mode. The results (Figures 9.9 and 9.10) showed that flux improvement by ozonation was also achieved in MF and UF operated in this mode.

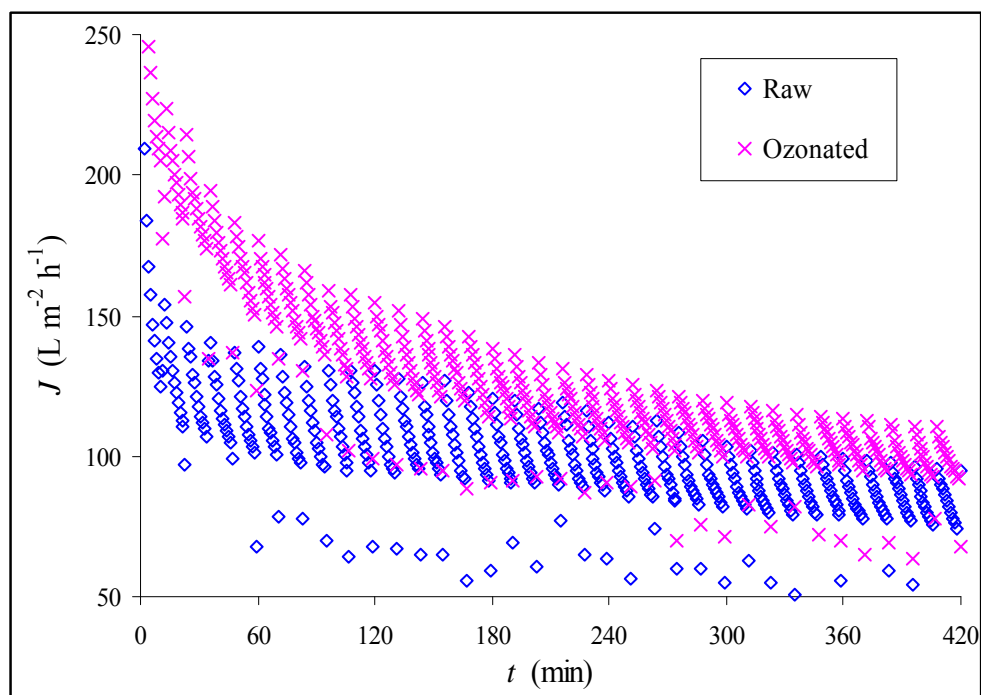


Figure 9.9. Effect of ozonation on the permeate flux

in cross-flow MF with rapid back-flushing

(Cross-flow velocity = 1.8 m s^{-1} , TMP = 20 kPa, back-flush pressure = 600 kPa,

back-flush frequency = 12 min^{-1} , back-flush duration = 1 second)

(Samples collected on 09 September 2011, their characteristics are shown in Appendix L)

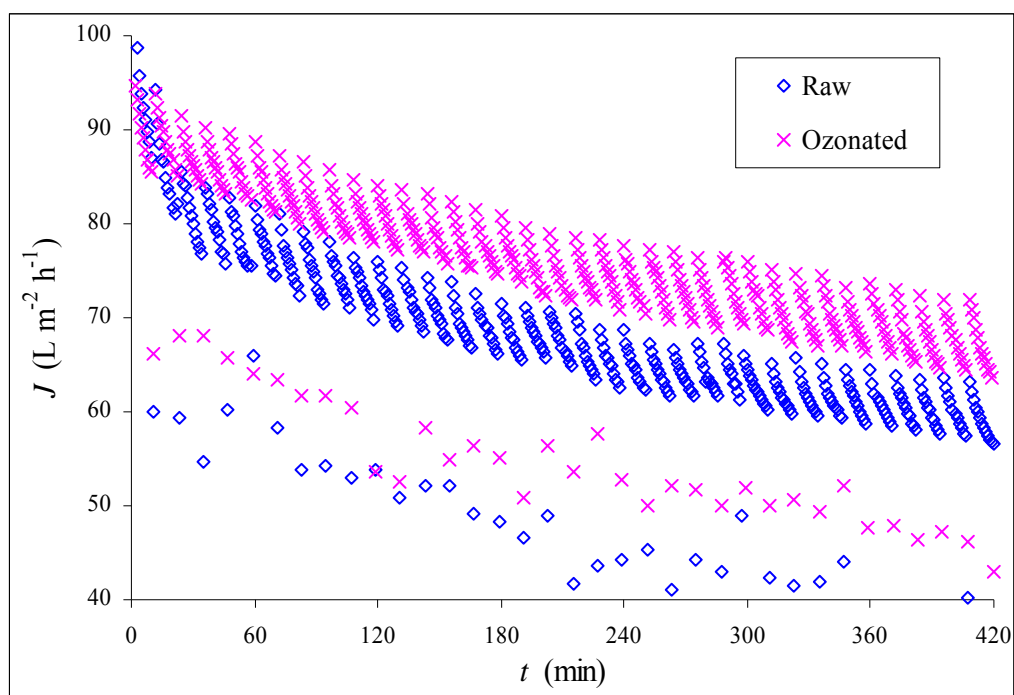


Figure 9.10. Effect of ozonation on the permeate flux
in cross-flow UF with rapid back-flushing

(Cross-flow velocity = 1.8 m s^{-1} , TMP = 30 kPa, back-flush pressure = 600 kPa,
back-flush frequency = 12 min^{-1} , back-flush duration = 1 second)

(Samples collected on 30 September 2011, their characteristics are shown in Appendix L)

9.4. Effect of feed coagulation with alum on flux performance in cross-flow MF

Ozonation (with or without subsequent BAC filtration) was the preferred pre-treatment for MF and UF for its ability to decolourise the raw effluent while improving the permeate flux. The product water would be suitable for non-potable reuse purposes (EPA Victoria 2003). Another method for colour removal is to treat the raw AS effluent with RO membranes. This method is energy-intensive. However, the final water product would have superior quality, which may meet the requirements for potable reuse purposes (Water Environment Federation 2006). If this option is selected, the raw AS effluent would need to be pre-treated to reduce fouling of the RO membrane. Currently, the most widely used processes for pre-treatment of RO feeds are coagulation-MF/UF followed by RO (Qin *et al.* 2004; Water Environment Federation 2006). Coagulation is intended to reduce fouling of the MF or UF membranes. For secondary effluents, the most popular process configuration is in-line coagulation (i.e., no allowance for the settling of coagulated matter) with low coagulant doses. In this section, the effect of coagulation with alum at a dose of 2.5 mg Al^{3+}

L^{-1} (without prior removal of the coagulated matter) on the permeate flux in MF (at a cross-flow velocity of 1.8 m s^{-1} and TMP of 20 kPa) was investigated. Short (2-hour) tests were conducted with the raw and the coagulated effluents without the application of rapid back-flushing. Longer (7-hour) tests with rapid back-flushing every 12 minutes were also carried out in an attempt to obtain flux profiles similar to those of pilot plants. The results (Figures 9.11 and 9.12) indicated that coagulation was an effective pre-treatment for fouling reduction in cross-flow MF with and without the application of rapid back-flushing. Similar to dead-end MF with the PVDF membrane (Chapter 5), the flux improvement by coagulation can be attributed to the removal of a proportion of biopolymers and HS from the raw AS effluent.

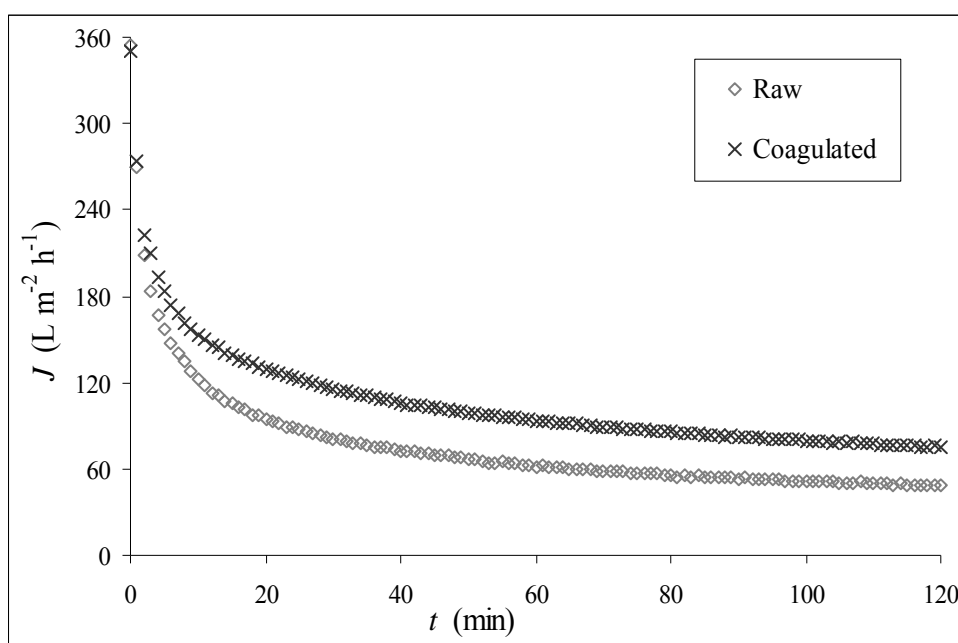


Figure 9.11. Effect of coagulation with alum on permeate flux in cross-flow MF without membrane back-flushing (Cross-flow velocity = 1.8 m s^{-1} , TMP = 20 kPa) (Sample collected on 30 September 2011)

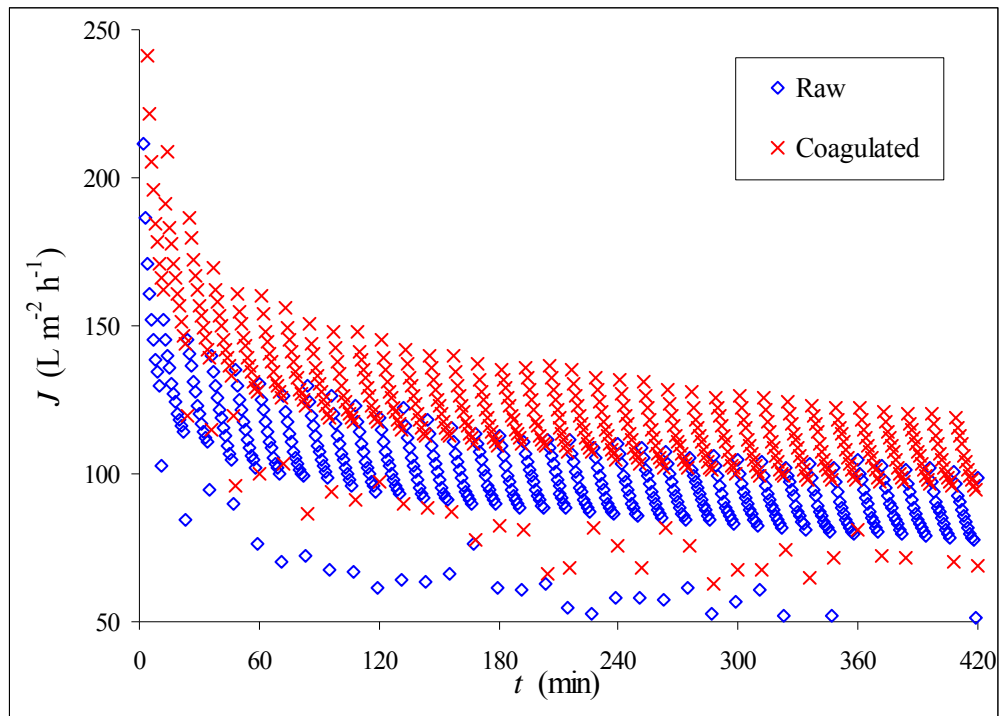


Figure 9.12. Effect of coagulation with alum on permeate flux

in cross-flow MF with membrane back-flushing

(Cross-flow velocity = 1.8 m s^{-1} , TMP = 20 kPa, back-flush pressure = 600 kPa,

back-flush frequency = 12 min^{-1} , back-flush duration = 1 second))

(Samples collected on 23 May 2011)

Chapter 9 Summary

This chapter was dedicated to fouling and fouling mitigation in cross-flow MF and UF of the AS effluent using tubular (single-channel) ceramic membranes. The MF membrane was made of α -alumina and its pore size was $0.1 \text{ }\mu\text{m}$. The UF membrane had a pore size of 20 nm and was made of zirconia coated on an alumina support. The majority of the tests were carried out at a cross-flow velocity of 1.8 m s^{-1} and TMP of 20 kPa (MF) and 30 kPa (UF).

Tests with the raw AS effluent with and without pre-filtration through $0.5 \text{ }\mu\text{m}$ glass-fibre filters showed that different from dead-end MF and UF with the 100 kDa (HFM-180) membrane, particles larger than $0.5 \text{ }\mu\text{m}$ made no contribution to the flux decline in cross-flow MF or UF. This was attributed to the cross-flow preventing the deposition of these particles on the membrane surface. The membrane foulants were identified as biopolymers (i.e., polysaccharides and proteins) and HS.

The effect of rapid membrane back-flushing, with the back-flush device being a piston driven by air pressure, on the flux performance was studied. It was found that back-flushing the membranes at 600 kPa for 1 second every 12 minutes resulted in significant flux improvement, which was attributed to the removal of the foulant layer on the membrane surface. However, it may be difficult to scale-up the back-flush system, as it has rarely been used in the treatment of surface water and municipal wastewater.

Of the two feed pre-treatments for colour removal, ozonation ($10 \text{ mg O}_3 \text{ L}^{-1}$, contact time 10 minutes) reduced membrane fouling, whereas adsorption with the AER ($10 \text{ mL resin L}^{-1}$, 20-minute contact time, 1 BV of the AER treated 1500 BVs of raw effluent) neither increased nor reduced the permeate flux. Similar to dead-end MF and UF with the polymeric membranes (Chapters 6 and 7), the flux improvement by ozonation was attributed to the breakdown of some biopolymers (i.e., proteins and polysaccharides) and HS to lower MW and less hydrophobic compounds. The ineffectiveness of the AER in fouling reduction can be explained by its inability to remove polysaccharides and proteins from the raw AS effluent.

Feed coagulation with alum at $2.5 \text{ mg Al}^{3+} \text{ L}^{-1}$ (without prior removal of the coagulated matter) significantly improved the flux performance of the MF membrane. This indicated an opportunity to utilise a coagulation/MF hybrid scheme with rapid back-flushing as a pre-treatment for RO for the production of high-quality recycled water which may be suitable for potable reuse purposes.

CHAPTER 10. CONCLUSIONS & RECOMMENDATIONS

Fouling of polymeric and ceramic membranes by raw and pre-treated activated sludge (AS) effluent was studied to obtain a more detailed understanding of the fouling mechanisms and the effects of different feed pre-treatments on membrane fouling in microfiltration (MF) and ultrafiltration (UF) of secondary effluent. The pre-treatments investigated included coagulation without removal of the coagulated matter prior to MF or UF, ozonation, and adsorption with an anion exchange resin (AER) or a powdered activated carbon (PAC). The dosages of ozone, AER and PAC were selected to reduce the true colour of the raw effluent by 75-80% (i.e., from 65–133 Pt-Co units to 15–25 Pt-Co units).

The research was divided into two parts. The first part dealt with dead-end filtration using polyvinylidene fluoride (PVDF) and polyethersulfone (PES) membranes – the most widely used membranes in surface water and municipal wastewater treatment. Two PVDF MF (0.1 μm) membranes, one was less hydrophobic (contact angle = 62°) than the other (contact angle $> 90^\circ$), and two hydrophobic PVDF UF membranes with different molecular weight cut-offs (MWCO) (50 kDa and 100 kDa) were used. A relatively hydrophilic PES UF membrane (MWCO = 30 kDa) was also investigated. The second part studied fouling and fouling mitigation in cross-flow filtration with ceramic membranes. Single-channel tubular membranes made of α -alumina (pore size = 0.1 μm) and zirconia (pore size = 20 nm) were used. The following conclusions were drawn from the experimental data:

10.1. Components in the effluent contributing to flux decline and fouling mechanisms

Both effluent organic matter (EfOM, materials smaller than 0.45 μm) and suspended solids (SS, particles larger than 0.5 μm) contributed to the flux decline in dead-end filtration of the effluent with the MF and the loose UF (100 kDa) membranes. However, SS did not contribute to the flux reduction on the tighter UF membranes (PVDF 50 kDa and PES 30 kDa) or in cross-flow filtration. Most of the flux decline by the SS was hydraulically reversible.

For both dead-end filtration with the polymeric membranes and cross-flow filtration with the ceramic membranes, biopolymers, which contained proteins and polysaccharides (molecular weight (MW) $\gg 20,000$ Da), and humic substances (HS, MW=1,000–20,000

Da) were the EfOM components responsible for fouling. The contribution of biopolymers to membrane fouling was much greater than that of HS, as indicated by the higher rejection of the former by the membranes. This was verified by the fact that the pre-treatments which removed more than 50% of the HS from the raw effluent but did not affect the biopolymers (i.e., pre-adsorption with the AER or the PAC) did not improve the membrane flux. Fouling by HS was mainly hydraulically irreversible, whereas biopolymers contributed to both hydraulically reversible and irreversible fouling. The majority of the biopolymers in the raw EfOM were isolated in the hydrophilic fraction, which meant that this fraction had the highest membrane fouling potential compared with the hydrophobic and transphilic fractions.

Flux data analysis showed that for dead-end MF, fouling of the membranes by the raw effluent was governed by pore adsorption and pore blocking during the first 20 minutes of filtration and then followed the cake filtration model. For the hydrophobic PVDF UF (100 kDa and 50 kDa) membranes, fouling switched from pore adsorption and pore blocking to cake filtration after the first 5 minutes of filtration. Fouling of the relatively hydrophilic UF (PES 30 kDa) membrane could be described by the cake filtration model throughout the course of filtration.

10.2. Effect of coagulation on membrane fouling

Coagulation with ACH and alum at $2.5 \text{ mg Al}^{3+} \text{ L}^{-1}$ significantly improved the permeate flux and reduced hydraulically irreversible fouling in dead-end MF and UF. The MF flux improvement was higher for alum than ACH, whereas the two coagulants had a similar flux enhancing effect in UF. Lowering the ACH dose to $1.0 \text{ mg Al}^{3+} \text{ L}^{-1}$ reduced the extent of fouling reduction by coagulation. Unlike MF fouling by the raw effluent, MF fouling by the coagulated effluent could be described by the cake filtration mechanism from the beginning of filtration. This was attributed to the coagulants destabilising the colloidal organic matter, including some biopolymers and HS responsible for membrane fouling in the raw effluent, and so causing the aggregation of these materials to form particles larger than the membrane pores. The reduction in the concentrations of the foulants and the early formation of the cake layer on the membrane surface enabled the improved flux and reduced hydraulically irreversible fouling. The reduction in irreversible fouling was much greater for the less hydrophobic MF membrane than the more hydrophobic counterpart. Coagulation reduced the rate of flux decline, but did not change the governing fouling

mechanisms in UF. This pre-treatment also resulted in significant flux improvement in cross-flow MF with the alumina membrane. However, a very high coagulant dose (approximately $40 \text{ mg Al}^{3+} \text{ L}^{-1}$) was needed to reduce the true colour of the effluent to the desired level (20–25 Pt-Co units).

10.3. Effect of ozonation and biological activated carbon (BAC) filtration on membrane fouling

Ozonation of the raw effluent at $10 \text{ mg O}_3 \text{ L}^{-1}$ for 10 minutes led to significant flux improvement for both dead-end and cross-flow filtration, which was attributed to the breakdown of a proportion of the biopolymers and HS to compounds with lower MW and hydrophobicity. BAC filtration of the ozonated effluent removed the majority of the particles larger than $0.5 \mu\text{m}$ and therefore led to further flux improvement in dead-end filtration with the MF and the loose UF (PVDF 100 kDa) membranes. However, this additional pre-treatment did not affect the flux of the tighter UF (PES 30 kDa) membrane. The hydraulically irreversible fouling of the membranes was reduced after ozonation, whereas BAC filtration did not affect this type of fouling. Similar to coagulation, the reduction in hydraulically irreversible fouling by ozonation was significantly greater for the less hydrophobic MF membrane than the more hydrophobic membrane. The unified membrane fouling index (UMFI) was found a useful tool for quantitative evaluation of the effectiveness of different feed pre-treatments on fouling reduction.

As ozonation of the raw effluent generated some low MW ($<500 \text{ Da}$) compounds (which were potentially biodegradable), this pre-treatment may accelerate membrane biofouling. The BAC filter showed potential to reduce biofouling since the filter removed the majority of the low MW compounds generated during ozonation.

10.4. Effects of adsorption pre-treatments on membrane fouling

Pre-treatments with the PAC and the AER to remove 75–80% of the true colour of the raw effluent neither reduced, nor worsened membrane fouling in dead-end filtration. This was attributed to the fact that although the AER and the PAC removed more than 50% of the HS from the raw effluent, they did not remove biopolymers – the largest contributors to membrane fouling. However, PAC adsorption may reduce membrane biofouling as it removed a significant proportion of the low MW ($<500 \text{ Da}$) compounds from the raw effluent. Similarly, cross-flow MF and UF tests showed that adsorption pre-treatment with the AER did not affect the permeate flux.

10.5. Effect of rapid membrane back-flushing on flux performance in cross-flow filtration

Back-flushing the ceramic membranes at 600 kPa for 1 second every 12 minutes resulted in significant flux improvement, which was attributed to the removal of the foulant layer on the membrane surface. The opportunity to combine coagulation or ozonation pre-treatment with rapid membrane back-flushing to maintain a high permeate flux in cross-flow filtration with ceramic membranes was demonstrated.

10.6. Chemical cleaning of the fouled membranes

Chemical cleaning of the 50 kDa PVDF and 30 kDa PES membranes fouled by the raw effluent was conducted. The most effective cleaning agents were NaOCl, sodium dodecyl sulphate (SDS), and Terg-a-zyme. The high cleaning efficiencies of the cleaners containing anionic surfactants (SDS and Terg-a-zyme) verified that hydrophobic attraction was the major force keeping the hydraulically irreversible foulants and the membranes together. The fact that these solutions turned yellow during the membrane cleaning experiment confirmed that HS played a role in causing internal adsorptive fouling.

10.7. Implications of these findings

Of the pre-treatments investigated, only those which led to the removal (coagulation) or breakdown (ozonation) of biopolymers reduced membrane fouling. Pre-treatments which do not affect the biopolymers in the secondary effluent are unlikely to improve the flux performance of the membranes. The results obtained in this study therefore imply that in MF and UF of secondary effluent (whether with polymeric membranes in dead-end mode or ceramic membranes in cross-flow mode), pre-treatment for fouling reduction should target the removal or the breakdown of the molecular structures of biopolymers (i.e., proteins and polysaccharides). For low colour secondary effluent, in-line coagulation would be the most appropriate pre-treatment for its simplicity and relatively low investment and operating costs. For secondary effluent with high colour, ozonation would be the pre-treatment of choice for its decolourising effect and potential fouling reduction. However, the addition of BAC filters downstream of the ozonation process may be needed to alleviate membrane biofouling. The BAC filters would retain the majority of the suspended solids from the ozonated effluent; therefore further flux improvement can be achieved if the downstream membranes are MF or loose UF membranes operated in dead-end mode. BAC

filtration is unlikely to have any significant impact on the permeate flux of tight UF (MWCO \leq 50 kDa) membranes and membranes operated in cross-flow mode.

The high effectiveness of SDS and Terg-a-zyme for removing hydraulically irreversible foulants indicated that these chemicals are promising alternative cleaning agents, particularly for membranes with low chlorine tolerance (e.g., those made from polypropylene).

10.8. Recommendations for future work

As shown in this study, biopolymers and a small proportion of HS in the secondary effluent were responsible for membrane fouling. Further analysis of these compounds is needed to reveal their detailed chemical compositions (e.g., types and molecular structures of polysaccharides and proteins) and their chemical reactivity. This knowledge would help to tailor pre-treatment for fouling reduction more effectively.

This research showed that the pre-treatments which removed more than 50% of HS but did not affect biopolymers did not reduce fouling in MF and UF of secondary effluent. However, the abundance of HS in secondary effluent and the high reactivity of HS towards common pre-treatment methods (including coagulation, oxidation, and adsorption with AERs and PAC) make it difficult to target only biopolymers to improve the efficiency of the pre-treatments. If novel pre-treatments with high selectivity for biopolymers can be found, the effectiveness of pre-treatments for fouling reduction would increase significantly.

According to the present study, less hydrophobic MF membranes are likely to benefit more from feed pre-treatments than more hydrophobic counterparts, as the hydraulically irreversible fouling of the formers tends to be less severe and more easily mitigated. However, most of the membranes used for MF of secondary effluent are made from hydrophobic materials (e.g., PVDF, PES, and polypropylene). Researchers have attempted to reduce the hydrophobicity of these membranes by different methods, such as surface coating with hydrophilic polymers (Du *et al.* 2009) and blending or grafting the base materials with hydrophilic copolymers and/or nanoparticles (Zhao *et al.* 2007; Li *et al.* 2009). The resulting membranes showed higher fouling resistance compared with the non-modified membranes (in most studies, fouling tests were done with bovine serum albumin

solutions). However, the use of these membranes has been limited at lab-scale level. Therefore, it is suggested that future research should focus on testing the practicability of these membranes in pilot-scale and full-scale MF and UF plants. It is envisaged that the use of less hydrophobic membranes would help to achieve the greatest reduction in irreversible fouling which can be obtained from feed pre-treatments such as coagulation or ozonation.

This study investigated the fouling of tubular ceramic membranes under particular MF and UF operating conditions which were selected based on current practice (as well as the capacity of the equipment). It is recommended that tests conducted under a wider range of operating conditions, including cross-flow velocity, TMP, and back-flush pressure, frequency and duration, are carried out in future studies to determine the optimal operating conditions for cross-flow filtration of secondary effluent. The advantage of the rapid back-flushing method used in this study over conventional back-flushing systems is the elimination of the need for a back-flush pump. The rapid action of the back-flush device also increases the time available for filtration. However, the use of this device, which was essentially a piston driven by air pressure, in full-scale filtration plants has not been reported. The practicability in scaling up this device would be an interesting subject for further investigation.

To date the use of ceramic membranes for MF and UF of municipal wastewater still remains at lab-scale and pilot-scale level. Therefore, it is not clear if these membranes can be cost competitive alternatives for the polymeric counterparts. As the cost of ceramic membranes has decreased considerably in the last few years (Pearce 2011), it is perhaps the right time to re-evaluate the possibility of using these membranes for this application.

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APPENDICES

Appendix A. Contact angles of the flat-sheet polymeric membranes

The contact angles of the virgin flat sheet membranes in this study were measured with an OCA20 contact angle meter (DataPhysics Instruments GmbH) using the sessile drop method with a Milli-Q water droplet volume of 10 μL . The contact angles (computed using the Young-Laplace equation) were taken within 5 seconds. Five measurements were carried out for each membrane. The results are shown in Table A1.

Table A1. Contact angle measurements for the flat-sheet polymeric membranes

Contact angle ($^{\circ}$)	VVLP	HFM-180	HFM-116	HFK-141
Replicate 1	59.9	82.6	66.8	40.7
Replicate 2	62.4	83.7	70.1	37.3
Replicate 3	61.5	86.0	66.4	41.0
Replicate 4	64.0	84.6	69.7	43.1
Replicate 5	63.6	80.9	66.9	41.7
Average	62 ± 2	84 ± 2	68 ± 2	41 ± 2

Some images taken from the contact angle meter are shown in Figure A1.

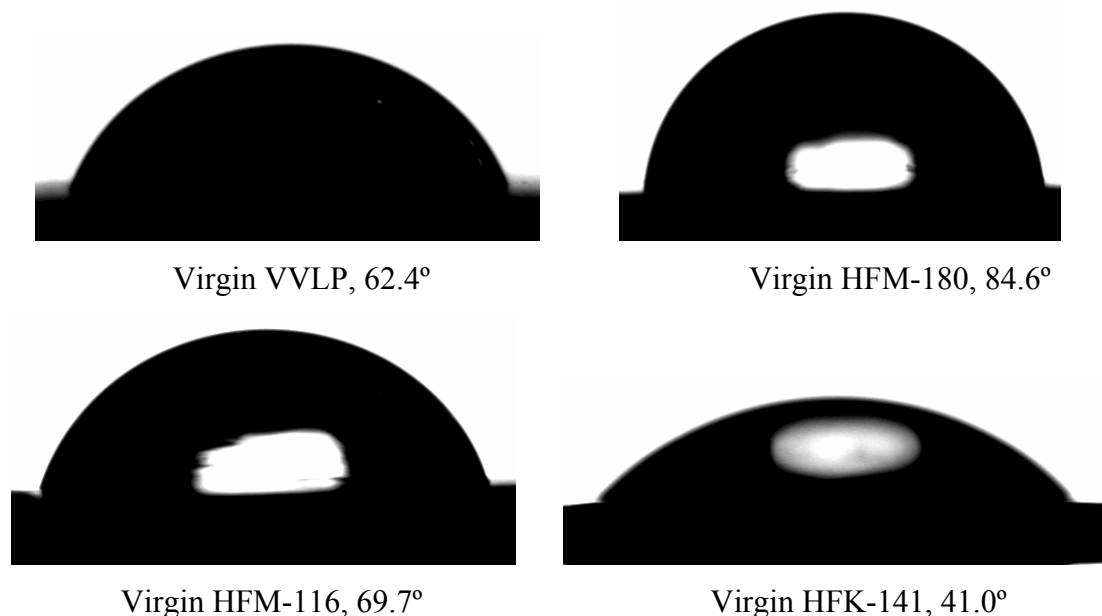


Figure A1. Images of water droplets on the virgin membrane surfaces taken by the OCA20 contact angle meter

Appendix B. Example of data processing for a filtration experiment

Date of experiment: 19 February 2010

Membrane type: HFM-180 (PVDF, MWCO = 100 kDa), filtration area = 13.4 cm²

Sample: Raw effluent

Operating conditions: transmembrane pressure = 110 kPa, temperature = 22 °C

1. Filtration of Milli-Q water using a virgin membrane – Determination of pure water flux of the virgin membrane J_0

Table B1. Flux data for the determination of the virgin membrane's pure water flux

Time, t (min)	Permeate weight (g)	Flux, (g/13.4 cm ² /min)
0	0	-
1	23.04	23.04
2	46.05	23.01
3	68.98	22.93
4	91.84	22.86
5	114.81	22.97
6	137.73	22.92
7	160.5	22.77
8	183.38	22.88
9	206.23	22.85
10	229.1	22.87

J_0 = Average of the last 3 flux data

$$= 22.87 \text{ (g/13.4 cm}^2\text{/min)}$$

$$= 1023.88 \text{ L m}^{-2} \text{ h}^{-1} \text{ (taking the density of the permeate as 1000 g L}^{-1}\text{)}$$

$$= 2.84 \times 10^{-4} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$$

Hydraulic resistance of the virgin membrane (R_m):

$$R_m = \frac{\Delta P}{\mu J_0} = \frac{110,000(Pa)}{0.000958(Pa.s) \times 2.84 \times 10^{-4} (m^3 m^{-2} s^{-1})} = 4.04 \times 10^{11} (m^{-1})$$

2. Filtration of the raw AS effluent – Plot of J/J_0 versus v curve and calculation of the resistance by total fouling and the UMFI for total fouling

Table B2. Flux data from the filtration test with the raw AS effluent and the HFM-180 membrane

Time, t (min)	Permeate weight (g)	Accumulated specific permeate volume, v (L m^{-2})	Flux, J ($\text{L m}^{-2} \text{h}^{-1}$)	Normalised flux, J/J_0
0	0	0	1023.88 ($= J_0$)	1
1	9.43	7.04	422.24	0.412
2	16.56	12.36	319.25	0.312
3	22.68	16.93	274.03	0.268
4	28.10	20.97	242.69	0.237
5	33.05	24.66	221.64	0.216
...
88	200.67	149.75	57.76	0.056
89	201.97	150.72	58.21	0.057

v = permeate volume/membrane area = $201.97 \text{ cm}^3/13.4 \text{ cm}^2 = 150.72 \text{ (L m}^{-2}\text{)}$ at the end of the run (89th minute)

Permeate flux at the end of the filtration run (J'):

$$J' = 58.21 \text{ L m}^{-2} \text{h}^{-1} = 1.62 \times 10^{-5} \text{ m}^3 \text{ m}^{-2} \text{s}^{-1}$$

Resistance by total fouling (R_{tf}):

$$R_{tf} = \frac{\Delta P}{\mu J'} - R_m = \frac{110,000(\text{Pa})}{0.000958(\text{Pa.s}) \times 1.62 \times 10^{-5}(\text{m}^3 \text{m}^{-2} \text{s}^{-1})} - 4.04 \times 10^{11}$$

$$= 6.70 \times 10^{12} (\text{m}^{-1})$$

The UMFI for total fouling = slope of the curve J_0/J versus v (Figure B1)

$$= 0.114 (\text{m}^2 \text{L}^{-1})$$

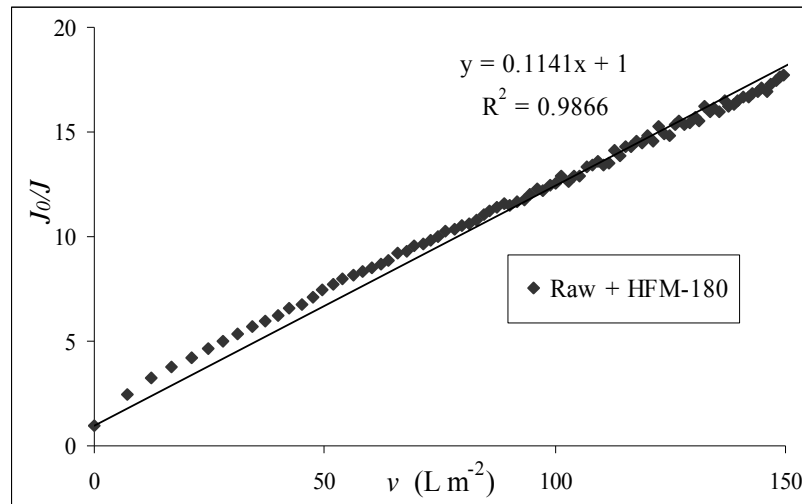


Figure B1. Calculation of the UMFI for total fouling

3. Determination of the pure water flux recovery (WFR) and the resistance by hydraulically irreversible fouling (R_{if})

The fouled membrane was backwashed with the permeate at 110 kPa for 5 minutes. The pure water flux of the backwashed membrane (J_{BW}) was then measured with Milli-Q water. The data are shown in Table B3.

Table B3. Flux data for the determination of the backwashed membrane's pure water flux

Time, t (min)	Permeate weight (g)	Flux, (g/13.4 cm ² /min)
0	0	-
1	9.63	9.63
2	19.24	9.61
3	28.88	9.64
4	38.49	9.61
5	48.23	9.75
6	57.88	9.65
7	67.50	9.62
8	77.00	9.5
9	86.55	9.55
10	96.12	9.57

J_{BW} = Average of the last 3 flux data

$$= 9.54 \text{ (g/13.4 cm}^2\text{/min)}$$

$$= 427.16 \text{ L m}^{-2} \text{ h}^{-1}$$

$$= 1.19 \times 10^{-4} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$$

Pure water flux recovery by backwashing (WFR):

$$WFR = \frac{J_{BW}}{J_0} = \frac{427.16}{1023.88} = 0.42$$

Hydraulic resistance by irreversible fouling (R_{if}):

$$R_{if} = \frac{\Delta P}{\mu J_{BW}} - R_m = \frac{110,000(Pa)}{0.000958(Pa.s) \times 1.19 \times 10^{-4} (m^3 m^{-2} s^{-1})} - 4.04 \times 10^{11} = 5.64 \times 10^{11} \text{ (m}^{-1}\text{)}$$

Appendix C. Sample calculation of the cleaning efficiency of the membrane cleaners

Date of experiment: 09 July 2010

Membrane type: HFM-116 (PVDF, MWCO = 50 kDa), filtration area = 13.4 cm²

Sample: Raw effluent

Operating conditions: transmembrane pressure = 110 kPa, temperature = 22 °C

1. Filtration of Milli-Q water using a virgin membrane – Determination of pure water flux of the virgin membrane J_0

Table C1. Flux data for the determination of the virgin membrane's pure water flux

Time, t (min)	Permeate weight (g)	Flux, (g/13.4 cm ² /min)
0	0	-
1	3.81	3.81
2	7.65	3.84
3	11.47	3.82
4	15.28	3.81
5	19.09	3.81
6	22.89	3.8
7	26.74	3.85
8	30.53	3.79
9	34.33	3.8
10	38.13	3.8

J_0 = Average of the last 3 flux data

$$= 3.80 \text{ (g/13.4 cm}^2\text{/min)}$$

$$= 170.00 \text{ L m}^{-2} \text{ h}^{-1} \text{ (taking the density of the permeate as 1000 g L}^{-1}\text{)}$$

$$= 4.72 \times 10^{-5} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$$

Hydraulic resistance of the virgin membrane (R_m):

$$R_m = \frac{\Delta P}{\mu J_0} = \frac{110,000(Pa)}{0.000958(Pa.s) \times 4.72 \times 10^{-5} (m^3 m^{-2} s^{-1})} = 2.43 \times 10^{12} (m^{-1})$$

2. Filtration of the raw AS effluent – Plot of J/J_0 versus v curve and calculation of the resistance by total fouling

Table C2. Flux data from the filtration test with the raw AS effluent and the HFM-116 membrane

Time, t (min)	Permeate weight (g)	Accumulated specific permeate volume, v ($L\ m^{-2}$)	Flux, J ($L\ m^{-2}\ h^{-1}$)	Normalised flux, J/J_0
0	0	0	170.00 ($= J_0$)	1
1	2.92	2.18	130.75	0.769
2	5.6	4.18	120.00	0.706
3	8.17	6.10	115.07	0.677
4	10.63	7.93	110.15	0.648
5	13.01	9.71	106.57	0.627
6	15.28	11.40	101.64	0.598
...
149	194.43	145.10	42.09	0.248
150	195.36	145.79	41.64	0.245

Permeate flux at the end of the filtration run (J'):

$$J' = 41.64\ L\ m^{-2}\ h^{-1} = 1.16 \times 10^{-5}\ m^3\ m^{-2}\ s^{-1}$$

Resistance by total fouling (R_{tf}):

$$R_{tf} = \frac{\Delta P}{\mu J'} - R_m = \frac{110,000(Pa)}{0.000958(Pa.s) \times 1.16 \times 10^{-5}(m^3 m^{-2} s^{-1})} - 4.72 \times 10^{12}$$

$$= 9.93 \times 10^{12}\ (m^{-1})$$

3. Determination of the pure water flux recovery (WFR) and the resistance by hydraulically irreversible fouling (R_{if})

The fouled membrane was backwashed with the permeate at 110 kPa for 5 minutes. The pure water flux of the backwashed membrane (J_{BW}) was then measured with Milli-Q water. The data are shown in Table C3.

Table C3. Flux data for the determination of the backwashed membrane's pure water flux

Time, t (min)	Permeate weight (g)	Flux ($\text{L m}^{-2} \text{h}^{-1}$)
0	0	-
1	1.97	88.21
2	3.98	90.00
3	5.97	89.10
4	7.99	90.45
5	10	90.00
6	12.04	91.34
7	14.06	90.45
8	16.09	90.90
9	18.13	91.34
10	20.17	91.34

J_{BW} = Average of the last 3 flux data

$$= 91.2 \text{ L m}^{-2} \text{h}^{-1}$$

$$= 2.53 \times 10^{-5} \text{ m}^3 \text{m}^{-2} \text{s}^{-1}$$

Pure water flux recovery by backwashing (WFR):

$$WFR = \frac{J_{BW}}{J_0} = \frac{91.2}{170} = 0.54$$

Hydraulic resistance by irreversible fouling (R_{if}):

$$R_{if} = \frac{\Delta P}{\mu J_{BW}} - R_m = \frac{110,000(\text{Pa})}{0.000958(\text{Pa.s}) \times 2.53 \times 10^{-4} (\text{m}^3 \text{m}^{-2} \text{s}^{-1})} - 2.43 \times 10^{12}$$

$$R_{if} = 2.10 \times 10^{12} (\text{m}^{-1})$$

4. Determination of the resistance by residual fouling (R_{res}) after chemical cleaning and the cleaning efficiency (E_{RW})

The backwashed membrane was soaked in 75 mL of 1.0 wt.% Terg-a-zyne solution (with gentle shaking in an orbital shaker at 100 rpm) for 45 minutes. The chemically cleaned membrane was then rinsed with Milli-Q water and its pure water was measured with Milli-Q water. The data are shown in Table C4.

Table C4. Flux data for the determination of the chemically cleaned membrane's pure water flux

Time, t (min)	Permeate weight (g)	Flux ($\text{L m}^{-2} \text{h}^{-1}$)
0	0	-
1	3.53	158.06
2	7.07	158.51
3	10.62	158.96
4	14.18	159.40
5	17.74	159.40
6	21.31	159.85
7	24.9	160.75
8	28.48	160.30
9	32.05	159.85
10	35.65	161.19

Pure water flux of the chemically cleaned membrane (J_c):

$$\begin{aligned}
 J_c &= \text{Average of the last 3 flux data} \\
 &= 160.4 \text{ L m}^{-2} \text{h}^{-1} \\
 &= 4.45 \times 10^{-5} \text{ m}^3 \text{m}^{-2} \text{s}^{-1}
 \end{aligned}$$

Pure water flux recovery by chemical cleaning:

$$WFR = \frac{J_c}{J_0} = \frac{160.4}{170} = 0.94$$

Resistance by residual fouling after chemical cleaning:

$$\begin{aligned}
 R_{res} &= \frac{\Delta P}{\mu J_c} - R_m = \frac{110000(Pa)}{0.000958(Pa.s) \times 4.45 \times 10^{-5} (m^3 m^{-2} s^{-1})} - 2.43 \times 10^{12} \\
 R_{res} &= 1.45 \times 10^{11} (m^{-1})
 \end{aligned}$$

Cleaning efficiency (E_{RW}) of the 1.0 wt.% Terg-a-zyne solution:

$$E_{RW} = \frac{R_{if} - R_{res}}{R_{if}} \times 100 = \frac{2.10 \times 10^{12} - 1.45 \times 10^{11}}{2.10 \times 10^{12}} = 93 \%$$

Appendix D. Effect of ozonation and BAC filtration on the effluent characteristics and the UMF_I for total fouling for the HFM-180 membrane

Table D1. Characteristics of the samples collected on 03 November 2008

Parameter	Raw effluent	Ozonated effluent	BAC filtrate
pH	7.5	7.6	7.1
DOC (mg L ⁻¹)	13.4	15.3	11.9
UVA ₂₅₄ (cm ⁻¹)	0.327	0.186	0.150
SUVA (L m ⁻¹ mg ⁻¹)	2.44	1.22	1.26
True colour (Pt-Co units)	89	28	25
Turbidity (NTU)	5.6	5.2	0.9

Table D2. Characteristics of the samples collected on 07 November 2008

Parameter	Raw effluent	Ozonated effluent	BAC filtrate
pH	7.6	7.7	7.3
DOC (mg L ⁻¹)	14.8	16.5	13.2
UVA ₂₅₄ (cm ⁻¹)	0.400	0.260	0.234
SUVA (L m ⁻¹ mg ⁻¹)	2.70	1.58	1.77
True colour (Pt-Co units)	118	27	24
Turbidity (NTU)	2.0	2.2	0.7

Table D3. Characteristics of the samples collected on 08 December 2008

Parameter	Raw effluent	Ozonated effluent	BAC filtrate
pH	7.5	7.8	7.2
DOC (mg L ⁻¹)	13.8	14.2	11.1
UVA ₂₅₄ (cm ⁻¹)	0.353	0.199	0.172
SUVA (L m ⁻¹ mg ⁻¹)	2.56	1.40	1.55
True colour (Pt-Co units)	90	19	16
Turbidity (NTU)	3.8	3.3	0.8

Table D4. Characteristics and UMFI for total fouling for the samples collected on 13 March 2009

Parameter	Raw effluent	Ozonated effluent	BAC filtrate
pH	7.8	7.6	7.1
DOC (mg L ⁻¹)	12.6	13.8	12.1
UVA ₂₅₄ (cm ⁻¹)	0.400	0.247	0.226
SUVA (L m ⁻¹ mg ⁻¹)	3.17	1.79	1.87
True colour (Pt-Co units)	123	27	25
Turbidity (NTU)	4.0	4.0	0.8
UMFI (m ² L ⁻¹) (HFM-180 membrane)	0.147	0.112	0.092

Table D5. Characteristics and UMFI for total fouling for the samples collected on 27 March 2009

Parameter	Raw effluent	Ozonated effluent	BAC filtrate
pH	7.8	7.7	7.3
DOC (mg L ⁻¹)	12.0	13.3	11.8
UVA ₂₅₄ (cm ⁻¹)	0.400	0.243	0.223
SUVA (L m ⁻¹ mg ⁻¹)	3.33	1.83	1.89
True colour (Pt-Co units)	112	26	25
Turbidity (NTU)	3.6	3.5	0.8
UMFI (m ² L ⁻¹) (HFM-180 membrane)	0.075	0.048	0.040

Table D6. Characteristics and UMFI for total fouling for the samples collected on 30 March 2009

Parameter	Raw effluent	Ozonated effluent	BAC filtrate
pH	7.6	7.5	7.2
DOC (mg L ⁻¹)	14.2	15.5	14.0
UVA ₂₅₄ (cm ⁻¹)	0.343	0.206	0.190
SUVA (L m ⁻¹ mg ⁻¹)	2.42	1.32	1.39
True colour (Pt-Co units)	90	19	18
Turbidity (NTU)	5.5	5.3	0.8
UMFI (m ² L ⁻¹) (HFM-180 membrane)	0.157	0.116	0.087

Table D7. Characteristics and UMFI for total fouling for the samples collected on 24 April 2009

Parameter	Raw effluent	Ozonated effluent	BAC filtrate
pH	7.6	7.6	7.2
DOC (mg L ⁻¹)	11.3	12.9	10.9
UVA ₂₅₄ (cm ⁻¹)	0.375	0.240	0.210
SUVA (L m ⁻¹ mg ⁻¹)	3.32	1.86	1.93
True colour (Pt-Co units)	118	28	26
Turbidity (NTU)	4.2	4.0	0.8
UMFI (m ² L ⁻¹) (HFM-180 membrane)	0.074	0.056	0.042

Table D8. Characteristics and UMFI for total fouling for the samples collected on 16 June 2009

Parameter	Raw effluent	Ozonated effluent	BAC filtrate
pH	7.2	7.3	6.5
DOC (mg L ⁻¹)	13.8	14.6	13.3
UVA ₂₅₄ (cm ⁻¹)	0.353	0.210	0.192
SUVA (L m ⁻¹ mg ⁻¹)	2.56	1.44	1.44
True colour (Pt-Co units)	90	19	16
Turbidity (NTU)	3.8	3.5	0.6
UMFI (m ² L ⁻¹) (HFM-180 membrane)	0.068	0.041	0.034

Appendix E. Effect of ozonation and BAC filtration on the DOC concentrations of the EfOM fractions as determined by resin fractionation

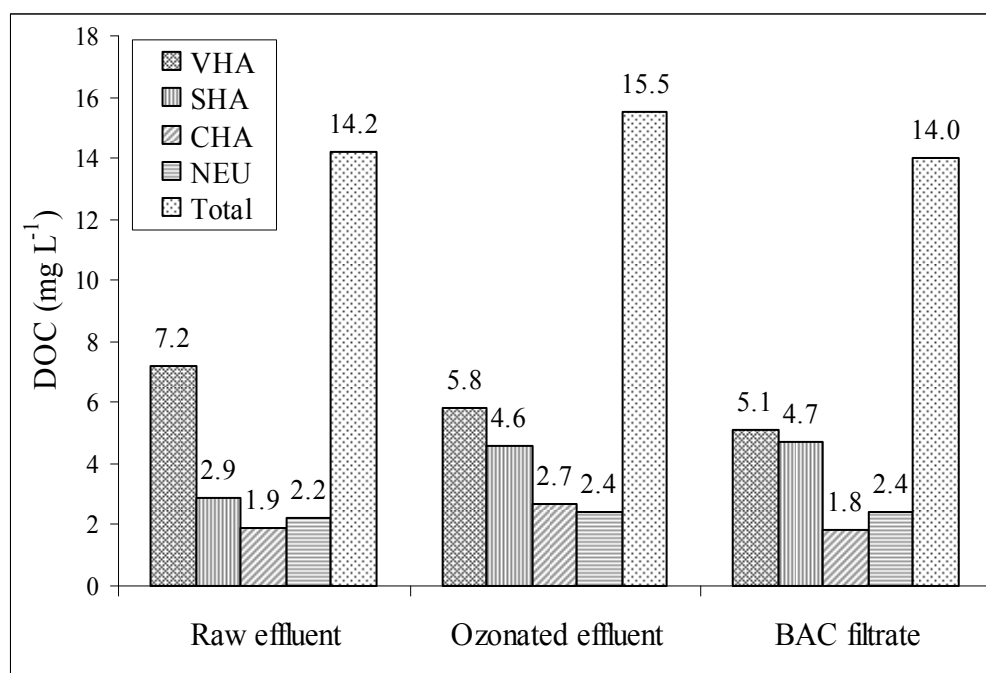


Figure E1. Effect of ozonation and BAC filtration on the DOC concentrations of the EfOM fractions of the raw effluent (Samples collected on 30 March 2009)

Appendix F. LC-OCD chromatograms of the samples listed in Table 6.3 but not included in Figure 6.2

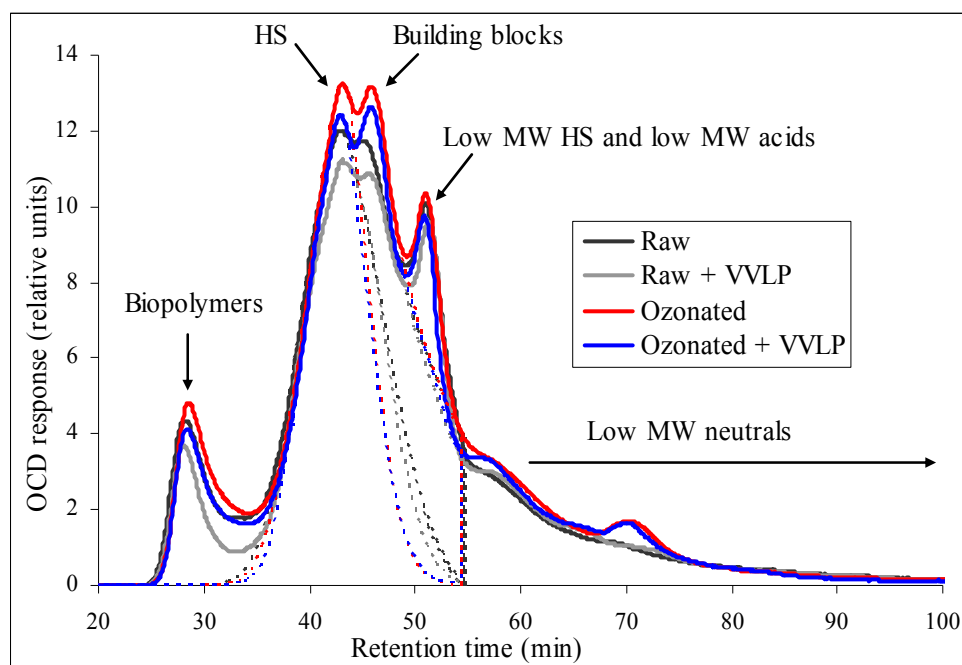


Figure F1. AMWDs of the raw and ozonated effluent and the corresponding permeates obtained from MF with the VVLP membrane

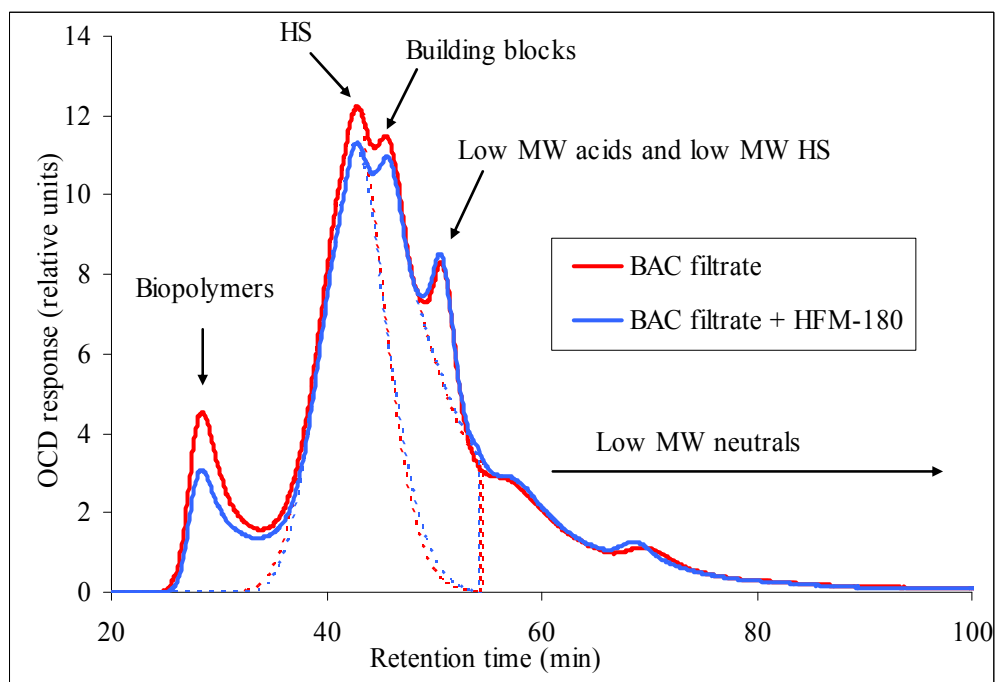


Figure F2. AMWDs of the BAC filtrate and the permeate obtained from UF with the HFM-180 membrane

Appendix G. Particle size distributions and zeta potentials of the raw effluent and the ozonated effluent

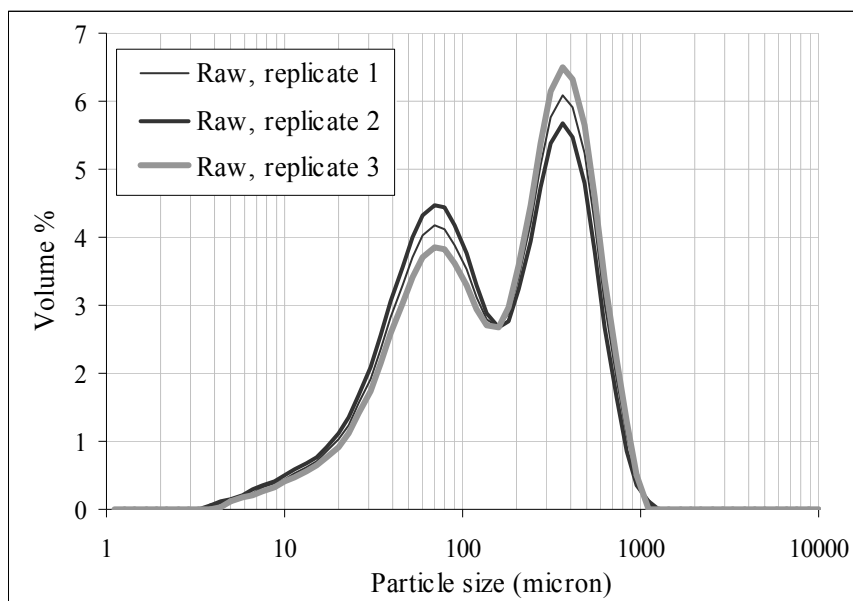


Figure G1. Particle size distributions of the raw effluent collected on 10 August 2009

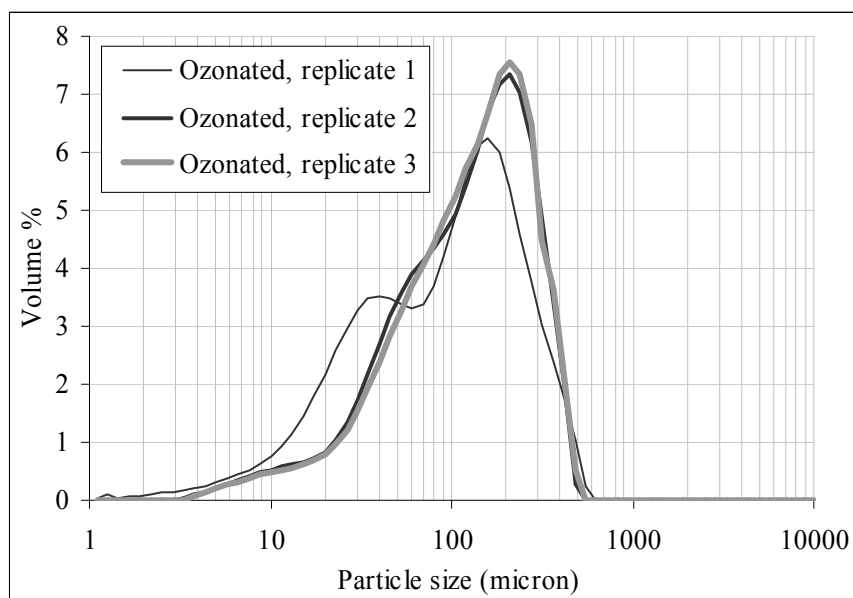


Figure G2. Particle size distributions of the ozonated effluent collected on 10 August 2009

Table G1. Effect of ozonation on the zeta potentials of the raw effluent

Zeta potential (mV)	Raw effluent	Ozonated effluent
Replicate 1	-13.4 ± 1.2	-14.7 ± 1.7
Replicate 2	-12.7 ± 1.0	-14.5 ± 1.3
Replicate 3	-13.4 ± 2.1	-14.0 ± 0.7
Replicate 4	-13.1 ± 1.4	-14.1 ± 2.1
Replicate 5	-13.3 ± 1.5	-14.0 ± 1.9
Average	-13.2 ± 1.4	-14.3 ± 1.5

***Appendix H. LC-OCD chromatograms of the ozonated effluent
and its MF permeate with the XUNP-003 membrane
(Samples listed in Table 7.2 but not included in Figure 7.3)***

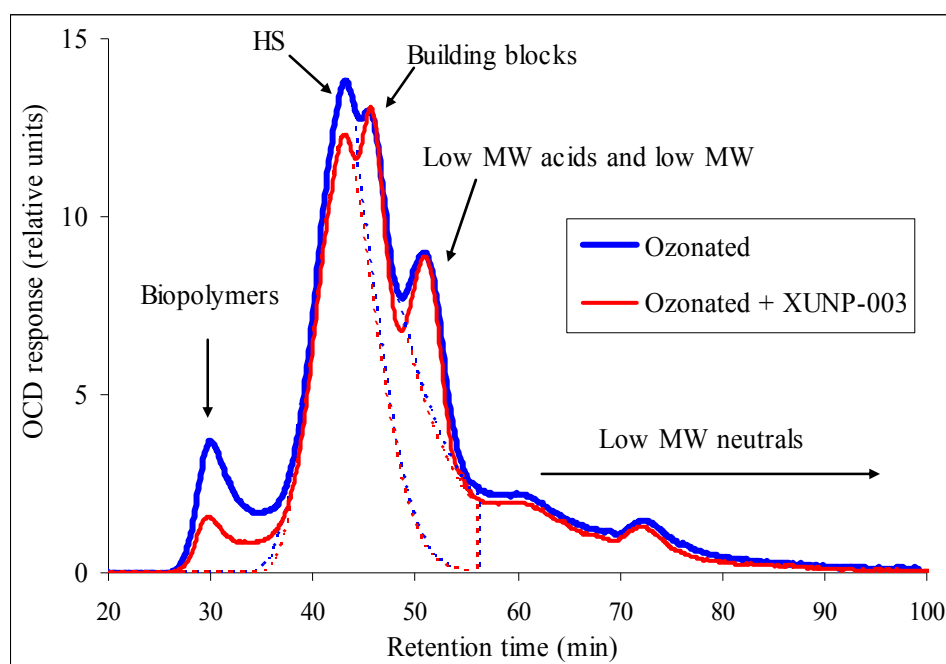


Figure H1. LC-OCD chromatograms of the ozonated effluent and the corresponding permeate from MF with the XUNP-003 membrane

***Appendix I. Characteristics of the samples used for the UF tests
shown in Figure 7.4***

Table II. Effect of ozonation and adsorption pre-treatment with the AER and the PAC on the characteristics of the raw effluent samples (samples collected on 01 April 2011)

Parameter	Raw	Raw + 10 mL AER L ⁻¹	Raw + 150 mg PAC L ⁻¹	Ozonated (Raw + 10 mg O ₃ L ⁻¹)
pH	7.3	7.5	7.4	7.4
DOC (mg L ⁻¹)	14.3	8.8	6.3	15.0
UVA ₂₅₄ (cm ⁻¹)	0.371	0.128	0.106	0.221
SUVA (m ⁻¹ mg ⁻¹ L)	2.59	1.45	1.68	1.47
True colour (Pt-Co units)	110	24	26	24
Turbidity (NTU)	6.6	N/M [*]	N/M [*]	N/M [*]

^{*}Not measured

Appendix J. Effect of cyclic chemical cleaning with SDS and Terg-a-zyme on the permeate flux of the HFM-116 membrane

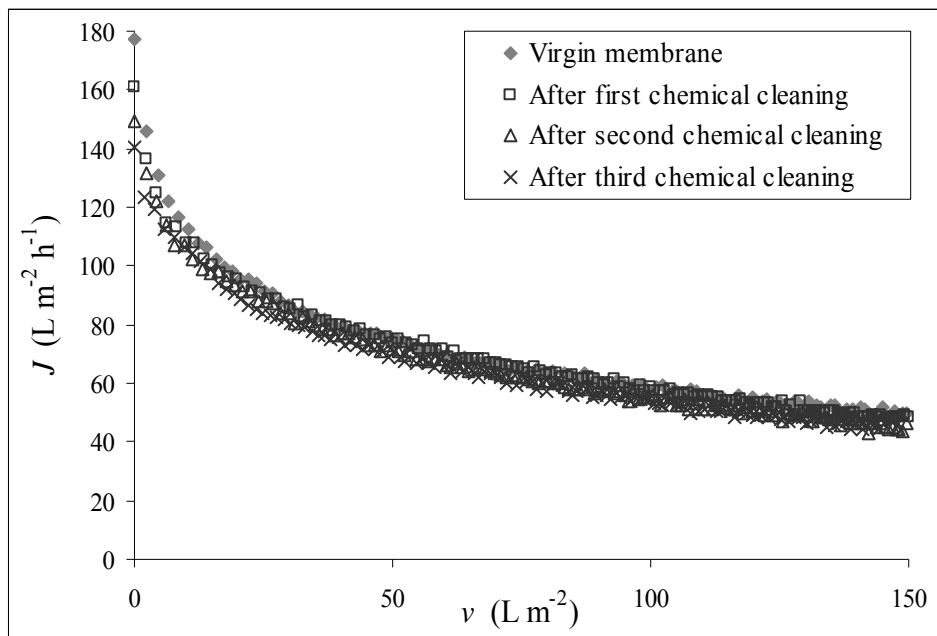


Figure J1. Effect of chemical cleaning with SDS on the permeate flux in UF of the raw effluent with the HFM-116 membrane over three cleaning cycles

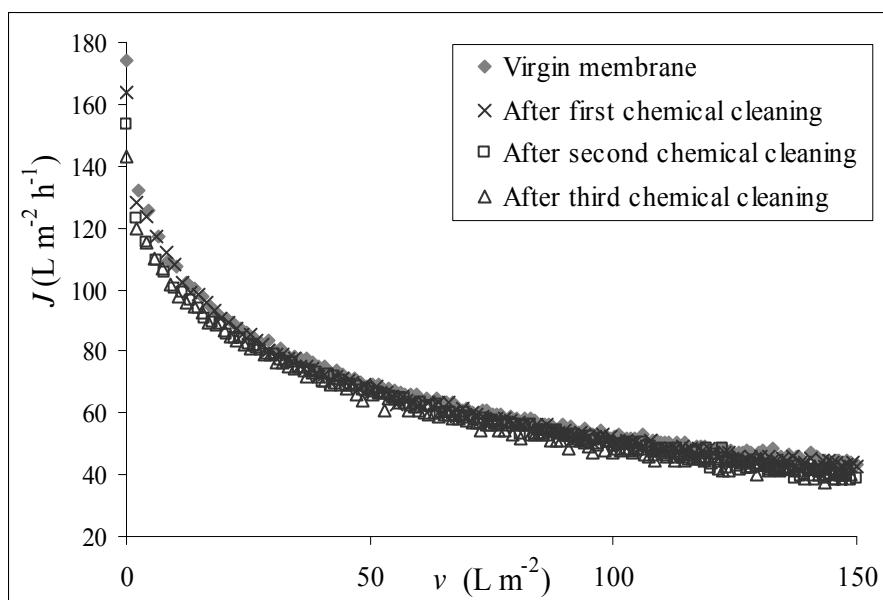


Figure J2. Effect of chemical cleaning with Terg-a-zyme on the permeate flux in UF of the raw effluent with the HFM-116 membrane over three cleaning cycles

***Appendix K. SEM images of the virgin and chemically cleaned
HFM-116 membrane samples***

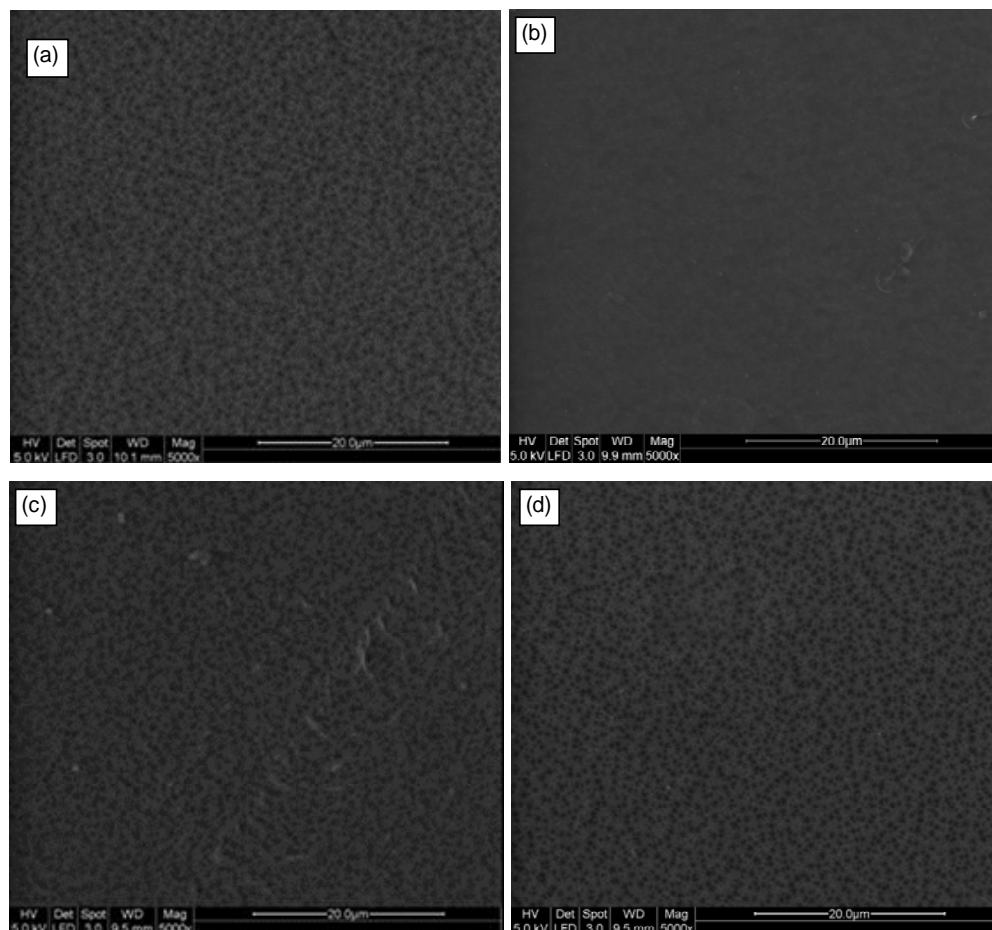


Figure K1. SEM images of the HFM-116 membrane

(a) Virgin, (b) Fouled by the raw effluent,

(c) After backwashing with the permeate, and (d) After cleaning with NaOH

Appendix L. Characteristics of the samples used in cross-flow filtration tests

Table L1. Characteristics of the raw effluent samples used in cross-flow filtration tests in Chapter 9

Sample collection date	DOC (mg L ⁻¹)	UVA ₂₅₄ (cm ⁻¹)	True colour (Pt-Co unit)	Turbidity (NTU)
15 April 2011	14.8	0.388	81	2.6
23 May 2011	12.1	0.388	108	3.2
08 July 2011	15.1	0.389	100	1.9
09 September 2011	12.2	0.371	90	3.5
30 September 2011	14.2	0.406	104	2.6

Table L2. Characteristics of the ozonated effluent samples used for Figures 9.9 and 9.10

Sample collection date	DOC (mg L ⁻¹)	UVA ₂₅₄ (cm ⁻¹)	True colour (Pt-Co unit)	Turbidity (NTU)
09 September 2011 (Figure 9.9)	11.9	0.249	22	3.5
30 September 2011 (Figure 9.10)	15.0	0.258	24	2.4