

IMPROVED MEMBRANE PRETREATMENT BY FLOATATION

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Master of Applied Science Thesis

Submitted to the School of Graduate Studies and Research
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In partial fulfillment of the requirements for the degree of
Master of Applied Science in Environmental Engineering

The degree is offered under Ottawa-Carleton Institute for Environmental Engineering
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ABSTRACT

Coagulation/flocculation/sedimentation is a common pretreatment process prior to microfiltration (MF) or ultrafiltration (UF) to alleviate membrane fouling, however there has been limited research on floatation as the pretreatment separation process. The main objective of this study is to compare sedimentation with floatation as part of the pretreatment for ultrafiltration of Ottawa River water (ORW) with relatively high natural organic matter (NOM) content. Water samples pretreated at two full-scale plants were subjected to multiple-day UF membrane fouling tests (constant flux with backwash and chemical cleaning) using an automated bench-scale UF hollow fiber membrane system.

For all the experiments, the transmembrane pressure (TMP) increased sharply during the beginning of the operation (~10 h), which indicated the adsorption was significant. In the later cycles, the TMP showed a more linear constant increase, which indicated the built up of the cake layers.

The total fouling index (TFI), hydraulically irreversible fouling index (HIFI) and chemical irreversible fouling index (CIFI) for floated water were much smaller than those of settled waters during both summer and winter testing. Thus, for this type of water coagulation/floatation pretreatment was superior process compared to coagulation/sedimentation, the decreased fouling appears to be linked to greater hydrophobic NOM removal by the coagulation/floatation. For all the tests, HIFI/TFIs were less than 0.1, which is to mean most of the fouling was reversible by hydraulic backwashing. Large fluctuation of backwash efficiencies with time were found for all the tested waters.

Enhanced chemical backwash with 100 ppm chlorine and chemical clean with 0.1N NaOH & 200 ppm chlorine were found to be very effective at reducing fouling for pretreated ORW. As expected longer filtration cycles resulted in greater fouling but with a slightly greater degree of hydraulically reversible fouling.

ACKNOWLEDGMENTS

I would like to thank my dear supervisor Dr. Roberto M. Narbaitz for giving me the opportunity to work on this project. His passion, knowledge, encouragement, support and guidance give me a great inspiration during my design, experiments and thesis writing. It has been an honour working with him. I really enjoyed our talks about family, he always can teach me no matter how to do the experiments but also how to enjoy life.

I would also like to thank the environmental engineering Technician Meghan Thomson for her help in the lab. I also would like to thank Dr. Dipak Rana from chemical engineering for his support and I enjoyed the coffee time with him.

And I would like to thank the members in Dr. Narbaitz's group, Steven Walker, Ladan Zoka and Juan Pablo Gonzalez Galvis. Steven and I entered the school at the same time and had classes together, he is the first friend I know in Canada, and he is very helpful. Steven built the filtration system and taught me a lot about the system and lab procedures. He is such a nice friend who I never forget. Juan helped me do the TOC fractionation, I really appreciate it.

I also would like to express my gratitude to Britannia water treatment plant and Aylmer water treatment plant for supplying the waters. I would like to thank all their staff.

I would like to thank my parents, my mother Junru Yin and father Xiangli Xu. I need to give an additional thanks to my dear husband Chen Chen and my little boy Eric Chen for their love, understanding, encouragement, and tremendous support during my study. I love them forever.

Finally, I would like to thank Ontario Graduate Scholarship Council for the financial support to me, and this project was funded by Natural Sciences and Engineering Research Council of Canada.

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ABBREVIATIONS

AF	Ottawa River water coagulated with alum + a polymer, flocculated and floated collected in Aylmer Water Plant
AFM	Atomic force microscopy
AS	Ottawa River water coagulated with alum + a polymer, flocculated collected from the Aylmer Water Plant and settled at the Univ. of Ottawa labs
BS	Ottawa River water coagulated with alum + a polymer, flocculated and settled collected from the Britannia Water Plant
BWE	Backwash efficiency
BWF	Backwash frequency
CA	Cellulose acetate
CC	Chemical cleaning
CIFI	Chemical irreversible fouling index
CIP	Chemical clean in place
Da	Daltons
DBPs	Disinfection by-products
DOC	Dissolved organic carbon
EBW	Enhanced backwash
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared
HA	Humic acids
HIFI	Hydraulic-irreversible fouling index
HPI	Hydrophilic fraction of natural organic matter

HPO	Hydrophobic fraction of natural organic matter
LMH	Unit for flux ($\text{L m}^{-2} \text{h}^{-1}$)
MBR	Membrane bioreactor
MF	Microfiltration
MFI	Modified fouling index
MIEX	Magnetic ion exchange
MW	Molecular weight
MWCO	Molecular weight cut off
NF	Nanofiltration
NMWCO	Normalized molecular weight cut off
NOM	Natural organic matter
NSF	Normalized specific flux
ORW	Ottawa River water
PAC	Powdered activated carbon
PAN	Polyacrylonitrile
PE	Polyethylene
PES	Polyethersulfone
POC	Particulate organic carbon
PP	Polypropylene
PS	Polysulfone
PVDF	Polyvinylidene fluoride
RC	Regenerated cellulose
RO	Reverse osmosis

SA	Sodium alginate
SDI	Silt density index
SEM	Scanning electron microscope
V	Specific volume (permeate volume/membrane area)
SUVA	Specific ultraviolet absorbance
TMP	Transmembrane pressure
TOC	Total organic carbon
TFI	Total fouling index
TPI	Transphilic fraction of natural organic matter
UV ₂₅₄	Ultraviolet absorbance at a wavelength of 254nm
UF	Ultrafiltration
UMFI	Unified membrane fouling index
WTP	Water treatment plant

NOMENCLATURE

BWE	Backwash efficiency (%)
CIFI	Chemical irreversible fouling index (m^2/L)
HIFI	Hydraulic irreversible fouling index (m^2/L)
NSF	Normalized specific flux (unitless)
J	Permeate flux: flow per unit area ($\text{L}/\text{m}^2/\text{h}$)
J_0	Permeate flux at time $t=0$ ($\text{L}/\text{m}^2/\text{h}$)
J_s	Specific flux J_s (h/m)
$J_{s 0}$	Initial specific flux when $t=0$ (h/m)
$J_{s V}$	Specific flux J_s when total permeate volume equal to V (h/m)
μ	Water viscosity ($\text{kg}/\text{m}/\text{s}$)
P_f	Pressure on the feed side (Pa)
P_p	Pressure on the permeate side (Pa)
r_{total}	Total rate constant (m^2/L)
R	Sum of resistance for membrane (L/m)
R_{cake}	Resistance coefficient due to cake formation on the membrane (L/m)
R_{CIFI}	Resistance coefficient due to irreversible fouling not restored by chemical cleaning (L/m)
R_{HIFI}	Resistance coefficient due to irreversible fouling not restored by hydraulic backwashing (L/m)
R_{mem}	Sum of resistance coefficient to the flow through a clean membrane (L/m)
TFI	Total fouling index (m^2/L)
TMP_0	Transmembrane pressure at time $t=0$ (Pa) ($\text{kg}/\text{m}/\text{s}^2$)

TMP	Transmembrane pressure through the membrane for total permeate volume equal to V being tested (Pa)
TMP _{fn}	TMP at end of filtration cycle n (Pa)
TMP _{in}	TMP at beginning of filtration cycle n (Pa)
TMP _{in+1}	TMP at beginning of filtration cycle n+1 (Pa)
UMFI	Unified Membrane Fouling index(m ² /L)
V	Specific permeate volume (L/m ²)

CHAPTER 1

INTRODUCTION

After several waterborne disease outbreaks in both developing and developed countries, people now recognize that conventional water treatment technology has some potential limitations. After the 2002 Milwaukee *Cryptosporidium* epidemic many new and upgraded drinking water treatment plants incorporated microfiltration (MF) and ultrafiltration (UF) membrane systems to insure effective *Cryptosporidium parvum*, *Giardia lamblia* and bacterial removal (Jacangelo et al., 1995; Zhou et al., 2003). These membranes' systems also produce very high quality water and they are less susceptible to fluctuations in water quality. However, one of the main obstacles in the operation of MF/UF processes is fouling; membrane foulants (i.e., colloidal or particulate matter, dissolved organics, and microorganisms) can reduce the water production rate or increase the energy requirements. Membrane fouling is inevitable, but there has been a great deal effort on minimizing its impact. The main tools used to reduce the impact of fouling are using different types of pre-treatment processes and using different operating conditions. The magnitude of the fouling and the effectiveness of the fouling minimization strategies are highly dependent on the raw water characterization.

Key operational variables are optimized to reduce fouling include: using different set permeate fluxes (Carrère et al., 2001; Guo et al., 2009 a; Lee et al., 2008; Walker, 2014; Waterman, 2008), backwashing and/or relaxation (De Souza & Basu, 2013; Jacangelo & Noack, 2005; Kim & DiGiano, 2006; Wu et al., 2008). In addition, membrane chemical cleaning plays an important role on membrane fouling control. The suitable chemical cleaning selection can maintain membrane permeability, save cost, and prolong membrane life spans (Kimura et al., 2004; McDonald & Robinson, 1993; Nguyen et al., 2011; Shi et al., 2014; Zhang et al., 2011).

Pretreatment prior to UF membrane processes will reduce particles and dissolved organic matter prior to membrane treatment, which results in a reduction of membrane

fouling. Coagulation/flocculation with or without sedimentation prior to membrane filtration is the most commonly implemented MF/UF pretreatment scheme for waters with significant NOM content. Floatation is a compact separation process, which is particularly suitable for waters with algae and cyanobacteria because the density of algae and cyanobacterial cells are low and these cells are easily floated. As one of the expected result of global warming is greater algal/cyanobacterial growth and greater algal/cyanobacterial challenges at water treatment plants, it is likely that floatation will become a more popular form of treatment. Floatation has received relatively little attention as a membrane pretreatment process (Amaral et al., 2013; Braghetta et al. 1997). Accordingly, Walker (2014) recently compared the effectiveness of floatation and sedimentation as pretreatment options for UF hollow fiber filtration of Ottawa River water (ORW). ORW is typical of Northern Canadian waters in that it has a low turbidity, low hardness, high color and high natural organic matter (NOM). As Walker's pretreatment (conducted at two closely located full-scale water treatment plants) used different coagulant aids, experiments need conducted to establish to what extent the observed improved performance was due to the coagulant aid or due to floatation. NOM amount and composition may vary seasonally, so the effectiveness of the different types of pretreatment may vary. In addition, Walker (2014) only considered one set of operating conditions and one type membrane cleaning strategy, it appears the later could be improved.

The objectives of this study are: a) to confirm the findings of Walker (2014), i.e., that floatation pretreatment is superior to sedimentation pretreatment for this relatively high NOM water; b) to evaluate the impact of seasonal water quality variations; c) to find a more effective chemical cleaning method for pretreated river water; and d) to study the effect of different filtration cycle lengths on the membrane performance. The basic hypothesis that floatation is superior to sedimentation as a membrane pre-treatment process for this type of waters. This thesis is written as a manuscript-based thesis, chapter 4 is a journal manuscript instead of a conventional results chapter.

CHAPTER 2

LITERATURE REVIEW

This literature review consists of three sections, introduction to membrane filtration technology, membrane fouling and hollow fiber membrane fouling control.

2.1 Introduction to Membrane Filtration Technology

Clean and safe drinking water has always been important to human health, but after several waterborne disease outbreaks in both developing and developed countries, people now recognize that the conventional water treatment technology has potential drinking water safety problems. One of the most common problems is caused by microorganisms, which includes viruses, bacteria and protozoa. For example, *Giardia lamblia* and *Cryptosporidium parvum* are very common protozoic pathogens which have high tolerance to chlorine disinfection. They are often detected in surface waters and in some treated drinking waters, and they have caused several outbreaks in North America (Hrudey & Hrudey, 2004; Jacangelo et al., 1995). The major size characteristics of these microorganisms are presented below (Fig. 2.1). The average size of viruses, bacteria, and protozoa are between 0.02 to 0.1, 0.3 to 50, and 50 to 500 μm , respectively. Conventional water treatment uses particle filtration that is not always capable of removing all of these microorganisms. As a result, membrane filtration processes have been increasingly used in water treatment (Vickers, 2005).

The main pressure-driven membrane processes listed in order of largest to smallest pore size are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). MF membranes range in size from approximately 0.05 to 10 microns. UF membranes are in the range of approximately 0.005-0.1 microns. MF/UF membranes remove suspended solids, protozoa, and bacteria through size exclusion (Vickers, 2005) (Fig. 2.1). They are ideal for the removal of these microorganisms from water and make treated water safer. Both of the tight MF and the loose UF membranes, as water safety barrier, have been used in many water drinking water treatment plants (MWH, 2005). It

should be noted that although membranes with pores sizes in the lower end of the UF membrane pore size range can achieve some virus removal, the majority of the UF membranes used in water treatment have pore sizes in the 0.01-0.02 μm size range and they are not very effective at removing viruses. The pore size of NF membranes is about 1-10 nm and they can remove divalent ions, including Ca^{2+} and Mg^{2+} , so NF membranes are often used for water softening (Fane et al., 2006). NF membrane can remove macromolecules, such as natural occurring organic matter (NOM), which are not removed well by UF and MF membranes. RO membranes pore size is less than 1 nm, so in addition to all of above mentioned contaminants they also remove monovalent ions, they are commonly used for water desalination (Fane et al., 2006).

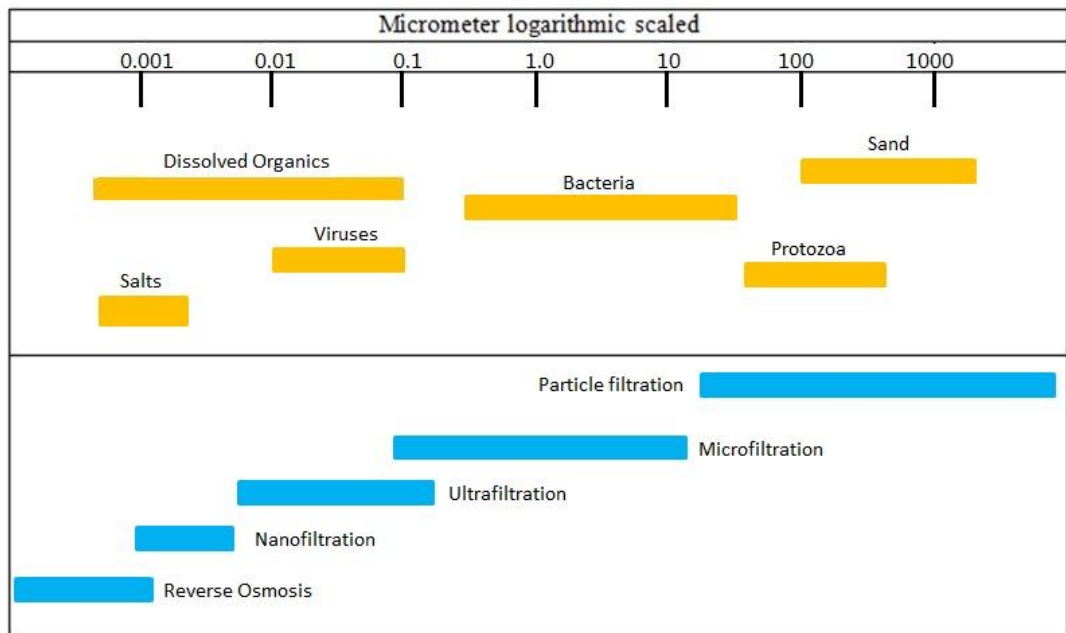


Fig. 2.1 Basic diagram of mass transport in a membrane (Vickers, 2005)

2.1.1 Definition of Ultrafiltration Technology

Ultrafiltration (UF) is a type of low pressure membrane filtration technology which uses hydrostatic pressure to force a solution through a semipermeable membrane. A semipermeable membrane is a thin layer of material which can separate substances in solution, they are categorized based on the molecular size of the solutes they can remove. The index used for this purpose is the molecular weight cutoff (MWCO), which is the size

of solutes which the membrane can remove 90%. A 100 kDalton (Da) MWCO UF membrane means that when water containing a solute with a molecular weight of 100 kDa is fed to the UF membrane, 90 percent of the solute will not pass through the membrane.

Although the UF membrane primary removal mechanism is size exclusion, sometimes they can effectively retain smaller solutes than the MWCO by static repulsion between the solute and surface of the membrane. The layers of foulant material that accumulate on the surface of a membrane may also boost the removal beyond that expected from the MWCO (Shi et al., 2014).

Compared to conventional clarification and disinfection processes, UF technology has many advantages. First, it can effectively remove bacteria and protozoa without using chemical disinfectants and thus avoids producing harmful disinfection by-products (DBPs). Second, it consistently produces a high quality effluent even when there are significant fluctuations in the influent water quality, this is not the case for conventional water treatment processes. Thirds, it uses less chemicals. Fourth, it has a smaller foot print. And finally it can be easily automatized.

2.1.2 Classification of Ultrafiltration Membrane

Membrane can be classified in several ways, UF membranes themselves can categorized based on the membrane configuration, the driving force, filtration types, and membrane materials. Most membranes are made from polymeric materials, but there also ceramic membranes in the market, this thesis concentrates on polymeric membranes.

2.1.2.1 Membrane Configurations

For drinking water applications UF membranes available in the following membrane configurations: spiral wound (flat sheet), tubular, hollow fiber membrane modules.

Spiral wound membrane modules are made from flat sheet membranes, but in a form of a hollow core containing many pairs of membrane sheets separated by a highly porous spacer layers plate as shown as Fig. 2.2. Feed enters one end of the element and flows through the feed channels towards the other end of the module, as it does due to the

pressure a fraction of the fluid passes through the membrane and into the permeate collection spacers, that lead the permeate to the central core tube, and exit as permeate. Spiral wound membranes have a cross-flow pattern, the feed is passed through a membrane, the solids being trapped in the filter and the concentrate being released at the other end.

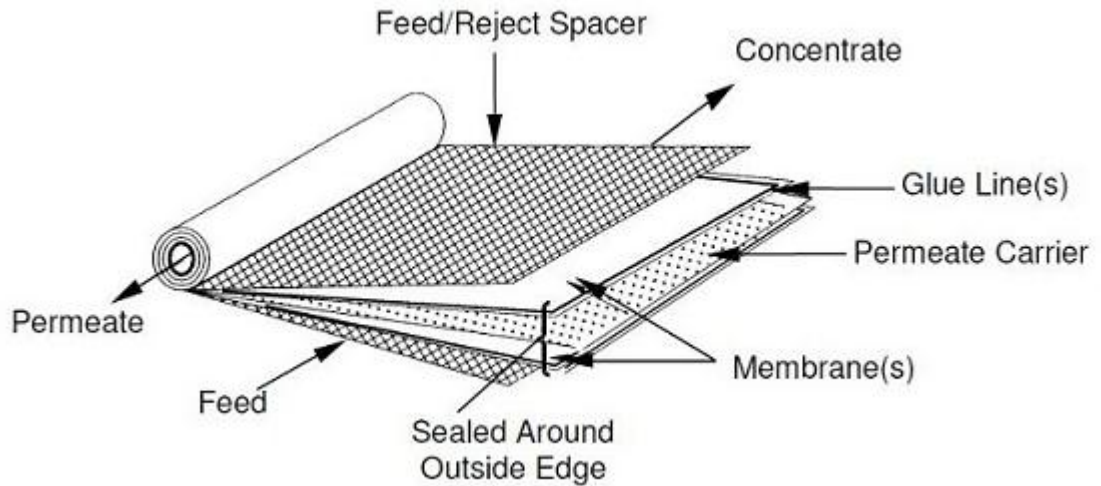


Fig. 2.2 Spiral wound membrane module (USEPA, 2005)

Tubular membranes are placed inside support porous tubes, and these tubes are placed together in a cylindrical shell to form the unit module. Tubular membranes have a diameter of about 5 to 15 mm, they are usually operated in a cross-flow pattern. Tubular membranes do not allow backwash because of the membrane coating is not bound strongly enough to be backwashed (Pearce, 2011).

In water treatment the most common type of UF membranes configuration used are hollow fiber membranes, which consists of hundreds to thousands of small tube-like fibers. These fibers are sealed into cartridges and the units have many cartridges. The inner fibers diameter is usually 0.8/0.9 mm, and the outer fiber diameter is 1.3/1.4 mm (Pearce, 2011). Because of high surface to volume ratio, hollow fibers modules are compact, cost-effective and energy-effective method for treating large volumes of feed (MWH, 2005). Because of the fibers bi-directional strength, they offer flexibility in terms of the system configuration or the system operation (MWH, 2005). The key advantage of hollow fibers is they can be backwashed to maintain the stability (Pearce, 2011). Hollow fiber membranes have been successfully employed in industrial water, industrial wastewater, and beverage processing applications, as well as municipal drinking water and wastewater treatment plants.

2.1.2.2 Driving Force

In terms of driving force UF hollow fiber systems can be classified into vacuum (submerged) and pressure membrane systems. In pressure driven units the pressurized feed goes to the inside of the fiber and flows through the fiber wall to the outside of the fiber (inside-out flow). In vacuum driven systems, a vacuum pump is connected to the inside of the hollow fibers and it draws the water from the outside of the fiber through the wall of the hollow fiber (outside-in flow). Inside-out flow systems have better control over module hydrodynamics to avoid dead-end zones and they flush particles from the membrane module more easily. However, outside-in flow usually produces lower head loss in the membrane module (Vickers, 2005).

2.1.2.3 Filtration Types

Membrane systems can be operated either through dead-end filtration or through cross-flow filtration. In cross-flow filtration, the feed flow travels tangentially across the surface of the membrane, thus, turbulence of the feed flow minimizes the deposition of filtered material on the filter surface, and allows the flow to remain constant. However, the principal disadvantage of this approach is the production of permeate is too low compared to dead-end filtration because the majority of the liquid flow exits the unit without going through the membranes, this flow is called the retentate. Dead-end filtration is different from cross-flow filtration, the flow direction is perpendicular to the membrane surface, and the retained particles are rapidly trapped on the surface, forming what is called a cake. The main advantage is dead-end filtration allows all of the feed to become permeate (MWH, 2005). In cross-flow systems only a fraction of the feed becomes permeate. Compared to cross-flow filtration, dead end filtration is particularly effective when feed water has a low level of foulants. So dead-end filtration is normally used for surface water filtrations, pretreatment for seawater RO, and tertiary wastewater filtrations (Remize et al., 2010).

2.1.2.4 Membrane Materials

Polymeric membranes are manufactured from different materials by different membrane suppliers. These include polysulfone (PS), polyethersulfone (PES), polyvinylidene fluoride (PVDF), polypropylene (PP), polyacrylonitrile (PAN), polyethylene (PE), and cellulose acetate (CA) (Vickers, 2005). The right material should be chosen based on their advantages and disadvantages for a particular application and to facilitate operation and maintenance. PVDF, PES and PS membranes are the most materials used in water treatment membranes because they can be safely exposed to chlorine, PVDF and PES being the most resistant (Clochard et al., 2004). PVDF hollow fibers are used predominantly in outside-in hollow fiber systems, while PS and PES hollow fibers are used predominantly in inside-in systems (Pearce, 2011).

2.2 Membrane Fouling

The biggest technical challenge in using membranes is membrane fouling, that is to say the increase in transmembrane pressure (TMP) or the reduction of permeate flux because of the accumulation of particles on the membrane or within the membrane pores. Membrane fouling leads to the increase of operational costs because of the need for frequent backwashing, regular chemical cleaning and the eventual replacement of the membrane. Although membrane fouling is an inevitable process, understanding the fouling mechanism, and developing effective fouling control strategies are particularly important. Membrane fouling can be classified into reversible fouling and irreversible fouling. Hydraulically reversible fouling can be recovered by hydraulic backwash; hydraulically irreversible fouling cannot be restored by hydraulic backwash. However, part of the hydraulically irreversible fouling may be recovered by chemical cleaning, so hydraulically irreversible fouling can be subdivided into chemically reversible fouling and chemically irreversible fouling. Fouling mechanism, membrane foulants and natural organic matter, and assessment methods of membrane fouling will be discussed in following sections.

2.2.1 Fouling Mechanism

The deposition of particles on the membrane surface or inside the membrane pores cause membrane fouling. The basic membrane fouling mechanisms include pore adsorption, pore blocking, and cake layer (Hermia, 1982; Vickers, 2005). Pore adsorption (also known as standard blocking) presumes that particles are smaller than the pores and they are deposited on the pore walls, so the pore cross section is reduced. Pore blocking, which includes complete blocking and intermediate blocking, presumes that particles completely or partially block the entrance to the membrane pores, because parts of pores are sealed, the total number of pores available for the water flow is reduced. Cake layer presumes that particles precipitate to form a permeable cake layer on the surface of the membrane and this layer results in a further resistance to flow through the membrane.

2.2.2 Membrane Foulants and Natural Organic Matter

The principal membrane foulants are particulates, inorganic precipitates, organic foulants and biological growth. In the treatment of surface waters by MF and UF membranes the principal foulants are inorganic precipitates and natural organic matter (NOM) (Guo et al., 2009 b; Huang et al., 2007; Lee et al., 2008; Qi et al., 2013; Tian et al., 2013 a; Yuan & Sydney, 2000; Zularisam et al., 2007). Which substances are the principal foulant depends on the water quality characteristics of the water being treated. NOM is a complex mix of organic compounds with different molecular weight (MW), different functional groups (phenolic, hydroxyl, carbonyl groups and carboxylic acid).

The most common classification of NOM is by its reaction to acidification: humic acids (HA) and fulvic acids are two main components. The HA can be precipitated by acidification while fulvic acids cannot (Gjessing, 1976). NOM can be further classified into three fractions: hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) (Zularisam et al., 2007). HPO is mostly composed of humic and fulvic acids, while HPI is mostly composed of polysaccharides, amino acids, protein (Zularisam et al., 2007). TPI is defined with MW in between hydrophobic and hydrophilic fractions.

NOM varies with the different sources, such as (1) allochthonous NOM including terrestrial, vegetative debris; (2) autochthonous algae NOM, and (3) wastewater organic matter (Huang et al., 2007). Furthermore, the NOM characteristics from a given source may change with time (Huang et al., 2007).

Many previous studies have tried to investigate the key fraction of NOM causing fouling. HPO has been reported as responsible for membrane fouling (Katsoufidou et al., 2005; Lee et al., 2008; Tian et al., 2013 a; Yuan & Sydney, 2000). Tian et al. (2013 a) observed that HA alone exhibited higher fouling potential than when HA was filtered together with a protein (bovine serum albumin) or a polysaccharide (dextran), the reasons may be protein and polysaccharide could interfere with the strong interactions of HA and membrane. Yuan & Zydney (2000) also found a significant fouling during filtration of an Aldrich HA solution through a 30, 50,100, 300 kDa PS membrane, they observed HA had a significant effect on fouling for the larger MWCO membranes, especially. It should be noted that Aldrich HAs are of terrestrial sources and are not considered to be representative of aquatic HAs. While Guo et al. (2009 b) studied six different NOM model compounds (fulvic acid, tannin, aniline, citric acid, polysucrose and oligopeptide) to represent different hydrophobicity in surface water by PVC hollow fiber membranes, they reported the hydrophobic neutral compounds caused the most fouling when they were be tested individually. However, the HPI DOM mixture caused faster fouling than hydrophobic DOM mixture when they were tested together.

Recently, different results were reported, many researchers claim that the principal membrane fouling in treating surface waters is caused by HPI (Qi et al., 2013; Zularisam et al., 2007; Yamamura et al., (2014). Zularisam et al. (2007) also carried out the UF hollow fiber experiments using the soft, rich in NOM surface water from Ulu Pontian River in Malaysia, they found that the HPI fraction fouled more than the HPO and TPI fractions. However, HPO fraction was not controlling because it presents a smaller fraction of NOM than HPI fraction.

But Qi et al. (2013) reported the results of HPI accounted for the majority of the fouling regardless the different membrane materials (PVC, PVDF and PS) used in bench-scale UF hollow fiber system when treating surface water from the Songhua River in China which has high content of DOC (7.72–7.83 mg/L), although HPO is the majority fraction

of DOC in the river. Yamamura et al., (2014) found the HPI fraction exhibited higher fouling potential than HPO regardless of the water sources (four different surface waters: Toyohira River with low concentration of NOM (0.8 mg/L TOC), Lake Inbanuma with heavy eutrophication (5.7 mg/L TOC), Kushiro River with 0.9 mg/L TOC, Yodo River water with 1.8 mg/L TOC) and membrane materials (PE, PVDF, PAN, and PES). In all of the four water sources, HPO fraction is the largest fraction. The primary components causing the irreversible fouling were identified as carbohydrate and proteins.

Based on the inconsistent results above, the primary NOM contributor of membrane fouling still remains to be determined by further research. The composition of NOM not only changes with locations but also with time, so it is of interest to study the impact of seasonal water quality changes and in particular the various NOM components have an membrane fouling.

2.2.3 Assessment Methods of Membrane Fouling

The assessment methods of membrane fouling include flux or TMP real time observation method, fouling index measurements and microscopic observation method.

2.2.3.1 Flux or TMP Real Time Observation Methods

Depending on the type of membrane system fouling can be quantified in terms of flux decline or TMP. For constant pressure systems, such as those frequently used in research, fouling is measured in terms of flux decline. In constant flux systems, such as most hollow fiber systems used in water treatment, fouling is quantified in terms of the increase in TMP.

2.2.3.2 Fouling Index and Measurements

Fouling is quantified in terms of the silt density index (SDI), the modified fouling index (MFI), single and combined blocking law models, the unified membrane fouling index (UMFI), and the resistance-in-series model index.

2.2.3.2.1 Silt Density Index and Membrane Fouling Index

SDI and MFI are the most widely applied methods to measure the particulate fouling potential of feed water. In both tests, a water sample is filtered through a 0.45 μm microfiltration membrane in dead-end flow setup at constant pressure to measure the particulate fouling potential of the sample. The SDI does not distinguish between blocking and cake filtration fouling mechanisms occurring during the test, and it cannot be used as part of a mathematical model to predict the rate of flux decline due to particulate fouling. Conversely, the MFI assumes fouling occurs due to the cake filtration mechanism and is dependent on the foulant particle size. It is effective for waters containing particulate and colloidal matters but not for organic matter in the water (Koo et al., 2013). Boerlage et al., (2002) tested with ultrafiltration (UF) membrane instead of microfiltration membrane and developed MFI-UF index, they found MFI-UF index was never stable for PS membrane testing tap water.

2.2.3.2.2 Single and Combined Fouling Mechanism Models

These methods are based on the blocking laws (Hernia, 1982). The fouling mechanisms can be classified in to four categories: standard blocking, complete blocking, intermediate blocking and cake filtration (Bolton et al., 2006). Some researchers attributed membrane fouling to one single mechanism including the cake filtration model, the pore narrowing (standard blocking) model and the complete pore blocking model (Muthukumaran et al., 2014). The regression of the flux or TMP data is used to assess the suitability of the models, and obtain the fouling rate coefficients. The best fitting model is presumed to indicate the controlling fouling mechanism.

Many studies reported that membrane fouling depended on the membrane material, feed solution and membrane configuration (Bolton et al., 2006; Mah et al., 2012; Wang et al., 2012). Wang et.al (2012) studied the fouling mechanisms of two flat membranes (PES and regenerated cellulose (RC)) with molecular weight cut off (MWCO) of 100, 30, and 10 kDa for treating succinic acid fermentation broth in UF system, they found that based on modeling their filtration tests the predominant fouling mechanism for PES 30 kDa and RC 10 kDa was complete blocking, for PES 100 kDa was intermediate blocking. The

performances of hollow fiber PS membranes were investigated in cross-flow UF for the processing of depectinized pineapple juice. The results revealed that hollow fiber membrane performance was controlled by a cake filtration mechanism, while ceramic tubular membrane performance was controlled by a pore blocking fouling mechanism (Barros et al., 2003). Taniguchi et al. (2003) also found cake layer formation was predominant of fouling of UF membranes by the reservoir water.

Four membrane fouling mechanisms can occur individually or in combination (Bolton et al., 2006; Muthukumaran et al., 2014; Wang et al., 2012). According to Muthukumaran et al. (2014), fouling due to standard blocking was predominant for ceramic MF membrane, whereas, fouling due to the combined standard blocking and cake layer were predominant for ceramic UF membrane in the treatment of secondary effluent. On the other hand, complete blocking was predominant for the performance of polymeric PES UF membrane. Bolton et al. (2006) fit the four individual mechanisms and combined mechanisms to data for the fouling of 0.22 μm pore size PVDF membrane in the sterile filtration of human plasma IgG and the viral filtration of bovine serum albumin. They observed the combined cake layer and complete blocking provided the best fits. In many cases fouling may not be caused by a single predominant mechanism, a combination of several mechanisms may be important.

More intensive studies about the transition in fouling mechanism by testing surface water in MF were performed by Yamamura et al., (2007). They hypothesized the following fouling mechanism: the membrane pores firstly blocked by relatively large particles meanwhile the inner pores were narrowed by small particles, and eventually a cake layer built up on the membrane surface.

An important disadvantage of these models is that they were derived for constant pressure system, however analogous models have been developed for constant flux systems. Another key disadvantage of this approach is that different mechanisms may occur simultaneously or sequentially in the operation cycle. For example, in long filtration tests/cycles, such as multi-day tests, it is reasonable to expect that cake filtration is the dominant fouling mechanism, while pore blocking has a more dominant role during the initial part of the test. Furthermore, sometimes several blocking models yield equally good simulations of the data, so it is impossible to identify the controlling mechanism. So the

combined fouling mechanisms should provide better data fits than single models. On the contrary, many researchers found the combination of cake filtration and standard blocking fouling model did not improve the simulations obtained by single blocking law models (Muthukumaran et al., 2014; Pezeshk & Narbaitz, 2012; Walker, 2014).

2.2.3.2.3 Unified Membrane Fouling Index

UMFI is a tool of predicting the total fouling capacity of the feed water and assessing the performance of low pressure membranes. The UMFI assumes that cake filtration is the predominant fouling mechanism but includes a potential contribution from cake layer formation and pore blocking (Huang et al., 2009). To obtain UMFI plot the reciprocal of the normalized specific flux (J_0/J) versus accumulated specific permeate volume (V), i.e., the volume of permeate per unit membrane area (L/m^2). These variables are related are described by the linear relationship shown in equation 2.1, and UMFI (m^2/L) is the slope of the resulting line.

$$\frac{J_0}{J} = (UMFI) V + 1 = \frac{TMP}{TMP_0} \quad (2.1)$$

Where J_0 is the permeate flux at time $t = 0$ hour ($L/m^2/h$), J is the permeate flux through the membrane for the water being tested ($L/m^2/h$), V is the accumulated specific permeate volume (L/m^2), TMP_0 is the transmembrane pressure at time $t = 0$ hour (Pa), TMP is transmembrane pressure through the membrane for the water being tested when the membrane has produced a total permeate volume equal to V (Pa)(Huang et al., 2009)

Huang et al. (2009) used three UMFI's to describe the fouling rate during single filtration cycles. They are the total fouling index ($UMFI_T$), the hydraulically irreversible fouling index ($UMFI_R$), and the chemically irreversible fouling index ($UMFI_C$). These indices were calculated using the linear regression approach. However, the limitation of this method is it assumes cake layer is the principal fouling mechanism.

2.2.3.2.4 Resistance-in-Series Model Index

Yeh and Cheng (1993) developed a fouling index which is based on a resistance-in-series model. The flux, J , is described as:

$$J = \frac{TMP}{R \cdot \mu} \quad (2.2)$$

where J is flow per unit area ($L/m^2/h$ or $m^3/m^2/s$), TMP is transmembrane pressure ($kg/m/s^2$), μ is the water viscosity ($kg/m/s$), R is the total flow resistance coefficient (m^{-1}). To allow more direct comparison between systems operating at different pressures, the specific flux J_s is often used (h/m). It is defined as

$$J_s = \frac{J}{TMP} = \frac{1}{R \cdot \mu} \quad (2.3)$$

In addition the fluxes, which may change with time, are often normalized by dividing them by the initial flux, so

$$NSF = \frac{J_s|_v}{J_s|_0} \quad (2.4)$$

where NSF is normalized specific flux (unitless), $J_s|_0$ is the initial specific flux (h/m), $J_s|_v$ is the specific flux (h/m) at any time when the specific volume is V (L/m^2) (i.e., permeate volume/membrane area).

Substituting equation 2.3 into equation 2.4 obtains

$$NSF = \frac{\frac{J}{TMP}}{\frac{J}{TMP_0}} = \frac{TMP_0}{TMP} \quad (2.5)$$

Where TMP_0 (Pa) is the initial TMP (Pa) for the clean membrane to obtain the flux J

This model assumes that R is the sum of flow resistance for the clean membrane (R_{mem}) (L/m), the resistance due to the cake formed on the membrane that is removed by hydraulic backwashing (R_{cake}) (L/m), the resistance due to irreversible fouling not restored by hydraulic backwashing (R_{HIFI}) (L/m), and the resistance due to irreversible fouling not restored by chemical cleaning (R_{CIFI}) (L/m), as summarized in equation (2.6):

$$R = R_{mem} + R_{cake} + R_{HIFI} + R_{CIFI} \quad (2.6)$$

Fouling resistance increases linearly with permeate volume, $R_i = r_i \cdot V$, where r_i is a rate constant (m^2/L). The total resistance can also be expressed as:

$$R = R_{mem} + r_{total} \cdot V \quad (2.7)$$

Where r_{total} is total rate constant. Combining equation 2.3 and 2.7 yields,

$$J_s = \frac{1}{\mu \cdot (R_{mem} + r_{total} \cdot V)} \quad (2.8)$$

Substituting to equation 2.4

$$\frac{1}{NSF} = \frac{J_s|_v}{J_s|_0} = \frac{(R_{mem} + r_{total} \cdot V) \cdot \mu}{R_{mem} \cdot \mu} = 1 + \left(\frac{r_{total}}{R_{mem}}\right) \cdot V \quad (2.9)$$

Different fouling indices can be calculated using the data from different operational cycles and cleaning steps. For single filtration cycles between hydraulic backwashes, the total fouling index (TFI) (m²/L) can be related to the normalized specific flux (NSF) and the specific volume (V) as follows:

$$\frac{1}{NSF} = 1 + (TFI) \cdot V \quad (2.10)$$

For multiple backwash cycles in between chemical cleanings, which is referred to as one chemical cleaning cycle (CC cycle), the hydraulic-irreversible fouling index (HIFI) (m²/L) can similarly be expressed as follows:

$$\frac{1}{NSF} = 1 + (HIFI) \cdot V \quad (2.11)$$

Average values for all data for a series of CC cycles can be used to determine the chemical irreversible fouling index (CIFI) (m²/L):

$$\frac{1}{NSF} = 1 + (CIFI) \cdot V \quad (2.12)$$

If the plot of (1/NSF) versus V is linear, the fouling indices can be calculated using linear regression. If the relationship is not linear, then the first and the last ten points can be used to determine the average value of the fouling indices.

Nguyen *et al.* (2011) and Walker (2014) found the TFI values variations were very significant between each hydraulic backwash cycle because of different effectiveness of the hydraulic backwash cycle. They compared the HIFIs of raw and coagulated water from same water plant, smaller HIFI of coagulated water than raw water indicate that the coagulation pretreatment can reduce hydraulic-irreversible fouling. They found excellent linear fit between inverse normalized specific flux and specific volume, suggesting resistance-in-series model could be used to describe chemical-irreversible fouling. Zupancic *et al.* (2014) and Lin *et al.* (2014) also found the HIFI and CIFI can effectively assess membrane performance and predict the optimal membrane operation, e.g. hydraulic backwash or chemical cleaning.

2.2.3.3 Microscopic Observation Methods

Field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and fourier transform infrared (FTIR) spectroscopy are used to assess the membrane fouling performance (Koo et al., 2013).

Natural organic matters (NOM) are recognized as one of the major foulants that block the membrane pore and reduce permeate flux. Some researchers studied the effect of NOM on membrane fouling and investigate the membrane fouling behavior of combined foulants (Xiao et al., 2013). Xiao et al. (2013) analyzed the surface and cross-section of a virgin and fouled membrane plus the fouling layer on the membrane surface by FESEM and FTIR, respectively. They found small molecules of HA and sodium alginate (SA) mixture were transported more easily than HA alone into membrane pores and caused internal and/or pore entrance blockage, leading to a rapid reduction of the effective filtration area.

2.2.3.4 Conclusions of the Fouling Analysis

Although the flux or TMP real time monitoring methods are easy, they cannot provide a simple quantitation of fouling. Fouling indices, such as the SDI, are conducted at a constant pressure in membrane filtration system and mostly used for RO membranes. MFI only assumes cake layer is the dominant mechanism and applies for high solid concentration feed. MFI-UF index can be used for UF but it still has to be conducted at a constant pressure, while most water treatment UF membrane systems operate with a constant flux and varying TMP with time. Single fouling models based on the blocking law assume that only one fouling mechanism is controlling, this is probably not realistic. And when regressing experimental data with single or combined blocking law models, the quality of the fit of alternative models is often quite similar so this approach does not yield a definitive answer as to the controlling mechanism. Furthermore this approach can only be applied to one filtration cycle, while hollow fibre systems operate many cycles per day and the fouling (and thus the controlling mechanisms) may change from the initial cycles to subsequent cycles (Waterman, 2008). Moreover, UMFI is also derived from blocking law which assumes cake layer is major fouling mechanism. The UMFI approach can be adapted to both constant flux and pressure operation so it seems more appropriate than

earlier approaches. The resistance-in-series model has the same mathematical form as the UFMI, but it is superior in that it does not assume a specific fouling mechanism. In conclusion, resistance-in-series model is a promising fouling analysis method.

2.3 Hollow Fiber Membrane Fouling Control

In hollow fiber UF membrane treatment applications the impact of fouling can be reduced by adjusting operating conditions and using the appropriate pretreatment.

2.3.1 Operating Conditions

The main operation methods can be used to alleviate the membrane fouling in hollow fiber membrane systems are varying the filtration parameters, using hydraulic backwashes, chemical cleaning, relaxation and air scouring.

2.3.1.1 Filtration Parameters

Filtration parameters include constant pressure or constant flux modes, different filtration cycle length, different set permeate fluxes, and so on.

Carrère et al. (2001) found that in the clarification of lactic acid fermentation broths using a cross-flow MFunit, the resistance of the cake formed during constant pressure filtration was higher than that observed during constant flux operation. Lee et al. (2008) also tested low DOC content surface water using different MF and UF flat sheet membranes, compared constant pressure and constant flux tests, and suggested that constant flux mode performed better than constant pressure one. Thus, most hollow fiber systems operate in the constant flux mode.

The operational flux rate depends on the membrane, the feed quality and the degree of pretreatment provided. Frequently, flux rate sensitivity tests are conducted to estimate the maximum flux rate for which the TMP is not disproportionate high. This is referred to as the operational critical flux, and to minimize the impact of fouling systems should operate at a flux that is below the critical. Waterman (2008) compared the fouling rate of four different constant fluxes (50, 70, 100 and 120 LMH) in the filtration of Ottawa River

water (ORW) using a 70 kDa MWCO PES hollow fiber membrane, and he found the fouling rate increased with increasing operating flux. In filtering ORW using a 100kDa PES membrane Walker (2014) found that the operational critical flux was approximately 79 LMH and there was a big differences in membrane performance between subcritical operations (50LMH) and supercritical operation (100 LMH). The comparisons of different constant permeate fluxes (60 and 100 LMH) were conducted by Guo et al. (2009 a) in treatment two surface waters: a) Luan River, which has a high algae contents; and b) Huang River; which has a high content of low molecular weight organic components. They reported operation at a higher constant permeate flux fouled membranes more readily than the lower permeate flux.

2.3.1.2 Backwashing, Air Scouring and Relaxation

Backwashing and/or relaxation periods are standard operating steps used in most membrane filtration systems to reduce fouling. Backwashing is reversing permeate through the membrane (Zsirai et al., 2012). Periodical backwashing can alleviate the aggregation of the particles on the membrane surface or in the membrane pores, the reverse direction flow can cause higher backwashing pressure to clean foulants effectively. The operation consists of a 15 to 60 minutes long filtration cycle followed by a 1-5 minutes long backwash at two to three times the permeate flowrate (MWH 2005). The filtration cycle length between backwashes varies depending on the feed (Jacangelo et al., 2005). Kim and DiGiano (2006) found 10 minutes of filtration cycle time between backwashing could reduce the fouling rate compared to 15 minutes of filtration cycle time in a two-fiber bench-scale UF system treating secondary waste water effluent. Waterman (2008) studied 15, 30 and 60 minutes of BWF between backwashing at a flux of 100 LMH (above the operating critical flux) in a bench-scale hollow fiber membrane system, the results showed that shorter filtration cycle times between backwashing reduced the fouling.

Wu et al., (2008) reported backwashing was effective in removing the cake layer, and backwashing fluxes had a greater impact than the duration for fouling control. Waterman (2008) also studied the effect of backwash duration time of 1 and 2 minutes on the membrane performance. He found that the increase in backwash duration time from 1 to 2 minutes could only reduce the fouling to a small extent. Because different compounds

have different fouling mechanisms, the appropriate conditions should be optimized for the water and pretreatment in question.

Relaxation is the intermittent pause of permeation, permits some flux recovery if the membrane is immersed (Zsirai et al., 2012). Wu et al., (2008) compared the membrane performance of filtration with relaxation and backwashing to the continuous filtration mode in a lab-scale aerobic membrane bioreactor (MBR), optimized relaxation could reduce membrane fouling effectively, but long and frequent relaxation would cause severe fouling. The influence of relaxation was studied in immersed hollow fiber membrane bioreactors, they found relaxation did not have a significant impact on the reversible and irreversible fouling, backwashing performed better than relaxation in reversing fouling (Zsirai et al., 2012). De Souza and Basu (2013) studied the impacts of relaxation parameters on UF membrane fouling reduction in drinking water treatment, they found lower fouling with the continuous flow mode compared to the dead end mode, and the longer duration of relaxation (15 minutes) found to be beneficial for fouling reduction compared to using a 5 minutes.

Air scouring involves injecting air bubbles intermittently or continuously to the membrane module, usually combined with backwashing, to promote higher turbulence at the membrane surface and improve the cleaning efficiency (Shi et al., 2014). Backwash can be combined with air for inside-out configuration which applies high velocity backwash followed by air flush to expel water from fiber. For outside-in configuration, air scouring is commonly used to clean the membrane (Pearce, 2011). In a bench-scale hollow fiber PVDF UF study conducted by Li et al. (2014), the hydraulically irreversible fouling could be reduced by either intermittent coarse bubble or by large pulse bubble sparging compared to operation without air scouring was applied. Overall, currently there are still some challenges in air scouring since the potential damage to membrane. De Souza and Basu (2013) also studied the impacts of combination of backwash, air scouring and relaxation on membrane performance, the combination of the three operations proved to be better in reducing fouling compared to air assisted backwashing only and air assisted relaxation only.

2.3.1.3 Chemical Cleaning

Membrane chemical cleaning plays an important role on membrane fouling control. Suitable chemical cleaning selection can maintain membrane permeability, save costs, and prolong membrane life (Shi et al., 2014). Many chemical reagents are commercial available, they fit within six categories: alkalis, acids, oxidants, surfactants, chelants and enzymes (Shi et al., 2014). Alkalis are primarily used to clean membranes fouled by organic and microbial foulants. Acids are commonly used to dissolve metal oxides and inorganic salts. Chelants have good capacity for complexing metals (Shi et al., 2014). The main function of oxidants, such as NaOCl and H₂O₂, is the oxidation of organics. Enzymes are used to catalyze proteins. The chemical cleaning procedure selection is very important for membrane filtration because it impacts membrane performance and prolongs membrane life.

Much research has focused on the chemical cleaning of fouled membranes. Zhang et al. (2011) tested NaOH, HCl, EDTA and NaOCl, they found that 100 ppm NaOCl was very effective in cleaning UF membranes used in the treatment of algal-rich water. Kimura et al. (2004) studied different chemical cleaning reagents for PS UF membranes used in treating Chitose River water, which has high concentrations of dissolved organic matter, manganese, and ammonia nitrogen. This 0.01M NaOH and 500ppm NaOCl were effective in restoring membrane permeability. They also found that NaCl and EDTA were not effective. Nguyen et al. (2011) performed chemical cleaning in the form of 20 minute-long enhanced backwashes every 24 hours with 100 ppm NaOCl, and 20 minutes with deionized waters rinses for membranes used to treat natural surface waters. The North Bay (ON) water is clear, low NOM content water (McDonald & Robinson, 1993). They developed different maintenance operations for their the membrane filtration racks: enhanced flux maintenance with the addition of 300 ppm NaOCl and clean-in-place (CIP) which involves recirculating a 2% citric acid solution for 20 minutes and then the membrane are soaked with water to neutralize the pH. After the citric acid procedure, 1% NaOH combined with 1000 ppm NaOCl solution are recirculated for 20 minutes and then the membrane are soaked with water to neutralize the pH.

Ottawa River water (ORW) has significant NOM content and relatively high color. And the ORW NOM was predominately hydrophobic in nature (Pezeshk & Narbaitz, 2012). NOM is known as the main contributor for the membrane fouling, theoretically alkalis and oxidants are effective. However, according to Walker (2014), 0.1N NaOH cleaning was fairly effective in restoring their Raw ORW-fouled PES membranes. However, the NaOH cleaning did not work very effectively for the pre-treated waters, and did not restore all the permeability of membranes used to treat raw ORW. Further investigation into alternative cleaning procedures is required for the pre-treated waters.

2.3.2 Pretreatments

In addition to the operational conditions, pretreatments (e.g., coagulation/sedimentation, adsorption, pre-oxidation) can reduce the membrane fouling to various degrees.

2.3.2.1 Coagulation with or without Sedimentation

Coagulation/flocculation/sedimentation remains the most common processes used to remove turbidity and NOM in water treatment. Aluminum sulfate (alum) and other chemicals (ferric salts, polymer) are added to water to form "flocs". The flocs become heavy enough to settle down to the bottom during the sedimentation and flocs are separated from the main water stream.

In order to minimize the formation of DBPs many water treatment plants optimizing coagulation for the removal of NOM rather than just turbidity removal. This generally requires significantly higher coagulant doses and is referred to as enhanced coagulation. This results in larger flocs.

Coagulation has been widely used in the UF system, depending on the raw water, the coagulated/flocculated water may be directly exposed to the membrane or it may get settled prior to membrane filtration. Whether sedimentation is included or not affect the size and characteristics of the flocs that one tries to develop in the coagulation/flocculation process. Applying coagulation before UF has been suggested by Jacangelo and Laine (1994), they found coagulation prior to hollow fiber UF could increase the TMP in 102

LMH constant flux tests. It appeared that alum had clogged the membrane pores and caused an increase in fouling. However, Done et al., (2007) used pre-coagulation method prior to PVDF flat sheet UF membranes, and presented coagulation without settling could remove the hydrophobic and neutral hydrophilic NOM, which resulted in the improvement of membrane flux. Huang et al. (2011) studied the effect of coagulation mechanism on membrane permeability in coagulation-assisted microfiltration for spent filter backwash water recycling, and claimed that coagulation improved the flux decline effectively, coagulation without sedimentation can improve the membrane performance because of the formation of less compressible cake layer. In addition, some researchers found sedimentation after coagulation can improve the membrane performance to some extent. Jung et al., (2006) reported coagulation with sedimentation before flat sheet UF membrane could reduce membrane fouling due to the increase in particle size. However, Park et al. (2002) applied coagulation and coagulation with sedimentation prior to hollow fiber inside-out UF system for drinking water production, and found coagulation was more effective than coagulation with sedimentation in improve the membrane permeability. But Liang et al. (2008) had somewhat different results, they compared three different pretreatments (coagulation, coagulation/sedimentation and coagulation/sedimentation/filtration) in three different UF pilot plants to treat algae-rich reservoir water and found coagulation/sedimentation was the best pretreatment in terms of water quality and fouling reduction. Moon et al. (2009) also found the similar results; they presented coagulation/sedimentation pretreatments performed better than UF without pretreatments in water production and DOM removal for drinking water treatment.

Coagulation with or without sedimentation can be used as one of the effective pretreatments of UF system, but the performance depends on the types of the coagulants, proper coagulant dosage, and the mixing time and so on.

Many studies have focused on optimize the coagulant dose in order to reduce the membrane fouling in the downstream treatment of membrane filtration (Aguilar et al., 1996; Lee et al., 2009; Shon et al., 2005; Tran et al., 2006). However, Ma et al., (2014) found the most serious membrane fouling happened when there was hydrophobic HA in the feed water with low doses of coagulant, which is to mean that a higher coagulant is necessary.

Due to their relatively large pore size water treatment UF and MF membranes only remove 10 to 20% of the incoming NOM. For the treatment of waters with significant NOM concentrations water treatment plants using UF and MF membranes must incorporate a pretreatment scheme that optimizes NOM removal. This generally entails using coagulation/flocculation/sedimentation pretreatment with higher coagulant doses.

2.3.2.2 Preoxidation

Many papers have reported that preoxidants such as UV, chlorine, permanganate, and ozone can improve the membrane performance (Gao et al., 2011). Patrick et al. (2011) used UV irradiation as a pretreatment upstream from NF and found UV was able to reduce the biofouling effectively. Heng et al. (2008) found that the combined use of permanganate and chlorine could inactivate the algae cells and mitigate the UF algae fouling. Yu et al (2014) compared coagulation as pretreatment for UF with coagulation with a continuous low dose of NaOCl (1 mg/L as Cl), they found the addition of NaOCl reduced membrane fouling by inactivating bacteria in the influent and reducing the production of proteins and polysaccharides in the cake layer. Xu et al. (2014) found 1.5 mg/L Cl could effectively reduce the membrane fouling by the low NOM concentration Yangtze River raw water and scanning electron microscope (SEM) images showed that much the filtration cake consisted of looser fragments. Schlichter et al. (2004) also investigated the effect of ozone on the filtration and found 0.05 mg/L ozone could reduce ceramic MF and UF fouling. Although pre-oxidants were studied as an effective pretreatment of filtration, more consideration must be taken into account to other impacts such as DBPs production.

2.3.2.3 Adsorption

Activated carbon adsorption and magnetic ion exchange (MIEX) adsorption have also been studied as pretreatment methods for low pressure UF membranes. Powdered activated carbon (PAC) is the most popular adsorbent utilized in adsorption/UF systems, the PAC is used primarily to remove synthetic organic compounds, such as pesticides, or to remove NOM (Gao et al., 2011). This NOM removal was intended to reduce DBPs formation and reduce membrane fouling. Contradictory results have been presented on

the benefits of PAC pretreatment. Some found adsorption had no obvious effect on membrane fouling control (Berube et al., 2002; Lee et al., 2000; Mozia & Tomaszewska, 2004), however, Campinas & Rosa (2010) and Zhang et al. (2003) reported PAC could help control membrane fouling. The reason of the different results may be because the different types of PAC, different PAC doses, and different water characteristics.

The MIEX are polymeric anionic ion exchange resins that can remove negatively charged molecules like NOM. The water is mixed with these resins in a contact reactor and then separated in a magnetic separator/clarifier. Kabsch-Korbutowicz et al. (2006) compared the effect of MIEX resin and coagulation on the UF membrane performance, they found that MIEX resin is much more effective than coagulation in organic substances removal and fouling reduction. But there are only a limited number of studies on MIEX as a pretreatment process for MF/UF system, more research is still needed.

2.3.2.4 Flootation

Global warming is an important environmental concern. As a result of the global warming it is expected, that there will more intense storm event and longer dry periods in between such events. The slightly higher temperatures are also expected to lead to greater evaporation. These conditions seem likely to lead to greater algal growth, more algal/cyanobacterial blooms and more taste and odour events at water treatment plants. Also, due to the higher temperature cyanobacteria are expected to become dominant over algae. Cyanobacteria are concern not only due to taste and odour events, but also because they produce skin toxins, heptotoxins and neurotoxins. Cyanobacteria blooms have been observed in many places in the world, for example, severe cyanobacteria problems arose in Western Lake Erie in the summer of 2014, and led to a three-day drinking water consumption ban in Toledo, OH (Plumer, 2015).

Flootation is a compact separation process, which is particularly suitable for waters with algae because the densities of algae and cyanobacterial cells are low so these cells are easily floated. As a result of the expected greater algal growth and greater algal challenges at water treatment plants, it is expected that flootation will become a more popular form of treatment.

Braghetta et al., (1997) also suggested that floatation pretreatment reduced fouling in a pilot scale hollow fiber MF system compared with treatment of raw surface water (TOC = 5-8 mg/L). Amaral et al. (2013) compared flat sheet PVDF MF alone and floatation followed by MF to treat eutrophic lagoon water and found the MF +floatation was more effective than MF alone in terms of removal of cyanobacterial cells, color, turbidity, UV₂₅₄ and DOC. Floatation increased the initial flux during the first 10 minutes, but membrane fouling worsened the flux during the next 170 minutes. Their results may indicate the combination of floatation and low pressure membrane filtration can be a viable option in water treatment. Walker (2014) reported floatation may be helping to remove more hydrophobic NOM in ORW as well compared to sedimentation when he conducted hollow fiber membrane filtration for drinking water production. However, only single set of filtration conditions was tested by Walker, the chemical cleaning used was not very effective for pretreated ORW and the initial flux of his various runs were not the same. His experiments should be confirmed and expanded.

2.4 Conclusions

Membrane fouling is inevitable, instead of eliminating it, minimizing fouling is more important. NOM has been considered as the dominant foulant in many natural surface waters and the NOM fractions (HPO, TPI, and HPI) cause different types of membrane fouling. To minimize membrane fouling, coagulation with/without sedimentation prior to membrane filtration is often implemented as pretreatment. The literature review shows that the effectiveness of coagulation with or without sedimentation depends on the type of the membrane used, the characteristics of the water being treated, the coagulant dosage, and the settling time has been implemented. There are few studies comparing of membrane performance between coagulation/settlement and coagulation/floatation as pretreatments prior to membrane filtration of high HPO NOM surface waters. Thus, there is a need to further study floatation as a pretreatment option for UF and to study the impact of seasonal water quality changes on membrane fouling.

Furthermore, operational conditions can be optimized to reduce fouling as well, including filtration parameters, backwash, and chemical cleaning and so on. In this study,

the appropriate chemical clean strategy will be studied for pretreated ORW and the effect of different filtration cycle length (30, 60 and 90 minutes) on the membrane fouling will be discussed as well.

CHAPTER 3

EXPERIMENTAL METHODS

The purpose of this chapter is to describe the water sample collection, testing equipment, materials, methods and protocols that were utilized for this study.

3.1 Water Sample Collection

Ottawa River Water (ORW) was chosen for this study because: a) it is a typical Northern Canadian water; b) it has a high NOM content and a large hydrophobic (HPO) NOM fraction (Aiken et al., 1985; Pezeshk & Narbaitz, 2012), which should lead to relatively rapid fouling; and c) there are adjacent full-scale water treatment plants in the Ottawa River that provide optimized coagulation/flocculation/sedimentation and coagulation/flocculation/floatation pretreated water for the ultrafiltration experiments. The Raw ORW and three different pretreated ORW sample types were collected from two water treatment plants, the Britannia WTP (serving Ottawa, Ontario) and the Aylmer WTP (serving Aylmer, Quebec). The Britannia WTP withdraws Ottawa River water less than 6 km downstream from the Aylmer WTP. That is to say the feed water to these two plants has the same water quality characteristics.

Raw ORW and ORW pretreated by the addition of alum and activated silica and then settled (referred to as BS) were collected from the Britannia Water Treatment Plant (WTP) in Ottawa, Ontario on September 4, 2014 (which was at end of summer) and January 7, 2015 which was in the winter (Fig. 3.1). In the summer, the chemical dosages used at this plant were 34 mg/L and 1.85 mg/L of alum and sodium silicate, respectively. The pH was adjusted to ~ 5.7 using 8 mg/L of sulfuric acid (H_2SO_4). In the winter, the chemical dosages of alum and sodium silicate were 30 mg/L and 2.25 mg/L, respectively. The pH was adjusted to ~ 5.7 using 8 mg/L of H_2SO_4 .

Two types of pretreated ORW from the Aylmer WTP, which uses floatation for separation, were also collected on September 4, 2014, and January 7, 2015. The first type of water sample collected, which is referred to as AF, consisted of floatation basin effluent, it was pretreated by the addition of alum and polymer coagulation/flocculation and then

separated by floatation (Fig. 3.1). The second type of sample, called AS, consisted of ORW also pretreated by the same alum-polymer coagulation flocculation as AF but the samples were collected before the floatation basin, and then they were settled for 24 hours in a 20 cm diameter plexiglass column at the University of Ottawa labs (Fig. 3.1). The Aylmer WTP uses 0.072-0.1 mg/L cationic polyacrylamide polymer (Superfloc C-492PWG, Kemira) as a flocculation aid and 35 - 37 mg/L alum as the coagulant. Although silica and polymers are potential membrane foulants, the quantities of these flocculant aids were small and presumably they were extensively removed by the sedimentation and floatation, so they are not expected to be major foulants. Water samples were stored in refrigerators at the University of Ottawa at 4 °C. Before testing, the water was transferred to the lab to reach room temperature (~20 °C).

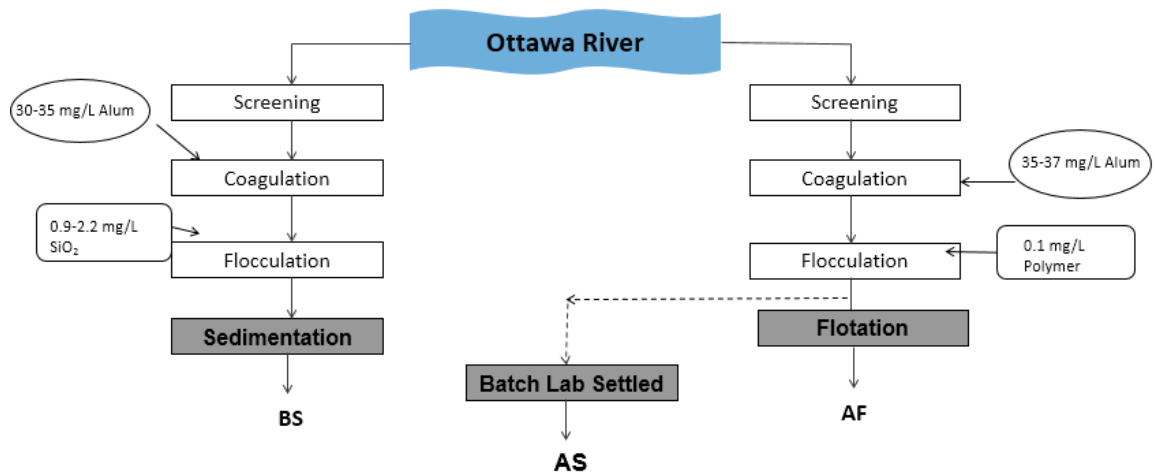


Fig. 3.1 Three pretreatment schemes

3.2 Membrane Module, Testing System and Testing Protocol

The evaluation of the UF membrane performance under different operating conditions and for different pre-treated waters was performed using an automated membrane testing system. The system and the testing procedures will be discussed in subsequent sections. The membrane module, which is central to the system's performance is described in the next subsection.

3.2.1 Membrane Module

For this study, membrane modules were constructed using six PES hollow fibers (Matrix Membranes, Oceanside, CA). The fibers were potted (i.e., the ends of the fibers glued into a fixed position in the module using epoxy) in a membrane module with effective lengths of 0.26 m and a total effective membrane area of 0.00392 m². The nominal molecular weight cut off (NMWCO) of the hollow fibers was 100,000 Da (<0.02 microns) (Matrix Membranes Inc., 2008). The inner fiber diameter is 0.8 mm and the outer fiber diameter is 1.4 mm. The membrane module housing was made with polyethylene tubing and plastic fittings. The module can be seen in Fig. 3.2. The far end of the fibers is sealed by the potting so the flow pattern within the module is inside-out dead-end mode (Fig. 3.3). That is the water can only enter into the fiber lumen at feed end of the module, it is then forced through the membrane fiber's walls into the module's shell and finally exits the module at the far end. The tubing used for the module is low density polyethylene. Tube diameters of 0.63, 0.95 and 1.27 cm were used in the various parts of the module.

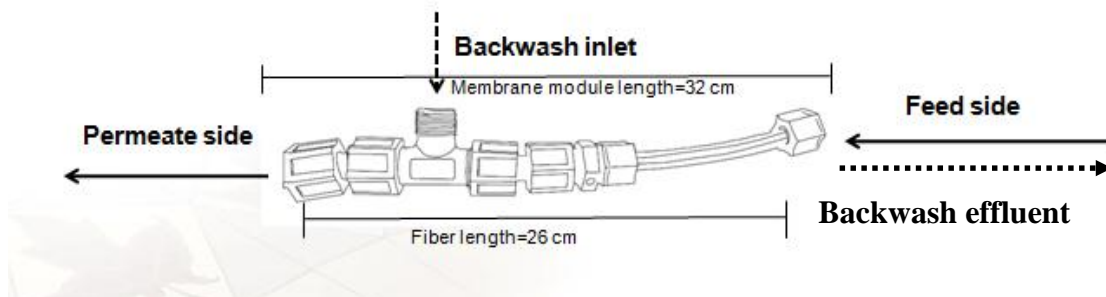


Fig. 3.2 UF hollow fiber membrane module design used in all filtration experiments

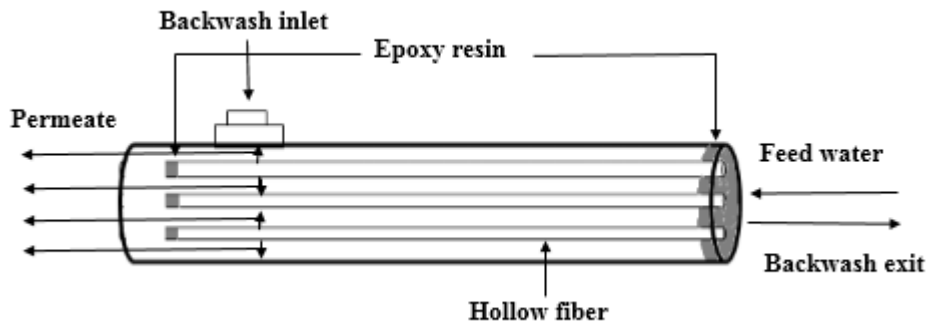


Fig. 3.3 Schematic diagram of the inside-out hollow fiber module

3.2.2 Membrane Filtration Testing System

Fig. 3.4 depicts the automated bench-scale hollow fiber UF system designed and built for this study by Walker (2014). The membrane filtration system uses 0.63, 0.95 and 1.27 cm diameter stainless steel and polyethylene tubing to connect different parts of the system. The system has two subsystems, the filtration and backwash subsystems (Fig. 3.4). The flow path for the filtration subsystem is shown as the thick solid lines. The subsystem is driven by a peristaltic pump (**PU1**) (L/S Easy-Load II, EW-77250-62, Cole-Parmer, Montreal, QC) that transfers the water from the feed reservoir through a number of different units. In sequence, these units are a pulse dampener (EQ-30610-37, Cole-Parmer, Montreal, QC), a pressure transducer (**P1**) (PX209-030G10V, Omegadyne Inc., Laval, QC), a three-way solenoid valve (**V1**) (Series 8320, Red Hat, ASCO), the membrane module, a two-way solenoid valve (**V2**) (Series 8262/8263, Red Hat, ASCO). The permeate was collected in a glass container and the permeate mass was measured by a top-loading balance (K-11018-12, Cole-Parmer, Montreal, QC). The balance is connected to a computer and Labview program that calculates the permeate mass flowrate.

The flow path for backwash subsystem is shown in Fig. 3.4 by the thick dashed lines. Because the small membrane area of the modules, the filtration cycles do not produce sufficient permeate to use for backwashing, accordingly RO water was used for backwashing. The RO water used was produced by passing distilled water through a RO system (LC-380PP, TOPWAY GLOCAL, INC., Brea, California). The TOC ranged from 0.05 and 0.1 mg/L. The backwash sub-system was driven a variable speed peristaltic pump (**PU2**) (FPUDVS2007, Omegadyne Inc., Laval, QC) that withdrew the RO water from the RO water reservoir and delivered it sequentially through a pulse dampener (EW-30610-37, Cole-Parmer, Montreal, QC), a two-way solenoid valve (**V3**) (Series 8262/8263, Red Hat, ASCO), a pressure transducer (**P2**) (PX209-030G10V, Omegadyne Inc., Laval, QC), through the membrane module, a three-way solenoid valve (**V1**) (Series 8320, Red Hat, ASCO) and finally into a waste container. During the backwash cycle the water entered the module (Fig. 3.3) through its side port into the membrane shell, then travelled through the fiber walls into the fiber lumen and exited the fibers through their open end at the feed

end of the module. From there the backwash water is redirected by a solenoid valve into a waste container.

Filtration and backwashing were automated through a LabView control program. Two separate pressure transducers were used to record the filtration and backwash pressures. Two pulse dampeners were used to reduce the pulsation. The UF system was automatically controlled by a LabView software which can input the operating parameters: feed flowrate, filtration cycle length, backwash flowrate and record the data including TMP, flux, backwash pressure, mass of permeate collected, etc. The system operates to maintain a constant permeate flux, Labview controls the output of the peristaltic pumps that drive the flow through the system.

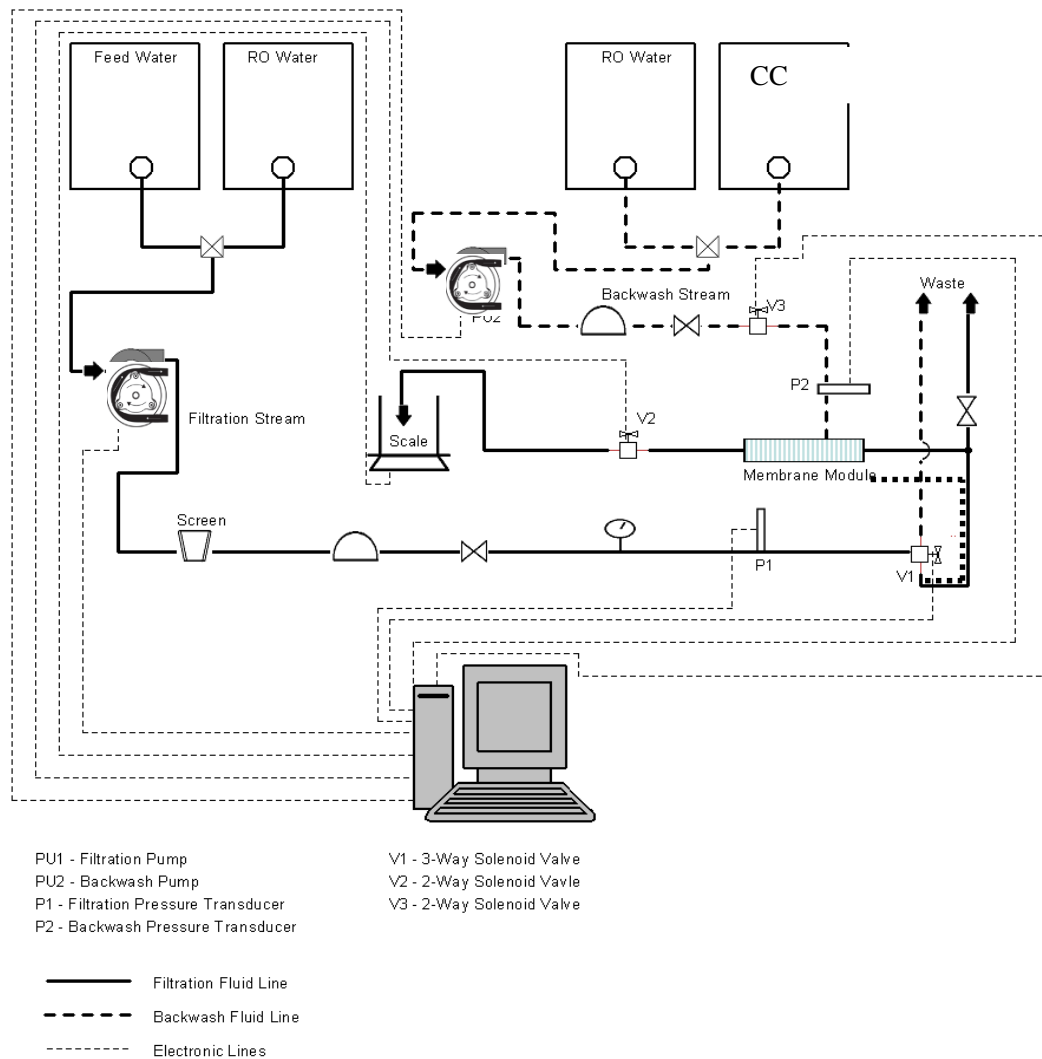


Fig. 3.4 Schematic diagram of the UF bench-scale system layout (Walker, 2014)

3.3 Experimental Design and Procedures.

The main stages of this ORW UF filtration study were: a) an optimization of the chemical membrane cleaning for the membranes fouled with ORW; b) a comparison of the impact of the filtration cycle lengths on UF membrane performance using water samples collected during the summer; and c) a comparison of the impact of the type pretreatment on UF membrane performance using water samples collected during the summer and winter. Each of these stages involved a number of multi-day UF filtration tests and each of these tests involved several activities. Firstly, the UF system was cleaned thoroughly and assembled, the second step involved the preparation of the membrane module. The third step involves conditioning the membrane. At last, this was followed by multi-day filtration experiments. Each test was conducted using a new membrane module.

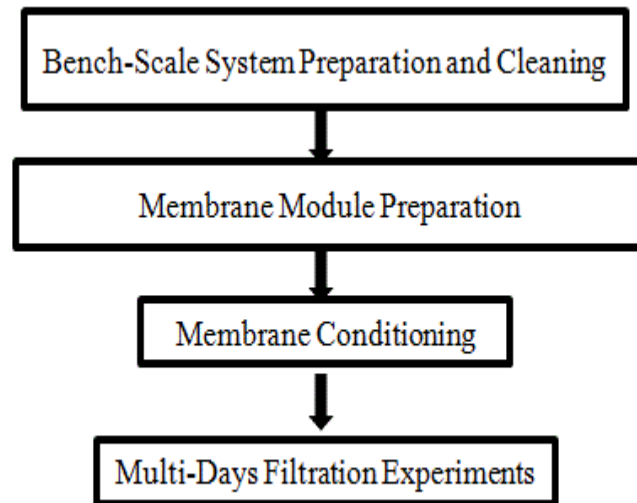


Fig. 3.5 Experimental procedure involved in conducting the multiday filtration experiments

3.3.1 Bench-scale UF System Preparation and Cleaning

Before each experiment, a thorough cleaning procedure was performed to make sure the whole system was clean so that contamination would not impact the experimental results. The reservoir container containing the feed water, backwash RO water and chemical enhanced backwash water were scrubbed and cleaned with liquid detergent and rinsed by RO water. The whole UF system was taken apart; all tubing was cleaned by pipe cleaner using liquid detergent solution. And then the tubing was rinsed with RO water. The pressure transducers and the solenoid valves were taken apart and cleaned with an ultrasonic cleaner (Bransonic 220, Branson Ultrasonics, Danbury, USA) for 10 minutes, then rinsed with RO water and allowed to dry. After every component of the UF system was cleaned, the system was assembled together and 10 ppm chlorine solution was circulated through the system for 1 hour, and finally the system was circulated by RO water.

3.3.2 Membrane Conditioning

Each filtration experiment was conducted with a new module. The membrane modules were described in section 3.2.1. The manufacturer pretreated the new ultrafiltration membrane fibers with a glycerol solution to coat the pore structure and prevent drying of the membrane. The glycerol must be thoroughly removed from the membrane prior to use. The glycerol-removing methodology recommend by the supplier was followed, about 2 L of RO water was pumped through the membrane at a maximum pressure of 34.5 kPa (5 PSI). Membrane was impermeable for the first hour, and the pressure had to be released frequently to avoid exceeding 34.5 kPa (5 PSI) pressure limits. Then membranes become more permeable, the flux increases to maintain a pressure of 34.5 kPa (5 PSI) until the pressure becomes stable with time and 2 L of RO water was filtered through the modules.

3.3.3 Optimization of Chemical Cleaning Methods

Prior to the main multi-day UF filtration tests described in the next subsections, two multi-day filtration tests were conducted to assess different chemical cleaning strategies. The filtration conditions for these tests were the same as those in subsequent tests (section 3.3.4), i.e., the filtration system was operated in an inside-out dead-end flow mode, at constant permeate flux of 50 LMH, and started with 30 minute-long RO water filtration then switched to floated ORW. The test lasted four days incorporating 30 minute long filtration cycles followed by 2-minute backwash cycles. The differences with the later tests was that the 20 minute-long chemical enhanced backwash performed at the end of the first day and the second day had different chlorine concentrations (10, 50, 100 and 200 ppm chlorine) and the 20 minutes chemical cleaning steps performed at the end of the third day (0.1 N NaOH & 200 ppm chlorine solution and 3% citric acid). The citric acid cleaning steps were added to ascertain if inorganic fouling was significant in this application.

3.3.4 Multi-Day Filtration Experiment Testing Protocol

For all filtration experiments, the bench-scale membrane filtration system was operated in inside-out dead-end flow mode, at constant flux of 50 LMH and started with 30 minute-long RO water filtration then switched to pretreated ORW. They involved four or five days of continuous operation and incorporated daily chemical enhanced backwashes and one chemical cleaning. Chemical enhanced backwash involved 20 minute backwashing with a 100 ppm chlorine solution and 20 minutes backwashing with RO water. Chemical cleaning involved 20 minute backwash recirculation with 0.1 N NaOH & 200 ppm chlorine solution and 20 minutes backwashing with RO water.

3.3.4.1 Seasonal Effect of Different Pretreatments on Membrane Performance

For the summer water samples, four-day long filtration experiments were conducted to compare the effect of different two pretreatments (floatation versus sedimentation) on membrane fouling. In these tests backwashing was conducted every 30 minutes for 2 minute using RO water at a flowrate of 200 LMH (i.e., four times the filtration flowrate). Chemical enhanced backwash was performed at the 24th and 48th hour. Chemical

recirculation cleaning was conducted at the 72nd hour during the 4-day long experiment. The pretreated waters tested in this phase of the study were AF, AS and BS, so as to compare the impact of floatation versus sedimentation pretreatment. The AS tests, which involved water using the same coagulation and flocculation as AF, were performed to test the possibility that the differences between BS and AF were due to the differences in the coagulant aid chemicals as opposed to differences in the separation processes.

For the winter water sample testing, the AB, AS and BS comparison involved 5-day experiments instead of 4-day experiments. Backwashes were also conducted every 30 minutes for 2 minute using RO water at a flowrate of 200 LMH. Chemical enhanced backwash was performed every 24 hours at the 24th and 48th hour. Chemical recirculation cleaning was conducted at 72nd and 96th hour during the 5-day long experiment. Both the summer and winter ultrafiltration experiments were conducted at room temperature.

3.3.4.2 Effect of Different Filtration Cycle length on Membrane Performance

The effect of different duration filtration cycles was studied using AF water collected during the summer. Three 4-day long filtration tests were conducted using different filtration cycle durations (30, 60 and 90 minutes) and 2 minutes long backwashing cycles. The filtration rate was 50 LMH and backwash flux 200 LMH. Chemical enhanced backwashes were performed at the 24th and 48th hour. A chemical recirculation cleaning was conducted at 72nd hour during the 4-day long experiment.

3.4 Analytical Methods for Water and Permeate Characterization

The water samples were analyzed for pH, alkalinity, hardness, ultraviolet absorbance, turbidity, TOC and DOC.

3.4.1 pH

The pH of all of the water samples were measured using a pH meter (Accumet model 910, Fisher Scientific, Hampton, NH). Measurements were conducted in triplicates.

3.4.2 Ultraviolet Absorbance at 254nm and Specific UV-Adsorption (SUVA)

Ultraviolet Absorbance at 254nm (UV_{254}) was measured using a UV spectrophotometer (HACH DR-5000, Loveland, CO). A 10mm path length quartz cell was used. Measurements were conducted in triplicates. SUVA was determined by dividing the UV absorbance at 254nm by the DOC (mg/L) concentration of the samples.

3.4.3 Turbidity

Turbidity was measured by using a Hach 2100AN Turbidimeter (Loveland, CO) for all water samples. The turbidimeter was calibrated with the following concentration standards supplied by Hach: <0.1 NTU, 20 NTU, 200 NTU, 1000 NTU, 4000 NTU, and 7000 NTU before measuring the samples. Measurements were conducted in triplicates.

3.4.4 Alkalinity, Total Hardness and Chlorophyll A

Alkalinity was measured using the titration based methods described in section 2320 B of Standard Methods, total hardness was measured using the titration based methods described in section 2340 C of Standard Methods and chlorophyll a was measured using the spectrophotometric method described in section 10200 H of Standard Methods (APHA/AWWA/WEF, 2012).

3.4.5 Total Organic Carbon (TOC)

The TOC concentrations of the samples were measured using a UV-persulfate oxidation based TOC analyzer (Phoenix 8000, Tekmar-Dohrmann, Cincinnati, OH, Model 14-7045-000). This analyzer follows the standard method 5310 C (APHA/AWWA/WEF, 2012).

3.4.6 Dissolved Organic Carbon (DOC)

DOC is TOC of water samples filtered through a 0.45 μm cellulose membrane (Millipore Corporation, Bedford, MA 01730) filter. The filtration was performed in a filtration cell (Amicon 400mL ultrafiltration stirred cell, Amicon Corp., MA), pressure

created by nitrogen gas was the driving force of the filtration. The effluent produced was analyzed with the TOC analyzer (Phoenix 8000, Tekmar Dohrmann, Cincinnati, OH, Model 14-7045-000).

3.4.7 Natural Organic Matter (NOM) Fractionation Characterization

NOM was characterized into hydrophobic, transphilic and hydrophilic NOM using XAD-4 and XAD-8 resins (Fisher Scientific, Hampton, NH). In this approach the NOM was quantified in terms of the TOC concentrations. Because the summer samples were contaminated, only the winter water samples were fractionated. The procedure used for NOM characterization in this study was adapted from Thurman and Malcolm (1981). The method is described in detail in Appendix A.

3.5 Evaluation of Membrane Performance

The membrane performance was evaluated in terms of the transmembrane pressure, the backwash efficiency, the resistance in series fouling indices, and the contaminant rejections.

3.5.1 The Transmembrane Pressure (TMP)

TMP was calculated by subtracting the pressure on the permeate side of the membrane (P_p) (Pa) from the pressure on the feed side of the membrane (P_f) (Pa) (MWH,2005).

$$TMP = P_f - P_p \quad (3.1)$$

3.5.2 Backwash Efficiency (BWE)

BWE may be calculated by the changes in transmembrane pressure (TMP) occurring in successive filtration cycles. A TMP increase during the filtration cycle is due to the particles deposited on the membrane surface or in the membrane pores.

The backwash efficiency (BWE) for the hydraulic backwashes of each experiment was calculated using the following equation

$$BWE = \frac{TMP_f - TMP_n}{TMP_f - TMP_i} \times 100 \quad (3.2)$$

Where TMP_n is the TMP at the beginning of filtration cycle n+1, TMP_i is the TMP at the beginning of filtration cycle n, and TMP_f is the TMP at the end of filtration cycle n (Chellam et al., 1998). If the TMP at the beginning of cycle (n+1) is the same as the TMP at the beginning of cycle (n), backwash can be considered 100% efficient.

3.5.3 Resistance-in-Series Model Index

The membrane performance was also evaluated in terms of resistance-in-series fouling indices described in section 2.2.3.2.4.

CHAPTER 4

IMPROVED MEMBRANE PRETREATMENT BY FLOATATION

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4.1 Abstract

Pretreatment by coagulation/flocculation/sedimentation is often used to alleviate membrane fouling, however there has been limited research on floatation as the pretreatment separation process. The main objective of this study is to compare sedimentation with floatation as part of the pretreatment for ultrafiltration (UF) of a river water with relatively high natural organic matter (NOM) content. Water samples pretreated at full-scale plants were subjected to multiple-day UF membrane fouling tests (constant flux with backwash and chemical cleaning) using an automated bench-scale UF hollow fiber membrane system. Based on the samples tested, coagulation/floatation pretreatment resulted in less fouling than coagulation/sedimentation during both summer and winter testing. The improved performance appears to be linked to greater hydrophobic NOM removal by the pretreatment. Most fouling could be reversed by hydraulic backwashing and chemical cleaning. Enhanced chemical backwash with 100 ppm chlorine and chemical clean with 0.1N NaOH & 200 ppm chlorine were found to be very effective at reducing fouling for pretreated water. As expected, longer filtration cycles resulted in greater fouling but with a slightly greater degree of hydraulically reversible fouling.

Highlights:

- An appropriate chemical clean strategy for pretreated Ottawa River water was identified.
- Flootation is a better pretreatment than sedimentation for hollow fiber UF systems.
- Total fouling indices in winter are much higher than summer, for all waters.
- The main fouling resistance is due to hydraulically reversible fouling.
- The degree of fouling is proportional to the hydrophobic NOM of the water.

Keywords: Hollow fiber ultrafiltration membrane, membrane fouling, coagulation/flocculation/flootation, resistance-in-series fouling index

4.2 Introduction

Clean and safe drinking water has always been important to human health, but after several waterborne disease outbreaks in both developing and developed countries, people now recognize that the conventional water treatment technology has serious potential drinking water safety issues (Vickers, 2005). As a result, microfiltration (MF) and ultrafiltration (UF) have been increasingly used in drinking water production for the removal of particles, colloidal species, protozoa and bacteria from surface or ground water (Jacangelo & Laine, 1994; Vickers, 2005). The effective removal of *Giardia lamblia* and *Cryptosporidium parvum* is a key advantage of these membrane processes (Jacangelo et al., 1995). One of the main concerns in the operation of MF/UF processes is fouling; i.e., membrane foulants (such as colloidal or particulate matter, dissolved organics, and microorganisms) accumulate in the pores and the surface of membranes reducing the water flux or increasing the energy requirements. The principal type of foulant will depend on the feed water quality; natural organic matter (NOM) has been considered as the principal foulant in many natural surface waters (Qi et al., 2013; Zularisam et al., 2007).

Membrane fouling is inevitable, so there has been a great deal of effort to minimize its impact. The main tools used to reduce the impact of fouling are using different types of pretreatment processes and using different operating conditions. Key operational conditions that can be optimized to reduce fouling include: using lower permeate fluxes (Carrère et al., 2001; Guo et al., 2009; Lee et al., 2008; Walker, 2014; Waterman, 2008), backwashing and/or relaxation (De Souza & Basu, 2013; Jacangelo & Noack, 2005; Kim

& DiGiano, 2006; Wu et al., 2008). In addition, membrane chemical cleaning plays an important role on membrane fouling control. The suitable chemical cleaning selection can maintain membrane permeability, save cost, and prolong membrane life spans (Kimura et al., 2004; Nguyen et al., 2011; Shi et al., 2014).

Pretreatment prior to UF membrane processes will reduce membrane fouling due to the removal of particles and dissolved organic matter, and results in improved membrane performance. Coagulation/flocculation with or without sedimentation prior to membrane filtration are the most commonly implemented MF/UF pretreatment processes for waters with significant NOM content. Inconsistent results in the effectiveness of coagulation with or without sedimentation have demonstrated that effectiveness depends on the type of membrane used, the characteristics of the different waters being treated, the coagulant type and dosage, and the different settling times implemented (Done et al., 2007; Huang et al., 2011; Jacangelo & Laine, 1994; Liang et al., 2008; Park et al., 2002). Floatation is a compact separation process, which is particularly suitable for waters with algae and cyanobacteria because their low density cells are easily floated. As one of the expected results of global warming is greater algal growth and greater algal challenges at water treatment plants, it is likely that floatation will become a more popular form of treatment (Amaral et al., 2013). There has been relatively little research on floatation as a form of pretreatment for MF/UF (Amaral et al., 2013; Braghetta et al., 1997). Walker (2014) compared the effectiveness of floatation and sedimentation as pretreatment options for hollow fiber UF of relatively high NOM water and found floatation to be superior. NOM concentrations and composition may vary in summer and winter as well, so the effectiveness of the different types of pretreatment may vary. In addition, Walker (2014) only considered one set of operating conditions and one type membrane cleaning strategy, which was not particularly effective.

The objectives of this work are: a) to confirm the findings of Walker (2014) on the impact of pretreatment, as performed at two nearby plants, on membrane filtration (, i.e., that floatation pretreatment is superior to sedimentation pretreatment for the same relatively high NOM water); b) to evaluate the impact of seasonal water quality variations; c) to find a more effective chemical cleaning method for pretreated river water; and d) to

study the effect of different filtration cycle lengths between backwash (30, 60 and 90 minutes) on the membrane performance.

4.3 Materials and Methods

4.3.1 Water Tested

In order to confirm the Walker (2014) results, ultrafiltration experiments were conducted with new samples of the same Ottawa River Water (ORW) subjected to a number of different pretreatments. ORW was chosen because: a) it is a typical Northern Canadian water; b) it has a high NOM content and a large hydrophobic (HPO) NOM fraction (Aiken et al., 1985; Pezeshk & Narbaitz, 2012), which should lead to relatively rapid fouling; and c) there are adjacent full-scale water treatment plants in the Ottawa River that provide optimized coagulation/flocculation/sedimentation and coagulation/flocculation/floatation pretreated water for the ultrafiltration experiments. The four types of water samples collected were: a) alum coagulated and floated ORW (AF), which was collected from the Aylmer Water Treatment Plant (WTP) in Gatineau, Quebec; b) alum coagulated and settled water (BS) which was collected from the Britannia WTP in Ottawa, Ontario; c) alum coagulated ORW was collected from the Aylmer WTP and then settled in a 20 cm diameter column in the lab (AS), and d) raw ORW. UF experiments were conducted with the first three waters, the last water was collected and analyzed as a reference. The water samples were collected on September 4, 2014, which was at end of summer and January 7, 2015, which was in the winter, respectively. The Britannia WTP withdraws Ottawa River water less than 6 km downstream from the Aylmer WTP. That is to say the feed waters to these two plants have the same water quality characteristics.

The Britannia WTP services Ottawa with drinking water, and in the summer, it added 34 mg/L of alum and 1.85 mg/L of sodium silicate. In the winter, the chemical dosages of alum and sodium silicate were 30 mg/L and 2.25mg/L, respectively. The pH was adjusted to ~ 5.7 using 8 mg/L of sulfuric acid. The Aylmer plant added alum as the coagulant and a cationic polyacrylamide polymer (Superfloc C-492PWG, Kemira) as the coagulant aid in the flocculation prior to separation by floatation. The alum dosage was 35-37 mg/L and the polymer dosage was 0.072-0.1 mg/L. Walker (2014) tested these same waters and

found that floatation pretreatment was superior but the coagulant aid and their dosages were different at both plants. Accordingly, the current study wanted to clarify whether the better results arose from a better coagulation arrangement. To achieve this, membrane filtration tests were also conducted with water collected from the Aylmer WTP flocculation basin and settled it in a tall 20 cm dia. plexiglass column in the lab. As the Aylmer coagulation/flocculation was not optimized to produce large easily settled flocs, this water was allowed to settle overnight. Although silica and polymers are potential membrane foulants, the quantities of these flocculant aids were small and presumably they were extensively removed by the sedimentation and floatation, so they are not expected to be major foulants.

Water samples were stored in refrigerators at 4 °C. Before testing, the water was transferred to the lab to reach room temperature (~20 °C). The UF tests for both the late summer and winter waters were performed at room temperature. Standard methods were used to preserve the samples (APHA/AWWA/WEF, 2012).

4.3.2 Membrane and Module Configuration

The filtration experiments were conducted using small hollow fibre membrane modules constructed in our lab. The membrane module housing was made with polyethylene tubing and plastic fittings (Fig 4.1). The module contained six polyethersulfone (PES) hollow fibers (Matrix Membranes, Oceanside, CA) potted at the ends of the module giving the module an effective fiber length of 0.26 m (Fig. 4.1). The membrane fibers run from feed end to the permeate exit end of the module shown in Fig. 4.1, the fiber lumina are open in the feed side and potted closed at the permeate side. Thus, this results in dead-end filtration with an inside-out fiber flow pattern. The nominal molecular weight cut off (NMWCO) of the hollow fibers is 100,000 Da (<0.02 microns). The inner fiber diameter is 0.8 mm and the total effective membrane area of one module is 0.00392 m².

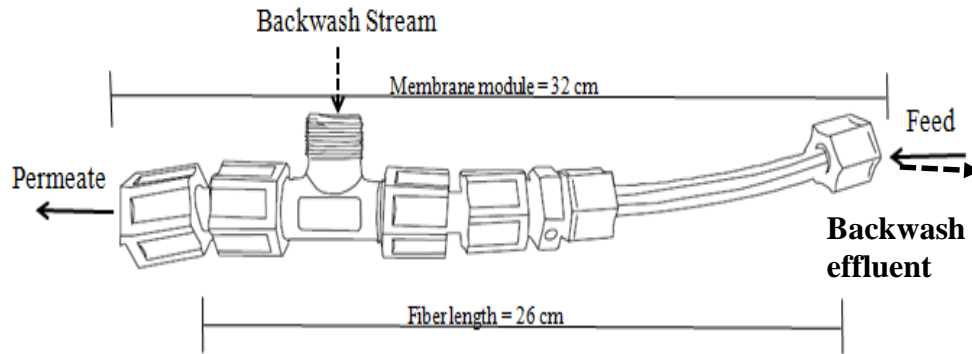


Fig. 4.1 Inside-out UF hollow fiber membrane module design used in dead-end filtration experiments

4.3.3 Ultrafiltration Bench-Scale System

The UF bench-scale filtration system (Fig. 4.2) used in these tests was developed by Walker (2014), and has two subsystems, filtration and backwash. The filtration subsystem is shown as thick solid lines, the backwash subsystem as thick dashed lines. Stainless steel and polyethylene tubing (0.63, 0.95 and 1.27 cm diameter) were used to connect different parts of the membrane filtration system. The feed water was pumped from the feed water reservoir using a peristaltic pump (**PU1**) (L/S Easy-Load II, EW-77250-62, Cole-Parmer, Montreal, QC) and it sequentially passes through a pulse dampener (EQ-30610-37, Cole-Parmer, Montreal, QC), a pressure transducer (**P1**) (PX209-030G10V, Omegadyne Inc., Laval, QC), a three-way solenoid valve (**V1**) (Series 8320, Red Hat, ASCO), the membrane module, and a two-way solenoid valve (**V2**) (Series 8262/8263, Red Hat, ASCO). The permeate was collected in a glass container and the permeate mass generated was measured by a top-loading balance (K-11018-12, Cole-Parmer, Montreal, QC).

The backwash subsystem takes reverse osmosis (RO) water from the RO water reservoir and pumps it through the membrane module in the opposite direction to the filtration mode. RO water was used as the backwash solution because the limited membrane area of the membrane modules did not permit the production of sufficient permeate to use for the backwash. The RO water used was produced by passing distilled water through a RO system (LC-380PP, TOPWAY GLOBAL, INC., Brea, California). The backwash system is driven by a variable speed pump (**PU2**) (FPUDVS2007,

Omegadyne Inc., Laval, QC) that pumps the RO water sequentially through a pulse dampener (EW-30610-37, Cole-Parmer, Montreal, QC), a two-way solenoid valve (**V3**) (Series 8262/8263, Red Hat, ASCO), a pressure transducer (**P2**) (PX209-030G10V, Omegadyne Inc., Laval, QC), through the membrane module, a three-way solenoid valve (**V1**) (Series 8320, Red Hat, ASCO) and finally into a waste container. Filtration and backwashing were automated through a LabView control program. Two separate pressure transducers were used to record the filtration and backwash pressures. Two pulse dampeners were used to reduce the pulsation caused by the peristaltic pumps. The UF system was automatically controlled by a LabView software program which: 1) inputs the operating parameters: feed flowrate, filtration cycle length, backwash flowrate; and 2) records the data including transmembrane pressure (TMP), flux, backwash pressure, mass of permeate produced, etc.

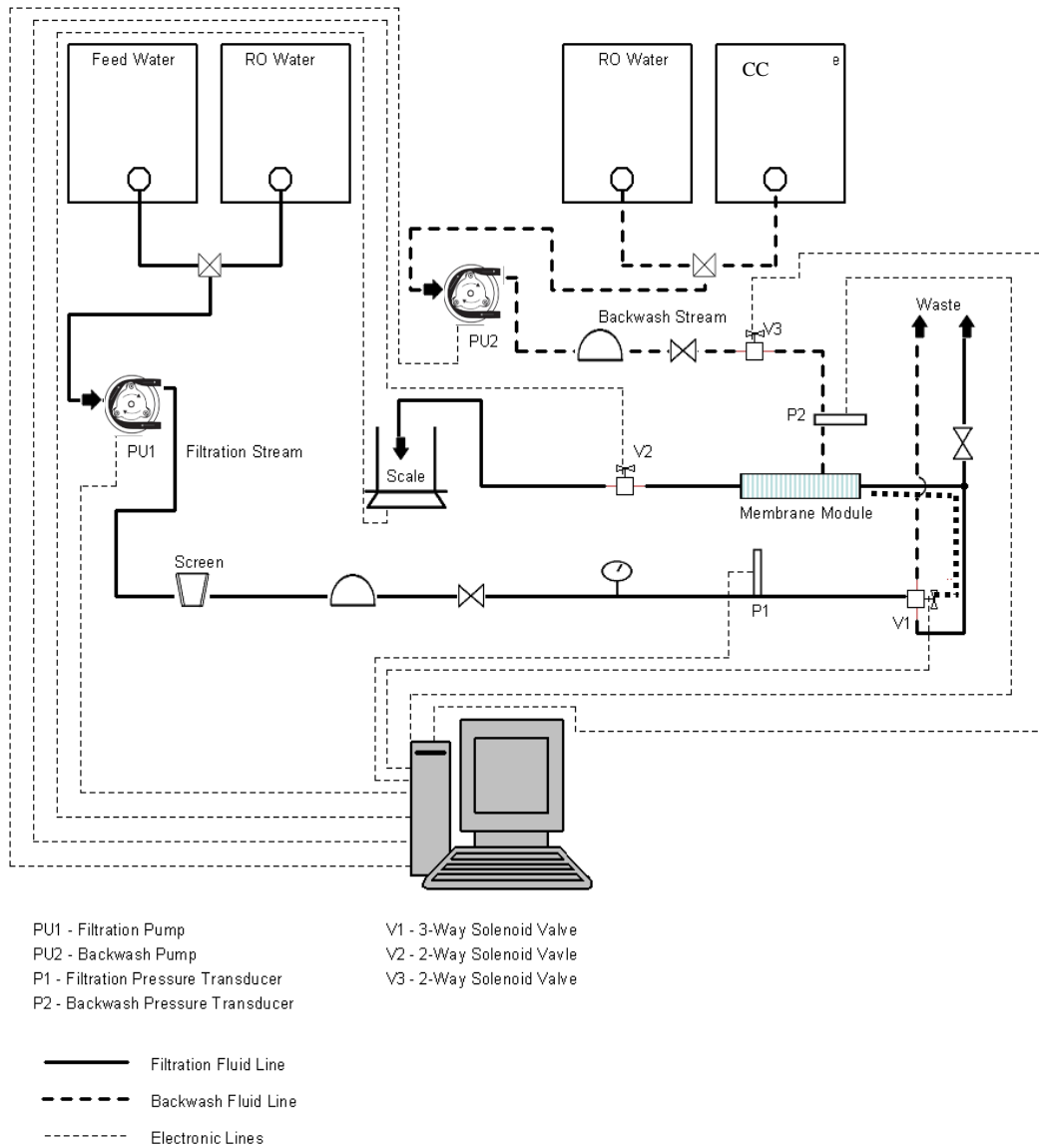


Fig. 4.2 Schematic diagram of the UF bench-scale system layout (Walker, 2014)

4.3.4 Experimental Plan

The experiments involved an evaluation of alternative cleaning methods, multi-day filtration tests to a) assess the impact of pretreatment; b) assess the impact of seasonal water quality variations; and c) assess the impact of filtration cycle length.

4.3.4.1 Cleaning Method Evaluation

Given that Walker (2014) observed that cleaning methods for this water/membrane combination could be improved, a chemical cleaning procedure sensitivity analysis was conducted. This sensitivity analysis involved two multi-day filtration tests incorporating the different enhanced backwashing and chemical cleaning solutions. The tests were conducted using the AF water collected during the summer. During the filtration, the membrane filtration system was operated in inside-out, dead-end mode with at constant flux of 50 LMH, started with 30 minute-long RO water filtration then switched to pretreated ORW, and the test lasted four days. At the end of each day, a 20 minutes chlorine solution enhanced backwash (EBW) was performed followed by 20 minutes backwashing with RO water. The efficiency of the enhanced backwash was assessed using different chlorine concentrations (10, 50, 100 and 200 ppm chlorine) at the end of a 24 hour period of operation. On other occasions, a 20 minutes recirculation chemical cleaning (0.1 N NaOH & 200 ppm chlorine solution and 3% citric acid) was performed; it was also followed by 20 minutes backwashing with RO water.

4.3.4.2 Multi-Day Filtration Experiment Testing Protocol

For all filtration experiments, the bench-scale membrane filtration system was operated in inside-out, dead-end mode with a constant flux of 50 LMH and started with 30 minute-long RO water filtration then switched to pretreated ORW. The experiments lasted four or five days and incorporated chemical enhanced backwashes or a chemical cleaning at the end of each day. Each run used a new membrane module. Chemical enhanced backwash involved a 20-minute backwash with a 100 ppm chlorine solution and a 20-minute backwash with RO water. Chemical cleaning involved 20-minute backwash recirculation with 0.1 N NaOH & 200 ppm chlorine solution followed by a 20-minute backwash with RO water.

4.3.4.3 Effect of Different Filtration Cycle Length on Membrane Performance

The effect of different filtration cycle lengths between backwashing on membrane fouling was studied using the AF water collected during the late summer. Runs were

conducted using a permeate flux of 50 LMH and 2 minute-long RO water backwashes performed every 30, 60 and 90 minutes. Chemical enhanced backwash was performed at the 24th and 48th hour. Chemical recirculation cleaning was conducted at the 72nd hour during the 4-day long experiments.

4.3.5 Analytical Methods

The pH was determined using a pH meter (Accumet model 910, Fisher Scientific, Hampton, NH). Turbidity was determined using a Hach 2100AN Turbidimeter (Loveland, CO). Total organic carbon (TOC) analysis was performed using a UV-persulfate oxidation based analyzer (Phoenix 8000, Tekmar Dohrmann, Cincinnati, OH, Model 14-7045-000). The dissolved organic carbon (DOC) was determined by filtering the water through a 0.45 µm cellulose membrane (Millipore Corporation, Bedford, MA 01730) and then performing TOC analysis on the filtrate. UV absorbance at 254nm was determined using a UV spectrophotometer (HACH DR-5000, Loveland, CO) with a 10mm path length quartz cell. The alkalinity, total hardness and chlorophyll A were determined according to the Standard Methods (APHA/AWWA/WEF, 2012). NOM was characterized into hydrophobic, transphilic and hydrophilic NOM using XAD-4 and XAD-8 resins (Fisher Scientific, Hampton, NH). The NOM fractionation/characterization procedure was adapted from that used by Thurman and Malcolm (1981).

4.3.6 Evaluation of Membrane Performance

The membrane performance was evaluated in terms of the transmembrane pressure (TMP), backwash efficiency (BWE), resistance-in-series fouling indices and permeate water quality.

4.3.6.1 The Transmembrane Pressure (TMP)

TMP was calculated by subtracting the pressure on the permeate side of the membrane (P_p) (Pa) from the pressure on the feed side of the membrane (P_f) (Pa) (MWH, 2005).

$$TMP = P_f - P_p \quad (4.1)$$

4.3.6.2 Backwash Efficiency (BWE)

BWE (%) was calculated by changes in TMP during the filtration cycles before and after each backwash event. TMP increases during the filtration cycles due to the particles/foulants being deposited on the membrane surface or in the membrane pores. The BWE for the hydraulic backwashes of each backwash cycle was calculated as:

$$BWE = \frac{TMP_{f_n} - TMP_{i_{n+1}}}{TMP_{f_n} - TMP_{i_n}} \times 100 \quad (4.2)$$

where $TMP_{i_{n+1}}$ is the TMP at the beginning of filtration cycle n+1, TMP_{i_n} is the TMP at the beginning of filtration cycle n, and TMP_{f_n} is the TMP at the end of the filtration cycle n (Chellam et al., 1998). If the TMP at the beginning of cycle (n+1) is the same as the TMP at the beginning of cycle (n), backwash can be considered 100% efficient.

4.3.6.3 Resistance-in-Series Model Index

The flux, J, is described as:

$$J = \frac{TMP}{R \cdot \mu} \quad (4.3)$$

where J is flow per unit area (L/m²/h or m³/m²/s), TMP is transmembrane pressure (kg/m/s²), μ is the water viscosity (kg/m/s), R is the total flow resistance coefficient (m⁻¹). To allow more direct comparison between systems operating at different pressures, the specific flux J_s is often used (h/m). It is defined as

$$J_s = \frac{J}{TMP} = \frac{1}{\mu \cdot R} \quad (4.4)$$

In addition the fluxes, which may change with time, are often normalized by dividing them by the initial flux, so

$$NSF = \frac{J_s|_V}{J_s|_0} \quad (4.5)$$

where NSF is the normalized specific flux (unitless), $J_s|_0$ is the initial specific flux (h/m), $J_s|_V$ is the specific flux (h/m) at any time when the specific volume is V (L/m²) (i.e., permeate volume/membrane area).

Substituting equation 4.4 into equation 4.5, for constant flux systems one obtains

$$NSF = \frac{\frac{J}{TMP}}{\frac{J}{TMP_0}} = \frac{TMP_0}{TMP} \quad (4.6)$$

Where TMP_0 (Pa) is the initial TMP (Pa) for the clean membrane to obtain the flux J

Yeh and Cheng (1993) developed a fouling index which is based on a resistance-in-series model. This model assumes that R is the sum of flow resistance for the clean membrane (R_{mem}) (L/m), the resistance due to the cake formed on the membrane that is removed by hydraulic backwashing (R_{cake}) (L/m), the resistance due to irreversible fouling not restored by hydraulic backwashing (R_{HIFI})(L/m), and the resistance due to irreversible fouling not restored by chemical cleaning (R_{CIFI})(L/m), as summarized in equation (4.7):

$$R = R_{mem} + R_{cake} + R_{HIFI} + R_{CIFI} \quad (4.7)$$

Fouling resistance increases linearly with permeate volume, $R_i = r_i \cdot V$, where r_i is a rate constant (m^2/L). The total resistance R (L/m) can also be expressed as:

$$R = R_{mem} + r_{total} \cdot V \quad (4.8)$$

Where r_{total} is total rate constant (m^2/L). Combining equation 4.4 and 4.8 yields,

$$J_S = \frac{1}{\mu \cdot (R_{mem} + r_{total} \cdot V)} \quad (4.9)$$

Substituting to

$$\frac{1}{NSF} = \frac{J_S|_V}{J_S|_0} = \frac{(R_{mem} + r_{total} \cdot V) \cdot \mu}{R_{mem} \cdot \mu} = 1 + \left(\frac{r_{total}}{R_{mem}} \right) \cdot V \quad (4.10)$$

Different fouling indices can be calculated using the data from different operational cycles and cleaning steps. For single filtration cycles between hydraulic backwashes, the total fouling index (TFI) (m^2/L) can be related to the normalized specific flux (NSF) and the specific volume (V) as follows:

$$\frac{1}{NSF} = 1 + (TFI) \cdot V \quad (4.11)$$

For multiple backwash cycles in between chemical cleanings, which is referred to as one chemical cleaning cycle (CC cycle), the hydraulic-irreversible fouling index (HIFI) (m^2/L) can similarly be expressed as follows:

$$\frac{1}{NSF} = 1 + (HIFI) \cdot V \quad (4.12)$$

Average values for all data for a series of CC cycles can be used to determine the chemical irreversible fouling index (CIFI) (m^2/L):

$$\frac{1}{NSF}=1+(CIFI)\cdot V \quad (4.13)$$

If the plot of $(1/NSF)$ versus V is linear, the fouling indices can be calculated using linear regression. If the relationship is not linear, then the first and the last ten points can be used to determine the average value of the fouling indices as suggested by Nguyen et al. (2011).

4.4 Results and Discussion

4.4.1 Water Quality Characterization

Table 4.1 summarizes the average measured water quality parameters. Raw ORW was characterized by high concentrations of TOC, low alkalinity and low hardness. Given the proximity of the two water treatment plants, the raw water at both plants has essentially the same characteristics. The Chlorophyll A concentrations in Ottawa River water were very low (Table 4.1), the late summer timing of the sampling may have contributed to the low values. It should be noted that floatation was incorporated into the Aylmer plant because it is a compact separation process and not because there are significant algal problems in the Ottawa River. Given the low algal, alkalinity and hardness concentrations and the relatively high NOM concentrations, NOM is expected to be the principal foulant.

Although the coagulation/flocculation of Aylmer water was not optimized for settling, the water quality characteristics for the two settled waters were very similar. Except for turbidity, the overall percent differences between the two settled waters was 7.18%. It should also be acknowledged that the coagulation/flocculation at the two treatment plants differed not only on the coagulant aid type but also in the process characteristics (e.g. hydraulic versus mechanical flocculation). Thus, the differences between two different coagulation/flocculation pretreatment systems have a relatively small impact on their water quality.

The slightly higher NOM concentrations in the winter samples of the raw ORW water might result from a concentration effects associated with lower river flowrates, although the two sets of concentrations are comparable. Pretreatment by sedimentation and floatation can be considered as effective pretreatment methods because they achieved substantial reductions in turbidity, UV_{254} , TOC, DOC, particulate organic carbon (POC) and specific UV absorbance (SUVA). The TOC removal rates by different pretreatment

approaches were approximately 60%. Moreover, the TOC removal rates in summer were a little higher than in winter (Table 4.1). The winter TOC percent removals by the three pretreatment alternatives were very similar (59.7-62.5%) (Table 4.1).

The seasonal water quality changes were relatively small except UV_{254} and SUVA (i.e., the UV_{254}/DOC ratio). High UV_{254} absorbance removal rates (up to 80%) were observed, UV_{254} absorbance values in winter were higher than summer for all the pretreatment options (Table 4.1). Meanwhile, the lower SUVA values were found in summer than winter. SUVA is an indicator of HPO, which is the dominant foulant in many natural surface waters (Uyak et al., 2008). AF had lower UV_{254} and SUVA values than BS and AS in both the summer and winter testing (Fig. 4.3). Based on the lower UV_{254} and SUVA values in AF, less fouling can be expected in the ultrafiltration of AF than for AS and BS. The SUVA values of the two settled waters were very similar indicating that the difference in the coagulant aids and other coagulation/flocculation characteristics did not have a significant impact.

Table 4.1 ORW and pretreated ORW quality characteristics in different seasons

Parameter Seasons	Raw ORW		AF ORW		BS ORW		AS ORW	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	6.77±0.07	7.70±0.07	6.48±0.06	7.54±0.10	6.48±0.10	6.86±0.10	6.47±0.10	7.15±0.11
Turbidity(NTU)	1.63±0.03	3.56±0.06	0.29±0.01	0.52±0.09	0.72±0.03	0.88±0.14	0.42±0.01	0.74±0.14
Alkalinity(mg CaCO ₃ /L)	28.6±0.50	26.0±0.05	3.10±0.10	3.33±0.65	3.73±0.25	2.33±0.65	3.50±0.20	3.00±0.57
Total Hardness(mg/L)	37.80±0.30	34.67±3.46	32.70±0.60	33.33±1.31	36.60±2.40	28.60±3.46	35.50±2.60	28.67±4.71
UV ₂₅₄ (cm ⁻¹)	0.25±0.001	0.32±0.001	0.03±0.001	0.06±0.002	0.05±0.004	0.08±0.002	0.05±0.002	0.07±0.001
TOC(mg/L)	7.18±0.01	8.23±0.08	2.05±0.08	3.09±0.04	2.52±0.19	3.32±0.04	2.45±0.01	3.13±0.04
DOC(mg/L)	7.09±0.02	8.16±0.06	1.96±0.02	3.07±0.01	2.41±0.02	3.27±0.01	2.34±0.04	3.08±0.01
HPO(mg/L)	N/A	6.33±0.10	N/A	1.54±0.03	N/A	2.37±0.06	N/A	2.28±0.06
TPI(mg/L)	N/A	1.08±0.07	N/A	0.81±0.04	N/A	0.33±0.04	N/A	0.23±0.11
HPI(mg/L)	N/A	0.74±0.05	N/A	0.72±0.07	N/A	0.57±0.08	N/A	0.58±0.15
Particulate OC(mg/L)	0.086	0.073	0.04	0.02	0.08	0.05	0.075	0.046
SUVA(L/mg/m)	3.56	3.92	1.68	1.89	2.24	2.51	2.17	2.34
Chlorophyll A(µg/L)	4.27	N/A	LOD	N/A	2.40	N/A	2.13	N/A
TOC removal (%)	N/A	N/A	72.36	62.47	64.87	59.69	65.91	61.98
UV ₂₅₄ removal (%)	N/A	N/A	80.47	81.87	80.34	74.37	79.81	77.50

LOD-below the limit of detection

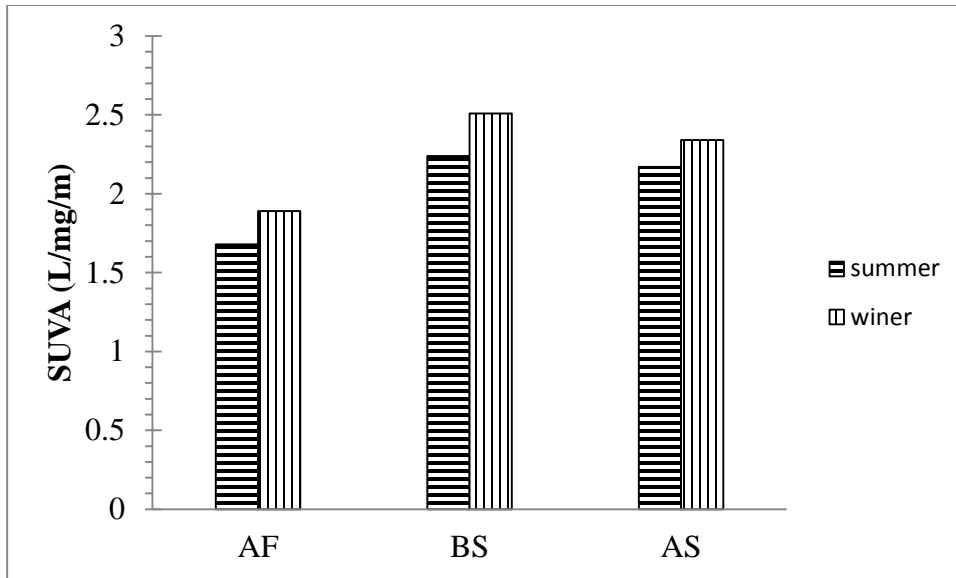


Fig. 4.3 SUVA values for the pretreated ORW in summer and winter

4.4.2 Studies on Chemical Cleaning Strategies on Pretreated Ottawa River Water

The filtration experiments consisted of filtration cycles followed by a backwashing cycle, a process that was continuously repeated until an enhanced backwash step or chemical cleaning step was performed. During each filtration cycle, the TMP increased with time, which significantly decreased when a hydraulic backwash was performed. The computerized filtration system monitored the TMP every 2 seconds. To avoid overcrowding the TMP versus time graphs, only a fraction of the data was plotted and the above described pattern is not obvious. During the filtration experiments evaluating the impact of different chlorine concentrations in the enhanced backwash solution, the TMP increased rapidly during the first 10 hours of operation and then gradually reached 50-60 kPa in 24 hours, before the first enhanced backwashing (Fig.4.4 and 4.5). The differences in the TMP between the runs on the first day may be the result of slight differences between the modules used. As shown in Fig. 4.4 there was no apparent TMP reduction after the 10 ppm chlorine enhanced backwash. This is consistent with the findings of Walker (2014) for the same type of water and membrane. Enhanced backwashes with 50, 100 and 200 ppm chlorine solutions decreased the TMP by 14.4%, 24.8% and 26.6%, respectively (Fig.4.4 and 4.5). The 200 ppm chlorine backwash performed only slightly better than 100

ppm chlorine solution, thus the latter appears to be a suitable enhanced backwashing solution.

As shown in Fig. 4.4 and 4.5, the 0.1N NaOH & 200 ppm chlorine backwash recirculation produced a TMP decrease of approximately 45% to about 30 kPa; which is almost the original value of the membrane TMP at the beginning of the operation (25 kPa). 0.1N NaOH & 200 ppm chlorine recirculation cleaning was found to be very effective for floated water. It is worth mentioning that Walker (2014) found a 0.1N NaOH static soaking cleaning was not effective in cleaning membranes that treated floated ORW. The reason could be static conditions used by Walker are less effective than the recirculation cleaning used in this study, however using the combination of NaOH and chlorine may be more important factor in the significantly better cleaning observed in the current study. A study of Liu et al. (2001) also found that membrane cleaning using the combination of caustic and chlorine was more effective than caustic alone and chlorine alone for the fouled membrane. The cleaning efficiency depends on how cleaning chemicals interact with fouling materials (Shi et al., 2014). Because NaOH can change the structure of NOM, make the fouling layer looser, and increase the solubility of the NOM, while the simultaneous chlorine addition can oxidize NOM and increase membrane hydrophilicity, the membrane permeability can be restored to a greater extent by the synergism of caustic plus chlorine cleaning. Thereafter, TMP increased quickly to return to the original value before chemical cleaning.

A citric acid recirculation cleaning step both before (Fig. 4.5) and after (Fig. 4.4) the NaOH & chlorine recirculation step was not effective. This is not surprising given that the main cleaning target of citric acid is the dissolution of inorganic salts and metal oxides (Shi et al., 2014), and the pretreated waters have a low mineral content (i.e., hardness of about 33 mg/L as CaCO₃ and alkalinity of about 3 mg/L as CaCO₃).

Based on the chemical cleaning results, 100 ppm chlorine solution was chosen for the daily enhanced backwashes and 0.1N NaOH & 200 ppm chlorine solution was chosen for the chemical recirculation cleaning steps.

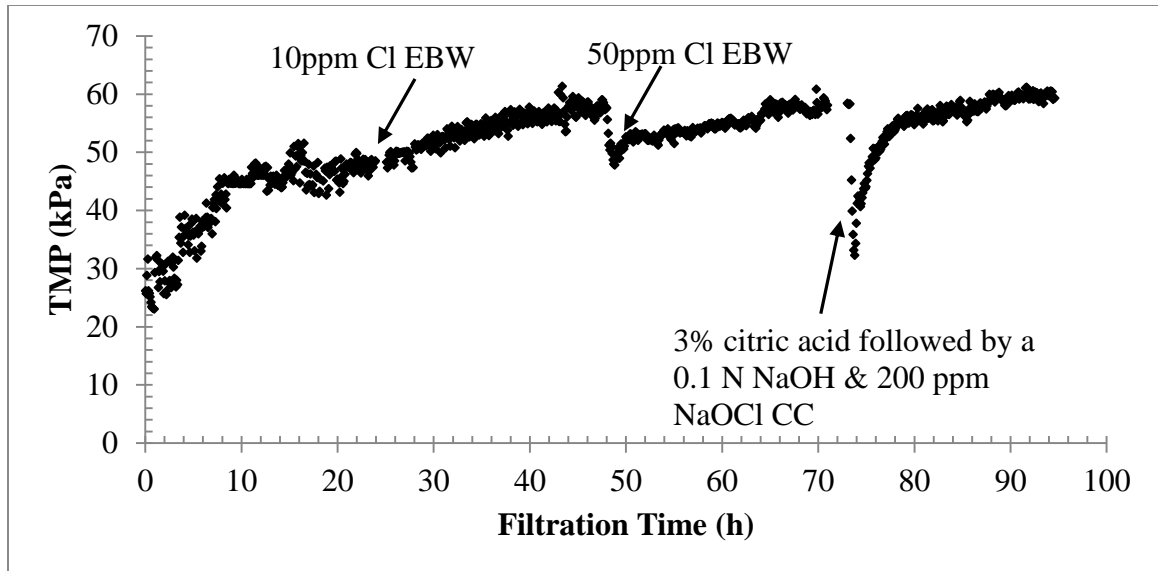


Fig. 4.4 Results of the first filtration test with different chemical cleaning steps

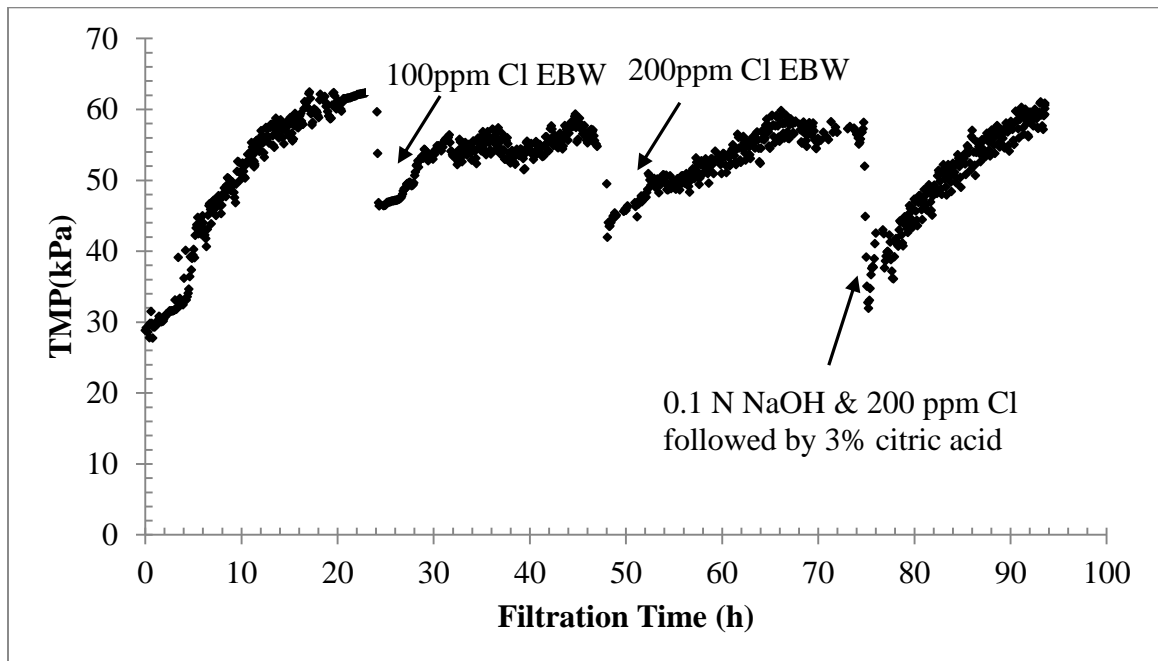


Fig. 4.5 Results of the second filtration test with different chemical cleaning steps

4.4.3 Seasonal Effect on Membrane Performance for Ottawa River Water

The influence of two different pretreatment methods (floatation versus sedimentation) on UF filtration performance in summer and winter was shown in Fig. 4.6 and 4.7. For all

the pretreatment alternatives considered, TMP increased with time, and it was significantly decreased by the chemical enhanced backwashing and chemical cleaning steps performed at the end of each day. Thus, indicating the great effectiveness of these types of cleaning. In all cases, TMP sharply increased during the beginning of the operation (about 10 h), which may indicate that adsorption is significant. It should also be noted that for each water, during several operational cycles immediately following chemical cleaning, TMP increased at a more rapid rate than in subsequent cycles. The more rapid increase may also indicate that adsorption occurred. The later cycles showed a fairly constant linear TMP increase, which may indicate the build-up of a cake layer. In addition, the TMP increase was greater during the initial day of operation than in subsequent days possibly indicating that there was some fouling that was irreversible based on this type of cleaning.

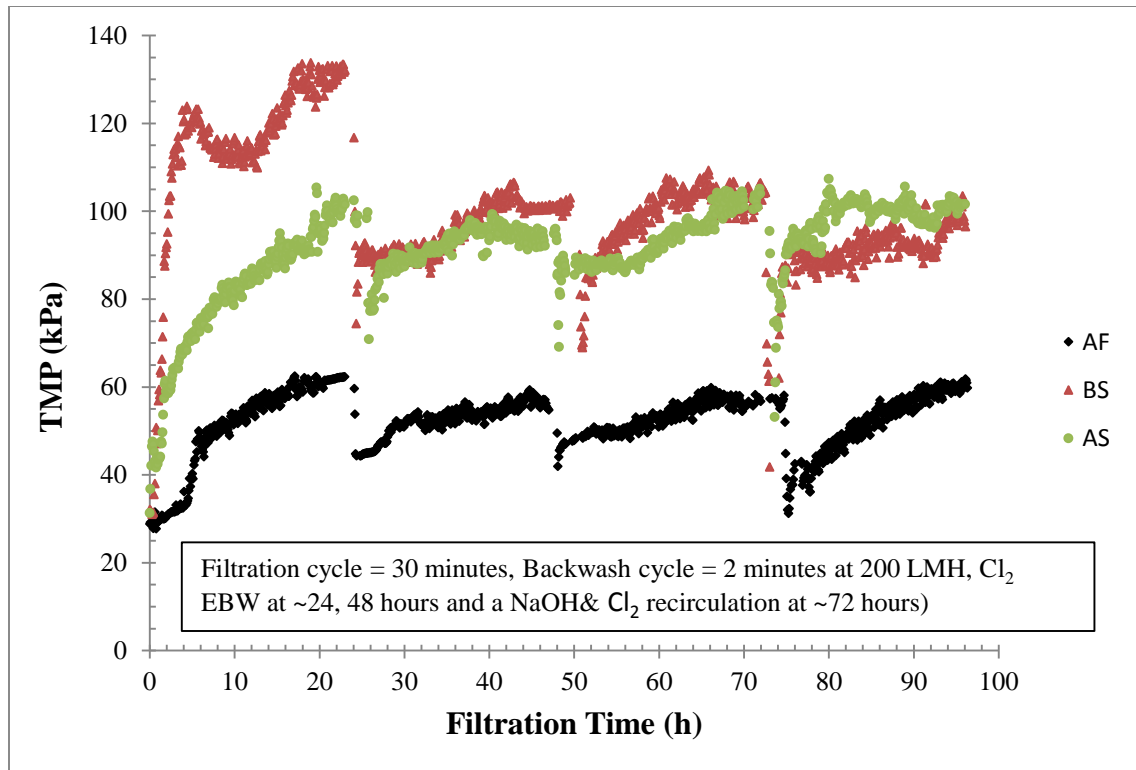


Fig. 4.6 Four-day 50 LMH filtration summer experiment results.

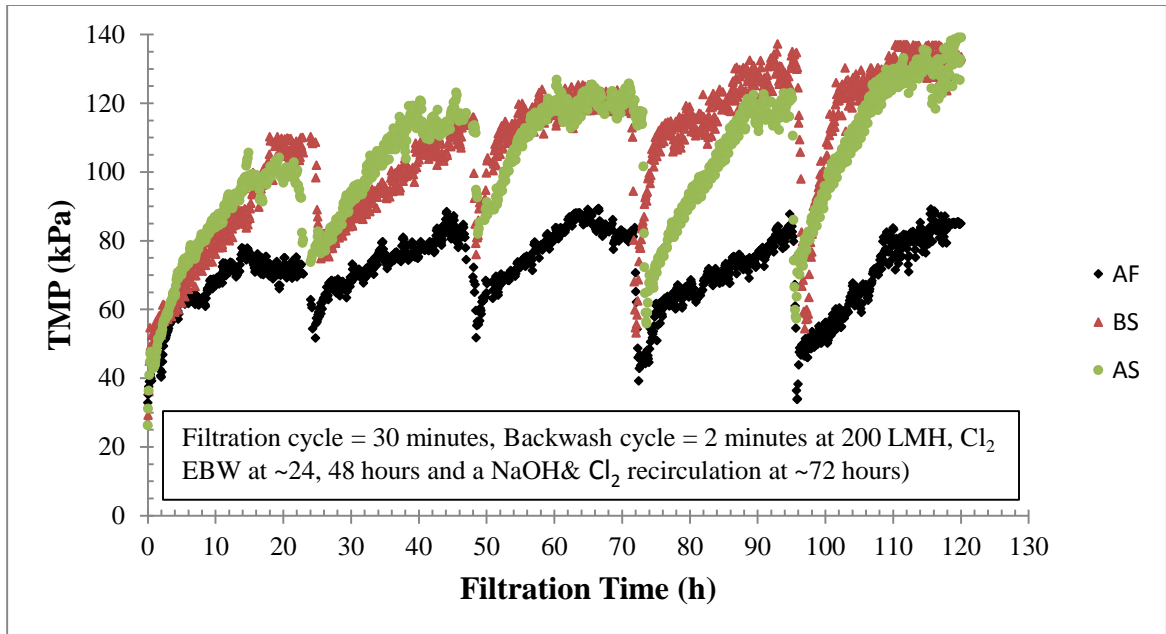


Fig. 4.7 Five-day 50 LMH filtration winter experiment results

The greater TMP rise for membrane filtration of the settled water than the floated water indicates that the former had greater fouling characteristics. This was the case for both the summer and winter samples, and it confirmed the findings of Walker (2014). Although during the first 24 hours settled water (BS) showed a higher fouling than settled water (AS), they produced about the same extent of fouling from the 25th hour onward in summer (Fig. 4.6). Over the duration of the summer experiments, the membrane TMP increased from about 30 to 100 kPa for both of BS and AS, while it increased from about 30 to 60 kPa for AF. For each system the maximum TMP at the end of each day were approximately the same (Fig. 4.6). Given the very similar water quality characteristic of the two settled water, the similarity of the TMP profile of the two settled waters should not be surprising. The improved membrane performance of the floated water seems to be related to the lower TOC and SUVA values achieved by this type of pretreatment.

In winter, the AF TMP increased from 30 to 80 kPa while for the settled ORWs the TMP increased from 30 to 140 kPa (Fig. 4.7), thus AF is superior regardless of the season. In addition, for the winter AS and BS pretreatments the TMP increased to higher levels each day despite the enhanced backwashes and chemical cleanings, while in summer the

TMP increased to approximately the same values at the end of 2nd, 3rd and 4th days. Accordingly during winter conditions in order to maintain more stable operation for membrane systems with sedimentation pretreatment the cleaning strategy should be modified slightly or the flux should be decreased slightly.

The average chemical backwash efficiencies of the chlorine enhanced backwashes for AF, BS and AS were 27.7 (29.9), 33.2 (33.3) and 29.4 (28.0) %, respectively in summer (winter). Thus, the chemical backwash efficiencies of this cleaning procedure were very similar for the three pretreatment options and the effectiveness did not significantly change with the seasons. The combined 0.1 N NaOH & 200 ppm chlorine recirculation step was found to be very effective for pretreated ORW and they almost recovered the entire membrane permeability. The TMP reductions in summer (and winter) were 46.4 (57.3), 60.5 (57.1) and 48.9 (52.9) % for AF, BS and AS, respectively. Thus, the effectiveness of the recirculation cleaning was influenced more by the type of pretreatment and seasons than by the chemical enhanced backwashes (i.e. the TMP decrease in figure 4.6 after 72 hour is much greater than that achieved after 24 and 48 hours). The greater winter fouling may be related to greater SUVA values; unfortunately, the fractionation of the summer samples was not possible so the impact of HPO concentrations during the summer cannot be established.

The fouling test results showed floatation is the preferred technology for pretreatment of UF to treat ORW, because of its lower NOM concentrations in floated ORW. This will be investigated in greater detail later.

4.4.3.1 Backwash Efficiency (BWE)

During the first ten hours of the operation, the BWE increased gradually for all the waters, presumably because the backwash pressure needs time to build up and make the backwashing more effective (Walker, 2014). BWE greatly fluctuates throughout the duration of each experiment, for example, the BWE for the Aylmer floated water fluctuated wildly from 35 to 100% over most of the experiment (Figure D. 1-6 in Appendix D). Walker (2014) and Nguyen (2011) also found the same trend.

Fig. 4.8 shows the average and 95% confidence intervals of BWE for the three pretreatment options. The AF's BWE was significantly higher than that of BS and AS for

both the summer and winter testing. The BWE of the two settled waters were very similar, and due to the overlapping 95% confidence intervals, the BWE for each pretreatment option is statistically the same during the two seasons. The confidence intervals are relatively small. This in part due to a) the large number of points (n) involved; and (b) the sample standard deviation gets divided by the square root of n as part of the confidence interval calculation.

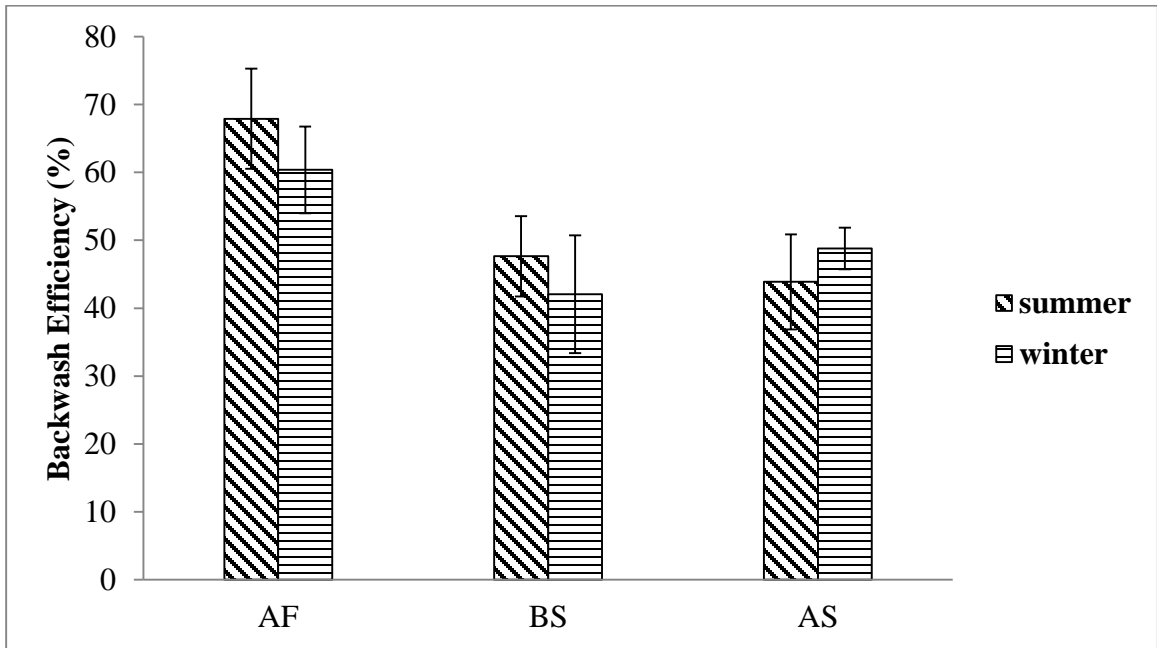


Fig. 4.8 Average values of BWE of Aylmer Floated, Britannia Settled and Aylmer Settled ORW in summer and winter experiments. Error bars represent the 95% confidence interval

4.4.3.2 DOC Fractionation

DOC fractionations were performed on the pretreated waters and UF permeates. Unfortunately, the summer samples were contaminated, so only the results for the winter waters are presented. The NOM fractionations of the winter pretreated water and in the UF effluent were shown in Table 4.2. As shown in Table 4.2 the three types of pretreatments had similar TOC removals (59.7 to 62.5%), and the membrane treatment improved the

TOC removal rate by approximately 10%. This low concentration TOC percent removals were expected given the relatively large MWCO of the membrane; typical percent TOC removals for UF water treatment applications is in the order of 5 to 20% (Pearce, 2011). The HPO removal by the AF pretreatment was slightly higher than for BS and AS (75.6% versus 62.6% and 64%). The HPO in AF is much less than that in BS and AS, which is consistent with the results of UV_{254} and SUVA data for pretreated waters (Table 4.1). However, the percent TPI removals by AF pretreatment were lower than those achieved by the BS and AS pretreatments (25.5% versus 69.1% and 78.3%). The HPI removals followed the same pattern (3.3% versus 23.7 and 21.9%). Accordingly the settled water had a higher HPO content and lower TPI and HPI content, thus HPO is a much larger fraction of NOM than for the floated water. Braghetta et al. (1997) reported floatation could remove significant HPO through bubble attachment to hydrophobic particle surfaces.

The UF membrane filtration increased the HPO, HPI and TPI percent removal of the pretreated waters to different degrees. However, because of the relatively small TOC values of the HPI and TPI fractions and the error in TOC analysis, there is greater uncertainty about the magnitude of these fractions. The mg/L HPO removals by the membranes were higher than the other two components. Thus more mass of HPO was retained by the membranes and thus it is likely that HPO is the main fouling fraction. This would explain the fact that floated pretreated water, which exposed membranes to lowest HPO concentrations, also caused the lowest level of membrane fouling. Other researchers also found the HPO fraction might be primarily responsible for membrane fouling (Katsoufidou et al., 2005; Lee et al., 2008; Tian et al., 2013; Yuan & Sydney, 2000).

Table 4.2 Combined (pre-treatment (Pre) + membrane (mem) filtration) NOM removals for each water

Treatments	TOC Removal rate(%)	HPO Removal rate (%)	HPO Removal amount (mg/L)	TPI Removal rate (%)	TPI Removal amount (mg/L)	HPI Removal rate (%)	HPI Removal amount (mg/L)
Pre(AF)	62.47	75.62	4.79	25.40	0.27	3.33	0.02
Pre(BS)	59.69	62.56	3.96	69.13	0.75	23.71	0.18
Pre (AS)	61.98	63.99	4.05	78.28	0.85	21.86	0.16
Mem(AF)	11.20	5.80	0.37	27.99	0.30	38.69	0.29
Mem(BS)	9.05	6.65	0.42	5.97	0.06	28.57	0.21
Mem(AS)	8.45	8.42	0.53	12.28	0.13	1.95	0.01
Pre+Mem(AF)	73.67	81.42	5.16	53.39	0.57	42.02	0.31
Pre+Mem(BS)	68.74	69.21	4.38	75.10	0.81	52.28	0.39
Pre+Mem(AS)	70.43	72.41	4.58	90.56	0.98	23.81	0.17

4.4.3.3 Fouling Resistance Analysis

The fouling resistance potential of each water was assessed by the application of resistance-in-series fouling indices. If the plot of $(1/NSF)$ versus specific volume (V) is linear, the fouling indices are calculated by linear regression using all the data. If the data shows a nonlinear pattern, the slope value was determined using the average of first and last 10 points (Yeh & Cheng, 1993). The results of the analysis are presented in Table 4.3.

TFI is a measure of the total fouling capacity of feed water. TFI, i.e., the slope of the above relationship, was calculated the slope using the average of the first ten and the last ten points within each hydraulic backwash cycle to reduce the impact of noisy data. Some hydraulic backwashing steps were ineffective, i.e., leading to negative values of TFI, i.e., the resistance after a hydraulic backwash was higher than prior to the hydraulic backwash. In the current analysis the negative TFI values, as well as the outliers, were excluded. Outliers are defined as any data point that deviates by more than three standard deviation from the average values. The average TFI values for AF were three times lower than that for AS and BS in the summer and two times lower in the winter. Moreover, the average TFI values for all the waters in winter were higher than in summer. The TFIs varied significantly from one cycle to the next, as illustrated by wide confidence limits. These large variations are consistent with the results of Nguyen et al. (2011). The significant

variation in the TIF values is probably due to the different hydraulic backwash efficiencies between each cycle.

HIFI was calculated using the linear regression method on the $1/NSF$ versus V data from the multiple hydraulic backwash cycles conducted over 24 hours without chemical cleaning. The chemical enhanced backwash was performed at the end of Day 1 and 2 and the chemical recirculation cleaning was conducted at the end of Day 3 or/and 4. The volume of water treated in one day was 1200 L/m^2 (i.e., $50 \text{ LMH} * 24 \text{ hours}$ of actual filtration), so the HIFI analysis was performed for every 1200 L/m^2 of permeate throughput. The average hydraulically irreversible fouling was greater for the settled waters than for the floated water (summer BS HIFI / summer AF HIFI = $15.0/6.0 = 2.5$ times, AS 1.8 times; winter BS 2.6 times, and AS 2.4 times (Table 4.3)). Moreover, although the confidence limits were overlapping, the average winter HIFI values were higher than those in the summer. The pattern of the BWE results coincided with the results of HIFI analysis. Due to the greater BWE, AF had a lower HIFI value.

Due to the lower fouling and lower fouling indices for the membrane filtration of floatation pretreated water, floatation may produce less foulants that sorb on the membrane (based on smaller HPO fraction), or foulants that form less compact cake layers. Floatation pretreatment resulted in less hydraulic irreversible fouling than sedimentation regardless of the type of coagulants used.

The HIFI/TFI ratios for the three waters (Table 4.3) ranged from 0.06-0.09 in summer to 0.07-0.10 in winter, which are of the same order of magnitude as those reported by Nguyen et al. (2011) for their hollow fiber bench-scale 42 LMH 4-day experiments for a natural surface water. Thus, the HIFI/TFI ratios suggest that during the summer about 90-94% of the total fouling was reversible by hydraulic backwashing, which implied that the main fouling resistance is due to hydraulically reversible fouling. This is much larger than the average BWE that ranged from 42-68%. The reason for these differences merits for their research, it may be related to: a) the 2-point approach of calculating the BWE and the variability of the TMP data immediately after backwashes, b) BWE is a different analysis method from the resistance-in-series fouling indices. Walker (2014) arrived at a different conclusion in spite of having very similar BWE values, the primary reason for his conclusion appears to be that a different analysis approach was followed.

The enhanced backwashing CIFI (or $CIFI_{EBW}$) values of the first three days of operation were used to determine the $CIFI_{EBW}$ in summer and winter. The CIFI for the two chemical clean steps, $CIFI_{CC}$, were based on the average values of the last two chemical cleaning cycles of the runs with winter water. Each data point represents one chemical cleaning. For BS summer water, the average $CIFI_{EBW}$ value of the first chemical cycle was much higher than the following two cycles. One would normally expect the first cycle pressure increase to actually be lower than subsequent cycles. This may be due to incomplete membrane stabilization, so it took a longer time to achieve more stable TMPs. Thus, only the data from the second and third chemically-enhanced backwash as were used to calculate the summer $CIFI_{EBW}$ values reported in Table 4.3. The summer $CIFI_{EBW}$ value of AF was much less than that of BS and AS (Table 4.3). The values of $CIFI_{EBW}/HIFI$ for all of the three different pretreated ORW were about 0.10, which indicated only 10% of productivity cannot be recovered by chemical enhanced backwash, so the chemically enhanced backwashes (100 ppm chlorine) was very effective in restoring the membrane permeability for pretreated ORW in summer (Table 4.3).

In winter, the $CIFI_{CC}$ value of AF was much less than that of BS and AS (Table 4.3). The values of $CIFI_{EBW}/HIFI$ for all of the three different pretreated ORW were approximately 0.25, which indicated about 75% of productivity can be recovered by chemical enhanced backwash, which is significantly lower than in the summer (Table 4.3). The values of $CIFI_{CC}/HIFI$ were much less than the values of $CIFI_{EBW}/HIFI$ (Table 4.3), which was expected as chemical cleaning is more effective than enhanced backwash.

A comparison of the fouling indices in summer and winter yields the following results. The total fouling is higher in winter than in summer (Table 4.3). The hydraulically irreversible fouling is about the same in summer and winter (Table 4.3), which also can be explained by the similar backwash efficiencies during the summer and winter tests (Fig. 4.8). Chemically irreversible fouling ($CIFI_{EBW}$) in winter is higher than summer as well (Table 4.3). As shown by Fig. 4.9 there is a fairly linear relationship between TFI and SUVA and between HIFI and SUVA, suggesting that the fouling is significantly linked to SUVA, which is representative of the HPO fraction.

Table 4.3 Fouling indices

	AF		BS		AS	
	Summer	Winter	Summer	Winter	Summer	Winter
TFI×10 ⁻⁴ (m ² /L)	63.9±5.6	110.2±11.7	182.5±21.9	209.6±24.4	178.3±19.5	206.9±16.0
HIFI×10 ⁻⁴ (m ² /L)	6.0±3.5	7.6±2.0	15.0±8.5	20.0±6.3	10.9±2.9	18.4±5.5
CIFI _{EBW} ×10 ⁻⁴ (m ² /L)	0.4	2.0	0.9	5.0	1.0	5.0
CIFI _{CC} ×10 ⁻⁴ (m ² /L)	N/A	0.3	N/A	2.0	N/A	4.0
HIFI/TFI	0.09	0.07	0.08	0.10	0.06	0.09
CIFI _{EBW} /HIFI	0.11	0.26	0.06	0.25	0.09	0.27
CIFI _{CC} /HIFI	N/A	0.04	N/A	0.10	N/A	0.21

(The mean ± 95% confidence intervals)

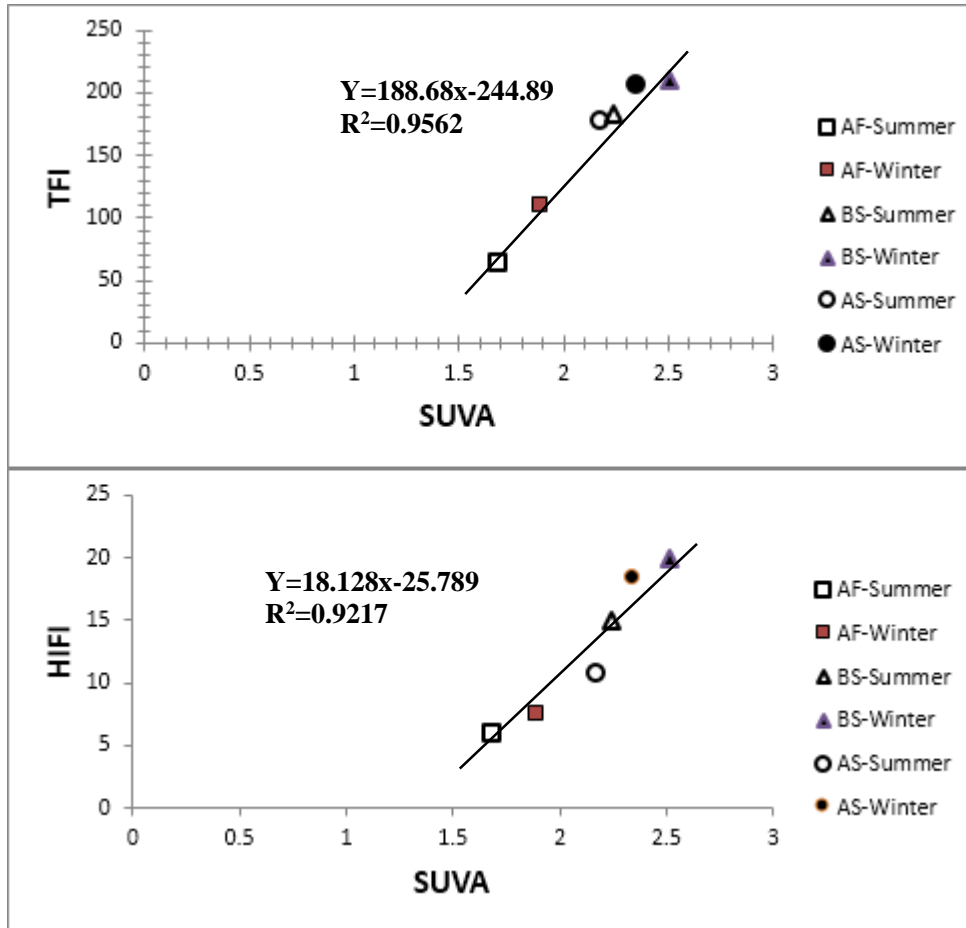


Fig. 4.9 The relationships between TFI and SUVA (a) and between HIFI and SUVA (b)

4.4.4 Effect of Different Filtration Cycle Length on Membrane Performance

The impact of filtration cycle length was assessed using 4-day UF filtration tests with AF pretreated water collected during the summer. Fig. 4.10 shows the TMP increase as the filtration cycles increase from 30, to 60 and 90 minutes. The fouling increased dramatically with increasing filtration cycle duration. At the beginning of all of the experiments, TMPs of three waters with different backwash frequency started from a similar TMP (~30 kPa), and then the TMPs significantly increased during the first 24 hours of operation. The greater the filtration cycle length the greater the TMP increase. This may be because adsorption takes place during the starting phase of the experiment (Katsoufidou et al. 2005).

And BWE for the 30, 60 and 90 minutes filtration cycles showed large fluctuations throughout the duration of the experiment. The average BWE decreased as the filtration cycle length increased. Because of the large fluctuations the confidence limits of BWE are rather wide. Although the BWE confidence limits for the 60 and 90 minute runs overlapped (so they are statistically the same), the BWE values for the 30-minute filtration cycle run were significantly higher (Fig. 4.11).

With a longer filtration time there may be more accumulation of cake material and the formation of a more compact cake that may be more difficult to hydraulically backwash. For all waters, TMP increased with time and dropped dramatically after chemical enhanced backwashing and chemical recirculation (Fig. 4.11).

The enhanced backwashing was able to reduce the TMP by 33.2%, 26.4% and 23.5% for floated ORW with backwash frequency of 30, 60 and 90 minutes, respectively. Combined chemical recirculation performed at 72nd hour reduced the TMP by 46.4, 35.6 and 41.9% for backwash frequencies of once every 30, 60 and 90 minutes, respectively. As mentioned before, synergism of NaOH and chlorine could be the reason why the cleaning efficiency of combined chemical recirculation was better than chlorine enhanced backwashing.

The results demonstrated that longer filtration cycles resulted in more membrane fouling. This finding agrees with the results of Kim and DiGiano (2006) and Waterman (2008), they found shorter filtration cycle lengths between backwashes reduced membrane

fouling. The reasonable explanation could be that with longer filtration cycles, fouling was accelerated through cake compression. So it was more difficult to clean the accumulated cake layer. It is worth to mention that TMP of the 30 minutes filtration cycles increased more slowly between chemical enhanced backwashes; it seemed it could maintain the slow increase rate for longer time as shown by the small slope of the TMP in Fig. 4.10.

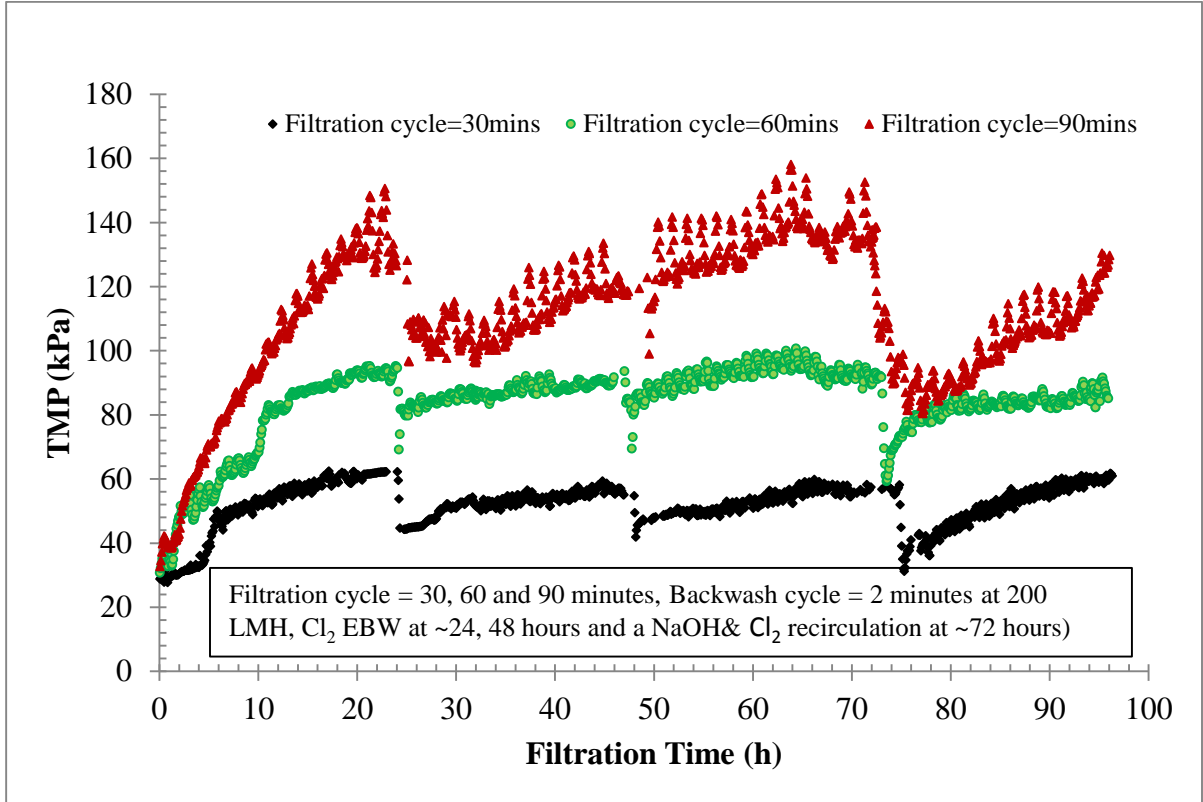


Fig. 4.10 Four-day 50 LMH filtration experiment results: effect of filtration cycle length

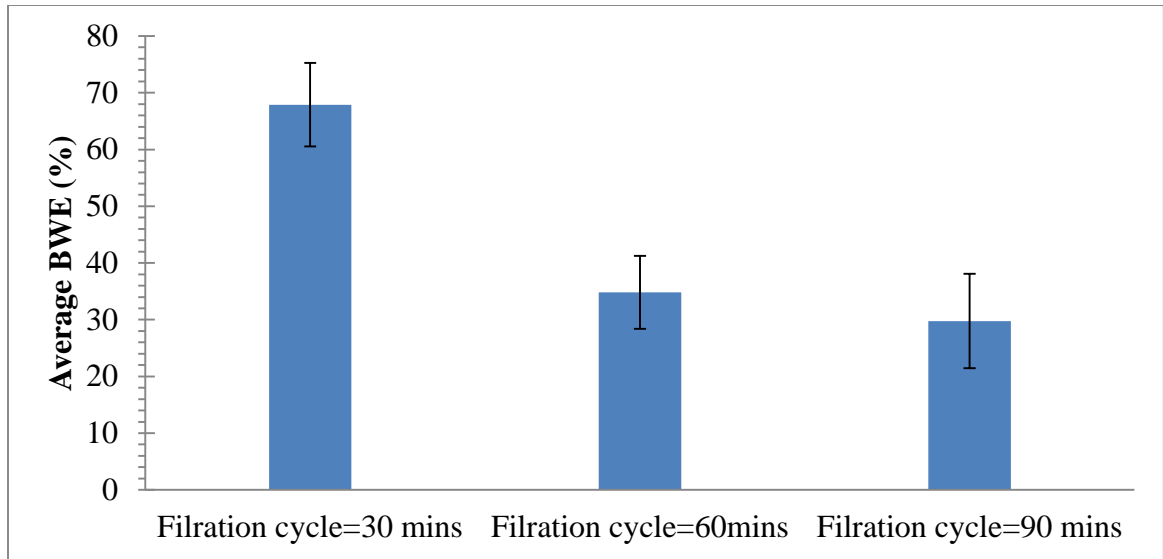


Fig. 4.3 Average values of BWE of Aylmer Floated ORW (Filtration cycle = 30 ,60 and 90 minutes, Backwash cycle = 2 minutes at 200 LMH, 20 minutes Chlorine enhanced backwash at ~24, 48 hours and a 20 minutes NaOH&Cl recirculation after ~72 hours, error bars represent the 95% confidence interval

4.4.4.1 Fouling Resistance Analysis

As shown in Table 4.4, the TFI, HIFI and CIFI increased with increasing backwash filtration cycle duration, thus there was more total, hydraulically irreversible and chemically irreversible fouling observed when longer filtration cycle times were used (Table 4.4). As mentioned before, it is likely that the longer filtration cycles resulted in a thicker cake and/or greater cake layer compression.

The average HIFI value of floated ORW for the 30 minute filtration cycles was much lower than that with longer filtration cycles (60 and 90 minutes) (Table 4.4). There was no significant difference in the ratio of HIFI/TFI (0.06-0.09) for the ORW subjected to different backwash frequencies. Based on the HIFI/TFI ratio, about 91, 93 and 94% of the fouling could be reversed by hydraulic backwash when the filtration cycle duration was 30, 60 and 90 minutes, respectively. Thus, longer filtration cycles increased the fouling but also resulted in a greater fraction of the fouling that was hydraulically reversible. Longer filtration likely resulted in a thicker cake layer, and a larger fraction of total foulants within the cake layer which is much easier backwashed. The results confirm the supplier's (Matrix Membranes Inc.) suggestions that operating longer filtration cycles could alleviate the hydraulically reversible fouling. As mentioned in section 4.4.3.3, although backwash

efficiencies (68, 35 and 29% for FT with 30, 60 and 90 minutes) were lower than the HIFI/TFI ratio, they are different measures of backwash efficiency.

Filtration cycles of 30 minutes caused the lowest chemical irreversible fouling. $CIFI_{EBW}$ values increased with the increasing filtration cycle length (Table 4.4). Based on the $CIFI_{EBW}/HIFI$ ratio, the chemical enhanced backwashing could reverse around 89, 78 and 70% of the hydraulic irreversible fouling in the 30, 60 and 90 minute filtration-cycle runs, respectively, since $CIFI_{EBW}/HIFI$ was 0.11, 0.22 and 0.30, respectively (Table 4.4).

In general, the permeate quality was very stable regardless of the operational conditions and seasons. Up to 75% TOC removal and approximately 95% UV_{254} removal was achieved by UF plus pretreatment. And the turbidity of permeate was less than 0.2 NTU for all of the samples.

Table 4.4 Fouling indices for different backwash frequency of Aylmer Floated ORW

Fouling indices	Filtration cycle = 30 minutes	Filtration cycle = 60 minutes	Filtration cycle = 90 minutes
$TFI \times 10^{-4}$ (m ² /L)	63.9 ± 5.6	129.2 ± 31.9	218.7 ± 45.9
$HIFI \times 10^{-4}$ (m ² /L)	6.0 ± 3.5	9.25 ± 5.1	13.2 ± 9.1
$CIFI_{EBW} \times 10^{-4}$ (m ² /L)	0.4	2.0	4.0
HIFI/TFI	0.09	0.07	0.06
$CIFI_{EBW}/HIFI$	0.11	0.22	0.30
$CIFI_{EBW}/TFI$	0.006	0.016	0.019

(The mean ± 95% confidence intervals)

4.5 Conclusions

This bench-scale study evaluated the impact of sedimentation and floatation pretreatment on the performance of a hollow fiber UF membrane system treating ORW which has substantial NOM content and a high hydrophobic NOM content. The coagulation/flocculation/sedimentation and coagulation/flocculation/floatation pretreatment conducted at two adjacent full-scale water treatment plants greatly reduced the NOM concentrations of these waters. The pretreatment resulted in TOC and UV_{254} absorbance removals in the 60-70% and 75-80% range, respectively, so there still remains significant amount of NOM which can foul the membranes. Based on the samples collected at the two treatment plants, the main conclusions of this study are:

1. The UF hollow-fiber filtration tests confirmed the findings of Walker (2014) that for this type of water, coagulation/flocculation/floatation provides better pretreatment than coagulation/flocculation/sedimentation. The superiority was evident from the lower TMP developed, the greater backwash efficiency, the lower total fouling indices, hydraulically irreversible fouling indices and the lower chemically irreversible fouling indices.
2. The improvements of coagulation/flocculation/floatation were observed during both seasons. The superiority appears to be linked to the floatation pretreatment's greater removal of the hydrophobic NOM fractionation.
3. Except for UV₂₅₄ and SUVA increases, the seasonal water quality changes were relatively small. However, the UF membrane fouling was significantly higher in winter than in summer for the three pretreatments options studied. The membrane filtration of the settled waters in winter showed a day after day TMP increase, while in summer the TMP increased to approximately the same level each day. It appeared that the differences in the fouling were linked to SUVA, an indicator of the hydrophobic NOM fraction.
4. The 100 ppm chlorine as a chemical enhanced backwash reagent and the 0.1N NaOH & 200 ppm chlorine chemical cleaning solutions identified in the initial experiments were very effective at reducing TMP and fouling during the summer for all the pretreatment options. The recirculation chemical cleaning steps reduced the TMP by approximately 45%. For the winter samples these chemical cleaning steps were also effective for the floated water, however for the settled waters a more aggressive cleaning procedure or a lower operating flux is necessary to maintain day-to-day constant maximum TMP levels.
5. Based on the fouling indices, about 90-94% of the total fouling was reversible by hydraulic backwash, although the average backwash efficiencies were below 68%. These differences require further investigation. Hydraulically irreversible fouling and chemically irreversible fouling were slightly higher in winter than in summer.
6. As expected, longer filtration cycles resulted in higher TMP increases, higher fouling indices (TFI, HIFI and CIFI), a slightly greater fraction of the fouling being hydraulically reversible and a lower fraction that is chemically irreversible.

To assess the universality of these results it is recommended that further testing be conducted with ORW and other water with high hydrophobic NOM content. In addition, testing of the same pretreatment alternatives should be conducted with algal impacted waters.

4.6 Acknowledgements

The authors would like to thank the Natural Sciences and Engineering Research Council of Canada for its financial support of this research and the Ontario Graduate Scholarship for the financial support of the lead author.

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CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This bench-scale UF membrane system was used to compare the effect of sedimentation and floatation pretreatment on the performance treating ORW which has substantial NOM content and a high hydrophobic NOM content. Based on the samples tested, the following conclusions were drawn from water characterization test, fouling experiments, backwash efficiency calculation and resistance-in-series model calculation:

1. Both of the coagulation/flocculation/sedimentation and coagulation/flocculation/floatation pretreatment conducted at two adjacent full-scale water treatment plants greatly reduced the NOM concentrations of these waters. The TOC and UV₂₅₄ absorbance removal rates were in the 60-70% and 75-80% range, but there still remains significant amount of NOM which can foul the membranes.
2. The UF hollow-fiber filtration tests confirmed the findings of Walker (2014) that for this type of water, coagulation/flocculation/floatation provides better pretreatment than coagulation/flocculation/sedimentation. The superiority was evident from the lower TMP developed, the greater backwash efficiency, the lower total fouling indices, hydraulically irreversible fouling indices and the lower chemically irreversible fouling indices.
3. The superior performance of coagulation/flocculation/floatation were observed during both seasons. The superiority appears to be linked to the floatation pretreatment's greater removal of the hydrophobic NOM fractionation.
4. The UF membrane fouling was significantly higher in winter than in summer for the three pretreatments options studied. Although UV₂₅₄ and SUVA increases in winter, the seasonal water quality changes were relatively small however. The membrane filtration of the settled waters in winter showed a day after day TMP increase, while in

summer the TMP increased to approximately the same level in each of operation. It appeared that the differences in the fouling were linked to SUVA, an indicator of the hydrophobic NOM fraction.

5. The 100 ppm chlorine as a chemical enhanced backwash reagent and the 0.1N NaOH & 200 ppm chlorine chemical cleaning solutions identified in the initial experiments were very effective at reducing TMP and fouling during the summer and winter filtration tests for all the pre-treatment options. The recirculation chemical cleaning steps reduced the TMP by approximately 45%.
6. Based on the fouling indices, about 90-94% of the total fouling was reversible by hydraulic backwash, although the average backwash efficiencies were below 68%. These differences require further investigation. Hydraulically irreversible fouling and chemically irreversible fouling is slightly higher in winter than in summer.
7. As expected, longer filtration cycles resulted in higher transmembrane pressure increases, a greater fraction of the fouling being hydraulically reversible and a lower fraction that is chemically irreversible.

5.2 Recommendations

Future work will include:

1. To verify the universality of the above conclusions for high hydrophobic NOM waters the tests should be repeated for waters with similar characteristics from different locations. The evaluation of the alternative pretreatment methods should be expanded to different types of waters, such as algal impacted water.
2. The new membrane conditioning method should be improved.
3. Because the summer samples were contaminated, the fractionation of TOC in summer were not tested, the comparison of TOC fractionation in different seasons should be conducted.

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APPENDIX A: XAD-4/XAD-8 Fractionation

The tendency of XAD-8 resin is to adsorb the hydrophobic fraction of NOM, and the tendency of XAD-4 is to adsorb the transphilic fraction (Croue et al., 2000). The XAD-4/XAD-8 fractionation method was adapted from Thurman and Malcolm (1981):

1. XAD-8/XAD-4 Resin Preparation:

- i. Load column make sure the valve is turned off to prevent column from running dry. Load column with resin to appropriate volume. The resin was cleaned according to the manufacturer's 0.1 N NaOH for 1-3 hours. Take samples of the feed and the effluent, lower their pH to around 7 with 1M HCL acid and measure DOC concentrations. The difference between the feed and effluent should be no more than a few hundred ppb.
- ii. Rinse column with five column volumes of hot MQ water. Remove the column from the stand, seal with stopper and shake vigorously.
- iii. Rinse column once with 10% 1M HCL acid solution.
- iv. Pass MQ water through the column. If the differential DOC is too high, repeat steps ii) and iii). Repeat this until effluent and influent have the similar DOC concentrations.

2. Fractionation processes in this study was shown in fig.A.1:

- a. Filter at least 400 mL water sample with a 0.45 μm membrane filter to remove precipitates.
- b. Adjust the pH of the water sample to below pH=2 with 10% 1M HCL.
- c. Pass the water sample through the column. Allow the first 100 ml to go to waste, this is to elute the remaining MQ water in the column.
- d. Pass the remaining 300 ml of sample through the XAD-4 column and XAD-8 column 2 more times sequentially, elute HPO from column XAD-4 and elute TPI with 0.1 N NaOH from column XAD-8 with 0.1 N NaOH.
- e. Conduct DOC analysis of the effluent (HPI), elute TPI and elute HPO.

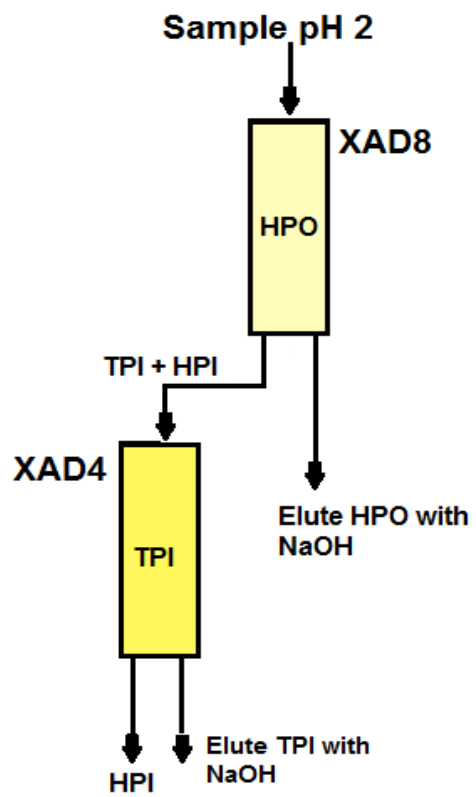


Fig. A.1 XAD-8/XAD-4 fractionation

APPENDIX B: Critical Flux

Because of the inevitability of membrane fouling, the optimization of operational conditions is very important to minimize membrane fouling. The definition of critical flux is “a flux below which a decline of flux with time does not occur; above it fouling is observed” (Field et al., 2006). One of the methods to determine the critical flux in water treatment is the constant flux experiments (Choi & Dempsey, 2005; Tiranuntakul et al., 2011). It can be conducted by setting a low constant flux, once a pseudo-steady state has reached; the rate of change of TMP was recorded for an adequate amount of time (generally 15 minutes). Then the flux was increased and this procedure continued in a step-wise fashion. The cycles of increasing flux and recording the rate of TMP increase are repeated many times. Then the rate of TMP increase versus flux is plotted. A linear relationship can be found for fluxes below the critical operational flux and a second linear relationship for fluxes above the critical operational flux (Choi & Dempsey, 2005; Tiranuntakul et al., 2011). Calculations are then performed to find the intersection of the two straight lines. The permeate flux at which the two lines intersected is defined as the critical operational flux.

Stoller and Chianese (2007) used spiral wound ultrafiltration membrane to test the critical flux of olive washing wastewater, they found flocculation pretreatment can improve the critical flux by 40%. The reasons may be because they used the different method to determine critical flux and the olive washing wastewater was fairly high in organic matter (i.e., COD ~ 800 mg/L). The nature of fouling in it is different from surface water.

Walker (2014) used the same method to test Raw ORW and found the critical flux was 79 LMH. Waterman (2007) determined the critical flux of Raw ORW to be 75 LMH. The operational critical fluxes of AF, BS and AS ORW were 82, 72, 70 LMH, respectively according to Fig. B.1, B.2, B.3. These values are consistent with the degree of fouling caused by the various pretreated feeds discussed in chapter 4. The operational critical flux for pretreated water would be expected to be higher than that for the raw water. In this study, the operational critical flux test was not performed for raw ORW. However, Walker (2014) conducted such test for Ottawa River water and the same type of membrane and he

obtained an operational critical flux of 79LMH. The relatively higher than expected value may be due to differences in water quality, slight differences in the membrane modules and the interpretation as to what is the linear range of the fluxes.

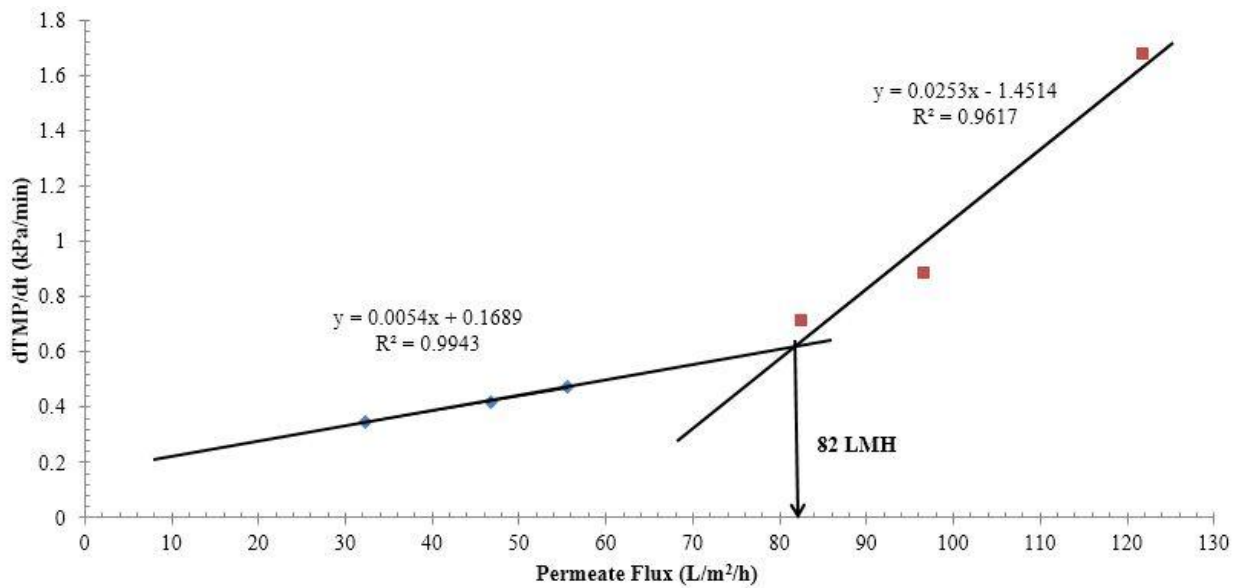


Fig. B.1Determination of critical flux of AF ORW in summer

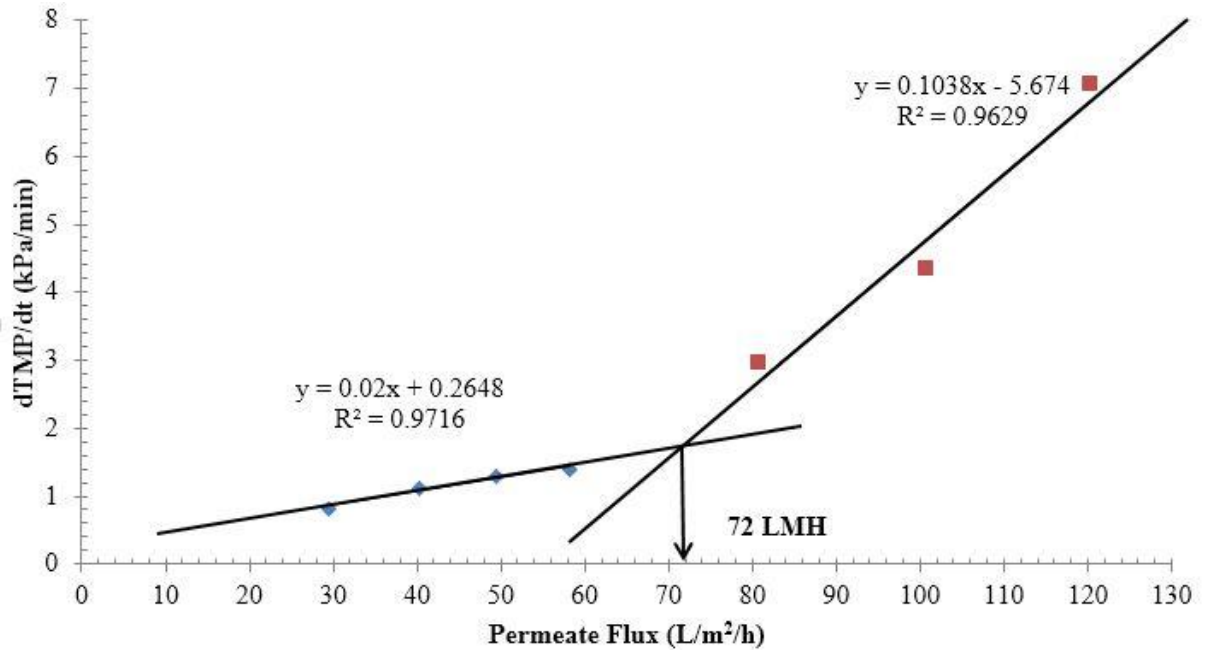


Fig. B.2 Determination of critical flux of BS ORW in summer

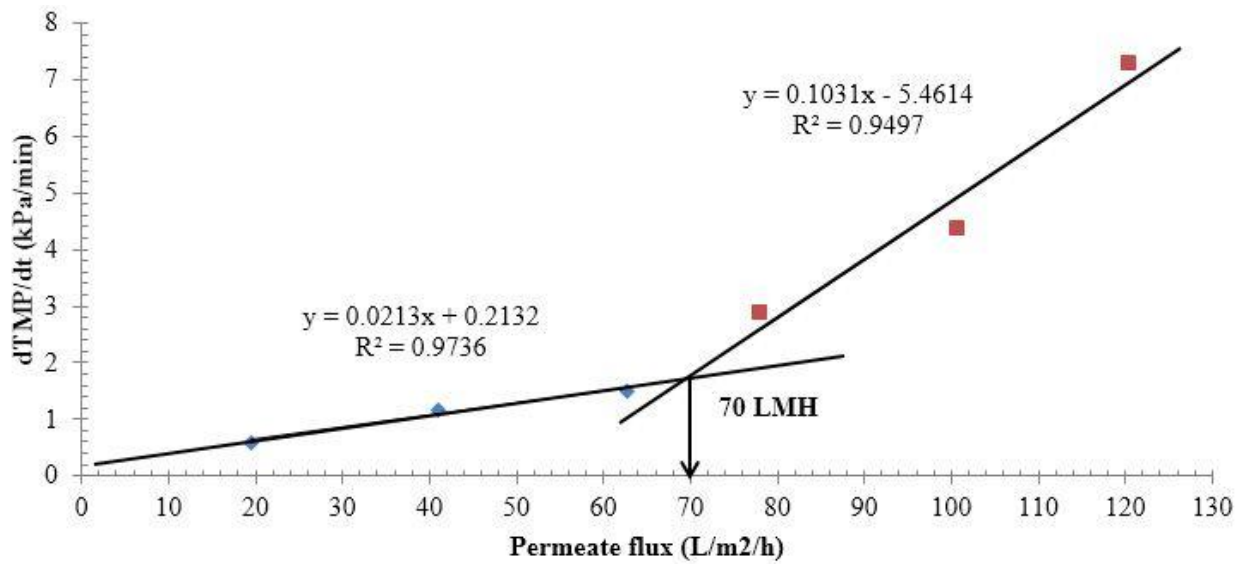


Fig.B.3Determination of critical flux of AS ORW in summer

APPENDIX C: TFI, HIFI and CIFI Calculations

The fouling indices TFI, HIFI and CIFI are calculated based on the slopes of the $1/\text{NSF}$ versus specific volume (V , permeate volume per unit membrane area) at different times of the multi-day filtration runs.

TFI is a measure of the total fouling capacity of feed water. As the $1/\text{NSF}$ versus V data for the entire experiments were non-linear in nature, TFI, i.e., the slope of the above relationship, was calculated using the average of the first ten and last ten points within each hydraulic backwash cycle. Because the experiment was conducted 4 or 5 days, there were approximately 200 filtration-backwashing cycles. The significant variation in TFIs was shown in Fig. C.1 to Fig. C.8 no matter different pretreatments and filtration cycle lengths were applied in different seasons.

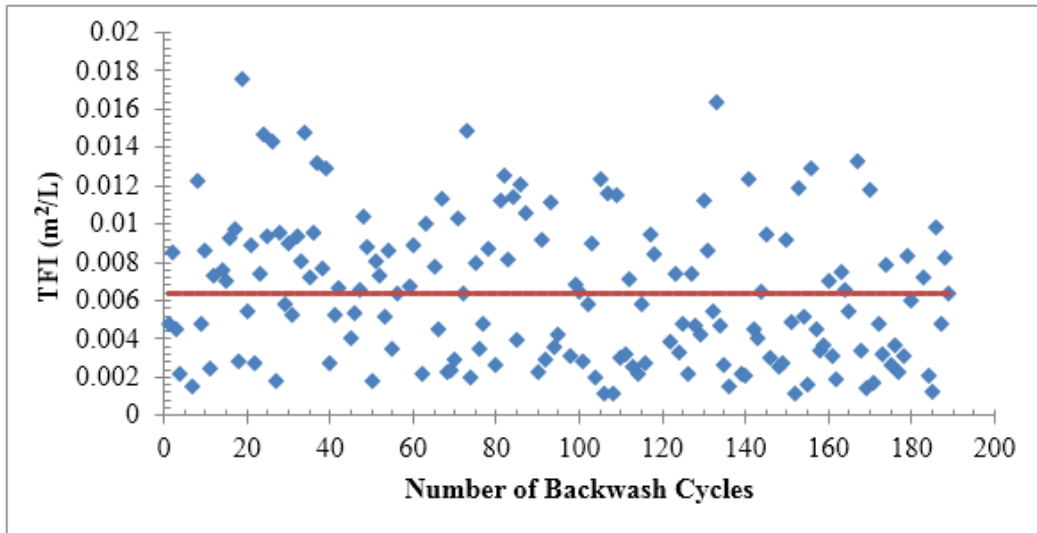


Fig. C.1 TFI values of AF in summer (50 LMH, Filtration cycle=30 minutes, 4 day experiment) (The straight line represents the mean value of TFIs)

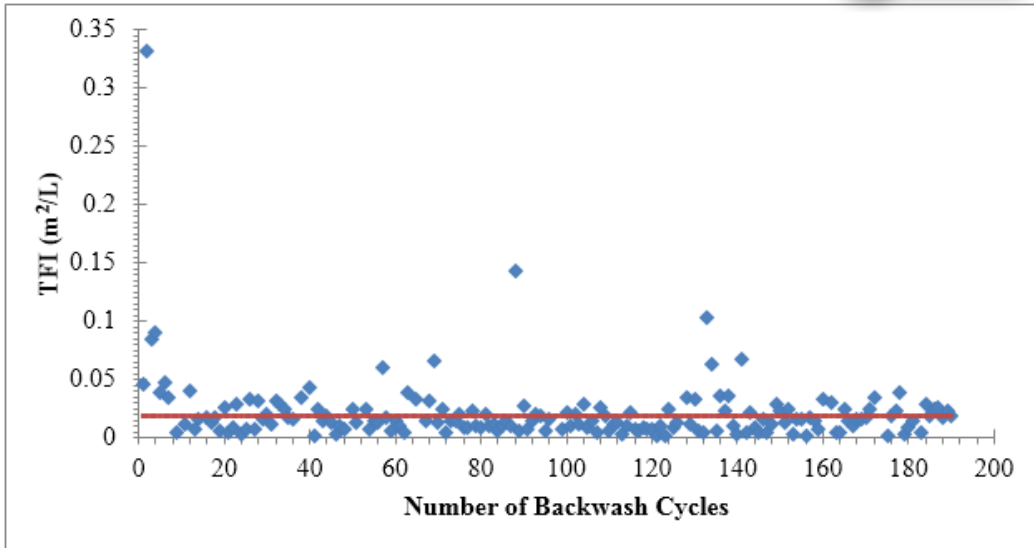


Fig. C.2 TFI values of BS in summer (50 LMH, Filtration cycle=30 minutes, 4 day experiment) (The straight line represents the mean value of TFIs)

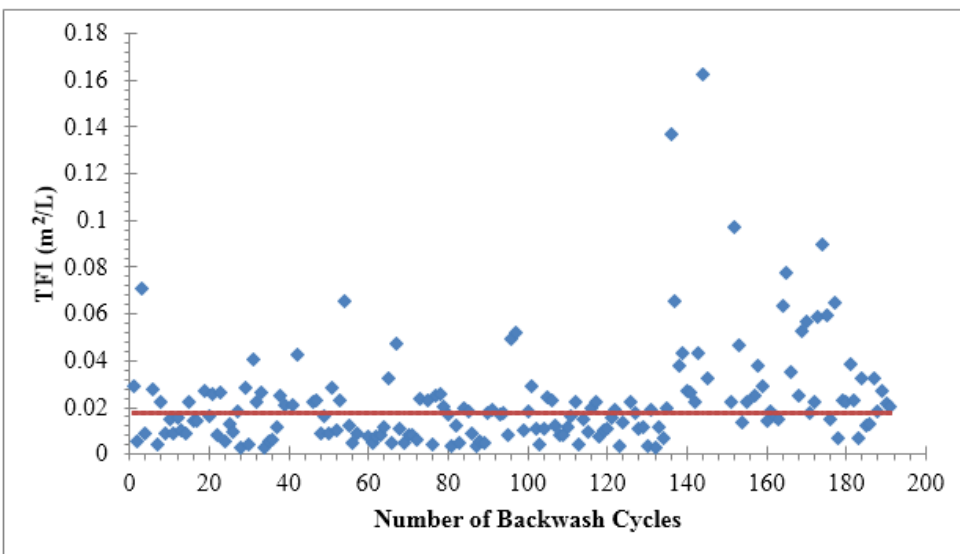


Fig. C.3 TFI values of AS in summer (50 LMH, Filtration cycle=30 minutes, 4 day experiment) (The straight line represents the mean value of TFIs)

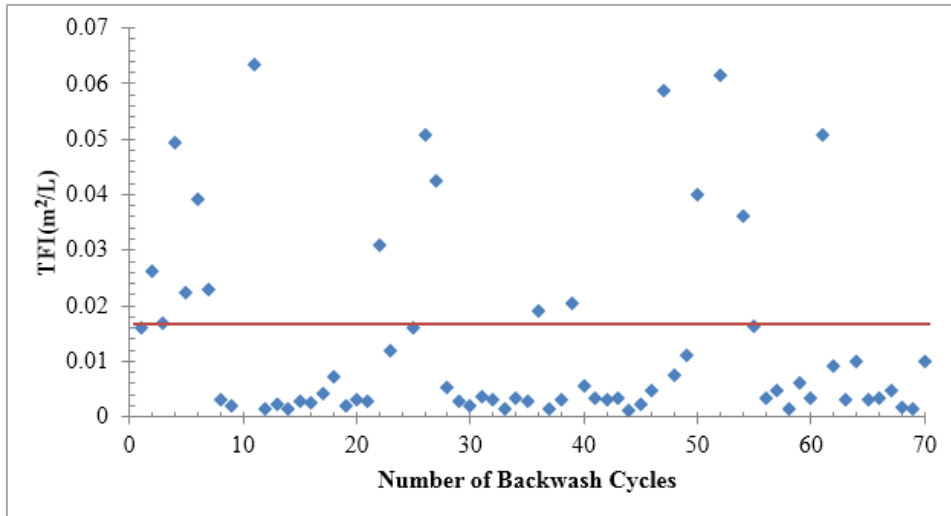


Fig. C.4TFI values of AF in summer (50 LMH, Filtration cycle=60 minutes, 4 day experiment) (The straight line represents the mean value of TFIs)

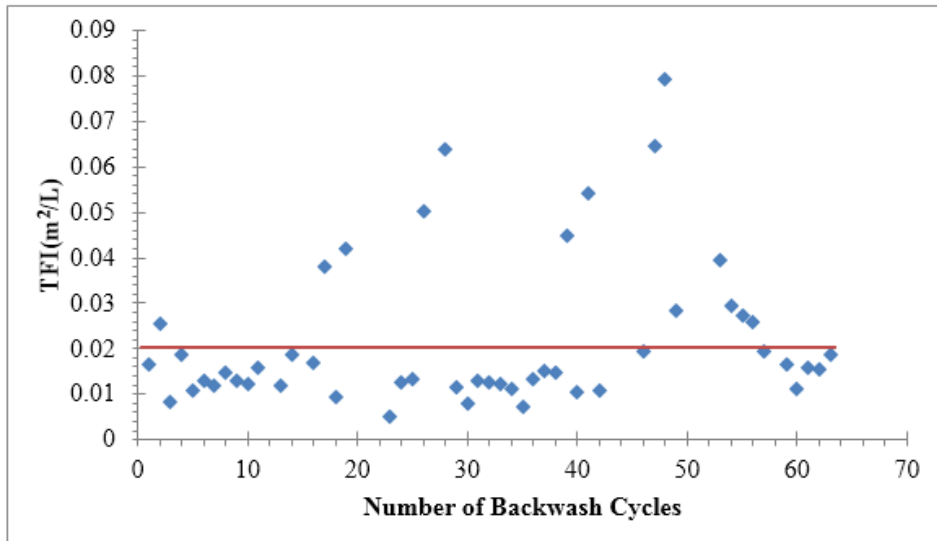


Fig. C.5TFI values of AF in summer (50 LMH, Filtration cycle=90 minutes, 4 day experiment) (The straight line represents the mean value of TFIs)

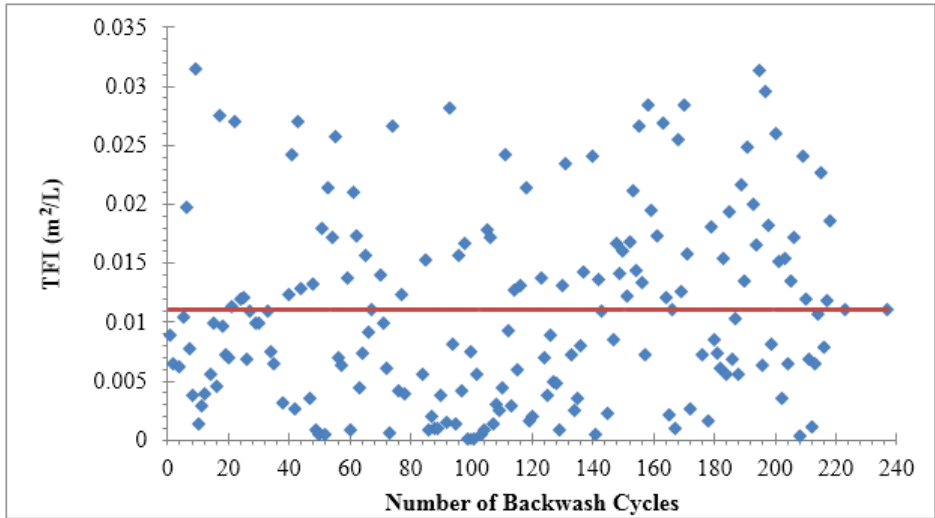


Fig. C.6TFI values of AF in winter (50 LMH, Filtration cycle=30 minutes, 5 day experiment) (The straight line represents the mean value of TFIs)

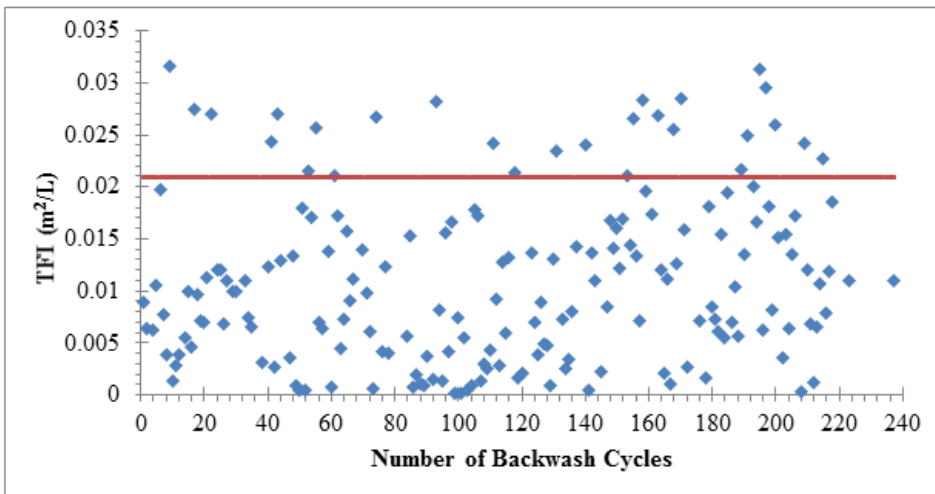


Fig. C.7TFI values of BS in winter (50 LMH, Filtration cycle=30 minutes, 5 day experiment) (The straight line represents the mean value of TFIs)

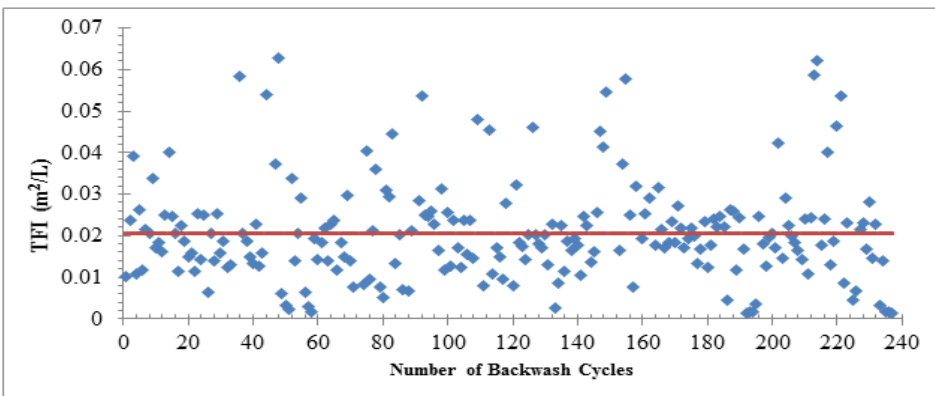


Fig. C.8TFI values of AS in winter (50 LMH, Filtration cycle=30 minutes, 5 day experiment) (The straight line represents the mean value of TFIs)

The hydraulically irreversible fouling index (HIFI) was calculated based on $1/NSF$ versus V data for filtration/backwashing cycles in between enhanced chemical backwashes and chemical backwashes. Figure C.9 showed this type of graph for the winter AF pretreated water, which is representative of that for all the pretreatment options studied. Although the relationship was not entirely linear, it was approximated by fitting a straight line for all the backwashing cycles in between each chemically enhanced backwash or chemical cleaning. They are shown in figure C.9 as straight line and are accompanied by the linear regression equation and R^2 of the line. The slopes of these lines are the HIFI; for example for the first day of operation which ended with the first chemically enhanced backwash HIFI was found to be 0.007.

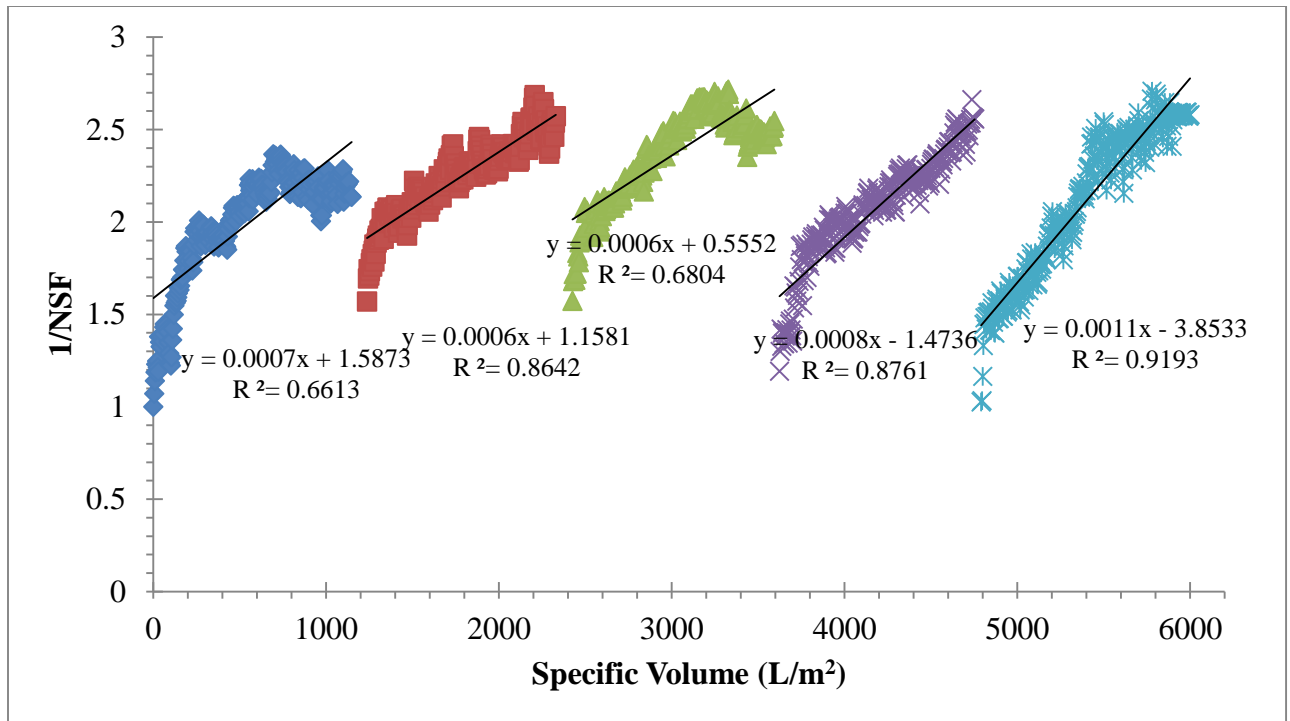


Fig. C.9 HIFI values of AF in winter (50 LMH, Filtration cycle=30 minutes, 5 day experiment)

The chemically irreversible fouling indices (CIFI) were calculated based $1/NSF$ data immediately before and after a chemical cleaning step. Each data point is the average value of one chemical cleaning cycle in winter for AF, BS and AS (Fig. C.10). $CIFI_{EBW}$ and $CIFI_{CCare}$ shown in figure C.10 as straight lines and are accompanied by the linear regression equation and R^2 of the line. The slopes of these lines are the CIFI.

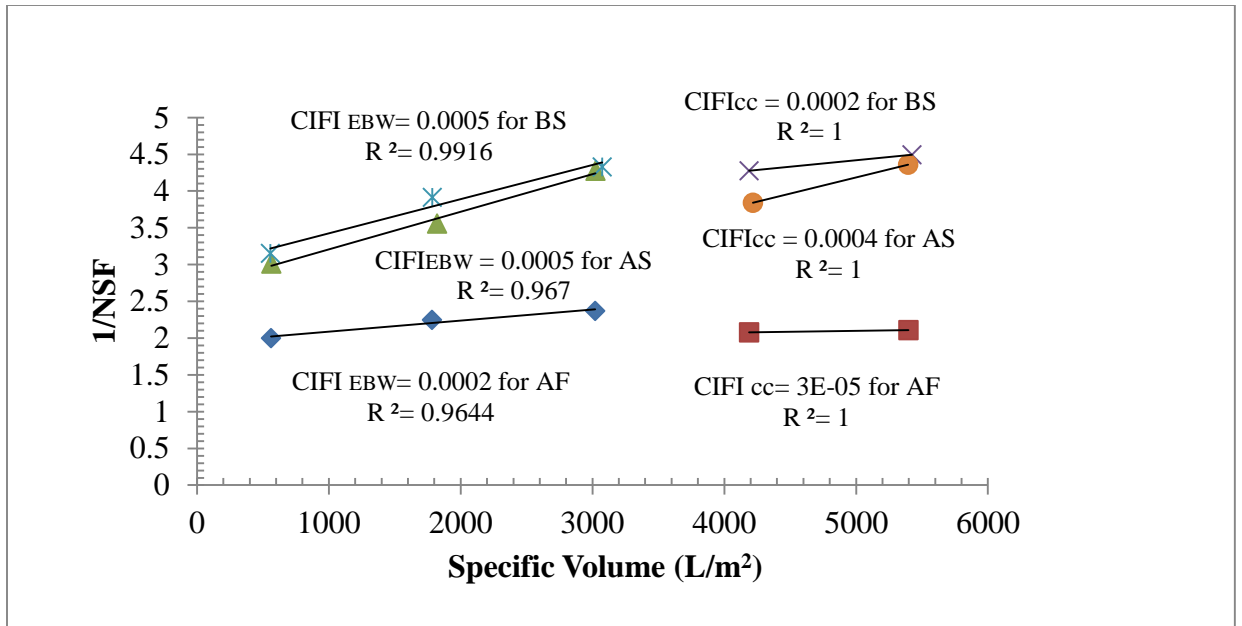


Fig. C.10 CIFI of AF, BS and AS in winter

APPENDIX D: Backwash Efficiency

AAs shown in Fig. D. 1-6 BWE showed large fluctuations throughout the duration of the experiment. Although the big fluctuations were found for each experiment, the superior performance of shorter filtration cycle was still shown in Fig. D.7.

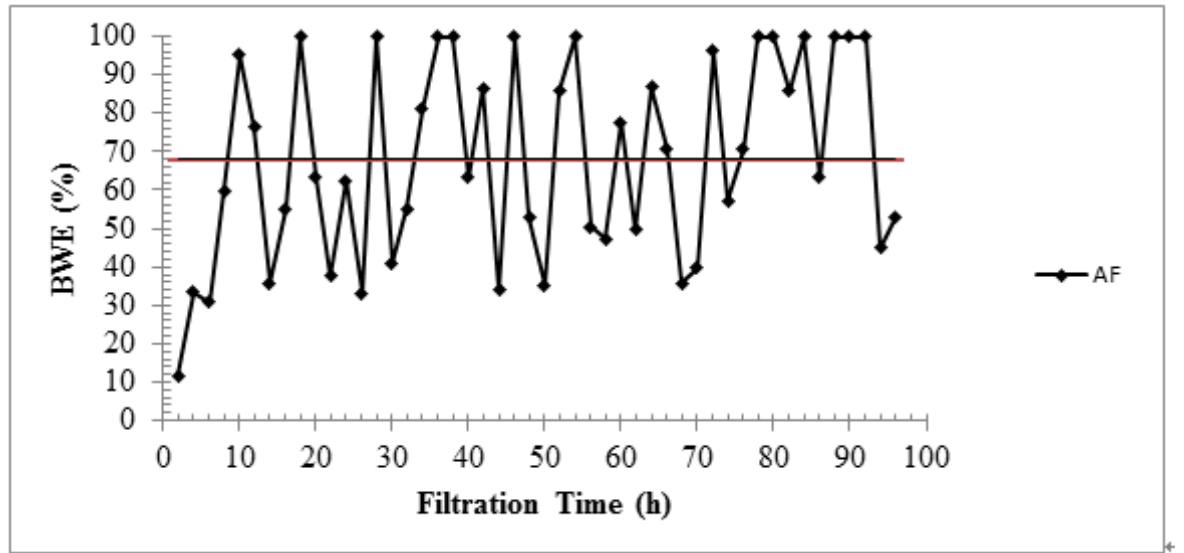


Fig. D.1BWE of AF using the values recorded every 2 hours (The straight line represents the mean value of BWE)in summer

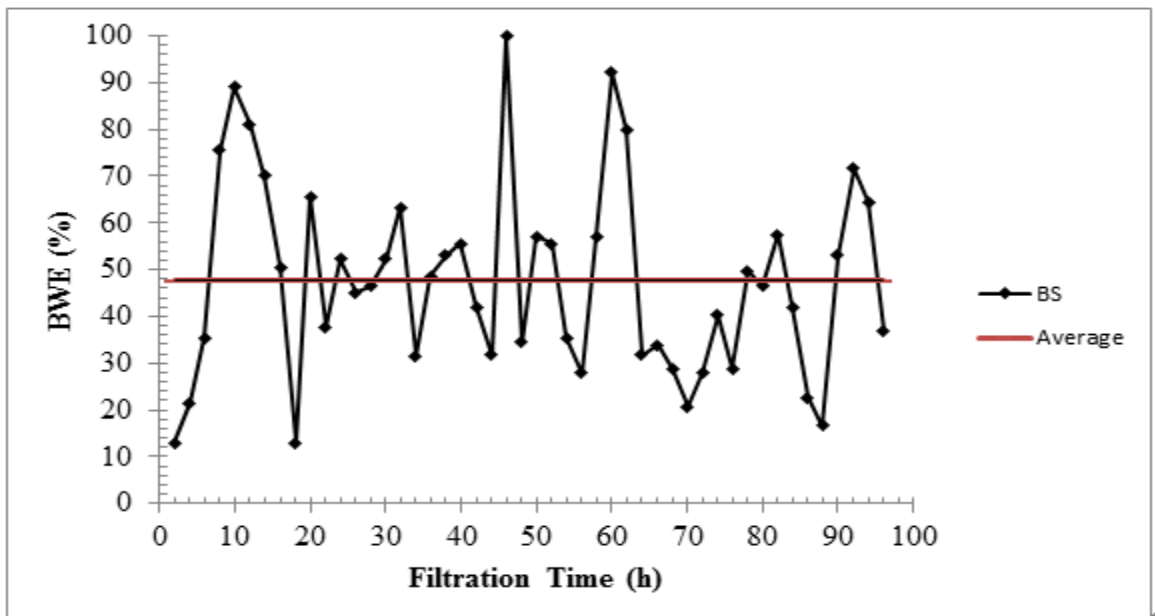


Fig. D.2BWE of BS using the values recorded every 2 hours(The straight line represents the mean value of BWE)in summer

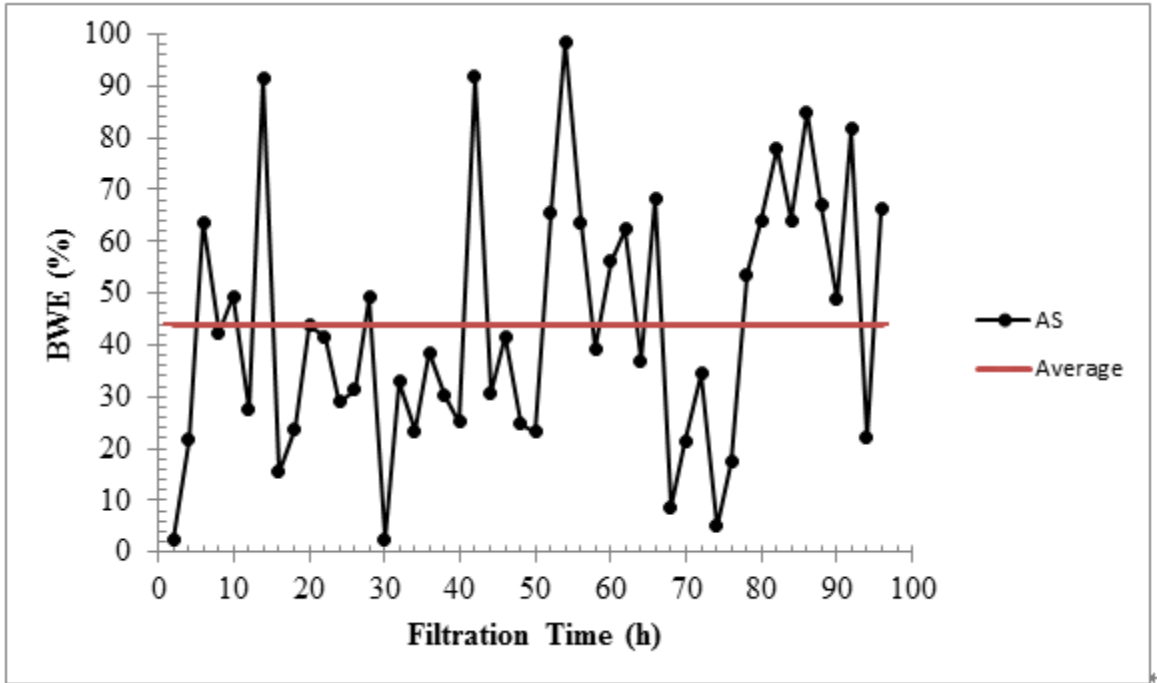


Fig. D.3 BWE of AS using the values recorded every 2 hours (The straight line represents the mean value of BWE) in summer

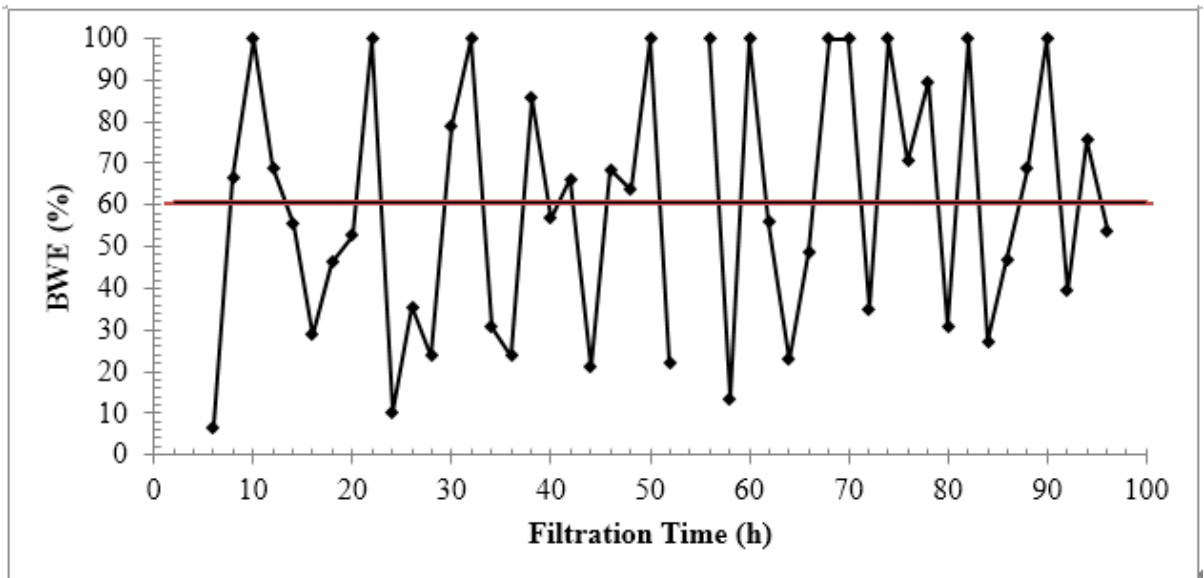


Fig. D.4 BWE of AF using the values recorded every 2 hours (The straight line represents the mean value of BWE) in winter

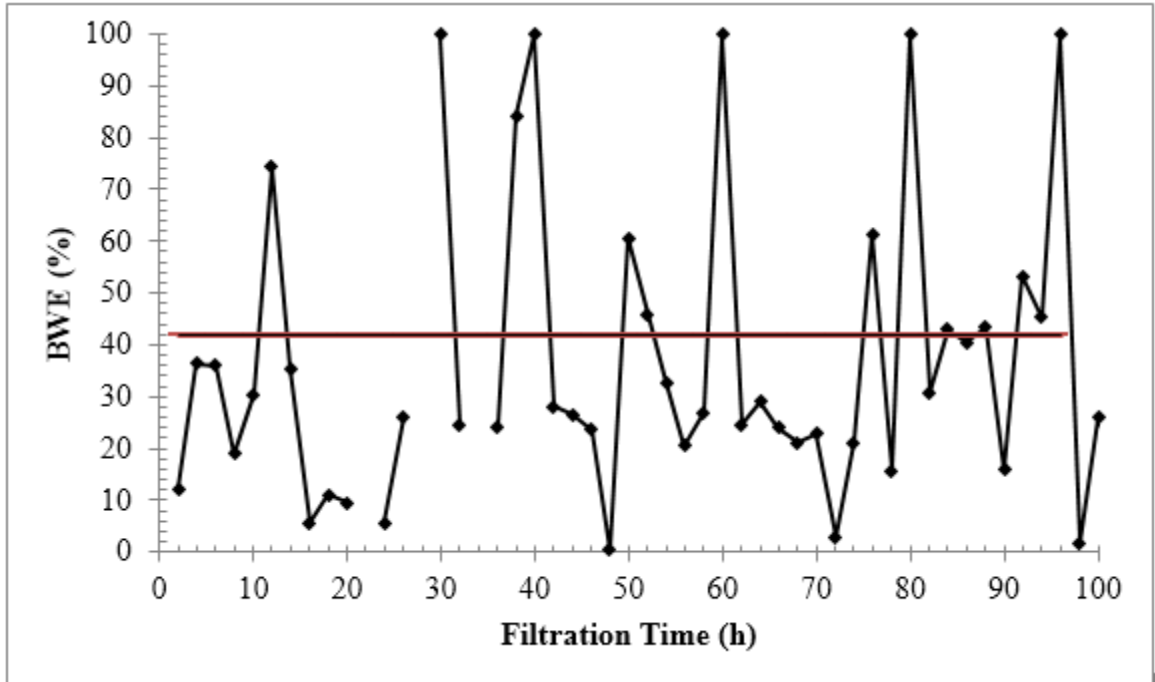


Fig. D.5 BWE of BS using the values recorded every 2 hours (The straight line represents the mean value of BWE) in winter

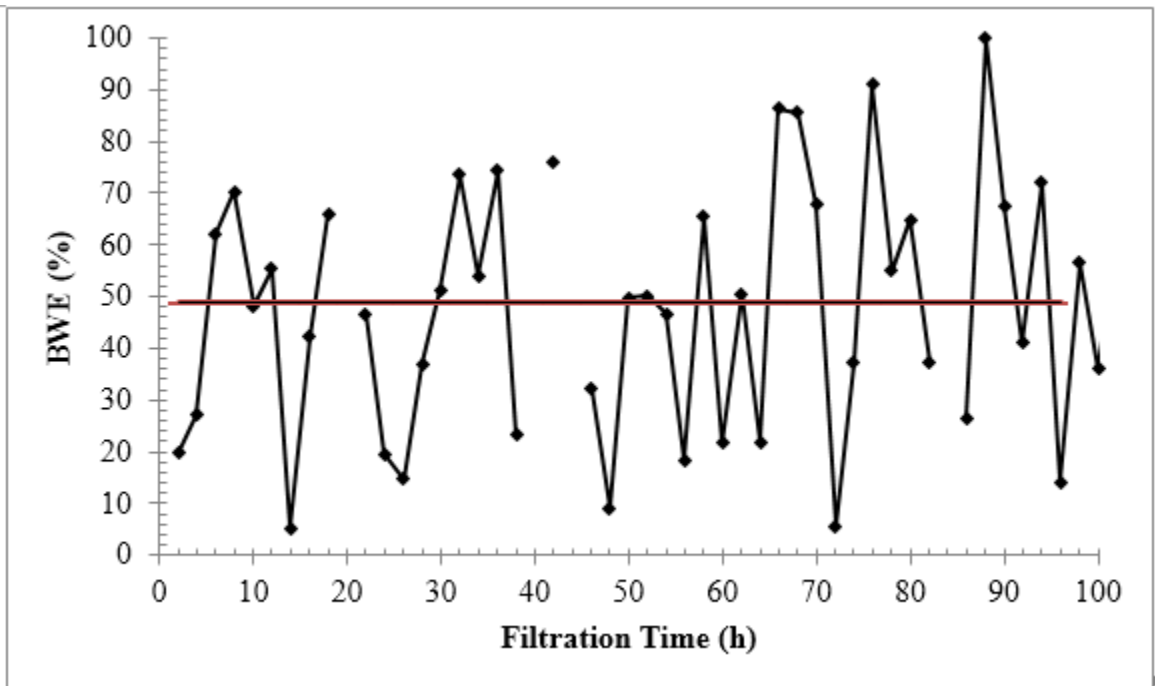


Fig. D.6 BWE of AS using the values recorded every 2 hours (The straight line represents the mean value of BWE) in winter

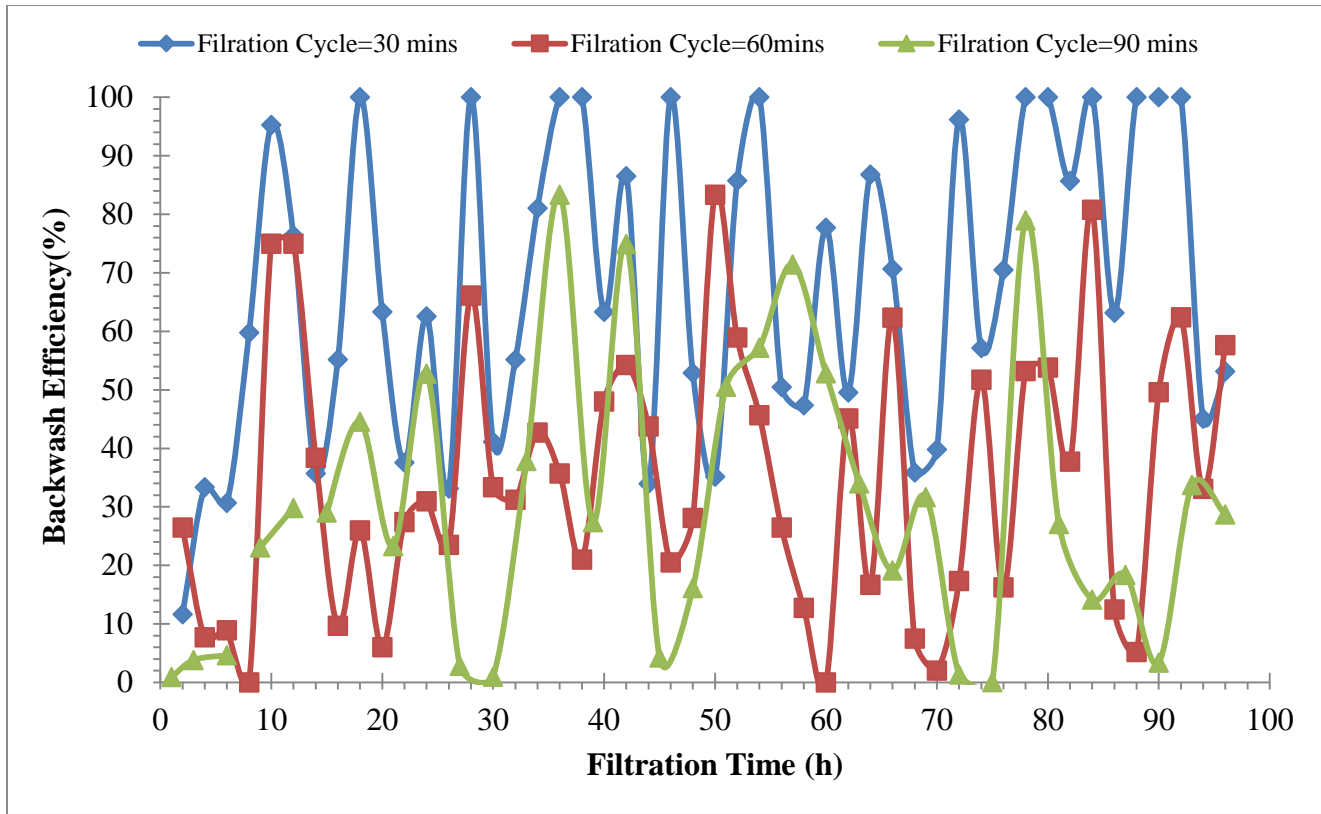


Fig. D.7 BWE of AF using the values recorded every 2 hours: effect of different filtration cycle length in summer