HOLLOW FIBER ULTRAFILTRATION OF OTTAWA RIVER WATER: IMPACT OF DIFFERENT PRE-TREATMENT SCHEMES

By

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ABSTRACT

To minimize membrane fouling many water treatment plants pre-treat water prior to microfiltration (MF) or ultrafiltration (UF). Coagulation/flocculation/sedimentation is a common form of pre-treatment, but little research has been conducted on floatation as a part of the pre-treatment. The objective of this thesis is to compare pre-treatment with floatation and with sedimentation for Ottawa River water, a typical Northern Canadian water with a high natural organic matter (NOM) content and a large hydrophobic (HPO) NOM fraction. Fouling tests consisted of multiple filtration/backwashing cycles performed by an automated bench-scale UF hollow fiber membrane system. Test were conducted with Ottawa River water (ORW) and ORW subjected to three different types of pre-treatment conducted at closely-located full-scale water treatment plants, including one using floatation. Both Alum pre-treatments resulted in decreases in NOM (63% and 68% TOC) and HPO NOM (56% and 68%TOC) which helped to reduce fouling. However, the remaining NOM and HPO NOM still caused significant hydraulically and chemical irreversible fouling.

The water pre-treated with floatation produced the least severe hydraulically irreversible fouling for all experiments while Raw ORW produced the highest. During the early stages of membrane filtration (~10 hours), the TMP sharply increases which may imply that adsorption is dominant. Statistical analysis during the initial stages of filtration showed that the HPO fraction of NOM was linked to hydraulically irreversible fouling, which may be attributed to adsorption. Raw ORW also had the highest hydraulically reversible fouling while all pre-treatments were able to reduce this type of fouling. Statistical analysis suggested that the transphilic (TPI) fraction of NOM and particulate organic carbon (POC) were responsible for hydraulically reversible fouling during subcritical flux experiments, which may be attributed to cake formation on the membrane surface. It was found that for all waters and experiments, hydraulically irreversible fouling was greater than hydraulically reversible fouling. This may be because of the high HPO concentrations in the ORW. Hydraulically reversible fouling and backwash efficiencies were found to fluctuate with time. It is hypothesised that the cake formation adheres to the membrane surface and is not fully removed until enough backwash pressure has developed. Further investigation into alternative cleaning procedures is required as the NaOH cleaning was not very effective for some of the pre-treated waters.

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ABBREVIATIONS

Alum F	Ottawa River water coagulated with alum + a polymer, flocculated and floated
Alum S	Ottawa River water coagulated with alum + silicate, flocculated and settled
BWE	Backwash Efficiency
CIP	Chemical clean in place
Da	Dalton
DAQ	Data acquisition
DOC	Dissolved organic carbon
EOM	Extracellular organic matter
FSS	Flat sequence structure
HPI	Hydrophilic fraction of natural organic matter
HPO	Hydrophobic fraction of natural organic matter
Iron	Ottawa River water coagulated with ferric sulfate coagulant + silicate, flocculated and settled
K_{CIR}	Chemically irreversible membrane fouling resistance (m^{-1})
K_{CR}	Chemically reversible membrane fouling resistance (m^{-1})
K_{HIR}	Hydraulically irreversible membrane fouling resistance (m^{-1})
KHP	Potassium hydrogen phthalate
K_{HR}	Hydraulically reversible membrane fouling resistance (m^{-1})
LMH	Unit for flux ($L\ m^{-2}\ h^{-1}$)
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
NMWCO	Nominal molecular weight cut-off

NOM	Natural organic matter
NSF	Normalized specific flux
OC	Organic carbon
ORW	Ottawa River Water
PES	Polyethersulfone
POC	Particulate organic carbon
PS	Polysulfone
PVDF	Polyvinylidene fluoride
Raw ORW	Raw (untreated) Ottawa River Water
RO	Reverse Osmosis
SUVA	Specific ultraviolet absorbance
TMP	Transmembrane pressure
TOC	Total organic carbon
TPI	Transphilic fraction of natural organic matter
UV254	Ultraviolet absorbance at a wavelength of 254nm
UF	Ultrafiltration

CHAPTER 1

INTRODUCTION

In March 1991 there was a very large outbreak of gastroenteritis in Milwaukee, Wisconsin, due to a Cryptosporidium infection that was transmitted through the drinking water supply. It was estimated that 403,000 people became ill (Mac Kenzie, et al. 1994). In the aftermath of the incident, many engineers resorted to implementing microfiltration (MF) and ultrafiltration (UF) membranes in new and upgraded water treatment plants as a way to avoid such incidents. This led to a tremendous growth in the use of these low pressure membranes. A membrane is a semi-permeable barrier that allows the passage of some constituents and the rejection of others. UF membranes are effective at producing consistent high quality water and removing harmful contaminants such as bacteria, protozoa, some viruses, some particles, and some natural organic matter (NOM) (MWH 2005). However, membranes do have limitations, in particular they are susceptible to fouling. Membrane fouling is the result of foulants and particles building up on the membrane surface restricting flow, plugging the membrane pores, or adsorbing within the membrane pores. Fouling requires periodic membrane cleaning and may result in premature membrane replacement. It has been concluded that membrane fouling is extremely complex, is often influenced by many parameters, and depends on the source water, membrane characteristics and the system's operating conditions (Metsamuuronen et al. 2014; Zularisam et al. 2011; Laine et al. 1989).

One of the main membrane foulants in surface waters is NOM (Uyak et al. 2014; Aoustin et al. 2001). NOM is very complex and varies depending on the soil characteristics in which it comes in contact, the time of the year and landscape (Gjessing 1976). NOM is commonly categorized into three fractions: hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI). Many researchers have found that the HPI fraction is the most influential NOM fraction in membrane fouling (Qu et al. 2012; Zularisam et al. 2007; Huang et al. 2007). Conversely, many researchers have also found that the HPO fraction of NOM is mainly responsible for membrane fouling (Gray & Bolto 2004; Jones & O'Melia 2001; Lin et al. 1999). Not many studies show that the TPI fraction of NOM contributes to membrane fouling, however, Bessiere et al. (2009) found that the TPI fraction of NOM was largely responsible for membrane fouling.

The principal approaches to minimize the impact of fouling are hydraulic backwashes, chemical cleanings and pre-treatment. Hydraulic backwashes remove particulate build up on the membrane surface by forcing membrane permeate in the opposite direction of filtration. The membranes are subjected to 1 - 5 minute long hydraulic backwashes every 15 minutes to 2 hours using 2-3 times the filtration flow rate. (MWH 2005). However, hydraulic backwashes generally do not reduce the transmembrane pressure (TMP) to its original value for constant flux systems, i.e., there is some hydraulically irreversible fouling and the membrane performance diminishes over time. Eventually, chemical backwashes or chemical soaks are required to reduce the effects of membrane fouling (Amy 2008). The chemical agent used for chemical cleans is chosen based on what is fouling the membrane and the membrane manufactures recommendations. Even after chemical cleans however, some fouling may persist, commonly referred to as chemically irreversible fouling (MWH 2005).

The third approach to reduce the impact of membrane fouling is to pre-treat the source water prior to membrane filtration. Coagulant/flocculation pre-treatment coupled with membrane filtration have shown promising results as higher quality membrane permeate is produced and membrane fouling is reduced (Guigui et al. 2002; Braghetta et al. 2001; Robert et al. 1999). However, there are studies that have also found that implementing coagulant/flocculation prior to membrane filtration results in an increase of membrane fouling (Liu et al. 2005; Schafer et al. 2001; Shorney et al. 2001). One explanation for an increase in membrane fouling after coagulation/flocculation was due to the coagulants forming a sticky floc complex which further restricts flow through the membrane (Adham et al. 2006). To maximize the efficiency of the pre-treatment in many cases the coagulated/flocculated water is settled prior to membrane filtration. Floatation is an efficient and more compact alternative to sedimentation, and has the added advantage that is a better separation process for algae. Little research on floatation as a form of membrane pre-treatment for algae impacted waters was identified in the literature (Pera do Amaral et al. 2013; Teixeira & Rosa 2006).

The objective of this thesis is to use an automated bench-scale UF hollow fiber system to compare the impact of pre-treatment with floatation versus sedimentation for a colored river water. Ottawa River water (ORW) was chosen as the challenge water because; a) its relatively high NOM and hydrophobic (HPO) content and resulting high fouling potential; and b) there are full-scale treatment plants treating ORW using coagulation/flocculation/sedimentation and coagulation/flocculation/floatation within close proximity of each other. It was hypothesised that floatation as a pre-treatment prior to membrane filtration would improve membrane performance. Membrane fouling for each water was assessed. The different types of membrane fouling; hydraulically irreversible, hydraulically reversible, chemically irreversible and chemically reversible were determined. Statistical analysis was conducted attempting to link membrane fouling with different water quality characteristics. This thesis is organized as a manuscript-based thesis, chapter 4 is a journal manuscript instead of a conventional results chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Membranes used in Water Treatment

A membrane is a thin semi-permeable barrier that allows the passage of some constituents and the rejection of others. Membrane filtration takes place when a feed water is forced through the thin wall of the membrane. The water solution that is forced through the membrane wall is called permeate and the water solution that remains on the feed side of the membrane is called retentate. The membrane surface is a continuous mass with interconnected voids, also known as pores. There are four main categories of membranes used in the water treatment industry: Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), and Reverse Osmosis (RO). RO membranes are primarily used in the desalination of salt water and NF membranes are usually applied to the treatment of brackish waters and for membrane softening. In recent years, MF and UF membranes have become increasingly popular in the water treatment industry for the treatment of surface waters (MWH 2005). A general comparison of the four main categories of membranes can be seen in table 2.1.

Table 2.1. General comparison of membrane processes

Membrane Process	Pore Size (nm)[a]	MWCO (Da)[b]	Typical Transmembrane Pressure (kPa)[c]	Species Retained[d]
Microfiltration	50 to 100	> 500,000	21 to 340	Particles, Sediment, Algae, Protozoa, Bacteria
Ultrafiltration	5 to 50	> 5,000	50 to 500	Small colloids, Viruses
Nanofiltration	2 to 5	> 400	340 to 1,030	Dissolved organic matter, Divalent ions
Reverse Osmosis	< 1	> 50	860 to 4,140	Monovalent species

[a]According to (Fane et al. 2006); [b]According to (Lonsdale H.K 1986); [c]According to (Bergman 2005); [d]According to (MWH 2005)

There are many ways to construct MF and UF membranes with several different configurations. Consequently this results in a variation in membrane properties such as pore structure, pore size, pore-size distribution, porosity, tortuosity and thickness. The flux and retention properties are a function of the membrane properties (Fane et al. 2011).

UF membranes are not uniform throughout the depth of the membrane, they are asymmetric. The top layer of the membrane is called the active layer. The active layer characteristics consist of narrow pore ranges, low porosity and small void dimensions. The bottom layer is called the support layer. Its characteristics consist of a high porosity and large void dimensions. The filtration takes place in the active layer. Since the active layer pores are so small, it has very little to no mechanical strength, hence why the support layer is necessary. Generally, the direction of the flow for an asymmetric membranes can only go one way, through the active layer first and then the supporting layer. If the direction of filtration was reversed, the support layer would clog resulting in the detachment of the active layer from the membrane. To prevent this, some commercial asymmetric membranes have two active layers, one of each side of the support layer (MWH 2005).

2.1.1 Membrane Configurations

There are many different membrane configurations that offer different properties. Choosing a configuration is usually based on the characteristics of the intended application. For instance, one configuration type may be stronger than the rest and can handle higher pressure applications, where another membrane configuration is more compact and is preferred for space limited applications. The most common membrane configurations used in water treatment are based on hollow-fiber membranes. Hollow-fiber membranes are hollow tubes that have a diameter of 0.5 mm to 2 mm. This type of configuration is desirable in water treatment due to its high membrane area to module volume ratio, also called membrane packing density (MWH 2005). In addition, hollow fiber systems can be hydraulically backwashed to help minimize fouling

Other less common configurations in fresh water treatment include but are not limited to: flat sheet, tubular, and spiral wound. The flat sheet membrane is usually a one layer flat sheet often used in laboratory filtration. They are also used in low volume industrial applications such as small wineries. The tubular membranes are tubes with several channels that run through. Usually the tubular membranes are made of inorganic material such as ceramic or minerals. These membranes are desirable for applications with extremely high solute concentrations. There are number of small treatment systems that utilize the FYNE system, a polymeric nanofiltration tubular membrane system, for the treatment of low-solids high-NOM waters. Spiral wound membranes consist of several layers of flat sheet membranes rolled into one cylindrical module. These membranes are often used in NF and RO application type treatments (MWH 2005).

2.1.2 Flow Regimes of Hollow Fiber Membrane Modules

Hollow fiber systems operate in a semi-batch fashion with a filtration cycle followed by a reverse filtration (backwash) step. There are four possible flow configurations for hollow-fiber membranes: outside-in dead-end, inside-out dead-end, outside-in cross-flow and inside-out cross-flow. Inside-out is when the feed enters the inside of the fibers and permeates to the outside. The inside-out configuration is pressure driven. Outside-in is when the membranes are submerged in a tank, the feed is on the outside of the fibers and permeates to the inside. This type of configuration is driven by a vacuum. Generally, outside-in systems can treat more water at the same flux because they have a larger membrane surface area. However, due to the increase in large particle concentration on the feed side of the membrane, there are periodic wastages from the tank (Davis 2011).

The dead-end modules are designed so that there is only one entrance and one exit for the fluid to travel, the feed stream enters and permeate stream exits. Therefore, all of the feed stream is converted to permeate. (Davis 2011; MWH 2005) In the cross-flow design there is one entrance for the feed stream, an exit for the waste stream and another exit for the permeate stream (Davis 2011; MWH 2005). This results in only a small amount of the feed stream being converted to permeate.

2.2 Membrane Fouling

2.2.1 Introduction to Membrane Fouling

Like many technologies, membranes experience a loss of performance which most commonly is the cause of membrane fouling. In constant flux experiments fouling will result in a TMP increase with time and in constant TMP experiments fouling will result in a flux decline with time (MWH 2005). Fouling can be classified into two categories: reversible and irreversible. Reversible fouling is defined by the fouling in which membrane permeability can be restored through hydraulic backwashes or chemical cleans. Irreversible fouling is the fouling that persists after the cleaning procedure (hydraulic or chemical) is performed. Eventually, the membrane will need to be replaced as cleaning strategies will become ineffective (Amy 2008).

Much research has gone into studying what exactly is responsible for membrane fouling. Studies have shown that membrane fouling is very complex, i.e., many factors can influence the rate and severity of fouling (Metsamuuronen et al. 2014; Zularisam et al. 2011; Waterman 2007; Zularisam et al. 2006; Laine et al. 1989). Some of these factors include the presence of natural organic matter (NOM) in the feed solution, the zeta potential of the membrane surface, certain organic and inorganic constituents, and operational flux.

2.2.2 Critical Flux

During filtration, membranes tend to foul. Instead of trying to prevent the inevitable, there are design and operational measures that can be taken to help minimize membrane fouling. One method is to reduce the flux through the membrane. However, how does one know what will be the optimal flux for the system, i.e., the largest flux possible while minimizing membrane fouling. The 'Critical Flux' can be defined as, 'a flux below which a decline of flux with time does not occur; above it fouling is observed' (Bacchin et al. 2006; Field et al. 1995).

Knowing the critical flux, the system operational parameters can be designed to operate in a sub-critical state with the objective of reducing operational costs and ultimately membrane fouling. There are several methods used in the determination of the critical flux. One method is directly observing the membrane. The direct observation through the membrane method involves looking through a microscope at an anopore membrane, which becomes transparent when wet, to analyze the particulate build up (cake formation) on the surface of the membrane. Unfortunately, this method is restricted to membranes which are transparent (Bacchin et al. 2006). Also, the analysis of particulate matter that could potentially be building up within the pores of the membrane, which can be expressed as standard blocking (Liu & Kim 2008), cannot be accounted for.

One of the more popular methods for determining the critical flux in water treatment, perhaps due to its simplicity, is the flux-pressure observation experiments (Bacchin et al. 2006). The flux-pressure experiments can be conducted by either setting the flux or pressure constant. Setting a constant pressure will result in a steady state flux, meanwhile setting a constant flux will result in a steady state pressure. The constant pressure experiment is recommended when the feed solution contains components that show little absorbability to the membrane, however, this may not be possible depending on the characteristics of the water to be treated. Constant flux experiments are recommended when complex suspensions are present (Bacchin et al. 2006). Both techniques can be used to determine critical flux. However, it is noted that for UF membranes used for dilute feeds, such as in water treatment, conducting constant flux experiments to determine critical flux is preferred (Bacchin et al. 2006). This is because changes in TMP while maintaining a constant flux test can be observed more easily than small changes in flux during a constant pressure test, therefore constant flux tests are able to detect trace fouling more efficiently (Bacchin et al. 2006).

The constant flux-pressure experiments operate as follows; the flux is set low (<35 LMH); once the system has stabilized, record the TMP; Once an adequate amount of time (~15 minutes) has passed, enough to determine the rate of change of TMP, the flux is then increased, and the process is repeated. The cycles of increased flux and TMP measurement are repeated many times, the TMP increases with each subsequent cycle. The critical flux has been surpassed when the rate of change in TMP has dramatically increased. It is also beneficial to backwash between flux increases to remove particulate matter build up on the membrane (Bacchin et al. 2006).

2.2.3 Membrane Fouling and Blocking Laws

Membrane fouling is extremely complex, not one single water quality measurement (TOC concentration, UV absorbance, pH, Alkalinity, etc...) has been universally correlated with membrane fouling. Therefore, membrane fouling is thought to be a combination of several factors (Adham et al. 2006). Some of these factors may include but are not limited to: organic and inorganic components in the feed water, particulate size, membrane material, operational conditions, and whether or not pre-treatment, such as coagulation/flocculation, has been implemented prior to membrane filtration.

It has been proposed that there are four different blocking laws (or mechanisms) that can describe how a membrane fouls: 1) complete pore blocking, 2) intermediate pore blocking, 3) standard pore blocking and 4) cake layer formation (Liu & Kim 2008; Suarez & Veza 2000). The complete pore blocking law states that a particle newly arrived to the entrance of a pore only has one option – completely blocking and sealing a membrane pore. This law assumes that particles do not accumulate on top of one another and adsorption within the membrane pores does not exist. For intermediate blocking, a certain particle travelling towards the membrane can either find its way to the membrane surface and partially block a membrane pore, or attach onto other particles. This creates a competition between previously attached particles and membrane pores for the adsorption of new particles arriving. Standard blocking, or pore constriction, deals with smaller particles that find their way into the membrane pores, but instead of leaving the membrane with the permeate, they adsorb internally onto the membrane pore walls. This causes the membrane pores to become constricted and thus impeding the flow through the affected membrane pores. The cake model involves the accumulation of particulate matter overlaying the external membrane surface (filtration side of the membrane) so that multiple layers are formed. This cake layer restricts flow to the membrane surface thus creating additional hydraulic resistance (Huang et al. 2008).

Katsoufidou et al. (2005) attempted to identify the dominant fouling mechanisms through modeling. The modeling suggested that under all experimental conditions and using humic acid formulated solutions as the feed source, irreversible pore constriction (standard blocking), was significant. The modeling and experiments also suggested that standard blocking takes place early on during the experiments, but eventually slows down. This makes sense as adsorption sites become limited with time. Overall, cake layer buildup and standard blocking were the main fouling culprits.

2.2.4 Membrane Foulants

There are many water quality characteristics that make each water unique. In some cases, it is unclear how these water quality characteristics effect membrane fouling. Researchers have not had much luck in identifying consistent correlations between water quality characteristics and membrane fouling (Zularisam et al. 2006). This section discusses some of the parameters that have been linked to membrane fouling.

2.2.4.1 Particulate Size

While studying the effects of extracellular organic matter (EOM) on membrane fouling, Qu, et al. (2012) looked at the effects of different sized particulates on membrane fouling using a 100 kDa polyethersulfone (PES) UF flat sheet membrane. This was accomplished using a priori membrane fractionation to create solutions with particles of specific size ranges. It was found that the particles with sizes greater than 100 kDa were responsible for membrane fouling. This makes sense as both of these EOM particulate sizes are greater than the membrane pore size tested (100 kDa). Therefore it was concluded that EOM particulates larger than the membrane pore size was responsible for a large portion of reversible and irreversible membrane fouling (Qu et al. 2012).

Fan et al. (2001) also studied the effects of particle size on membrane fouling using water from the Maroondah reservoir. The large particles above the membrane pore size (> 30 kDa) were shown to be a major influence on membrane fouling, which is consistent with Qu et al. (2012)'s findings.

2.2.4.2 Membrane Characteristics

Even though a major factor in membrane fouling is what constituents are present in the feed water, there are characteristics of the membrane chosen for filtration that can have an effect. Amy (2008) looked at the fouling of membranes in the presence of NOM. Even though the main focus of his study was not to study the performance of one membrane versus the other, he was able to make some conclusions. He concluded that when NOM is present in the feed water (not fractioned): (1) microfiltration (MF) membranes are more prone to fouling than UF membranes; (2) the roughness of the membrane surface had a greater impact on membrane fouling than whether the membrane was hydrophobic or hydrophilic; (3) a greater membrane surface charge reduced fouling, i.e., zeta potential does affect membrane fouling; (4) smaller pore sizes are prone to greater hydraulically irreversible membrane fouling (Amy 2008).

Zularisam et al. (2007) used two different membranes (table 2.1) for the removal of different NOM fractions. The MRUTM66 membrane is more hydrophilic (smaller contact angle), has a smaller molecular weight cut off (MWCO), and has a less negative surface charge than the MRUTM55 membrane. However, it was found that the MRUTM66 membrane rejected less DOC than the MRUTM55 membrane, despite its lower MWCO. However, the MRUTM66 membrane was able to remove more of the HPI fraction than the MRUTM55 membrane. This can be explained by the MRUTM66 membrane’s lower surface charge - there is less repulsion between the foulant and the membrane surface. Zulariam et al. (2007) concluded that MRUTM66 membrane's main removal mechanism was size exclusion while the MRUTM55 membrane's was electrostatic interaction.

Table 2.2. Membrane characteristics - MRUTM55 vs. MRUTM66 (Zularisam et al. 2007)

Parameter	MRUTM55	MRUTM66
Membrane Type	Hollow fiber	Hollow fiber
Membrane Material	Polysulfone	Cellulose acetate
External diameter, μm	600	600
Internal diameter, μm	300	300
Contact angle	56	28
Zeta Potentual (mV @ pH 7)	-27	-15.4
MWCO, kDa	68	50
Pure water flux (LMH)	13.7	25.3
Pure water permeability (LMH/bar)	43	85

Another study illustrating the impact of membrane material was conducted at the University of New Mexico (Adham et al. 2006). Five different source waters with different characteristics were tested to see how they would affect membrane performance when comparing polysulfone (PS) and polyvinylidene fluoride (PVDF). It was found that the performance of each membrane material was different for each water. For some waters, PS membranes fouled less than the PVDF while for other water the PVDF fouled less. It was concluded that different source waters react with different membranes in different ways. The performance of a membrane material is source specific (Adham et al. 2006).

Fan et al. (2001) conducted fouling experiments using two different types of hollow fiber membranes. The two membranes tested were called GVHP and GVWP. The GVHP membrane's surface is hydrophobic and the GVWP membrane's surface is hydrophilic. It was found that the hydrophilic membranes performs better (fouls less) than the hydrophobic membrane when subject to both feed waters (raw and pre-filtered raw). Also, the GVWP membrane fouled significantly less when the feed water was pre-filtered. Similar findings were obtained by other researchers, as explained in a review paper by Zularisam et al. (2006).

2.2.4.3 Operational Conditions

Guo et al. (2009) studied the impact of operational characteristics of a UF membrane system on membrane fouling. The membrane used in the study was a hollow fiber PVC membrane with a MWCO of 80 kDa. The surface waters used were from the Luan River and the Huang River, which have high algae concentrations. The system was operated at two fluxes, 60 LMH and 100 LMH, to determine if the difference would have an impact on membrane fouling. The operating system was first ran over a short period of time with no backwashes to see the effects. It was found that the TMP increased only 0.05 bar over the duration of the short experiment for the 60 LMH flux, while the TMP increased 0.2 bar for the 100 LMH flux. Therefore, even during short filtration times, a higher flux causes more severe membrane fouling than lower fluxes (Guo et al. 2009). These results were confirmed by many others including Waterman (2007), who conducted experiments at different operational fluxes (below and above critical) for Ottawa River Water - TMP greatly increased when the system was operated at above the critical flux.

Waterman (2007) also studied the effect of filtration cycle length and backwash cycle length on PES hollow fibre membrane fouling using raw Ottawa River Water. The filtration cycle lengths used were 15 minutes, 30 minutes and 1 hour and the backwash cycle lengths were 1 minute and 2 minutes. It was found that increasing the filtration length also increased the TMP. Increasing the backwash cycle length did improve fouling conditions as the TMP was lower for 2 minute backwash experiments, however, improvements were minimal (Waterman 2007).

Long filtration experiments were also conducted by Guo et al. (2009), lasting 3 months. These experiments included hydraulic backwash cycles every 30 minutes and chemical cleanings with 30 ppm NaClO and NaOH after 8 hours of operation. It was found that the TMP for the 60 LMH flux increased, but fouling was reversible as TMP was restored to the initial TMP after hydraulic backwashes. For the 100 LMH however, the TMP increased and was not restored to the initial TMP after hydraulic backwashes. Even after the chemical cleaning the TMP was not restored. Therefore irreversible fouling was prevalent during the higher flux and not the lower flux (Guo et al. 2009). Amy (2008) states that different operational conditions, such has operating at a high flux, can exacerbate membrane fouling. However, Amy (2008) also states that the characteristics and source of NOM has a greater impact on membrane fouling than operational conditions.

2.2.4.4 Natural Organic Matter (NOM)

NOM is found in all surface and ground waters and can be extracted from organic compounds in soils. Soil extracted NOM has somewhat different characteristics from aquatic NOM. Waters with high concentrations of NOM appear to have a yellow-brown colour. The formation of NOM in soil depends on the plant-residue which in turn is dependent on temperature, humidity, chemical, physical and microbiological activity, and the age of the soil. Since the formation of NOM is very complex, the composition, concentrations, molecular weight distribution and functional groups of NOM in surface waters vary depending on location, time of the year, landscape, etc. (Gjessing 1976). Due its complex characteristics NOM cannot be characterized well with a single analytical method, accordingly NOM is generally quantified in terms of its total organic carbon (TOC) concentration. Others quantify NOM in terms of the dissolved (or filtered) organic carbon (DOC). To highlight how different the concentration of NOM can be throughout the year, Sharp et al. (2006) showed that for their raw feed water, the TOC concentration of NOM was 14.5 mg/L in December and 4.3 mg/L in September the following year. Other researchers have experienced similar fluctuations in NOM concentration in both the United States and Europe. One researcher found that the NOM concentration in the Santa Ana River increased from 2.2 mg TOC/L to 9 mg TOC/L between June 2000 and May 2002 (Sharp et al. 2006).

The amount of NOM that is present in waters is thought to be based on the mineral composition of the soils in which the NOM was extracted through infiltration and runoff. NOM may adsorb to the mineral lattice, by means of Van der Waals forced or hydrogen bonds, within the soil. Therefore, the higher the mineral content in the soil, the lower the quantity of NOM that may be extracted by water (Gjessing 1976).

One common way to classify NOM is by its reaction to acidification. There are two broad categories: humic acids and fulvic acids. The humic acids can be precipitated by acidification while fulvic acids cannot (Gjessing 1976). In areas with high peat content (i.e., swamps, bogs) it has been found that fulvic acid fractions dominant in NOM while in low peat content areas humic acids dominate (Yefimov & Vasil'kova 1971). These two broad categories of classification can be categorized even further into three NOM fractions that are commonly determined in water analysis. The three fractions are Hydrophobic (HPO), Hydrophilic (HPI), and Transphilic (TPI). The HPO fraction consists of the humic acid and fulvic acid fractions (carboxylic and phenolic functional groups), the TPI fraction contains lower aromatic compounds than the HPO and the HPI fractions consists of non-humic compounds (proteins, amino acids and polysaccharides) (Zularisam et al. 2011). The HPO fraction generally accounts for roughly around 50% of the total NOM fraction, HPI 25 - 40% and TPI roughly 25% (Zularisam et al. 2007). The high hydrophobic concentration is typical of northern waters. The DOC in high coloured waters in Canada, Scandinavia and Russia is typically 60 - 80% hydrophobic (Aiken et al. 1985).

As the TOC of a water is often used as synonymous to NOM, one should be aware that not all of the TOC in waters arises from humic and fulvic substances. So there is another method of classifying NOM (TOC), it based on from where the organic matter originates from. NOM can originate from three major sources in which they can be classified by. The first is allochthonous NOM, which is mainly produced by vegetative debris from terrestrial sources that run off or leach into the water system. The second type of NOM based on origin is autochthonous, which originates from algae and contains extracellular and intracellular macromolecules. The third type of OM is organic matter discharged via wastewater effluents (Amy 2008). Huang et al. (2007) took three different waters, all with different origins: (1) allochthonous NOM, (2) autochthonous NOM, and (3) wastewater organic matter, and found that the three waters produced very different results when treated using membrane filtration.

NOM is a known membrane foulant and many studies have been and are continuing to be conducted on the reasons of why and how NOM fouls membranes (Metsamuuronen et al. 2014; Uyak et al. 2014; Bessiere et al. 2009; Zularisam et al. 2006; Aoustin et al. 2001). Zularisam et al. (2007) studied the effects of the different fractionations of NOM using water from the Ulu Pontian River in Malaysia. The feed water was fractioned into HPO, TPI and HPI fractions using XAD-8 and XAD-4 resins. Each fraction was fed to the membrane separate of the other fractions in order to determine the individual fouling potentials. It was found that the HPI fraction fouled the membrane severely more than the HPO and TPI fractions. During a 120 minute experiment, the HPI fraction produced a flux decline of 52% versus only 35% and 20% for the HPO and TPI fractions, respectively (Zularisam et al. 2007). The HPI fraction of NOM was also found to contribute to membrane fouling more so than the other NOM fractions (HPO and TPI) (Qu et al. 2012; Huang et al. 2007).

Zularisam et al (2007) hypothesised that the reason the HPI fraction fouls more than the HPO and TPI fraction was due to the presence of high molecular weight components such as polysaccharides. Polysaccharides have a linear macromolecular shape and are relatively neutral, therefore they have a high adsorption potential. Amy (2008) concluded from his studies that the presence of polysaccharide-like and protein-like foulants that are responsible for membrane fouling are more likely to originate from microbial sources / algae (autochthonous NOM). Conversely, even though the HPI fraction was found to be the major culprit in membrane fouling, it also had a lower rejection percentage than the HPO and TPI fractions. Meanwhile, the HPO fraction experienced the highest rejection percentage. This phenomena is thought to be due to the electrostatic interactions between foulant and membrane surface. The HPO fractions are negatively charged, the HPI fractions are more neutral, while the membrane surface is also negatively charged. HPO fractions were repelled by the membrane surface and HPI fractions were not (Zularisam et al. 2007).

Lin et al. (1999) who also studied the effects of different NOM fractions found that the HPI fraction was responsible for membrane fouling. However, Lin et al. (1999) also found that the HPO fraction of NOM also contributed to membrane fouling. In fact, many studies have found that the HPO fraction is the main foulant or plays an important role in membrane fouling (Gray & Bolto 2004; Jones & O'Melia 2001; Crozes et al. 1993). The HPO fraction being more of a foulant than the HPI fraction was especially prevalent when the membrane used was hydrophobic (Nilson & DiGinao 1996).

Conversely to what other studies have found, the HPO or HPI fraction being the main influence on membrane fouling, Bessiere et al. (2009) concluded that it was the TPI fraction that caused the most severe membrane fouling. This was found by fractioning the NOM using XAD8 and XAD4 resins and then feeding the NOM fractions separately to the membrane to study their individual effects, much like the studies conducted by Zularisam et al. (2007) and Qu et al. (2012). Bessiere et al. (2009) also found that when all the NOM fractions were combined, such as in surface water, the TPI fraction had less of a fouling impact than it did when it was the only NOM fraction. Bessiere et al. (2009) suggested that when the TPI is combined with HPO and HPI, TPI has interactions with the HPO and HPI fractions and not just the membrane.

As well as conducting fouling experiments with different NOM fractions, Zularisam et al. (2007) conducted the experiments in such a way that different fouling resistances could be calculated. That is, fouling resistances caused by concentration polarization, cake layer formation, and adsorption. Zularisam et al. (2007) was able to conclude that the three different NOM fractions all had different fouling mechanisms. The HPO fraction's primary fouling mechanism is concentration polarization, HPI's is adsorption, and TPI's is cake formation.

Fan et al. (2001) conducted a fourth NOM fractionation step and fractioned the HPI NOM into HPI neutral and HPI charged by using a IRA-958 exchange resin. Dividing up the HPI fraction of NOM produced an interesting finding, the HPI neutral fraction had the highest membrane fouling potential while the HPI charged fraction had the lowest membrane fouling potential.

2.3 Controlling Membrane Fouling

Extensive research has been performed on how to control and mitigate membrane fouling since a solution for complete elimination has not yet been found. Many methods have proven effective and are often implemented. Such methods include but are not limited to; physical cake layer removal via hydraulic backwashes or abrasive sponge cleaning, enhanced chemical backwashes, chemical cleans (CIP), and pre-treatment to the feed water. The following subsections concentrate on the measures evaluated in this study.

2.3.1 Hydraulic Backwashes

The most common process at removing particulate buildup on the membrane surface is to physically remove it through hydraulic backwashes. A hydraulic backwash is essentially passing permeate or another source of clean water through the membrane in the opposite direction as filtration. In general, backwash frequency can be anywhere from 15 minutes to 2 hours and can last 1-5 minutes, the backwash flow rate is usually 2 to 3 times the permeate filtration flow rate (MWH 2005).

Much research has gone into the study of hydraulic backwash optimization (Zularisam et al. 2007; Waterman 2007; Crozes et al. 1997). Kennedy et al. (1998) determined that by producing a hydraulic backwash pressure of two and a half times that of the operational pressure, the membrane permeability was progressively restored. Zularisam et al. (2007) studied the effects of different NOM fractions on membrane fouling and fouling recovery. The flux recovery after hydraulic backwashes for the HPO fraction of NOM was found to be 2.6%, the TPI fraction 17.2% and HPI fraction 8.7%. Waterman (2007) looked at the effects of backwash frequency and backwash duration on membrane fouling restoration. It was found that the backwash frequency had a major influence on membrane fouling. 7.5-hour Experiments where backwashes were conducted every 15 minutes had a final normalized specific flux (NSF) of 0.5 - 0.6 after 7.5 hours, while experiments with backwashes every 1 hour ended with a NSF of 0.2 - 0.3. The backwash duration did have a small effect on the restoring membrane permeability, but increasing the backwash duration from 1 minute to 2 minutes did not increase the backwash efficiency significantly (Waterman 2007). Other methods that are performed for a similar purpose as hydraulic backwashes are aeration and membrane relaxation (De Souza & Basu 2013).

2.3.2 Chemical Cleaning

Membranes selectively allow some constituents to pass while rejecting others therefore resulting in membrane fouling. Even though hydraulic backwash cycles are frequently employed, it does not result in full flux recovery and it's fouling recovery efficiency diminishes over time and therefore requires the addition of chemical backwashes or chemical soaks to reduce the effects of fouling (Amy 2008).

In the literature it is apparent that much research is being conducted on which chemical cleaning process is most efficient. For instance, Nguyen et al. (2011) used 100ppm of chlorine solution (pH 9.9) for 20 minutes and then deionised water for 20 minutes. Nakatsuka et al. (1996) continuously injected 3-5mg/L of NaClO into the stream to inhibit the growth of bacteria on the membrane surface for surface water treatment of the Chitose river. Broens et al. (2012) conducted a chemical cleaning step in the filtration process that consisted of a caustic and acidic process. The caustic solution consisted of 400ppm of NaClO in water, after which NaOH was added to obtain a pH of 11.5. The acidic solution of comprised of HNO_3.

Kimura et al. (2004) assessed the cleaning efficiencies of different cleaning agents on an irreversible fouled flat sheet membrane subject to Chitose River water. The chemical cleaning agents used were: 0.1M NaCl, 20mM EDTA, HCl (at pH=2), Oxalic acid (at pH=2), 0.01M NaOH, and 500ppm NaClO. It was found that the NaCl and EDTA were not effective at all in restoring membrane permeability while the NaClO and NaOH cleaning solutions were effective at restoring membrane permeability (Kimura et al. 2004). Lee et al. (2001) also found that acid and caustic cleaning methods restored membrane permeability for membranes fouled by a highly hydrophobic surface water.

2.3.3 Coagulation/Flocculation to Reduce NOM

NOM removal is very important in water treatment because NOM reacts with chlorine and other chemical disinfectants forming many different potentially-harmful disinfection by-products. Its removal is also desirable because a fraction of the NOM gives water colour. NOM greatly reduces the capacity of activated carbon, which is used at some plants, and it is important membrane foulant One common and effective way at remove NOM along with turbidity in water is through the addition of coagulants that allow the particles and dissolved molecules to flocculate and be removed either by sedimentation or floatation (MWH 2005).

There are four main mechanisms in which the coagulation/flocculation destabilize particles: (1) compression of the electric double layer, (2) adsorption and charge neutralization, (3) adsorption and interparticle bridging, and (4) enmeshment in a precipitate (sweep floc). Adsorption and charge neutralization is when the particles are adsorbed onto the chemical added (coagulant or polymer) and thus neutralizing the previously negatively charged clay, humic acid, or bacterial particle. The neutralization of the particles allows for easier floc formation. Adsorption and interparticle bridging is similar to adsorption and charge neutralization with respect to the coagulant or polymer adsorbing to the particles. The difference with adsorption and interparticle bridging is the fact that the coagulant or polymer extends out of the particle and into the solution, almost like an arm. This coagulant or polymer arm extending off the particle can link up with another particle creating a bridge between the two. Sweep floc occurs when high dosages of coagulant are added to the water. The high dosages of coagulant create insoluble precipitates that become entrapped with the particulate matter and form amorphous precipitates. The amorphous precipitates grow, settled and drag other amorphous precipitates down (MWH 2005).

Since NOM can react with chlorine to create disinfection by-products, research has been conducted on how effective the coagulation/flocculation process is at removing NOM (Braghetta et al. 2001; Robert et al. 1999). It has been found that NOM removal by coagulation has more than one mechanism. For larger particles such as colloids, charge neutralization is dominant. For smaller dissolved particles the main removal mechanisms were found to be mainly adsorption and interparticle bridging (Randtke 1988).

It has been found that coagulation/flocculation are more effective at removing certain NOM factions over others. In fact, Sharp et al. (2006) also found that charge neutralization and adsorption and interparticle bridging were the main mechanisms in NOM removal. However, Sharp et al. (2006)'s research went one step further and found that the two mechanisms mentioned above were responsible at removing the HPO fraction of NOM. Fearing et al. (2004) also found that the coagulation/flocculation process was also effective at removing the HPO fraction and was relatively poor at removing the HPI fraction and non-acids. Thus, the concentration of DOC residuals post coagulation are equivalent to the HPI fraction concentration. Consequently, it may be concluded that the raw water HPI DOC fraction concentration is a good indicator of the post-coagulation DOC concentration (Sharp et al. 2006).

2.4 Membrane Performance

As previously discussed, membrane performance (membrane fouling) is a function of many parameters, such as but not limited to NOM concentration, fractionation and source, membrane characteristics, and operational parameters. Regardless what parameters are responsible for membrane fouling, membrane performance is continuously being assessed. There are many methods for showing and quantifying membrane fouling which makes comparing studies from different researchers a challenge. For instance, researchers such as Uyak et al. (2014) and Liu et al. (2011), chose to express the performance of their membranes by plotting experimental data using TMP on the y-axis and time on the x-axis. Others such as Kim & Dempsey (2013) have chosen to express their membrane's performance in terms of hydraulic resistance. Another common method for quantifying membrane performance is to graphically show the deterioration of relative flux or normalized specific flux versus time or specific volume, as was done by Waterman (2007) and Fan et al. (2001). A more recent approach used by Huang et al. (2008) and Nguyen et al. (2011) utilizes a performance measure called fouling indices. Regardless of which method is used to quantify membrane fouling, without standardizing how results are presented, it is sometimes difficult to compare membrane performance of separate studies conducted from different researchers. Therefore, in the following section, results are not presented for comparative purposes but to give insight on how membranes are performing in some studies.

2.4.1 Membrane Performance during Operation

Fan et al. (2001) conducted fouling experiments using UF hollow fibre membranes and three different raw water sources. The three waters subject to membrane filtration were the Maroondah Aqueduct (DOC 3.1 mg L^{-1}), Moorabool River (DOC 9.0 mg L^{-1}) and Mount Zero Reservoir (DOC 9.1 mg L^{-1}). As may be expected, the water from the Maroondah Aqueduct would produce the least severe fouling due it's DOC concentration being 1/3 the concentration of the other source waters. In fact, the water from the Maroondah Aqueduct did produce the least severe fouling, but only slightly. After 30 minutes of operation, all source waters resulted in the relative flux ($^{J}/_{J_o}$) to drop below 0.1.

Kim & DiGiano (2006) treated a raw water with a TOC concentration of 8.9 mg/L and reached a normalized specific flux of 0.28 after 16 hours of operation. Bessiere et al (2009) reached a normalized specific flux of 0.37 after filtering 1.55 g organic carbon / m^2 using raw water from Alberta Water Treatment Works (TOC = 9.8 mg/L). Carroll et al. (2000) also studied membrane performance using raw water from the Moorabool River (DOC = 9.0 mg/L) and found that their permeate flow rate dropped from 9.5 g/min to 1.7 g/min after 900 g (1286 L/m^2) of permeate was produced.

2.4.2 Coagulation/Flocculation Coupled with Hollow Fiber Membrane Filtration

Research has shown that using MF and UF membranes alone for the treatment of surface water is not adequate in meeting ever stringent guidelines and regulations. It is therefore becoming common practice to couple coagulation/flocculation with membrane filtration. Not only does the membrane produce a better quality of permeate when coupled with coagulation and flocculation (Guigui et al. 2002), but in most cases membrane fouling is reduced. Braghetta et al. (2001) found that using ferric salts as the coagulant improved membrane performance by reducing fouling and improved membrane flux by 25-50% when compared to the raw water. Many other researchers have also found that using coagulation ahead of membrane filtration reduced the severity of membrane fouling (Robert et al. 1999; Jack & Clark 1998; Laine et al. 1989).

Liu et al. (2011) studied the effects of coagulation/flocculation prior to membrane filtration by using alum as the coagulant and a synthetic humic rich solution. Two experiments were conducted, one addition of coagulation and two additions of coagulation. For the experiments where two additions of coagulant were used, injections were in two placed: (1) before the flocculation basin and (2) into the flocculation basin. It was found that one addition of coagulant reduced membrane fouling. After 300 hours of operation, the TMP for the one coagulant dose experiment was roughly 40 kPa while the TMP for the two coagulant dose experiment was roughly 25 kPa. A factor of 1.6 reduction in TMP when the second dose coagulant was added during flocculation. The explanation for this reduction in membrane fouling was due to floc size. The floc size produced from the addition of two coagulant doses was one half larger than the floc produced by only adding one coagulant dose. Therefore, it was concluded that larger floc produced less severe fouling. Even though the second coagulant dose improved membrane permeability, the DOC rejections were very similar (i.e., 67.6% and 67.1%) (Liu et al. 2011).

Even though the addition of coagulants is thought to improve membrane performance, this is not always the case. Interactions between NOM, coagulants, and membrane surfaces are very complex. Coagulation prior to membrane filtration can be very beneficial and efficient at reducing fouling but there are also studies suggesting coagulation has adverse effects on membrane performance. Liu et al. (2005) conducted a case study where ferric chloride was being used as a coagulant prior to membrane filtration. The TMP was increased when ferric chloride was used when compared to the raw water - the ferric chloride increased the severity of membrane fouling. It was hypothesised that the ferric chloride negatively affected membrane performance due to the very low alkalinity of the water which may have caused the ferric chloride and NOM to form fouling causes complexes. Shorney et al. (2001) and Schafer et al. (2001) used ferric sulfate and ferric chloride respectively, as coagulants prior to membrane filtration. In both cases the pre-treatment increased the severity of membrane fouling in MF and UF membranes. Adham et al. (2006) hypothesised that high doses of alum produce sticky Aluminum micro-flocs which form a cake layer on the membrane and thus fouling the membrane.

Research has also shown that coagulant dosage also has an impact on membrane performance when coupled with coagulation pre-treatment. Howe and Clark (2002), Judd and Hillis (2001) and Fu and Dempsey (1997) all found that the lowest coagulant dosage caused membranes to foul more than a higher coagulant dosage. Membrane fouling was worse than raw water when low doses of coagulant were added, while membrane fouling was better than raw water when high doses of coagulant were added. Bian et al. (1999) used PACl as the coagulant prior to membrane filtration and found the opposite as above. Low doses of PACl caused the membrane to foul less severely than high doses.

Howe and co-workers at the University of New Mexico conducted a very extensive research project looking at the effects on different waters and coagulants on membrane performance (Adham et al. 2006). The experiment utilized a bench-scale system that contained 1 membrane fiber per module, operated in the outside-in mode, and kept the TMP constant at 10 psi while flux was allowed to change. Five different water sources were used in the study, all with different characteristics: Medina River, Chattahoochee River, Seine River, Clackamas River, and the Waikato River. All waters were also pretreated with a coagulant and allowed to settle before membrane filtration. In four of the five waters, coagulation and sedimentation improved membrane flux when compared to the raw water. The only water that produced a more severe membrane fouling after pre-treatment was the Clackamas River (Adham et al. 2006). It may be concluded from these results that the effectiveness of coagulant pre-treatment is water specific.

There have been researchers that have used untraditional coagulants to aid in the flocculation of particles prior to membrane filtration. Both Qu et al. (2012) and Katsoufidou et al. (2005) added calcium to the feed solution before membrane filtration is that a divalent ion, like calcium, would decrease electrostatic repulsion between particulates and therefore increase the potential for flocculation. The effect of calcium on membrane fouling was seen to be different between reversible and irreversible fouling. It was seen that as calcium concentration increased, the reversible fouling increased while irreversible fouling decreased. These findings are supported by the fact that the calcium addition neutralized the particles resulting in flocculation and thus a greater deposition on the membrane surface (cake formation). Cake formation is seen to be a reversible foulant as it can readily be removed via hydraulic backwashes (Qu et al. 2012). Conversely, Amy (2008) added calcium to a NOM fractionated feed of HPO and found that the calcium did not increase the fouling because the charge on the particulates were reduced and therefore more easily passed through the negatively charged membrane surface.

Qu et al. (2012) found that as the calcium concentration increased, so did the NOM concentration in the permeate stream. The explanation for this was due to the fact that with no calcium, the negatively charged NOM particles would be rejected by the negatively charged membrane surface by electrostatic repulsion. When calcium was added, the particles were neutralized in order to flocculate. Some of the unflocculated neutral NOM particles were passing through the membrane. Conversely, Katsoufidou et al. (2005) found the opposite. When no calcium was added the NOM rejection was roughly 20% but when 2mM of calcium was added the NOM rejection reached as high as 75%.

2.5 Conclusions

One of the major challenges in membrane filtration is membrane fouling. NOM has been found to severely foul membranes and the NOM fractions (HPO, TPI, and HPI) cause different types of membrane fouling. Some studies suggest that the HPO fraction of NOM is mainly responsible for membrane fouling while others suggest it is the HPI fraction of NOM. This is particularly relevant the typical Northern Canadian waters, that have low turbidity, high colour, high NOM and high HPO content. To reduce the concentration of NOM and minimize membrane fouling, coagulation/flocculation pre-treatment prior to membrane filtration is often implemented. Studies show that the effectiveness of coagulation/flocculation at reducing membrane fouling varies depending on the membrane used, the water being treated, the coagulant dosage, and whether a separation process, such as settling, has been implemented. No studies were found in the literature comparing the effectiveness of coagulation/flocculation coupled with settlement versus coagulation/flocculation coupled with floatation as pre-treatments prior to membrane filtration of high HPO NOM surface waters. Thus, it is of interest to study the impact of pre-treatment of a colored river water incorporating floatation versus sedimentation on the performance of downstream hollow fibre UF membranes. The next chapter describes the materials and methods used for: (1) characterizing NOM to determine which fractions cause membrane fouling, and (2) determining the effectiveness of different pre-treatments (settlement versus floatation) on membrane performance.

CHAPTER 3

MATERIALS AND METHODS

The purpose of this chapter is to describe the equipment, materials, methods and protocols that were utilized for this study. The first part of this research consisted of reconstructing and programming a UF hollow fiber bench-scale membrane system. The system was programmed to mimic the operational conditions and constraints of a full-scale facility in that is capable of automatically performing filtration cycles and hydraulic backwashes based on filtration cycle time and/or maximum TMP. The second part of this research was to use the UF membrane system to conduct constant flux fouling experiments to assess membrane performance using Ottawa River water subject to three different types of pre-treatment. Each water was analyzed to determine how their characteristics varied.

3.1 Waters Tested

Ottawa River Water (ORW) was the challenge water chosen for this study because of its high colour and membrane fouling properties. ORW received three different pre-treatments: ORW with the addition of a ferric sulfate coagulant and silicate and then settled (Iron), ORW with the addition of alum and silicate and then settled (Alum S), and ORW with the addition of alum and a polymer and then floated (Alum F).

The Raw ORW (untreated) was obtained from the Britannia Water Treatment Plant in Ottawa, Ontario. The Britannia Water Treatment Plant (WTP) also has a pilot-scale study where ferric sulfate is being studied as an alternative to alum. The pilot plant was comprised of two treatment trains. The first treatment train mimicked the full-scale facility (conventional treatment train), which services Ottawa with drinking water, and uses alum as the primary coagulant. The pH was adjusted to ~ 5.7 using a dosage of 8.09 mg/L sulfuric acid (H_2SO_4). The dosages of Alum and silicate (SiO_2) were 34.9 mg/L (3.17 mg Al/L) and 0.91 mg/L, respectively. The second treatment train used ferric sulfate as the coagulant instead of alum. The pH was adjusted to ~4.8 using a dosage of 4.14 mg/L sulfuric acid (H_2SO_4). The dosages of ferric sulfate and silicate (SiO_2) were 46.91 mg/L (9.33 mg Fe/L) and 1.00 mg/L, respectively. Both the Alum (Alum S) and ferric sulfate (Iron) pre-treated waters were collected after settling and before the media filters.

The fourth water was obtained from the Aylmer Water Treatment Plant in Aylmer, Quebec, which also takes its water from the ORW 6 km upstream from the Britannia WTP. Thus, the feed water to this plant has the same water quality characteristics as that of the Britannia treatment plant - the Ottawa River. Alum was added as the coagulant as well as the polymer cationic polyacrylamide (Superfloc C-492PWG, Kemira) to help aid in the flocculation. The dosages added for the alum and polymer change depending on whether it is summer or winter. For these experiments the water was collected during the summer - the alum dosage was 32 - 34 mg/L and the polymer dosage was 0.7 mg/L. Instead of settling their water, the Aylmer plant used floatation for separation. The alum floated water (Alum F) was extracted after the floatation basin and before the sand filter.

3.2 Water Storage and Preservation

Immediately after water collection samples were stored in a cold room at the University of Ottawa at 4°C to retard potential biological degradation. One day prior to its use, the water was transferred to the lab and allowed to reach room temperature (~20°C). Standard methods were used to determine how to preserve the samples based on what analysis was to be conducted. (APHA/AWWA/WEF, 1998)

3.3 Cleaning of Glassware

It was imperative that the glassware used was cleaned to the point where nothing, such as organics absorbed to the glass surface, would leach into the samples resulting in artificially higher TOC concentrations. The cleaning procedure outlined below was adapted from Storrar (2005):

> (1) Glassware was rinsed with RO water then soaked in a bath of alkaline liquid detergent (Contrex, Decon Laboratories Inc.) and RO water.
> (3) The glassware was then rinsed with RO water and placed into a laboratory oven (Fisher Scientific) at 105°C until dry.
> (4) The dried glassware was filled with a chromic - sulfuric acid solution (Ricca Chemical Company) for a minimum of 1 hour.
> (5) The glassware was then drained of the chromic - sulfuric acid solution, rinsed with RO water 10 times, and placed again into the laboratory oven at 105°C until dry. Glassware was then ready for use.

The RO water used was produced by treating distilled water using an RO system (LC-380PP, TOPWAY GLOCAL, INC., Brea, California). The RO system is comprised of six stages: (1) sedimentation filter, (2) carbon block filter, (3 - 5) thin film composite membranes, (6) GAC carbon filter.

3.4 Ultrafiltration (UF) Hollow Fiber Membrane and Module

The hollow fiber UF membranes used in this study were supplied by Matrix Membranes, Oceanside, California. The membranes are made of polyethersulfone (PES) and are hydrophilic in nature. They are also double skinned, i.e., have a separation layer on both sides of the support layer so that they can be operated inside-out or outside-in, in this study they were used in inside-out flow pattern. The nominal molecular weight cut off (NMWCO) of the membrane fibers is 100,000 Da (<0.02 microns). The inner fiber diameter is 0.8 mm. According to the supplier, a 6 log reduction has been reported by independent laboratory tests for bacteria, cysts and turbidity (Matrix Membranes Inc., 2008).

The membrane module was constructed to operate with an inside-out dead-end flow regime. Six fibers were cut to a length of 30 cm. The modules were constructed with low density polyethylene tubing and plastic fittings. Two centimeters of the fibers on both ends of the module were epoxied resulting in an effective membrane fiber length of 26 cm. The resulting total effective membrane area of one module is 0.00392 m^2. The module can be seen in figure 3.1 below:

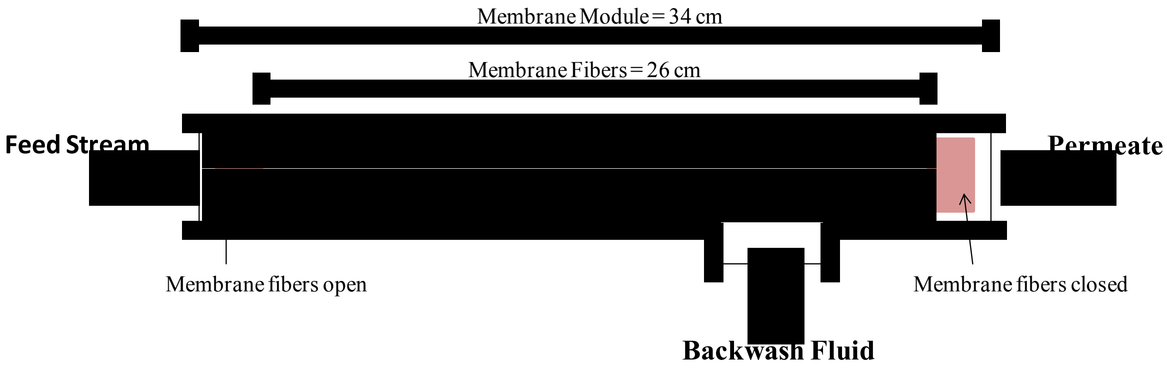

Figure 3.1. UF hollow fiber membrane module design used in all filtration experiments

3.5 UF Bench-Scale System

A bench-scale UF hollow fiber membrane treatment system was constructed by a former student (Waterman 2007), however, slight modifications were made. One of the phases of this research was to ensure that the bench-scale UF system simulated the operational characteristics of a full-scale facility. In doing so, numerous sensors and instruments were incorporated into the bench-scale system to either control or monitor operation. The bench-scale system was programmed to operate unsupervised switching from filtration cycles to backwash cycles while recording useful data, such as: TMP, flow rate and flux, and time of each filtration and backwash cycle.

3.5.1 Physical Components of the UF Bench-Scale System

The bench-scale system has two streams, filtration and backwash (figure 3.2). The filtration stream, which is shown by the thick solid lines, is comprised of a peristaltic pump (**PU1**)

(L/S Easy-Load II, EW-77250-62, Cole-Parmer, Montreal, QC), a 178 µm mesh strainer (K-29595-35, Cole-Parmer, Montreal, QC), 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), and a top-loading balance (K-11018-12, Cole-Parmer, Montreal, QC) which was used to measure the permeate mass flow rate.

The backwash stream, which is shown by the thick dashed lines, consists of a variable speed pump (**PU2**) (FPUDVS2007, Omegadyne Inc., Laval, QC), a pulse dampener (EW-30610-37, Cole-Parmer, Montreal, QC), a pressure transducer (**P2**) (PX209-030G10V, Omegadyne Inc., Laval, QC), and a two-way solenoid valve (**V3**) (Series 8262/8263, Red Hat, ASCO).

The tubing used for the system is low density polyethylene. Tube diameters of 1/4", 3/8" and 1/2" were used throughout the system. Originally, the system was comprised of transparent tubing, which was later replaced by black non-transparent tubing in an attempt to eliminate biological growth that was experienced between experiments.

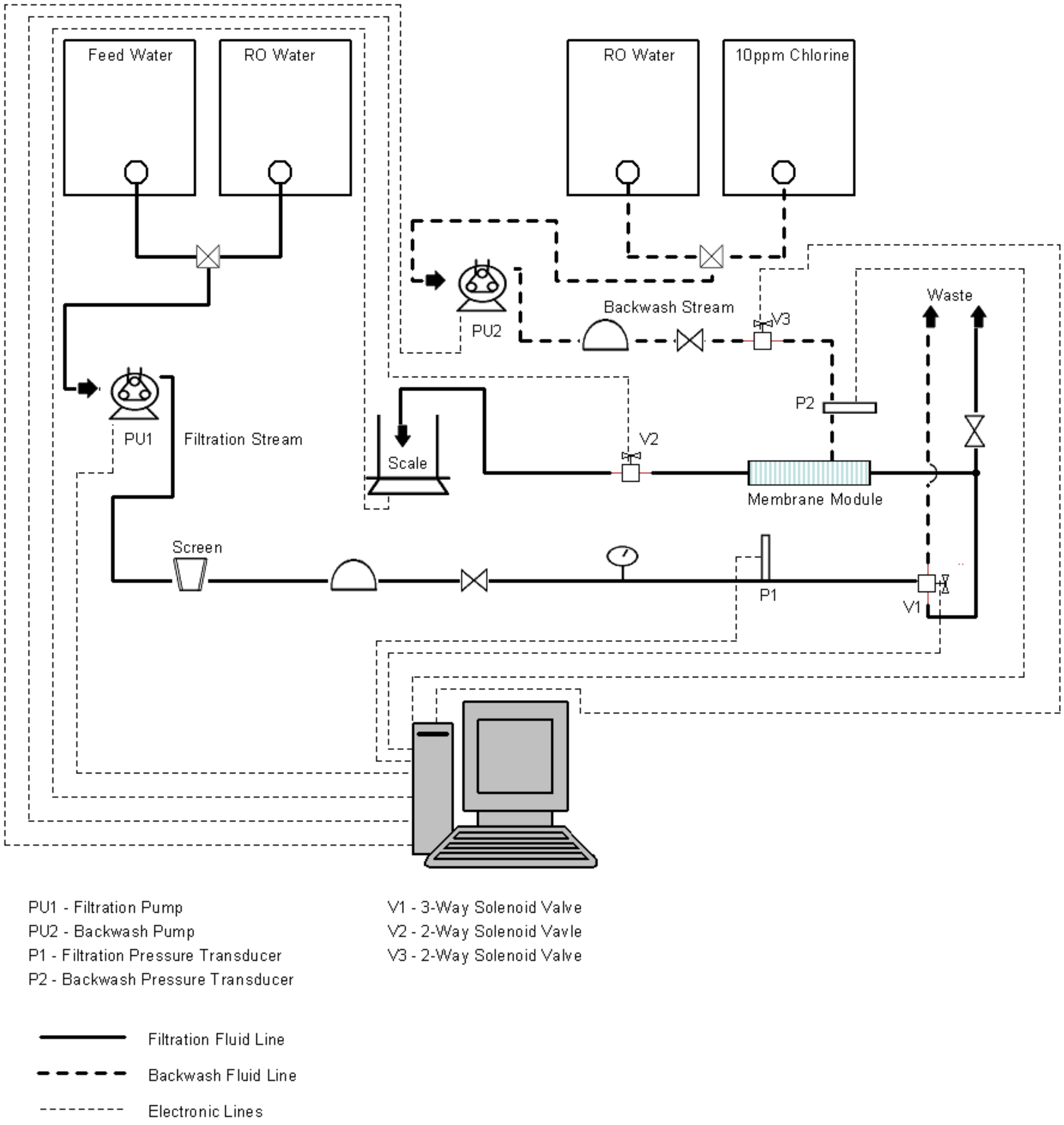

Figure 3.2. Schematic diagram of the UF bench-scale system layout

3.5.2 Programming of the UF Bench-Scale System

To simulate the operation of a full-scale facility, the system was programmed with a LabVIEW interface which was designed to allow the operator to control and visually monitor slight changes in operational parameters (using real time updated graphs). The 'Front Panel' is where the user can input operational parameters. The parameters that the program requires input for is the desired flow rate/flux for filtration and backwash, the time for each filtration and backwash cycle, the incremental increase / decrease of pump voltage based on the difference between actual and set flux, the membrane radius, length, and the number of membrane fibers. The front panel also allows the user to view the actual filtration and backwash flux, cycle duration (time), and TMP pressure.

The block diagram is where the behind the scenes programming takes place. The entire program is nested within a double flat sequence structured loop. The first flat sequence structure (FSS) loop is the filtration cycle and the second FSS loop is the backwash cycle. The FSS loop alternates between the first FSS and the second FSS based on given conditions. Inside both FSS loops there is a 'while loop'. For the filtration cycle, the 'while loop' will only terminate when a specified time (filtration time) has been reached or when the TMP reaches a certain value. When the 'while loop' is completed, the program switches from the first FSS loop to the second FSS loop where there is another 'while loop' with another termination condition (i.e., the inputted backwash time). When the second FSS loop terminates, the program goes back to the first FSS loop, and so on.

Every device that is used to either control the system or collect information from makes use of Data Acquisition (DAQ). DAQ is a process in which real time signals are converted into digital values, such as communicating to the pump what voltage to operate at or retrieving voltage readings from a device, such as a pressure transducer. Since the DAQ outputs and inputs voltages, the voltage relationship with that device had to be obtained from the manufacturer. The voltage relationships for the pressure transducers can be seen below:

Pressure transducers: $Pressure\ (PSI) = \frac{Voltage\ Reading}{0.3333}$

Obtaining and displaying a flow rate on the front panel from the scale was a challenge. The scale, which measures the mass of permeate collected, returned a mass to labVIEW. Calculating flow rate from the scale readings involved finding the change in mass over the change in time. To program this, two case structures were used to hold the first mass and first time value while waiting for the second mass and second time value. Then the program subtracted the second mass from the first mass and the second time from the first time - change in mass over change in time. The scale recorded a mass at very small (0.033 minutes) time intervals and the amount of permeate that the beaker on the scale collected varied. For example, the beaker may collect 3 drops of permeate during one time interval but may only collect 1 drop of permeate during the next time interval. As a result, the flow rate output from the scale on the front panel looked very noisy and varied which made it very hard to visually monitor and determine the actual flow rate. It was found that taking 20 consecutive flow rate readings and averaging them produced a less noisy and easily read result. To program this, a stacked sequence structure (SSS) loop was used with 19 sequences. The first 20 flow rate reading calculated from the scale would be stored in the SSS loop. Then, once 20 readings were obtained, all 20 values in the array are averaged and displayed in the front panel. The 21st calculated flow rate replaces the 1st flow rate, and an average is taken again and displayed, and so on.

The labVIEW program was also written to maintain constant flux, which was a challenge. The operator inputs a desired flow rate on the front panel. The program then takes that desired flow rate, and compares it to the actual flow rate. Is the actual flow rate within a certain range of the desired flow rate? If no, increase or decrease the voltage supplied (specified by the operator on the front panel) to the pump based on whether the flux is too high or too low. If yes, continue supplying the pump with the current pump voltage. The voltage increase and decrease is critical in maintaining constant flux as membrane fouling increases hydraulic resistance with time.

The program was effective in switching from filtration to backwash based on conditions provided by the operator. When the system switches from filtration to backwash, the voltage supplied to the filtration pump turns off, all 3 solenoid valves switch, and the voltage supplied to the backwash pump turns on. It should also be noted that all data is exported to Microsoft Excel.

3.6 Experimental Procedure

Conducting fouling experiments required numerous small but necessary steps. First, it was ensured that the physical membrane system itself was clean, and there was no leaching of organics. Then the membrane preservative was removed. Before fouling experiments could commence, the pure water flux and critical flux was found for RO water and Raw ORW, respectively. Fouling experiments that were conducted were 8-hour experiments and multi-day experiments. The experimental procedure can be seen in figure 3.3. It should be noted a new set of membrane fibers were used for every experiment.

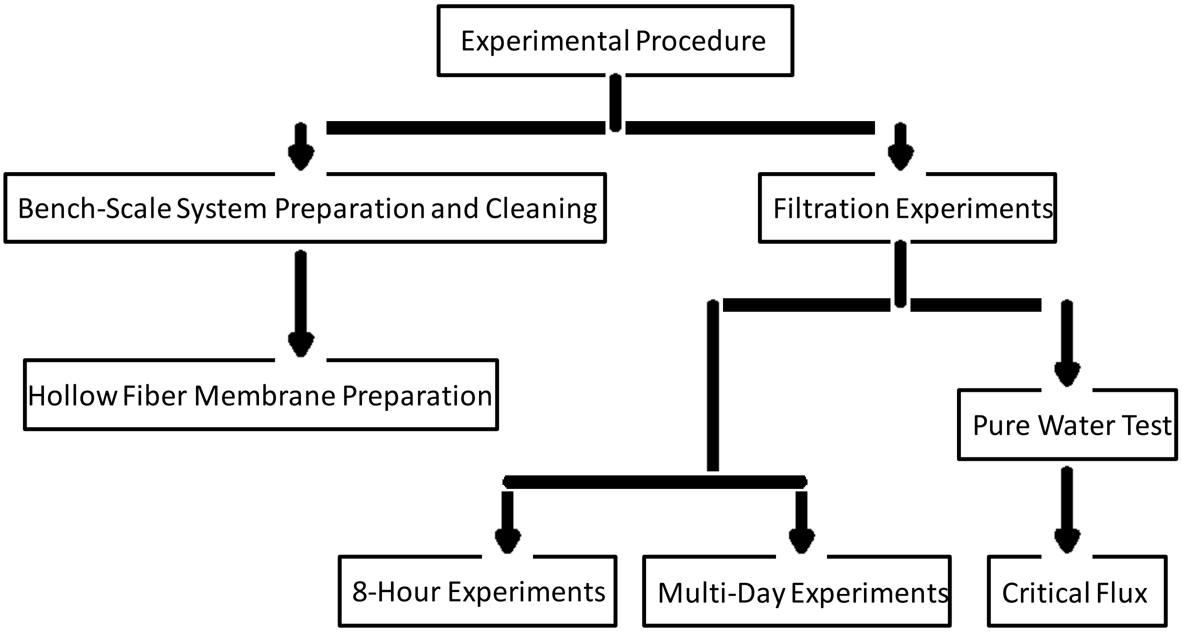

Figure 3.3. Experimental procedure layout schematic

3.6.1 Bench-Scale System Preparation and Cleaning

A cleaning procedure for the bench-scale UF system was implemented to ensure the system was clean after each experiment and would not impact the next experiment. It was imperative that the membrane system was cleaned so that nothing would leach during experiments resulting in; (1) additional fouling of the membrane, and (2) added organic carbon concentrations to the permeate stream. Frequent thorough cleanings were necessary to minimize biological growth. The membrane system was taken apart, all tubing was soaked in a liquid detergent solution bath. The tubing was then rinsed with RO water and abrasively cleaned with pipe cleaners to remove any adsorbed. The bottoms of the pressure transducers were allowed to sit in a beaker of liquid detergent solution, abrasively cleaned with pipe cleaners, then rinsed with RO water and allowed to dry. The solenoid valves were taken apart, placed in a beaker with a liquid detergent solution, and cleaned with an ultrasonic cleaner (Bransonic 220, Branson Ultrasonics, Danbury, USA) for 15 minutes. The water reservoirs containing the feed water, backwash RO water and chemical enhanced backwash feed were scrubbed and cleaned with liquid detergent and RO water. Once every component of the UF system was cleaned (minus the membrane fibers), the system was put back together and RO water plus 10ppm chlorine was ran through for several hours for a final flushing. The next experiment was then ready to commence.

3.6.2 Hollow Fiber Membrane Preparation

Before any experiment could be initiated, the glycerine preservative from the membrane fibers had to be removed. This was accomplished following the suppliers recommendations; run 2 L of RO water through the membrane at a maximum pressure of 34.5 kPa (5 PSI). This process took roughly ~10 hours. At the beginning the membrane was impermeable and the pressure had to be released frequently to avoid exceeding 34.5 kPa (5 PSI) pressure limit. Within the first hour, the membrane becomes permeable, but the flux is very low. Over time, the flux is increased to maintain a pressure of 34.5 kPa (5 PSI) until the pressure no longer drops with time and 2 L of RO water is filtered through. The membrane was stored over night in a refrigerator and in a 2ppm chlorine/RO water solution.

3.6.3 Filtration Experiments

The filtration experiments conducted comprised of membrane characteristic determination, experimental parameters, and fouling experiments. The pure water test was executed to determine the TMP and flux relationship for a new membrane. Any deviation from the pure water TMP at a certain flux was thought to be due to membrane fouling or loss of membrane integrity. The critical flux was determined for Raw ORW only to determine the two fluxes that the fouling experiments would be operated at - below and above critical. The critical flux was performed by the procedure outlined by Waterman (2007). The critical flux for pre-treated waters were expected to be different but they were not evaluated. Once the pure water test was complete and critical flux determined, the fouling experiments commenced.

3.6.3.1 Pure Water Test

A pure water test was conducted using RO water to determine the relationship between TMP and flux. According to the membrane supplier, the TMP - Flux relationship is linear between 0 - 413 kPa (0 - 60 PSI) (Matrix Membranes Inc., 2008). The pure water test was conducted by setting a flux, letting the system stabilize, and then recording the TMP. The flux was then increased, system allowed to stabilize, and the new TMP was recorded. Depending on the magnitude of flux increase, it would take the system 5 to 20 minutes to stabilize. This process continued until an adequate number of data points were obtained.

3.6.3.2 Critical Flux

The critical flux was obtained using the flux step method (Bacchin, et al., 2006). First the flux was set to a low value and the system's flux was allowed to stabilize, then the TMP was recorded for 15 minutes. This was followed by a 2ppm chlorine/RO solution enhanced backwash for 10 minutes. Then the system was switched to the filtration mode and the flux was increased, allowed to stabilize, then the TMP was recorded for 15 minutes. This process continued, increasing the flux after every backwash. The rate of fouling (TMP increase with time) at each flow rate was calculated and used the determination of the critical flux.

3.6.3.3 8-Hour Fouling Experiments

Two sets of 8-hour experiments were conducted for all waters (Raw ORW, Iron, Alum S, and Alum F) to determine the impact of sub-critical and supercritical flux on fouling. The subcritical flux was 50 L m^{-2} h^{-1} (LMH) and the supercritical flux was 100 LMH. The membranes were backwashed with RO water during the hydraulic backwashes (200 LMH) instead of using membrane permeate because of the low permeate volumes produced. No chemical cleans were conducted for these experiments. Membrane permeate samples were taken every 2 hours during the length of the experiment to determine TOC concentrations. The parameters inputted into the LabVIEW program are shown below.

Table 3.1. LabVIEW experimental input parameters for filtration experiments

Parameter	Input Value
Filtration Flow Rate (mL min^{-1})	3.267 (50 LMH) / 6.53 (100 LMH)
Filtration Time (min)	30
Hydraulic Backwash Flow Rate (mL min^{-1})	13.069
Hydraulic Backwash Time (min)	2
No. Of membrane fibers	6
Radius of one membrane fiber (m)	0.0004
Length of one membrane fiber (m)	0.26
Pump voltage increase/decrease	0.0001

3.6.3.4 Multi-Day Fouling Experiments

The 50 LMH 3 day experiments were conducted for all waters (Raw ORW, Iron, Alum S and Alum F) to assess membrane fouling over a longer period of time and the effectiveness of chemical cleaning. The membrane was backwashed with RO water during the hydraulic backwashes. A chemically enhanced hydraulic backwash was conducted after 24 hours of operation with a 10ppm chlorine - RO solution. The chemically enhanced hydraulic backwashes lasted 20 minutes and were followed by a 20 minute RO water rinse. A sodium hydroxide (NaOH) soak was conducted on the third day of the experiments because ORW is highly hydrophobic, which is desorbed in high pH environments. The membrane + module was removed from the bench-scale system and allowed to soak for 20 minutes in 0.1N

NaOH. The membrane and module were then reinstalled into the bench-scale system and rinsed for 20 minutes with RO water. Membrane permeate samples were taken every 2 hours during the duration of the experiment. The parameters inputted into the LabVIEW program are the same as in table 3.1.

3.7 Analytical Methods for Water and Permeate Characterization

3.7.1 Total Organic Carbon (TOC)

A TOC analyzer was used to quantify the concentration of NOM in each sample. The TOC analyzer used was a UV-persulfate oxidation based analyzer (Phoenix 8000, Tekmar Dohrmann, Cincinnati, OH, Model 14-7045-000). This method of TOC analysis follows the standard method 5310 C (APHA/AWWA/WEF, 1998).

The TOC analyzer was calibrated for the concentration range of 0.0001 ppm - 10 ppm. For the 0.0001 ppm standard RO water was used. For the standards 1 ppm, 2 ppm, 3 ppm, 4 ppm, 5 ppm, 6 ppm, 7 ppm, 8ppm, 9 ppm and 10 ppm, a 1 liter 1000 ppm potassium hydrogen phthalate (KHP) stock calibration solution was diluted.

3.7.2 Dissolved Organic Carbon (DOC)

The DOC was obtained by filtering the source water through a 0.45 μm cellulose membrane (Millipore Corporation, Bedford, MA 01730) and then performing TOC analysis on the filtrate. The membrane was placed into a filtration cell (Amicon 400mL ultrafiltration stirred cell, Amicon Corp., MA). The filtration cell came equipped with a magnetic stirrer that did not touch the membrane surface. The driving force through the membrane was pressurizing the filtration cell with nitrogen gas. The effluent produced was analysed with the TOC analyzer.

3.7.3 Natural Organic Matter (NOM) Characterization

NOM was characterized using XAD4 and XAD8 resins (Fisher Scientific, Hampton, NH). The procedure which was used for NOM characterization in this study was adapted from Thurman and Malcolm (1981). The method is described in detail in Appendix A.

3.7.4 Molecular Weight Distribution

Ultrafiltration membranes were used to determine the molecular weight distributions of each water. An Amicon 400mL ultrafiltration stirred cell (Amicon Corp., MA) was used with membranes with molecular weight cut-offs (MWCOs) of 30,000, 10,000, 5,000, 3,000 and 1,000 Daltons (Millipore, MA).

The membranes were coated with glycerin by the manufacturer to prevent drying. To remove the glycerin, the membranes were soaked in a beaker of RO water (glossy side down) for a minimum of 1 hour while changing the RO water 3 times. After the membranes were cleaned, the method chosen to conduct the MWCO fractionation was the in-series ultrafiltration method, which is commonly used according to the literature (Kitis, et al., 2002). Permeate and retentate were collected for analysis. The filtration proceeded sequentially from the highest MWCO to that with the lowest MWCO. Excess permeate produced by each filtration step was used as the feed to the next filtration with a lesser MWCO membrane.

3.7.5 General Water Quality Characteristics

A pH meter (Accumet model 910, Fisher Scientific, Hampton, NH) was used for all measurements. Turbidity was determined by using a Hach 2100AN Turbidimeter (Loveland, CO) for all samples. Before samples were analyzed, the instrument was calibrated using standards supplied by Hach: <0.1 NTU, 20 NTU, 200 NTU, 1000 NTU, 4000 NTU, and 7000 NTU. The method used to determine alkalinity was the Titration Method described in section 2320 B of Standard Methods (APHA/AWWA/WEF, 1998). The method used to determine total hardness was the EDTA Titrimetric Method in section 2340 C of Standard Methods (APHA/AWWA/WEF, 1998). To determine the zeta potential and conductivity of samples, a Zetasizer Nano Particle Analyser (Nano ZS, Malvern Instruments Ltd., Worcestershire, United Kingdom, Model ZEN3600) was used.

3.7.6 Total Iron

Total iron concentrations were determined for: Raw ORW, Iron, Alum S and Alum F and the membrane permeate from the Iron fouling experiments. The method used to determine total iron was the Phenanthroline Method in section 3500-Fe B in the Standard Methods (APHA/AWWA/WEF, 1998) and used a spectrophotometer (HACH DR-2800, Loveland, CO). The built in program (TPTZ Method, Method 8112) on the spectrophotometer was utilized. Each samples' pH was adjusted to between 3 and 4 using 10% HCl or 0.1 N NaOH before analysis. The sample was then added to the 10 mL sample cell followed by the addition of one 10 mL TPTZ iron reagent powder pillow. The sample was swirled for 30 seconds to ensure mixing and then let sit for 3 minutes to allow reaction. The sample cell was cleaned with kimwipes before insertion into the spectrophotometer and conducting the measurement.

Before each use, the spectrophotometer was calibrated using a stock iron solution. The stock iron solution preparation was followed from section 3500-Fe B of the Standard Methods (APHA/AWWA/WEF, 1998). The stock iron solution preparation steps and calibration relationships are displayed in Appendix B.

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

UV absorbance at 254nm was determined for all waters: Raw ORW, Iron, Alum S and Alum F. UV was determined by using a UV spectrophotometer (HACH DR-5000, Loveland, CO) with a 10mm path length quartz cell. The UV spectrophotometer was always zeroed using

RO water. A UV-TOC correlation was made for Raw ORW and its permeates, Alum S and its permeate and Alum F and its permeates, which can be seen in Appendix C. SUVA was determined by dividing the UV absorbance at 254nm by the DOC (mg/L) concentration of the samples.

3.7.8 Glycerol

Glycerol concentrations were determined by measuring the refractive index of the sample. The refractive index of water at 20°C is 1.3247 while the refractive index of glycerol at 20°C is 1.4229 (Rheims, et al., 1997). Any glycerol - water solution will have a refractive index between that of water and glycerol. The refractive index of known glycerol - water solutions were determined. The known glycerol - water solutions comprised of glycerol percentages of 0, 1, 2, 4, 6, 10 and 14. Measuring the refractive index of the samples was done by using a Bausch & Lomb ABBE-3L Refractometer.

3.8 Evaluation of Membrane Performance

For each experiment, pressure on the feed and permeate sides of the membrane were monitored and recorded by the LabVIEW operated bench-scale membrane system. The transmembrane pressure (TMP) was calculated by subtracting the pressure on the feed side of the membrane (P_f) by the pressure on the permeate side of the membrane (P_p) (MWH, 2005).

$$TMP = P_f - P_p \tag{3.1}$$

The backwash efficiency (BWE) for the hydraulic backwashes of each experiment was calculated. BWE was calculated using data from the hydraulic backwashes throughout the duration of each experiment. BWE was calculated as follows:

$$BWE = \frac{TMP_f - TMP_n}{TMP_f - TMP_i} \; x \; 100 \tag{3.2}$$

where TMP_f is the TMP at the end of filtration cycle n, TMP_i is the TMP at the beginning of filtration cycle n, and TMP_n is the TMP at the beginning of filtration cycle n+1 (Chellam, et al., 1998).

The NOM rejection was calculated as follows:

$$R = 1 - \frac{C_p}{C_f} \tag{3.3}$$

where C_p is the NOM permeate concentration (ppm) and C_f is the NOM feed water concentration (ppm) (MWH, 2005).

To numerically express the severity of different types membrane fouling, the resistance-in-series model was applied, adapted from MWH (2005) and commonly used by other researchers (Kim & Dempsey 2013; Dang et al. 2010; Ousman & Bennasar 1995). For the 8-hour experiments the total fouling was characterized by the total fouling resistance K_F which was determined at the end of each experiment by using the following equation:

$$J = \frac{TMP}{\mu(K_m + K_F)} \tag{3.4}$$

where J is the permeate flux (m^3 m^{-2} s^{-1}), TMP is the transmembrane pressure (kg s^{-2} m^{-1}), μ is the viscosity of water at 20°C (kg m^{-1} s^{-1}), K_m is the membrane resistance (m^{-1}), K_F is the total fouling resistance (m^{-1}). K_F is a time dependent, it depends on the TMP value at the time in question.

K_m is the hydraulic resistance of a virgin membrane when a foulant-free feed water (RO water) is filtered through the membrane, i.e. the pure water tests. K_m was determined by analyzing the pure water test and applying the following filtration equation:

$$J = \frac{TMP}{\mu(K_m)} \tag{3.5}$$

K_m was found to be $2.06\ x\ 10^{12}$ m^{-1} which is within the typical membrane resistance range for UF membranes ($1\ x\ 10^{12} - 1\ x\ 10^{13}$ m^{-1}) (Benjamin & Lawler, 2013).

For all experiments, hydraulic backwashes were employed to remove cake deposits on the membrane surface. Based on the effectiveness of the hydraulic backwashes, two forms of fouling were quantified, hydraulically reversible and hydraulically irreversible fouling. The following model was used to quantify these types of fouling as a function of time and at a specific point during the experiments:

$$J = \frac{TMP}{\mu(K_m + K_{HIR} + K_{HR})} \tag{3.6}$$

where K_{HIR} is the hydraulically irreversible fouling resistance (m^{-1}), and K_{HR} is the hydraulically reversible fouling resistance (m^{-1}). K_{HIR} and K_{HR} as a function of time was calculated using the TMP immediately before and after the hydraulic backwashes throughout the experiment. First, set the TMP to its value immediately after the hydraulic backwash, at this point K_{HR} is equal to zero as the hydraulic backwash removed that type of fouling. Then K_{HR} was calculated using equation 3.6 with the TMP value immediately prior to the hydraulic backwash. Hydraulically irreversible fouling is hypothesized to be primarily caused by adsorption and hydraulically reversible fouling is most likely due to cake formation.

In addition, based on the results of chemical cleanings the fouling can be further subdivided into chemically irreversible fouling and chemically reversible fouling. These two types of fouling were determined using the following model:

$$J = \frac{TMP}{\mu(K_m + K_{HR} + K_{CIR} + K_{CR})} \tag{3.7}$$

where K_{CR} is the chemically reversible fouling resistance (m^{-1}), and K_{CIR} is the chemically irreversible fouling resistance (m^{-1}). Note that this analysis can only be performed using TMP data immediately before and immediately after a chemical clean. K_{CIR} was calculated by applying equation 3.7 immediately after the chemical clean, so that K_{CR} is zero as the chemical clean removed this type of fouling. Then equation 3.7 was used at the point just prior to the chemical clean to calculate K_{CR} (Dang et al. 2010).

3.9 Statistical Analysis

To determine if there was a significant linear relationship between the independent variables x and the response variables y, t-tests were conducted. For every t-test conducted the null hypothesis was that the slope of the linear line between variables x and y was equal to 0.

Therefore, the null hypothesis states there is no linear relationship between x and y. The alternative hypothesis was that the slope of the linear line between x and y did not equal 0. Two-tailed tests were always conducted. The t-tests were performed using four sets of data points, one for each of the waters treated. Therefore, based on the critical values in the t-tables, with a degree of freedom (df) equalling 2 [df = number of data points (n) - 2] and with a 5% level of confidence, to reject the null hypothesis the t-value must be larger than 4.303 or smaller than -4.303 (Mendenhall, et al., 2009).

CHAPTER 4

HOLLOW FIBER ULTRAFILTRATION OF OTTAWA RIVER WATER: IMPACT OF DIFFERENT PRE-TREATMENT SCHEMES

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4.1 Abstract

To minimize membrane fouling many water treatment plants pre-treat water prior to microfiltration (MF) or ultrafiltration (UF). Coagulation/flocculation/sedimentation is a common form of pre-treatment, but little research has been conducted on floatation as a part of the pre-treatment. The objective of this study is to compare floatation with sedimentation as a pre-treatment for a highly coloured river water. Fouling tests consisted of multiple filtration/backwashing cycles performed by an automated bench-scale UF hollow fiber membrane system. Alum coupled with floatation (Alum F) produced the least severe hydraulically irreversible fouling and also produced the highest quality permeate based on total organic carbon (TOC) concentrations. The hydrophobic fraction of natural organic matter (NOM) was found to affect hydraulically irreversible fouling while transphilic NOM and particulate organic carbon affected hydraulically reversible fouling.

4.2 Introduction

Ultrafiltration (UF) membranes are effective at producing consistently high quality water and removing harmful contaminants such as bacteria, protozoa, some viruses, some particles, and some natural organic matter (NOM) (MWH 2005). However, membranes do have limitations, in particular they are susceptible to fouling. Membrane fouling is the result of foulants and particles building up on the membrane surface, plugging the membrane pores, or adsorbing within the membrane pores, all of which restrict the flow through the membrane. Membrane fouling is extremely complex, is often influenced by many parameters, and depends on the source water, membrane characteristics and the system's operating conditions (Metsamuuronen et al. 2014; Zularisam et al. 2011; Laine et al. 1989). One of the main known membrane foulants in surface waters is NOM (Uyak et al. 2014; Aoustin et al. 2001).

The principal approaches to minimize fouling are hydraulic backwashes, chemical cleanings and pre-treatment. Hydraulic backwashes remove particulate build up on the membrane surface by forcing membrane permeate in the opposite direction of filtration. The membranes are subjected to 1 to 5 minute-long hydraulic backwashes every 15 minutes to 2 hours using 2 to 3 times the filtration flow rate. (MWH 2005). However, hydraulic backwashes generally do not reduce the transmembrane pressure (TMP) to its original value, i.e., there is some hydraulically irreversible fouling and the membrane performance diminishes over time. Eventually, chemical backwashes or chemical soaks are required to reduce the effects of membrane fouling (Amy 2008). The chemical agent used for chemical cleans is chosen based on what is fouling the membrane and the membrane manufacturer's recommendations. Even after chemical cleans however, some fouling may persist, commonly referred to as chemically irreversible fouling (MWH 2005).

The third approach to reduce the impact of membrane fouling, is to pre-treat the source water prior to membrane filtration. Coagulation/flocculation as the pre-treatment coupled with membrane filtration have shown promising results as higher quality membrane permeate is produced and membrane fouling is reduced (Guigui et al. 2002; Braghetta et al. 2001; Robert et al. 1999). However, there are studies that have also found that implementing coagulation/flocculation prior to membrane filtration results in an increase of membrane fouling (Liu et al. 2005; Schafer et al. 2001; Shorney et al. 2001). One explanation for an increase in membrane fouling after coagulation/flocculation is that the coagulants form a sticky floc complex which further restricts flow to the membrane (Adham et al. 2006). To maximize the efficiency of the pre-treatment in many cases the coagulated/flocculated water is settled prior to membrane filtration (Adham et al. 2006). Floatation is an efficient and more compact alternative to sedimentation, and has the added advantage that it is a better separation process for algae. Little research on floatation as a form of membrane pre-treatment was identified in the literature (Pera do Amaral et al. 2013; Teixeira & Rosa 2006).

The objective of this study is to use an automated bench-scale UF hollow fiber system to compare the impact of pre-treatment with floatation versus sedimentation and for a colored river water. Ottawa River water was chosen as the challenge water because; a) its relatively high NOM content and fouling potential; and b) there are full-scale treatment plants using coagulation/flocculation/ sedimentation and coagulation/flocculation/floatation within close proximity of each other.

4.3 Experimental

4.3.1 Waters tested

This study used Ottawa River water (ORW) subjected to a number of different pre-treatments. ORW is a soft, low alkalinity water with a significant amount of colour, NOM, and more specifically hydrophobic NOM typical of northern waters (Aiken et al. 1985). This water was selected because; a) it's relatively high NOM content should lead to high fouling and shorter experiments; and b) the availability of water treatment plants treating the same river water using several types of processes, including one using floatation.

UF membrane tests were conducted using ORW subjected to four different types of pre-treatment: a) no pre-treatment (Raw ORW), b) ferric sulfate coagulated and settled water (Iron), c) alum coagulated and settled water (Alum S), and d) alum coagulated and floated water (Alum F). Raw ORW was obtained from the Britannia Water Treatment Plant (WTP) in Ottawa, Ontario. Iron and Alum S were collected from the Britannia WTP's pilot plant. The pilot plant consisted of two treatment trains, one mimicking the full-scale plant using alum coagulation and sedimentation (Alum S) and the second investigated iron coagulation and sedimentation (Iron) . For the Iron pre-treatment, the dosages of ferric sulfate and silicate (SiO_2) were 46.91 mg/L (9.33 mg Fe/L) and 1.00 mg/L, respectively. The pH was adjusted to ~4.8 using 4.14 mg/L of sulfuric acid (H_2SO_4). For the Alum S pre-treatment, the dosages of alum and silicate (SiO_2) were 34.9 mg/L (3.17 mg Al/L) and 0.91 mg/L, respectively, the same used in the full-scale plant. The pH was adjusted to ~ 5.7 using 8.09 mg/L of sulfuric acid (H_2SO_4). Both Alum S and Iron pre-treated waters were collected after settling and before the media filters.

The fourth water was obtained from the Aylmer WTP in Aylmer, Quebec, which also takes its water from the ORW less than 6 km upstream from the Britannia WTP. Alum was added as the coagulant as well as the polymer to help aid the flocculation. The water sample for these experiments were collected during the summer at which time the alum dosage was 33 mg/L (2.99 mg Al/L) and the cationic polyacrylamide (Superfloc C-492PWG, Kemira) polymer dosage was 0.7 mg/L. Instead of settling their water, the Aylmer plant uses floatation for separation. Alum F was extracted after the floatation basin and before the media filter.

4.3.2 Membrane and Module Configuration

Each experiment was conducted with a new membrane module which contains six hydrophilic polyethersulfone (PES) fibers supplied by Matrix Membranes, Oceanside, CA. The fiber's nominal molecular weight cut off (NMWCO) is 100,000 Da (<0.02 microns) and their inner fiber diameter is 0.8 mm. The membrane module was constructed to operate with an inside-out dead-end flow regime. Six fibers were cut to a length of 30 cm. The housing modules were constructed with low density polyethylene tubing and plastic fittings. Two centimeters of the fibers on both ends of the module were epoxied resulting in an effective membrane fiber length of 26 cm. The resulting total effective membrane area of one module is 0.00392 m^2. The module can be seen in figure 4.1 below:

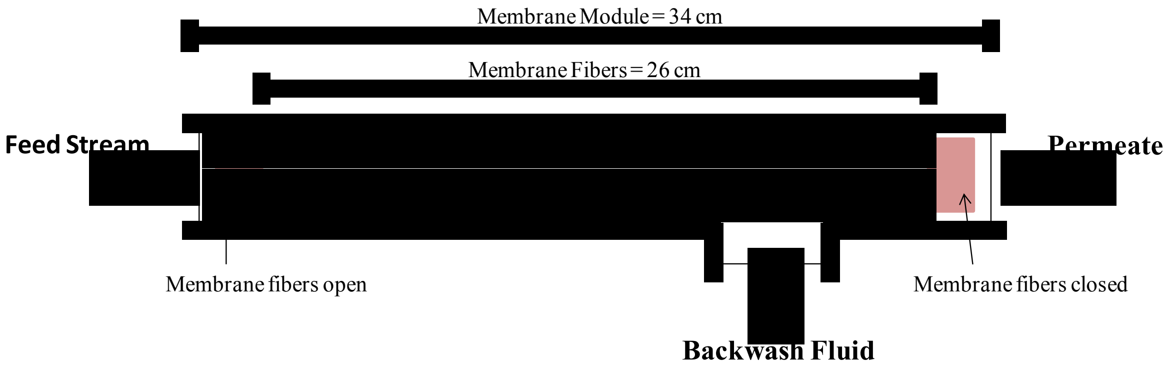

Figure 4.1. UF hollow fiber membrane module design used in all filtration experiments

4.3.3 Ultrafiltration (UF) Bench-Scale System

The experiments were conducted using the bench-scale UF hollow fiber membrane treatment system shown in Figure 4.2, which is a slightly modified version constructed by Waterman (2007). One of the challenges of this research was to ensure that the bench-scale UF system simulated the operational characteristics of a full-scale facility. In doing so, numerous instruments were incorporated into the bench-scale system to either control or monitor operation. A LabVIEW program was created to operate the bench-scale system unsupervised. It controls the filtration pump output to have a constant permeate flux and it automatically switches from filtration cycles to backwash cycles in an infinite loop while recording data, such as: TMP, flow rate and flux. Because of the low volume of filtrate produced by this six membrane fiber system, the backwashes were performed using RO water (i.e., distilled water passed through a reverse osmosis system).

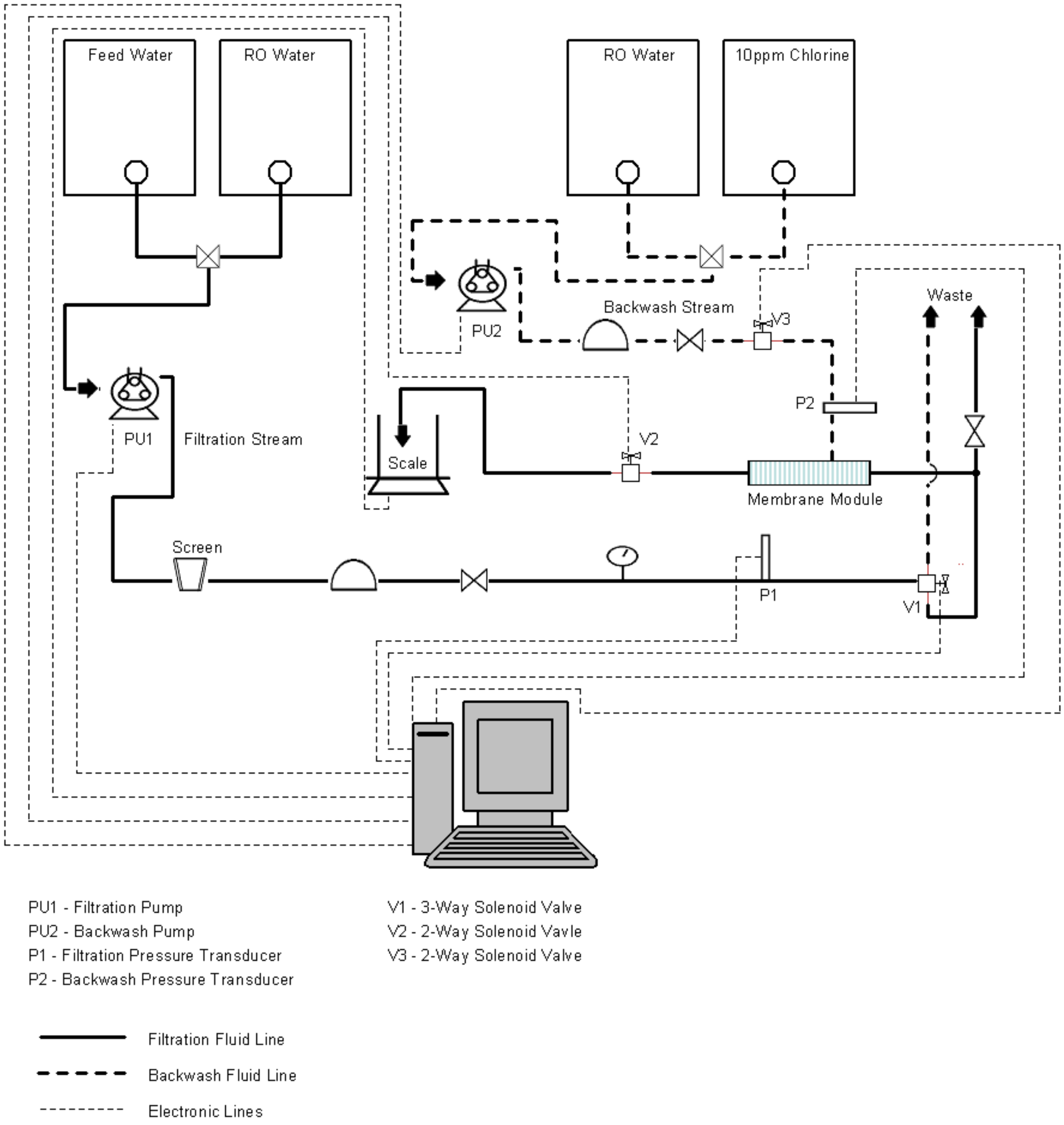

Figure 4.2. Schematic diagram of the UF bench-scale system layout

4.3.4 Experimental Plan

The filtration experiments conducted were pure water tests, a critical flux test, 8-hour long membrane filtration/fouling tests (below and above critical flux), and multi-day long membrane fouling tests incorporating a chemical clean. A pure water test was performed to determine the TMP and flux relationship for a virgin membrane and calculate the membrane resistance. This was accomplished by running reverse osmosis (RO) water through the membrane at a low flux. After recording the TMP for 15 minutes the flux was increased. This procedure continued in a step-wise fashion. During fouling experiments, any TMP deviation from the pure water TMP at a set flux was thought to be due to membrane fouling or loss of membrane integrity.

The 'Critical Flux' can be defined as, 'a flux below which a decline of flux with time does not occur; above it fouling is observed' (Bacchin et al. 2006; Field et al. 1995). However, techniques used to establish the critical flux show slight fouling below the critical flux. The critical flux was determined by performing the flux-TMP step method (Bacchin et al. 2006) for Raw ORW only, it was assessed to aid in the selection of two operational fluxes one below and one above the critical flux. The data from the critical flux experiment graphed in terms of change in TMP over change in time (dTMP/dt) versus permeate flux (LMH) to determine at what flux level the slope dramatically increases. The critical flux experimental results can be seen in figure 4.3. A linear relationship was found for fluxes below critical and those above critical. Calculations were performed to find the intersection of the two straight lines. The permeate flux at which the two lines intersected is the critical flux. The critical flux was found to be 79 LMH. Waterman (2007) who also conducted studies on UF hollow fiber UF membrane filtration used Raw ORW in his experiments and found the critical flux for his membrane to be 75 LMH.

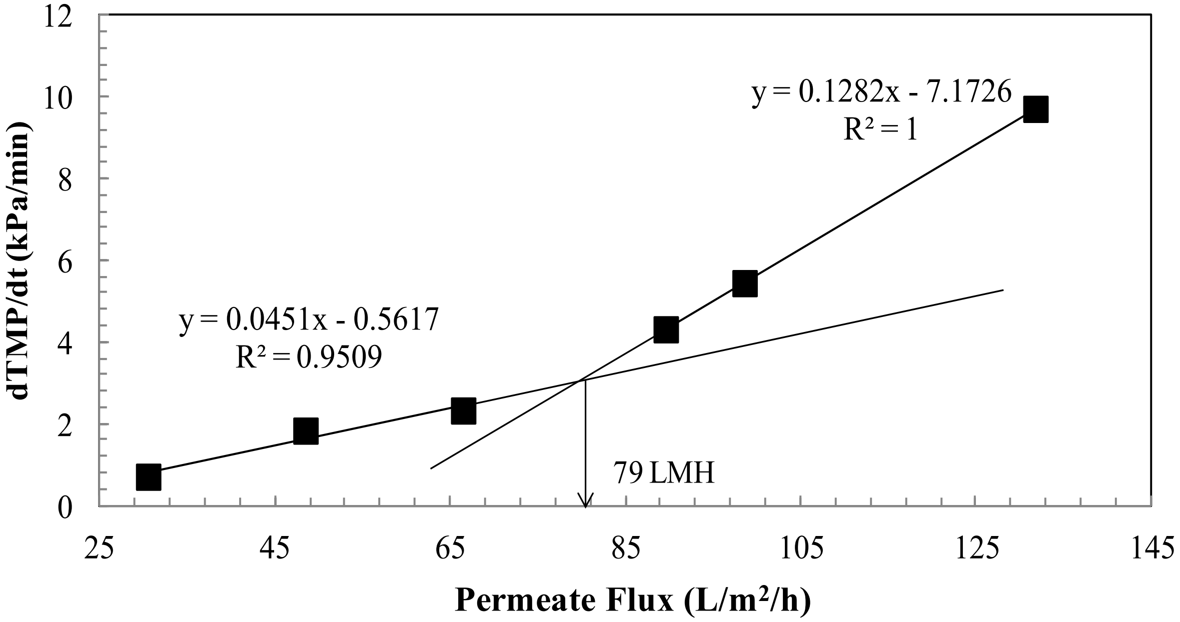

Figure 4.3. Determination of Critical Flux using the flux-TMP step method (Waterman 2007) for Raw ORW

Two 8-hour experiments were performed to assess membrane performance for each water, one at a sub-critical flux (50 LMH) and the other at super-critical flux (100 LMH). For each experiment, the filtration cycle duration was 30 minutes and the hydraulic backwash cycles (200 LMH) lasted for 2 minutes. No chemical cleans were conducted.

A multi-day experiment at 50 LMH was conducted for each water to assess membrane fouling over a longer period of time and to evaluate the impact of chemical cleaning. A chemically enhanced backwash was performed after 24 hours of operation and a 0.1N NaOH membrane cleaning procedure was performed after 40-42 hours of operation. The 2ppm chlorine enhanced backwash was conducted for 20 minutes as per Matrix Membrane's recommendations to reduce membrane fouling. A 0.1N NaOH clean was selected because ORW has high concentrations of hydrophobic NOM (HPO), and NaOH results in high pH conditions which HPO is less adsorbable. The filtration and backwash cycle durations were also 30 and 2 minutes, respectively. On the third day of experimenting the membrane module was taken out of the UF system and placed in a 0.1N NaOH bath (chemical clean) for 20 minutes, reconnected and then rinsed for 20 minutes with RO water prior to resuming operation.

4.3.5 Sample Collection and Analytical Methods

Sample collection and storage protocols were adapted from the Standard Methods (APHA/AWWA/WEF, 1998). A UV-persulfate oxidation based analyzer (Phoenix 8000, Tekmar Dohrmann, Cincinnati, OH, Model 14-7045-000) was used to quantify the concentration of total organic carbon (TOC) in each sample. The dissolved organic carbon (DOC) concentrations were obtained by filtering the sample through a 0.45 μm membrane (Millipore Corporation, Bedford, MA 01730) and then performing TOC analysis on the filtrate. Nitrogen gas was the driving force for the filtration cell (Amicon 400mL ultrafiltration stirred cell, Amicon Corp., MA). The particulate organic carbon (POC) is the difference between the TOC and the DOC. Molecular weight (MW) fractionations of the NOM in each water were performed using the same ultrafiltration membrane filtration cell with membranes with NMWCOs of 30,000, 10,000, 5,000, 3,000 and 1,000 Daltons (Da) (Millipore, MA). NOM was also characterized into hydrophobic (HPO), transphilic (TPI), and hydrophilic (HPI) fractions using XAD4 and XAD8 resins (Fisher Scientific, Hampton, NH). The NOM characterization procedure was adapted from Thurman and Malcolm (1981). 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). The zeta potential and conductivity were determined using a Zetasizer Nano Particle Analyser (Nano ZS, Malvern Instruments Ltd., Worcestershire, UK, Model ZEN3600). The total iron was determined by the Phenanthroline Method and using a spectrophotometer (HACH DR-2800, Loveland, CO). UV absorbance at 254nm was determined using a UV spectrophotometer (HACH DR-5000, Loveland, CO) with a 10mm path length quartz cell. The UV spectrophotometer was always zeroed using RO water. SUVA was determined by dividing the UV absorbance at 254nm by the DOC (mg/L) concentration of the samples. The alkalinity, total hardness, and total iron were determined according to the Standard Methods (APHA/AWWA/WEF1998).

4.3.6 Fouling Determination

For every experiment, the TMP was monitored and recorded by the LabVIEW-operated hollow fiber membrane filtration system. The TMP change with time was used to graphically show membrane fouling. To numerically express the severity of different types membrane fouling, the resistance-in-series model was applied (MWH 2005) and commonly used by other researchers (Kim & Dempsey 2013; Dang et al. 2010; Ousman & Bennasar 1995). For the 8-hour experiments the total fouling was characterized by the total fouling resistance K_F which was determined by using the following equation:

$$J = \frac{TMP}{\mu(K_m + K_F)} \tag{4.1}$$

where J is the permeate flux (m^3 m^{-2} s^{-1}), TMP is the transmembrane pressure (kg s^{-2} m^{-1}), μ is the viscosity of water at 20°C (kg m^{-1} s^{-1}), K_m is the membrane resistance (m^{-1}), K_F is the total fouling resistance (m^{-1}). K_F is a time dependent, it depends on the TMP value at the time in question.

K_m is the hydraulic resistance of a new membrane when a foulant-free feed water (RO water) is filtered through the membrane, i.e. the pure water tests. K_m was determined by analyzing the pure water test and applying the following filtration equation:

$$J = \frac{TMP}{\mu \cdot (K_m)} \Rightarrow K_m = \frac{TMP}{\mu \cdot J} \tag{4.2}$$

K_m was found to be $2.06\ x\ 10^{12}$ m^{-1} which is within the typical membrane resistance range for UF membranes ($1\ x\ 10^{12} - 1\ x\ 10^{13}$ m^{-1}) (Benjamin & Lawler, 2013).

For all experiments, hydraulic backwashes were employed to remove cake deposits on the membrane surface. Based on the effectiveness of the hydraulic backwashes, two forms of fouling were quantified, hydraulically reversible and hydraulically irreversible fouling. The following model was used to quantify these types of fouling as a function of time and at a specific point during the experiments:

$$J = \frac{TMP}{\mu(K_m + K_{HIR} + K_{HR})} \tag{4.3}$$

where K_{HIR} is the hydraulically irreversible fouling resistance (m^{-1}), and K_{HR} is the hydraulically reversible fouling resistance (m^{-1}). K_{HIR} and K_{HR} as a function of time was calculated using the TMP immediately before and after the hydraulic backwashes throughout the experiment. After a hydraulic backwash, K_{HR} is equal to zero. Therefore, calculating K_{HIR} is done by using the TMP immediately after a hydraulic backwash with equation 4.3. Then K_{HR} was calculated using equation 4.3 with the TMP value immediately prior to the hydraulic backwash. Hydraulically irreversible fouling is hypothesized to be primarily caused by adsorption and hydraulically reversible fouling is most likely due to cake formation.

In addition, based on the results of chemical cleanings the fouling can be further subdivided into chemically irreversible fouling and chemically reversible fouling. These two types of fouling were determined using the following model:

$$J = \frac{TMP}{\mu(K_m + K_{HR} + K_{CIR} + K_{CR})} \tag{4.4}$$

where K_{CR} is the chemically reversible fouling resistance (m^{-1}), and K_{CIR} is the chemically irreversible fouling resistance (m^{-1}). Note that this analysis can only be performed using TMP data immediately before and immediately after a chemical clean. K_{CIR} was calculated by applying equation 4.4 immediately after the chemical clean, so that K_{CR} is zero as the chemical clean removed this type of fouling. Then equation 4.4 was used at the point just prior to the chemical clean to calculate K_{CR} (Dang et al. 2010).

Backwash efficiencies (BWE) were calculated to assess membrane permeability recovery by hydraulic backwashes. BWE for individual backwash cycles were calculated as follows:

$$BWE = \frac{TMP_f - TMP_n}{TMP_f - TMP_i} \, x \, 100 \tag{4.5}$$

where TMP_f is the TMP (kPa) at the end of filtration cycle n, TMP_i is the TMP (kPa) at the beginning of filtration cycle n, and TMP_n is the TMP (kPa) at the beginning of filtration cycle n+1 (Chellam et al. 1998).

4.4 Results and Discussion

4.4.1 Water Quality

The water quality analysis results are presented in table 4.1. It was found that the TOC concentration of the Raw ORW was 6.78 mg L^{-1} and that pre-treatments reduced TOC by 33 ± 8.5%, 63 ± 9.9% and 68 ± 10.3% for Iron, Alum S and Alum F, respectively. Thus, the Alum F is the most effective pre-treatment in terms of TOC removal, but the Alum S pre-treatment was almost as effective. As expected, DOC, POC, pH and Alkalinity were also reduced by pre-treatment. Interestingly, both the Alum S and Alum F reduced turbidity, however, the Iron pre-treatment increased the turbidity. This trend was also found for the UV-254 and SUVA. These findings suggest that the iron (Fe) may have been interfering with the turbidity and UV-254 measurements and that the settling part of the Iron pre-treatment was not very effective. The latter would account for the much lower TOC and DOC removals produced by the Iron pre-treatment as opposed to the Alum pre-treatments. It is hypothesized that the turbidity of the Iron pre-treatment water is caused by iron (Fe)/NOM colloidal complexes. It must be stated that the Iron pre-treatment water was collected from a pilot plant which may have not been operating under optimum conditions. Thus, the results of the experiments conducted with Iron pre-treatment water should be considered with caution. Generally when a coagulant is added it is desirable to obtain a zeta potential within the range of -8 mV to +8 mV (optimal range) (MWH 2005). As can be seen in table 4.1, the only pre-treatment that produced a zeta potential within that optimal range was Alum S. However, the pre-treated waters in this study were collected after settling or floatation, therefore the neutral particles within the optimal range may have already been removed during the separation process leaving the more charged particles to remain in solution.

Table 4.1. Water quality characteristics compilation

Parameter	Raw ORW (Britannia WTP)	Iron	Alum S	Alum F
TOC (mg L^{-1})	6.78 ± 0.35 [*1]	4.54 ± 0.11	2.51 ± 0.10	2.15 ± 0.11
DOC (mg L^{-1})	6.07 ± 0.05	4.38 ± 0.04	2.45 ± 0.12	2.07 ± 0.10
POC (mg L^{-1})	0.71 ± 0.10	0.16 ± 0.10	0.06 ± 0.10	0.08 ± 0.12
pH	6.97 [*2]	4.36	6.56	6.46
Turbidity (NTU)	1.52 ± 0.10	4.48 ± 0.09	0.88 ± 0.14	0.37 ± 0.03
Alkalinity (mg $CaCO_3$ L^{-1})	30.5 ± 1.7	5.2 ± 3.0	1.4 ± 2.7	5.6 ± 2.7
Total Hardness (mg $CaCO_3$ L^{-1})	34.3 ± 1.7	37.7 ± 0.7	33.8 ± 5.1	24.7 ± 1.4
Zeta Potential (mV)	-26.10	-21.43	-5.44	-15.00
Conductivity (mS cm^{-1})	0.07	0.12	0.11	0.10
Total Iron (mg L^{-1})	0.37 ± 0.03	1.32 ± 0.20	0.11 ± 0.03	0.08 ± 0.03
UV-254 (cm^{-1})	0.25 ± 0.00	0.35 ± 0.00	0.06 ± 0.00	0.05 ± 0.00
SUVA (L mg^{-1} m^{-1})	4.16 ± 0.04	8.03 ± 0.16	2.50 ± 0.26	2.39 ± 0.15
Hydrophobic NOM (mg L^{-1})	4.97 ± 0.58	3.89 ± 0.15	2.20 ± 0.20	1.60 ± 0.20
Transphilic NOM (mg L^{-1})	0.65 ± 0.22	0.16 ± 0.10	0.02 ± 0.09	0.12 ± 0.09
Hydrophilic NOM (mg L^{-1})	0.45 ± 0.04	0.34 ± 0.11	0.24 ± 0.06	0.35 ± 0.09
TOC Removal (%)		33 ± 8.5	63 ± 9.9	68 ± 10.3

[*1] *- Values represent the mean value ± the 95% confidence interval*

[*2] *- Entities without ± correspond to single measurements*

NOM is composed of different fractions (HPO, TPI, and HPI), each of which are thought to affect membrane performance differently (Zularisam et al. 2007). The NOM fraction compositions for Raw ORW was found to be 82%, 11% and 7% for HPO, TPI and HPI, respectively. This is very similar to that found by Dang (2010) for Raw ORW. Table 4.2 shows the removal for NOM fractions by pre-treatment. Raw ORW has an HPO concentration of 4.97 mg/L - to reduce that by 3.37 mg/L is significant (achieved by Alum F). In general, it was found that all pre-treatments were fairly effective at removing the HPO and TPI NOM and not very effective at removing HPI NOM (table 4.2). Both Alum S and Alum F were more effective at removing the HPO fraction of NOM. The greatly decreased values of the SUVA for the Alum S and Alum F waters also attest to good HPO removals. The Iron pre-treatment was the least effective pre-treatment at removing the TPI fraction of NOM, while the Alum S pre-treatment was the most effective. For the HPI NOM removal, the Alum F and Iron performed the worst, while Alum S performed the best. Overall, on a mass basis the HPO fraction was best removed (1.08 - 3.37 mg/L) while the TPI fraction of NOM was best removed on a percentage basis as removals ranged from 76% to 98%. Even though pre-treatment was able to remove a portion of the HPO NOM, 78%, 44% and 32% remained in the Iron, Alum S and Alum F waters, respectively. For this reason, the pre-treated waters were expected to foul the membrane.

Table 4.2. NOM fraction removals for each pre-treatment method

Treatment	HPO Removal		TPI Removal		HPI Removal	
	(%)	(mg/L)	(%)	(mg/L)	(%)	(mg/L)
Iron	22	1.08	76	0.49	26	0.12
Alum S	56	2.77	98	0.63	47	0.21
Alum F	68	3.37	82	0.53	22	0.10

Molecular weight (MW) fractionations were also conducted on each water. It was found that for the Raw ORW, 10.5% of NOM was in particulate form (> 0.45µm); 9.1% is between 0.45µm and 30,000 Da; 14.2% between 30,000 Da and 10,000 Da; 31.2% between 10,000 Da and 5,000 Da; 15.6% between 5,000 Da and 3,000 Da; 8.6% between 3,000 Da and 1,000 Da and 10% smaller than 1,000 Da. These results vary slightly from those found by Dang (2010), the differences may be due to season and/or annual variations of NOM.

The MW fraction compositions for the Raw ORW are more evenly distributed when compared to the pre-treated waters. Alum F showed a clear shift towards smaller NOM molecules, which was expected given that larger molecules should be easier to coagulate and separate. The Iron pre-treatment showed two trends. The first, is a shift towards the smaller size fractions like in the other pre-treatments. The second is quite different from the Alum pre-treatments in that there is the formation of a very significant amount (44% of the DOC) of larger molecules (i.e., 30,000 Da to 0.45um range). It is hypothesized that this larger fraction is an iron-NOM colloidal complex (Al-Attas 2012; Gu et al. 1995) that give this water its higher turbidity and interferes with the UV measurements. With the exception of Iron, pre-treatment reduced the mass of NOM above 3,000 Da. For some MW size fractions, pre-treatment increase the NOM concentration, as seen (figure 4.4) for Alum S for the range 3,000 Da - 1,000 Da.

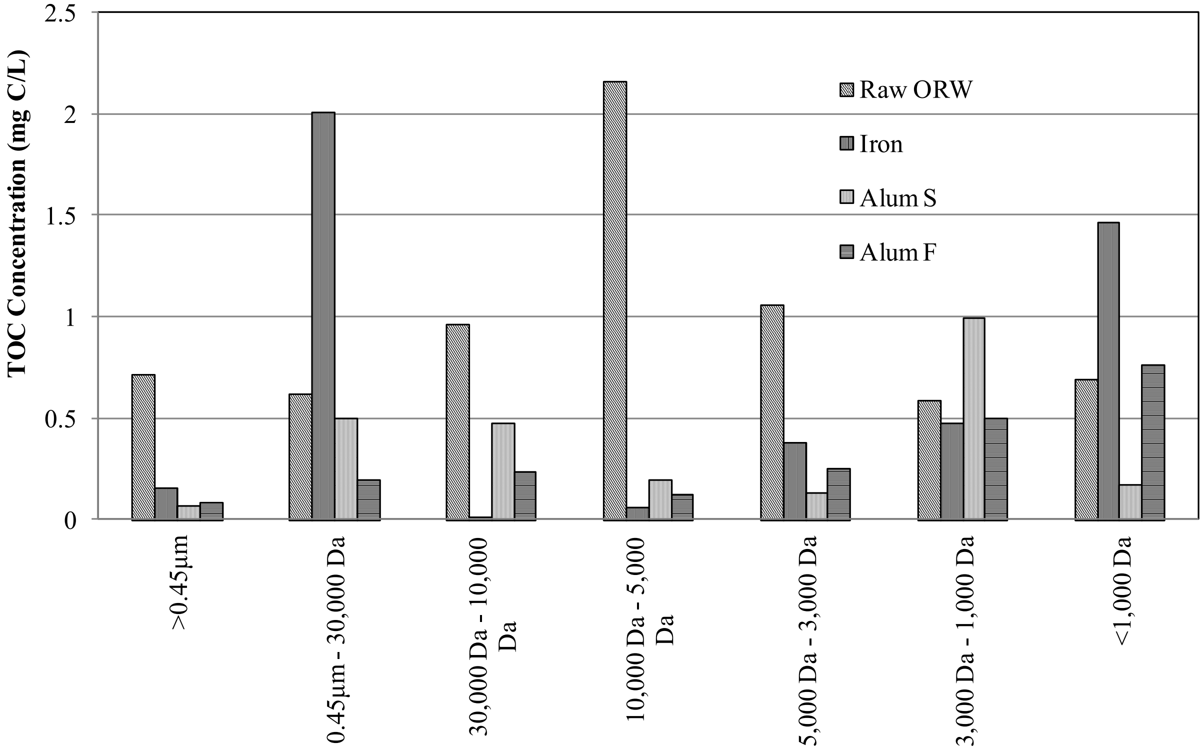

Figure 4.4. Molecular weight fraction results

4.4.2 Membrane Performance for the 8-Hour Experiments

For each water, an experiment was ran with an operational flux below critical (50 LMH) and above critical (100 LMH) (based on the critical flux for Raw ORW). For all waters, it was found that the flux above critical resulted in greater membrane fouling as expected, based on the critical flux theory (Guo et al. 2009; Waterman 2007). Figure 4.5 shows the TMP increases with time for Raw ORW and Alum F operating at 50 LMH and 100 LMH experiments. As the filtration system recorded the pressure measurements every 0.033

minutes, the amount of data collected is extremely large and would result in very crowded and unclear graphs. Accordingly, the graphs presented only include a limited number of data points. The magnified part in figure 4.5 shows that backwashing has a positive impact on the TMP, which is not very evident in most graphs. The 100 LMH run for Raw ORW clearly illustrates the beneficial impact of backwashing on the TMP. This figure shows that, as expected, the pre-treatment greatly decreases the TMP development and that increasing the permeate flux increases the fouling.

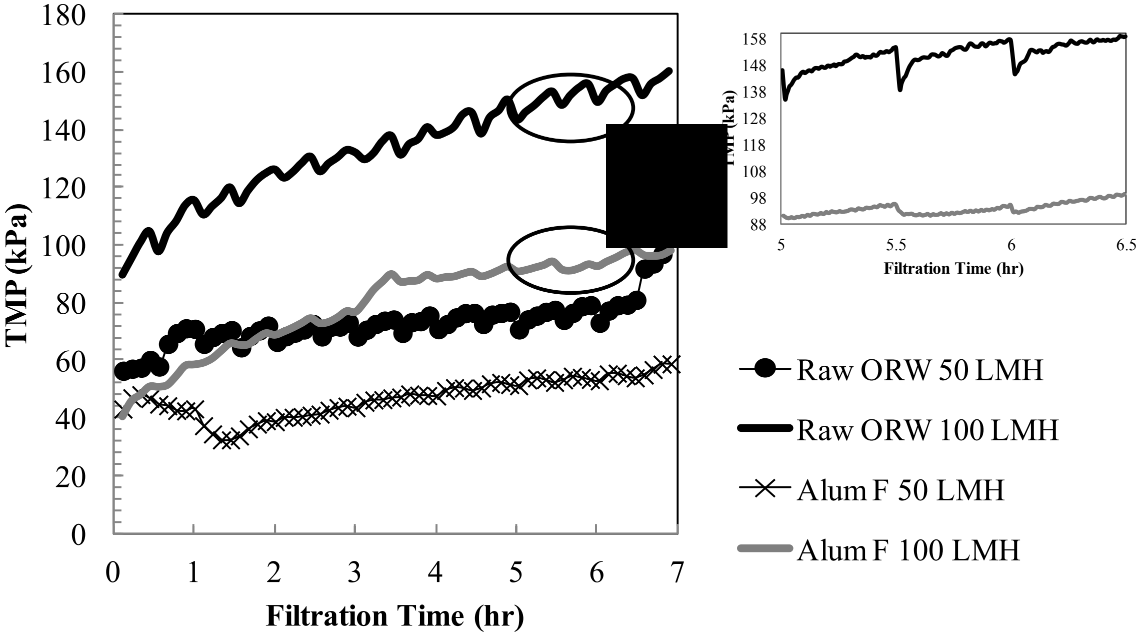

Figure 4.5. TMP versus filtration time for the 8-hour 50 LMH and 100 LMH experiments for Raw ORW and Alum F (Filtration cycle = 30 minutes, Backwash cycle = 2 minutes at 200 LMH)

4.4.2.1 Fouling Resistances

To quantify membrane fouling with time, total fouling resistance (K_F), hydraulically irreversible fouling resistance (K_{HIR}) and hydraulically reversible fouling resistance (K_{HR})

were calculated for both the 50 LMH and 100 LMH 8-hour experiments (figures 4.6 and 4.7). The significance of each fouling resistance with respect to membrane operation is as follows; the greater the K_{HIR} the greater the adsorption and thus greater the need for chemical cleans as hydraulic backwashes are ineffective; the greater the K_{HR} the more effective the hydraulic backwashes, presumably due to greater cake formation. Chemical cleans are undesirable because they increase the maintenance cost of membrane filtration, produce chemical waste effluents, and can decrease membrane productivity as membranes would be taken offline. Hydraulic backwashes also produce a concentrated waste effluent and decrease membrane productivity.

Based on figure 4.6 a), for the 50 LMH 8-hour experiments, Raw ORW produced the highest total fouling followed by Iron, Alum S and then Alum F. Figure 4.6 b) shows the increase of hydraulically irreversible fouling with time. Surprisingly Iron produced a higher K_{HIR} than Raw ORW. A possible explanation for this finding is that the turbidity-causing iron (Fe)/NOM complexes may be more easily adsorbed than the constituents in the Raw ORW. Alum S and Alum F produced lower K_{HIR}, meaning there is less foulant adsorption on the membrane. All waters show increasing K_{HIR} values with time, which may suggest that there are still vacant adsorption sites after 6-8 hours of operation at 50 LMH. Figure 4.6 c) shows the change of hydraulically reversible fouling (K_{HR}) changes with time. Cake formation for the Raw ORW starts high ($K_{HR} = 8.00\ x\ 10^{11}\ m^{-1}$) but decrease by a factor of two after 3 hours, after which time it is relatively constant. The hydraulically reversible fouling for the three pre-treated waters are considerably lower than that for the Raw ORW over the duration of the tests. All three pre-treated waters show similar hydraulically reversible fouling but K_{HR} values fluctuate with time. This may suggest that at times the pressure on the backwash-side of the membrane is not sufficiently large enough to dislodge all of the cake material. With time the cake material accumulates, further increasing flow resistance and at some point the pressure builds up and dislodges more of the accumulated cake. Comparing figures 4.6 b) and c), it can be seen that the majority of the resistance is due to hydraulically irreversible fouling as opposed to hydraulically reversible fouling. This indicates that hydraulic backwashes are not very effective at restoring membrane productivity. This finding is also supported by Waterman (2007) who also used Raw ORW in his studies.

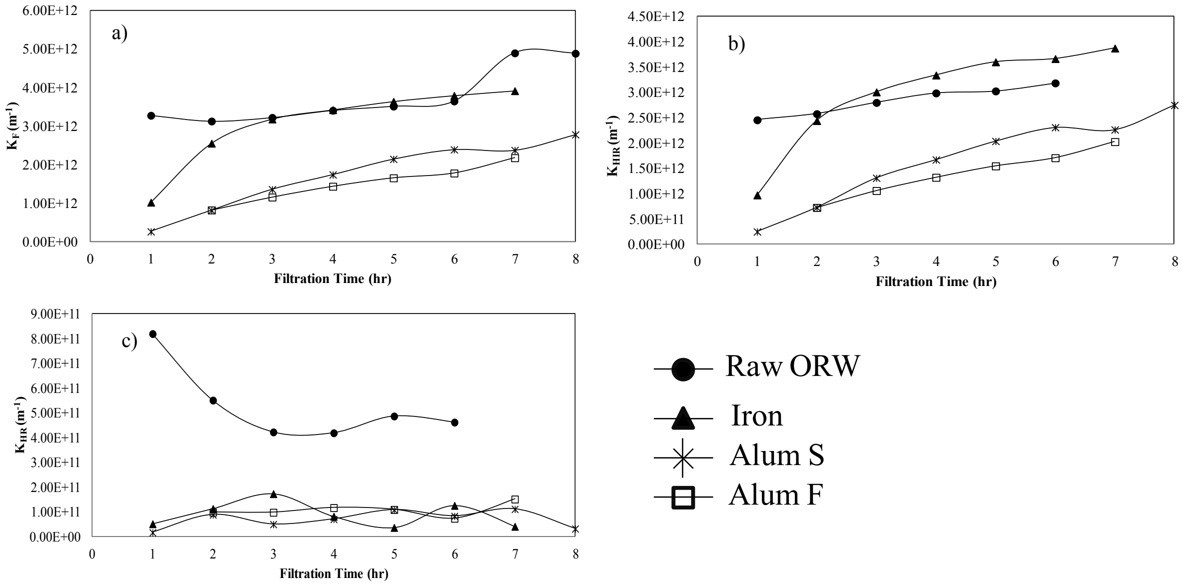

Figure 4.6. Fouling resistances for the 50 LMH 8-hour filtration experiments (Filtration cycle = 30 minutes, Backwash cycle = 2 minutes at 200 LMH): a) Total Fouling (K_F), b) Hydraulically Irreversible Fouling (K_{HIR}); and c) Hydraulically Reversible Fouling (K_{HR})

In the 100 LMH experiments it can be seen in figure 4.7 a) that Iron and Alum S led to greater fouling than Raw ORW while Alum F produced the lowest fouling. Even though the addition of coagulants as a pre-treatment is supposed to improve membrane performance, this is not always the case (Liu et al. 2005; Schafer et al. 2001; Shorney et al. 2001). As seen in figure 4.7 b), Iron and Alum S caused greater hydraulically irreversible membrane fouling than Raw ORW while Alum F produced the lowest hydraulically irreversible fouling. K_{HIR} increases with time for all waters, which again suggests that there are still adsorption sites on the membrane or within the pores available after 6-8 hours of operation at 100 LMH. Figure 4.7 c) shows K_{HR} with time - cake formation with time. Raw ORW produced the greatest cake formation followed by Iron/Alum S and then Alum F. K_{HR} fluctuates with time, as was the case for the 50 LMH 8-hour experiments. Again, when comparing K_{HIR} and K_{HR}, it can be seen that the majority of the resistance is due to adsorption, meaning hydraulic backwashes were ineffective at restoring membrane productivity. Waterman (2007) who conducted fouling experiments with Raw ORW also found this.

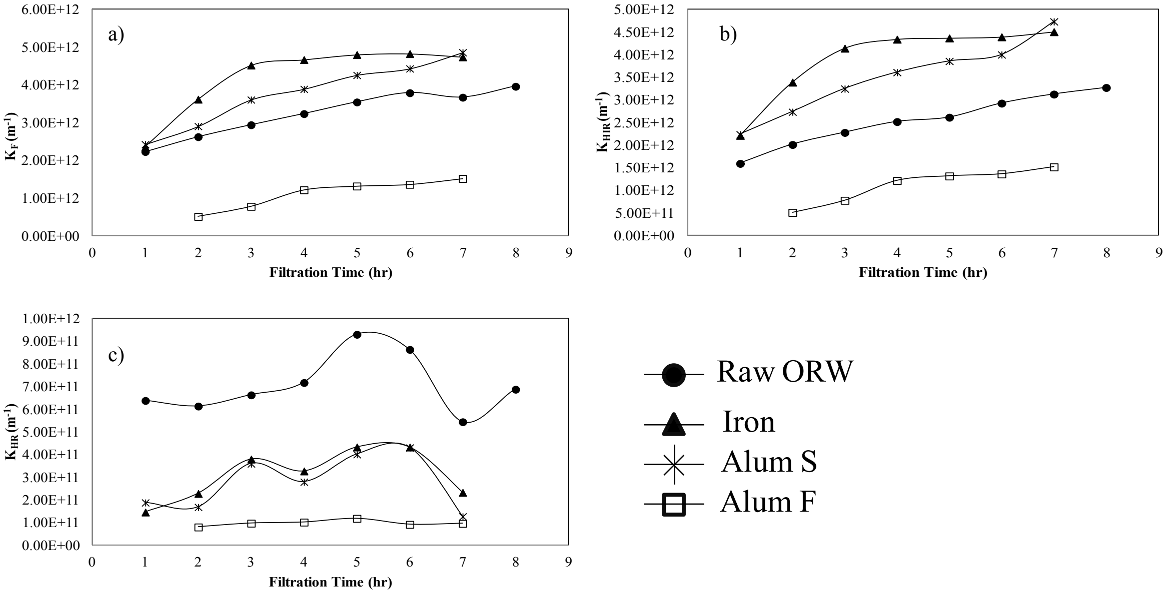

Figure 4.7. Fouling resistances for the 100 LMH 8-hour experiments (Filtration cycle = 30 minutes, Backwash cycle = 2 minutes at 200 LMH) : a) Total (K_F), b) Hydraulically Irreversible (K_{HIR}); and c) Hydraulically Reversible (K_{HR})

As seen in figures 4.6 and 4.7, different fouling trends become apparent between the 50 LMH and 100 LMH experiments. For the 50 LMH experiments, Raw ORW produced the highest total fouling while Iron produced the highest hydraulically irreversible fouling, while for the 100 LMH experiments, both Iron and Alum S produced higher total fouling and hydraulically irreversible fouling than raw ORW. At both 50 and 100 LMH, Alum F had the lowest total fouling resistance and the lowest hydraulically irreversible fouling. On the other hand, Alum S had among the lowest total fouling resistances at 50 LMH but among the highest at 100 LMH. The differences in the behaviour of Alum S and Alum F may be due to the nature, strength and reactivity of the of post sedimentation/flotation particles and is possibly related to the different coagulant aids utilized (i.e., silica versus a polymer).

Guo et al. (2009) found that operating at 60 LMH produced a more reversible type of fouling (K_{HR} - cake formation) while operating at 100 LMH produced a more adsorptive based fouling (K_{HIR}). In the case of this study, it can be hypothesized that for membrane filtration the higher pressures associated with a higher hydraulic loading (100 LMH) may result in foulants that adsorb more to the membrane or create a more compact cake that adheres more to the membrane surface.

4.4.3 Membrane Performance for the 50 LMH Multi-Day Experiments

For the 50 LMH multi-day experiments (figure 4.8) it was also found that the Raw ORW produced the most severe fouling, the Alum F produced the least severe fouling and the fouling by the Iron and Alum S waters fell somewhere in between. The large TMP decrease between 40-50 hours is due to an NaOH chemical clean and the small TMP decrease (~24 hours) is from a chlorine enhanced backwash. The NaOH chemical clean was able to reduce the TMP by 40%, 14%, 33% and 7% for Raw ORW, Iron, Alum S and Alum F, respectively. The TMP dramatically increases between 0 - 10 hours and thereafter the TMP increases slowly and gradually, especially for the pre-treated waters (figure 4.8). The initial TMP rise is most likely due to adsorption that takes place during the early stages of the experiment (Katsoufidou et al. 2005).

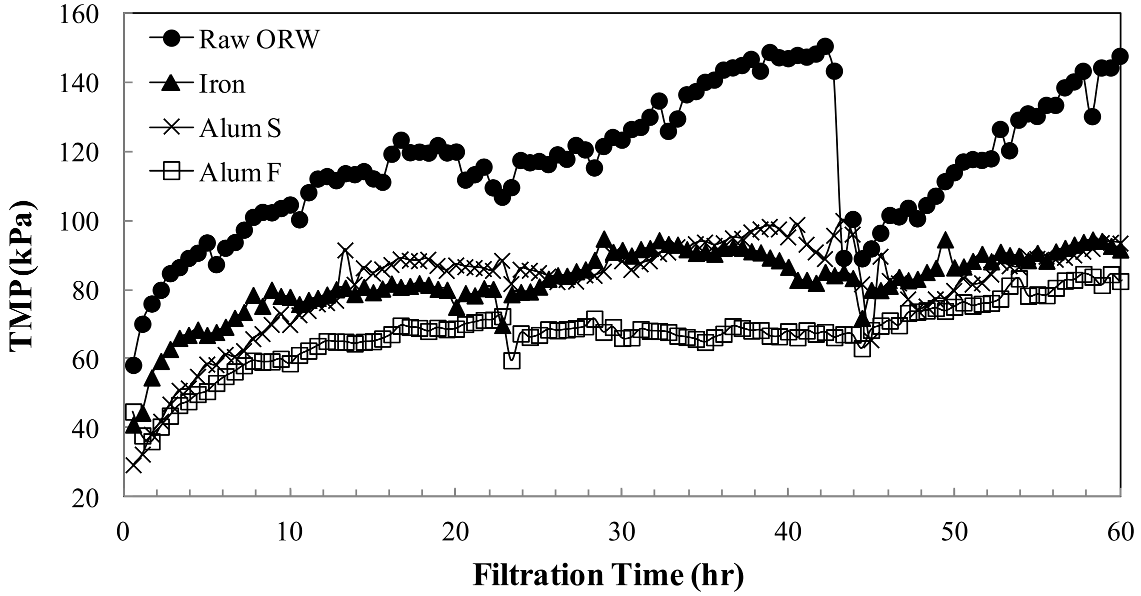

Figure 4.8. Multi-day 50 LMH filtration experiment results (Filtration cycle = 30 minutes, Backwash cycle = 2 minutes at 200 LMH, Chlorine enhanced backwash at ~24 hours and a NaOH chemical soak at ~42 hours)

4.4.3.1 Fouling Resistances

The membrane fouling resistances (K_F, K_{HIR} and K_{HR}) for the multi-day experiments were assessed with time, as shown in figure 4.9. With the exception of the iron pre-treated water, the patterns were similar to those observed during the 8-hour experiments. Figure 4.9 a) follows the same trend as figure 4.8 - expected as K_F is based on TMP. Figure 4.9 b) shows

K_{HIR} increases with time. As can be seen, Raw ORW produced the greatest K_{HIR} values and thus presumably resulted in the greatest amount of adsorption while Alum F produced the lowest. In the first 10 hours of operation, K_{HIR} increases significantly with time for all waters, which may suggest the available adsorption sites were being occupied and/or the larger pores within the membrane were being blocked. Between 10 and 20 hours, K_{HIR} for the three pre-treated waters becomes relatively steady, adsorption sites appear to have been occupied. The K_{HIR} for Raw ORW however, continues to increase with time. Figure 4.9 c) shows K_{HR} (resistance from cake formation) with time. Raw ORW produced the highest hydraulically reversible fouling while all three pre-treated waters produced significantly less. Again, the K_{HR} fluctuates with time, which may suggest that cake is not fully removed by hydraulic backwashes until a certain amount of cake resistance has formed and backwash pressure has built-up. For all waters, K_{HIR} was greater than K_{HR}, which implies that the main fouling resistance is due to hydraulically irreversible fouling.

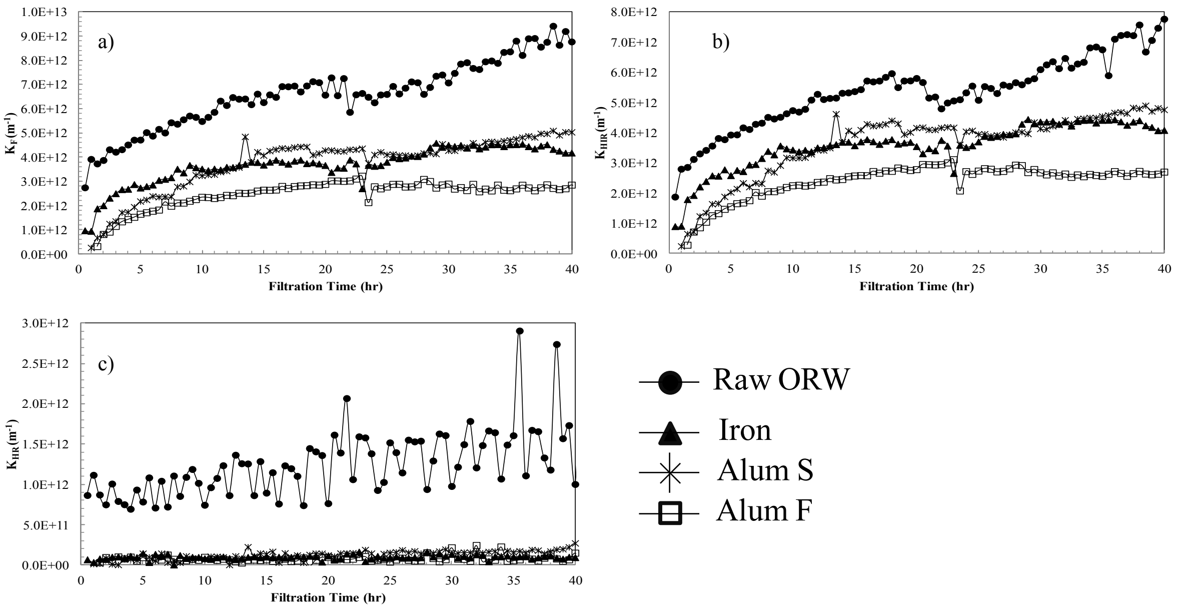

Figure 4.9. Fouling resistances for the 50 LMH multi-day experiments (Filtration cycle = 30 minutes, Backwash cycle = 2 minutes at 200 LMH): a) Total (K_F), b) Hydraulically Irreversible (K_{HIR}); and c) Hydraulically Reversible (K_{HR})

The hydraulically irreversible fouling resistance (K_{HIR}) can be categorized into two types: the chemically irreversible fouling and the chemically reversible fouling. K_{CIR} quantifies the fouling that persists after a chemical clean while K_{CR} quantifies the foulant removed by a chemical clean. A chlorine enhanced backwash was conducted, however, this cleaning method had minimal impact and therefore resistance analysis for it was not conducted. A single 0.1N NaOH chemical clean was conducted during the multi-day experiments and was seen to be effective at restoring some membrane permeability for Raw ORW (see figure 4.8), therefore resistance analysis was conducted. To compare K_{HIR}, K_{HR}, K_{CIR} and K_{CR}, fouling was assessed immediately before and immediately after the NaOH chemical cleaning step. These results can be seen in table 4.3. For all the pre-treated waters, it can be seen that K_{CIR} is greater than K_{CR}, which means that at an operation time of 40-42 hours, most of the fouling is chemically irreversible based on the 0.1N NaOH chemical clean conducted. For

Raw ORW, K_{CR} is greater than K_{CIR} which is consistent with the large decrease in TMP in figure 4.8. The greater K_{CR} value was expected as Raw ORW has a high HPO concentration - HPO being the more absorbable NOM fraction and desorbable by NaOH. Based on the chemical cleaning that was employed, Raw ORW produced the highest chemically irreversible and chemically reversible fouling while Alum F produced the lowest. The significance of this finding, assuming the chemical clean was optimized, is that operating with Raw ORW would result in membrane replacement earlier than the pre-treated waters, especially if operated with Alum F. Note that the 0.1N NaOH clean was conducted at slightly different times in the 40-42 hour range, thus differences in the timing of the TMP drop in figure 4.8. Since only one cleaning agent and method was applied, it cannot be concluded that chemical cleaning in general is effective or ineffective for this type of application.

Table 4.3 also shows the ratio of chemically irreversible fouling to hydraulically irreversible fouling. This ratio is a method in displaying chemical clean efficiency. The K_{CIR}/K_{HIR} ratio for Raw ORW is 0.51, meaning 51% of the adsorbed matter was not removed by 0.1N NaOH. Likewise, 77%, 55% and 91% of the adsorbed matter was not removed by 0.1N NaOH for Iron, Alum S and Alum F, respectively. Therefore, since the K_{CIR}/K_{HIR} ratio is smallest for Raw ORW, the 0.1N NaOH was most effective for this water and least effective for Alum F. For a different membrane and a different colored surface water Nguyen et al. (2011) calculated the ratio of chemically irreversible to hydraulically irreversible fouling (CIR/HIR) to be 0.19 for a chemical clean after 24 hours of operation - much smaller than the ratios calculated in this study. This suggests that the 0.1N NaOH chemical clean employed was a lot less effective than the 20 minute NaOCl chemical clean employed by

Nguyen et al. (2011) and suggests that other cleaning methods should be evaluated for ORW fouled membranes to establish if ORW NOM may be particularly prone to this type of fouling. Further research into which cleaning methods and agents are most beneficial for this water/membrane combination is recommended. The ratio of hydraulically reversible fouling to total fouling (K_{HR}/K_F) was also assessed. It was found that Raw ORW had the highest K_{HF}/K_F ratio of 0.11 meaning 11% of the total fouling is hydraulically reversible (associated with cake formation). All three pre-treated waters has significantly lower K_{HR}/K_F ratios. This finding is likely due to Raw ORW having the highest POC and TPI NOM concentrations, as these two water parameters are thought to contribute to cake formation on the membrane surface.

Table 4.3. Fouling resistance immediately prior and resulting from the NaOH chemical soak for the 50 LMH multi-day filtration experiments

Water	K_F (m^{-1})	K_{HIR} (m^{-1})	K_{HR} (m^{-1})	K_{CIR} (m^{-1})	K_{CR} (m^{-1})	K_{CIR}/K_{HIR}	K_{HR}/K_F
Raw ORW	8.36E+12	6.62E+12	9.07E+11	3.38E+12	4.07E+12	0.51	0.11
Iron	3.89E+12	3.80E+12	1.13E+11	2.94E+12	8.43E+11	0.77	0.03
Alum S	4.88E+12	4.64E+12	9.78E+10	2.50E+12	2.28E+12	0.54	0.02
Alum F	2.85E+12	2.61E+12	1.14E+11	2.39E+12	3.47E+11	0.91	0.04

4.4.3.2 NOM and Fractions Removal by Membrane Filtration

Membrane filtration achieved various amounts of NOM removal for all waters (table 4.1) calculated averaging TOC concentrations of the seven permeate samples collected. For the Raw ORW the TOC removal was 42%, which is a lot higher than the 15% ORW TOC removal reported by Waterman (2007) for a PES membrane with a smaller nominal MWCO

(70 kDa). The higher TOC rejection by the Matrix membrane used in this study may be due to electrostatic repulsion being the main removal mechanism. Dang et al. (2010) reported TOC removals for UF filtration with ORW between 72 - 80%, thus TOC removals obtained in the current study are reasonable. The above results demonstrate that membrane characteristics can have a significant impact on performance. The Iron pre-treatment alone removed significantly less TOC than the Alum S pre-treatment (table 4.1), presumably due to the poor separation in the pre-treatment step. However, as shown in table 4.4 when coupled with membrane filtration, the Iron pre-treatment improved the TOC removal from 33% to 66% and performed slightly better than Alum S. This may be due to the fact that the iron (Fe) present in the Iron water was forced to precipitate by the membrane. An orange precipitate was clearly evident in the tubing ahead of the membrane module when the system was dissembled at the end of the experiment. This precipitated iron (Fe) may be an iron (Fe)/NOM complex and therefore as the iron (Fe) was rejected so was the NOM. Evaluating different waters, Al-Attas (2012) and Gu et al. (1995) found that iron (Fe) forms an iron (Fe) /NOM complex with large MW fractions above 5,000 Da that are hydrophobic in nature. The current study's water analysis results coincide with these findings as the Iron water was found to have a large MW fraction above 30 kDa and a large HPO NOM concentration (table 4.1). The additional TOC removals resulting from membrane filtration of the Alum pre-treated waters were only 1% and 4% for Alum S and Alum F, respectively. It was found that Alum F (Alum + a polymer + floatation) with membrane filtration produced the highest TOC removal (72%) and DOC removal (69%) versus Alum S with 64% TOC removal and 60% DOC removal. Pera do Amaral et al. (2013) coupled dissolved air floatation (DAF) with MF and was able to achieve 52% DOC removal from fresh water while another study

from Teixeira & Rosa (2006) coupled DAF with NF and was able to achieve 72.5% DOC removal also from fresh water. However, these two studies used algal-impacted waters, which are expected to behave differently.

Table 4.4. Combined (pre-treatment + filtration) NOM removals for each water

Treatment	TOC Removal (%)	DOC Removal (%)	HPO Removal (%)	TPI Removal (%)	HPI Removal (%)
Iron	33	25	-	-	-
Alum S	63	59	-	-	-
Alum F	68	65	68	82	22
Raw ORW + Mem Filt	42	36	-	-	-
Iron + Mem Filt	66	62	-	-	-
Alum S + Mem Filt	64	60	-	-	-
Alum F + Mem Filt	72	69	69	94	23

4.4.4 Backwash Efficiency (BWE)

Backwash efficiency (BWE) was calculated for every experiment and water. This was accomplished by calculating the BWE for every second backwash cycle throughout the experiments. Results for the 50 LMH multi-day experiment can be seen in figure 4.10 and averaged BWE values of the entire experiment length can be seen in table 4.5. It is shown in figure 4.10 that the BWE fluctuate throughout the duration of the experiment, which coincides with the results of K_{HR}. The BWE with time trend supports the suggestion that cake formation is not fully removed by hydraulic backwashes until a certain amount of cake resistance has formed. It can also be seen in figure 4.10 that prior to 20 hours the differences in BWE between the waters is greater than the differences in BWE after 20 hours - especially for Alum S. As the experiments approach 40 hours, the BWE seems to converge and all waters produce similar BWEs. Caution should be taken when applying blocking law models or analyzing select hydraulic backwash data due to BWE fluctuations.

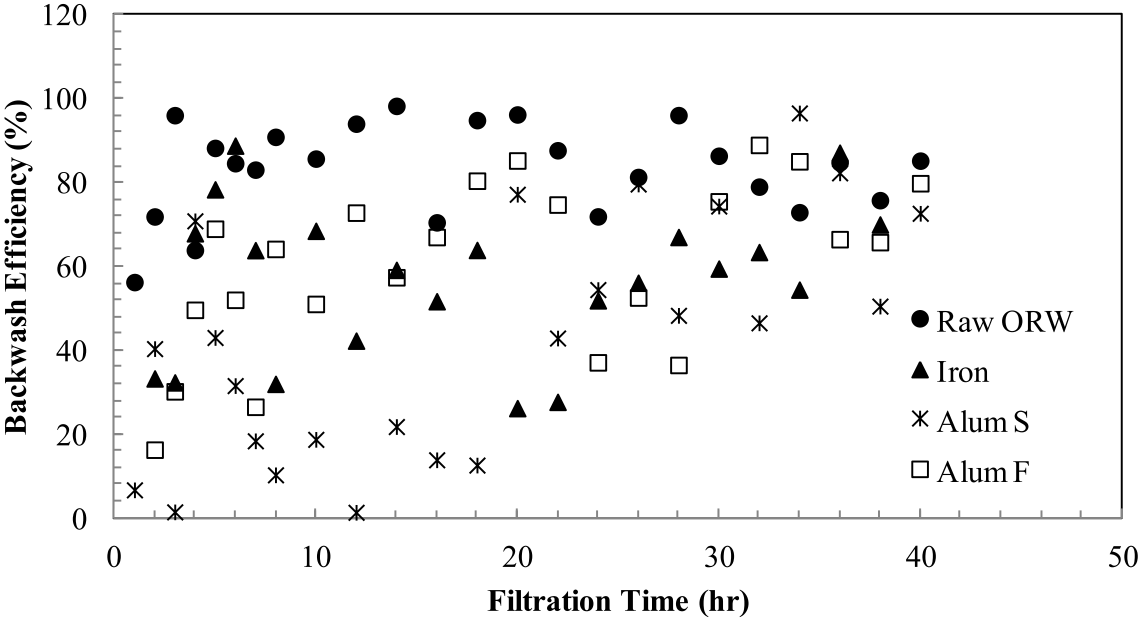

Figure 4.10. BWE calculated for the 50 LMH multi-day fouling experiments (Filtration cycle = 30 minutes, Backwash cycle = 2 minutes at 200 LMH)

Table 4.5 shows that the Raw ORW produced the highest BWE for all experiments in spite of having the largest fouling resistance. Raw ORW has the highest POC and TPI NOM concentration which would lead to greater cake formation (Zularisam et al. 2011) and as backwashing removes this cake formation, it is reasonable that Raw ORW has the highest BWE. Raw ORW also produced the most consistent BWE values between the three experiments when compared to the pre-treated waters, which can be seen from the standard deviation (STD) and the coefficient of variance (CV) values in table 4.5. Waterman (2007) who also conducted Raw ORW fouling experiments at 50 LMH (30 min filtration, 1 min backwash) and 100LMH (30 min filtration, 2 min backwash) using a different membrane found the average BWEs were 79% and 75-80% respectively, which is relatively close to the 83% found in this study.

The BWE of the 8-hour 100 LMH experiments were higher than those for the 8-hour 50 LMH experiments. This is possibly caused by the membrane being exposed to a greater mass of NOM (i.e., foulant) and results in greater cake formation which is presumably removed by the backwashing. Changes in fouling characteristics from increases in pressure and hydraulic loading (Guo et al. 2009) may also result in differences for BWE. The multi-day experiments resulted in greater average BWE. This may be attributed to the changing nature of fouling - cake-related fouling, which should be controlled by backwashing, becomes dominant.

Table 4.5. Average BWE, standard deviation, and coefficient of variance for the 8-hour 50 LMH and 100 LMH experiments and the 50 LMH multi-day experiments

Water	50 LMH 1-day			100 LMH 1-day			50 LMH 3-day		
	Avg (%)	STD	CV	Avg (%)	STD	CV	Avg (%)	STD	CV
Raw ORW	80	14	18	83	10	12	83	11	13
Iron	40	30	74	58	32	54	57	18	32
Alum S	40	23	59	51	29	56	42	29	68
Alum F	37	15	40	66	22	34	60	20	34

The ratios between BWE and K_{HR} were calculated for the multi-day 50 LMH experiments. This was done to determine if a correlation existed between BWE and K_{HR}, as these two variables should be related. As can be seen in figure 4.11, the BWE/K_{HR} ratios are very similar for the pre-treated waters and overlap when the ± 95% confidence intervals are applied, i.e. the BWE/K_{HR} ratios for the pre-treated waters are not statistically different. This indicates that a correlation exists between BWE and K_{HR} for the pre-treated waters but not for the Raw ORW. The BWE and K_{HR} may not correlate with each other for the Raw ORW due to the Raw ORW having much higher POC and TPI concentrations.

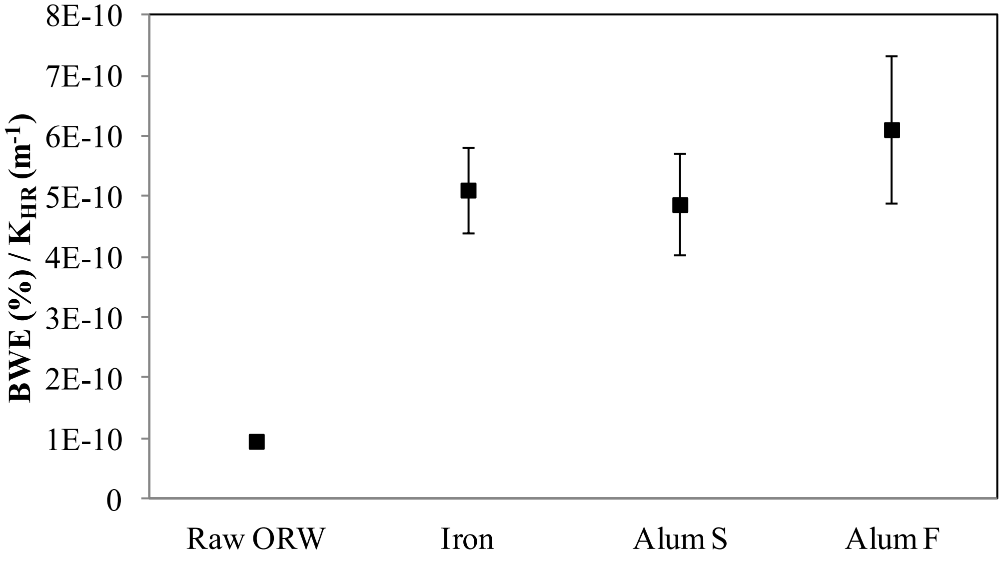

Figure 4.11. Average ratio value and ± 95% confidence interval for BWE/KHR for the 50 LMH multi-day experiments

4.4.5 Statistical Analysis

T-tests were conducted to help identify possible statistical relationships between the fouling resistances and different water characteristics. In order to conclude statistical significance, for a degrees of freedom equalling 2 [4 data points (n) - 2], the t-value must be greater than 4.303 or smaller than -4.303. Earlier analysis of the data showed that the Iron pre-treated water produced turbidity that interfered with UV-254 measurements. Therefore, some statistical analysis was also conducted when Iron data was excluded. In this case, t-values must be larger than 12.706 or smaller than -12.706 for statistical significance. Variables found to have statistical significance were also plotted for graphical inspection of linearity (Mendenhall, et al., 2009).

4.4.5.1 Impact of Water Characteristics on Fouling Resistances and BWE for the 8-Hour Experiments

T-test results for the 50 LMH 8-hour experiments are presented in Table 4.6. K_F has statistically significant relationships with TOC, DOC, HPO NOM, UV-254 (without Iron) and SUVA (without Iron). These findings show that a high TOC water will foul membranes more than a low TOC water. When the Iron data was excluded, statistical analysis showed that UV-254 and SUVA (indicators of HPO NOM) were strongly linked to K_F. Even though membrane fouling usually cannot be attributed to individual water characteristics, HPO NOM is often the main membrane foulant (Zularisam et al. 2011; Gray and Bolto 2004; Jones and O'Melia 2001).

Statistical significant relationships between K_{HIR} and HPO NOM, UV-254, UV-254 (without Iron) and SUVA (without Iron) were also found. This was expected as these parameters represent the HPO fraction of NOM, which is quite absorbable. Nilson & DiGiano (1996) also found the HPO fraction to contribute to fouling. Zularisam et al. (2007) believes that the HPI fraction of NOM is mainly responsible for adsorption because of its high polysaccharide-like and protein-like foulant properties (Amy 2008). Lastly, t-test results show a statistical relationship between K_{HR} and POC, TPI NOM, and UV-254 (without Iron). The K_{HR} relationship with POC and TPI NOM was expected as these two parameters are thought to contribute to cake formation on the membrane surface (Zularisam et al. 2007).

According to Zularisam et al. (2007) the HPO fraction of NOM is responsible for concentration polarization and therefore should be removed by hydraulic backwashes. T-tests were conducted on the average BWE and water characteristics. It was expected that BWE be statistically related to POC and TPO NOM, which was found to be the case.

For the 50 LMH experiments there were many statistically significant relationships, however, for the 100 LMH experiments, no statistically significant relationships were found between K_F, K_{HIR} and K_{HR} with any of the water characteristics. This is probably because operating below critical flux and above critical flux causes different fouling characteristics, as hypothesized by Guo et al. (2009). The 100 LMH experiments and water characterizations could not be repeated because we exhausted that water sample.

Table 4.6. t-values for fouling resistances and water characteristics for the 50 LMH 8-hour experiments

Parameter	K_F	K_{HIR}	K_{HR}	BWE
TOC	5.05	-	-	-
DOC	6.49	-	-	-
POC	-	-	13.32	10.80
Hydrophobic	8.16	4.47	-	-
Transphilic	-	-	8.82	5.70
UV-254	-	4.88	-	-
UV-254 (without Iron)	110.37	139.50	12.73	-
SUVA (without Iron)	72.26	418.17	-	-

NOTE: • Omitted values are statistically insignificant
• For a statistically significant linear relationship when Iron was excluded, -12.706 > t-value > 12.706. When the Iron was included, -4.303 > t-value > 4.303

4.4.5.2 Impact of Water Characteristics on Fouling Resistances and BWE for the Multi-Day Experiments

The t-test results for multi-day the fouling resistances and the feed water characteristics are presented in table 4.7. Average values for K_F, K_{HIR}, K_{HR}, and BWE were found from the beginning of the experiment up until the chemical clean (40 hours) and t-tests were conducted. T-tests were also performed for average values of K_F and K_{HIR} for 8 hours of operation to compare with the results of the 8-hour tests. Since only one NaOH chemical clean was conducted, only one value for K_{CIR} and K_{CR} was used for t-tests. No statistical significant relationships were found between K_{CIR} and K_{CR} and water quality characteristics. Limited data concerning chemical cleans may have influenced this.

The t-tests showed $K_{F\ (0\text{-}8\ hours)}$ was statistically related to TOC, DOC, HPO NOM, TPI NOM, UV-254 (without Iron) and SUVA (without Iron), the same as the 8-hour tests. This suggests that during the initial stages of the experiment the more adsorbable HPO fraction influences total fouling. For the 0 to 40 h period the only statistically significant relationship was with POC. A possible explanation for the significant relationship between POC and $K_{F\ (0\text{-}40\ hours)}$ is that the fouling resistance from K_{HIR} becomes relatively constant after 10-15 hours of operation. The fouling caused by adsorption no longer plays a significant role in membrane fouling resulting in POC becoming the main foulant during long filtration experiments. Next, the relationship between the water quality parameters and the hydraulically reversible and hydraulically irreversible fouling resistances were examined. $K_{HR\ (0\text{-}40\ hours)}$ was found to have a statistically significant relationship was POC, and TPI NOM. This was expected based on the literature and the findings from the 50 LMH 8-hour t-test results as these two parameters are responsible for cake formation (Qu et al. 2012; Zularisam et al. 2007). To compliment the findings for $K_{HR\ (0\text{-}40\ hours)}$, t-tests for BWE were also conducted. It was found that for the 50 LMH multi-day experiments, TPI NOM had a statistically significant relationship with BWE. It was also expected that POC have a significant relationship with BWE (based on the $K_{HR\ (0\text{-}40\ hours)}$ results), however, for the 50 LMH multi-day experiments, the POC t-value was slightly below the statistically significant threshold t-value. None of the water characteristics measured were found to have a statistically significant relationship with 0-40 hour K_{HIR} values, while the 0-8 hr K_{HIR} values were found to have statistically significant relationships with TOC, DOC, HPO NOM, UV-254 (without Iron) and SUVA (without Iron). The similarity in pattern with total fouling suggest that adsorption-related hydraulically irreversible fouling during the initial stages of the experiments was related to the HPO fraction of NOM. Also, the statistical analysis conducted for the $K_{HIR\ (0\text{-}8\ hours)}$ (8-hour and multi-day experiments) has shown that both experiments yielded similar results and that the HPO fraction of NOM is statistically responsible for hydraulically irreversible fouling within the first day of operation.

Table 4.7. t-values for fouling resistances and water characteristics for the 50 LMH multi-day experiments

Parameter	K_F		K_{HIR}		K_{HR}	BWE
	0-40 hours	0-8 hours	0-40 hours	0-8 hours	0-40 hours	0-40 hours
TOC	-	11.57	-	176.30	-	-
DOC	-	7.55	-	20.66	-	-
POC	4.46	5.10	-	-	11.59	*3.14*
Hydrophobic	-	4.70	-	7.90	-	-
Transphilic	-	4.50	-	-	7.04	4.70
UV-254 (without Iron)	-	174.70	-	61.85	-	-
SUVA (without Iron)	-	95.22	-	87.79	-	-

NOTE: • Omitted values are statistically insignificant

• For a statistically significant linear relationship when Iron was excluded, -12.706 > t-value > 12.706. When the Iron was included, -4.303 > t-value > 4.303

4.5 Conclusions

Ottawa River water is a coloured river water with a high hydrophobic fraction. This bench-scale study investigating the impact of different pre-treatments on Ottawa River water on hollow fiber UF membrane filtration found:

(1) Both Alum pre-treatments of the high TOC and HPO Ottawa River water at two different water treatment plants resulted in decreases in TOC (63% and 68%) and HPO NOM (56% and 68%). The pre-treatments helped to reduce fouling, however the remaining TOC and HPO NOM caused the hydraulically and chemical irreversible fouling to still be significant.

(2) The 50 LMH and 100 LMH 8-hour experiments showed different fouling trends which may suggest fouling characteristics change based on flux. It is hypothesized that waters subject to higher pressures associated with higher hydraulic loading during membrane

filtration may produce a foulant that is more difficult to hydraulically dislodge or more easily adsorbed to the membrane.

(3) The Alum F pre-treatment coupled with membrane filtration, which has not been researched for the treatment of high NOM and HPO waters until now, consistently showed better performance than the alternative pre-treatment options studied. It showed lower overall fouling and lower hydraulically irreversible fouling, possibly because this pre-treatment resulted in lower HPO and NOM concentrations. Thus, this thesis' hypothesis was correct. These results need to be confirmed for other similar waters and different membranes. As the water treatment plant with floatation used a different coagulant aid than the plant using sedimentation, experiments need to be conducted to establish to what extent the improved performance was due to floatation and due to the coagulant aid.

(4) Hydraulically reversible fouling and backwash efficiency were found to fluctuate with time. To accurately quantify this phenomena, the bench-scale membrane system needs to be operated for several days so representative backwash efficiency and hydraulically reversible fouling resistances can be generated. The fluctuations may imply that cake formation adheres to the membrane and is not fully removed until enough backwash pressure has developed.

(5) During the initial 8 to 10 hours of operation the fouling resistance increased at a significant rate, and from then on it was much more gradual. This suggests that fouling characteristics change with time. Thus, it is recommended that future fouling experiments be conducted lasting three days or more to obtain results that are more representative of full-scale performance.

(6) It was found that hydraulically irreversible membrane fouling was much greater than the hydraulically reversible membrane fouling for all the waters used in this study. This finding may be due to the fact that ORW has a high HPO concentration, which is the more adsorbable NOM fraction.

(7) Statistical analysis suggests that the HPO fraction of NOM was responsible for hydraulically irreversible fouling during the initial stages of membrane filtration (0 to 8 hours), which may be attributed to adsorption. It was also found that POC and TPI fractions of NOM during subcritical flux operation appear to be primarily responsible for the hydraulically reversible fouling, which may be attributed to the role of POC and TPI fractions in cake formation on the membrane surface. The HPO fraction of NOM was found to be statistically related to the total membrane fouling during the first 8 hours of operation, while POC was found to be statistically significant during the 40 hours of operation. This may suggest that after a certain time, there is a shift in which constituent is the main foulant - HPO NOM during the initial stages of membrane filtration and POC during the later.

(8) Further investigation into alternative cleaning procedures is required as the NaOH cleaning was not very effective for some of the pre-treated waters. For Raw ORW-fouled membranes the chemically reversible fouling resistance was greater than the chemically irreversible resistance. However, the opposite was observed for the pre-treated waters as the chemically reversible fouling resistance was quite a bit smaller than the chemically irreversible fouling resistance.

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CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

A bench-scale UF membrane system was successfully assembled and programmed to mimic the operation of a full-scale membrane treatment plant. The UF membrane system and membrane module proved effective at conducting fouling experiments using raw and pre-treated ORW. The following conclusions were drawn from pre-treatment analysis and fouling experiments:

(1) Both Alum pre-treatments of the high TOC and HPO Ottawa River water at two different water treatment plants resulted in decreases in TOC and HPO NOM, but significant concentrations remained. The pre-treatments helped to significantly reduce fouling.

(2) Operating below (50 LMH) and above (100 LMH) critical flux resulted in different fouling trends. It is hypothesized that waters subject to higher pressures and hydraulic loading during membrane filtration may produce a foulant that is more difficult to hydraulically dislodge or more easily adsorbed to the membrane.

(3) The Alum F pre-treatment coupled with membrane filtration, which has not been researched for this application until now, showed lower hydraulically irreversible fouling, perhaps due to having a lower HPO concentration, and slightly greater NOM removal. Since the Alum F pre-treatment (alum + polymer + floatation) consistently outperformed the other pre-treatments, further research should be considered to determine why.

(4) Hydraulically reversible fouling and backwash efficiency were found to fluctuate with time. This may imply that cake formation adheres to the membrane and is not fully removed until enough backwash pressure has developed.

(5) During the initial 8 to 10 hours of operation the fouling resistance increased at a significant rate, and from then on it was much more gradual. This suggests that fouling characteristics change with time. Thus, it is recommended that future fouling experiments be conducted lasting three days or more to obtain results that are more representative of full-scale performance.

(6) It was found that hydraulically irreversible fouling was greater than hydraulically reversible fouling for the membrane and waters used in this study. This finding may be due to the fact that ORW has a high HPO concentration which is the more adsorbable NOM fraction.

(7) Statistical analysis suggests that the HPO fraction of NOM was responsible for hydraulically irreversible fouling during the initial stages of membrane filtration (0 to 8 hours), which may be attributed to adsorption. It was also found that POC and TPI fractions of NOM appear to be primarily responsible for the hydraulically reversible fouling, which may be attributed to the role of POC and TPI fractions in cake formation on the membrane surface. The HPO fraction of NOM was found to be statistically related to the total membrane fouling during the first 8 hours of operation, while POC was found to be statistically significant during the 40 hours of operation. This may suggest that after a certain time, there is a shift in which constituent is the main foulant - HPO NOM during the initial stages of membrane filtration and POC during the later.

(8) Further investigation into alternative cleaning procedures is required as the NaOH cleaning was not very effective for some of the pre-treated waters. For Raw ORW-fouled membranes the chemically reversible fouling resistance was greater than the chemically irreversible fouling resistance. The opposite was observed for the pre-treated waters as the chemically reversible fouling resistance was quite a bit smaller than the chemically irreversible fouling resistance.

5.2 Recommendations

(1) Due to the differences in fouling with time it is recommended that experiments that are 3 days or longer be used instead of 1 day experiments. During the first day of operation adsorption is apparent and fouling has not stabilized.

(2) As permeate samples collected in the first day of operation indicated some organic compound leaching, future experiments should investigate the source of the leaching, possibly via GS-MS analysis of the leachate. Also as a precaution, leachate analysis should start in the second day of operation.

(3) It was found that the HPO fraction of NOM was responsible for hydraulically irreversible fouling and TPI was responsible for hydraulically reversible fouling. Two to five hour long filtration experiments should be conducted using separate NOM fractions to assess the fouling potential of each individual fraction.

(4) Create a membrane module that runs outside-in and compare the performance with the module used in this study on different pre-treatment methods.

(5) Use IRA-958 resins to further fraction the hydrophilic NOM into hydrophilic neutral and hydrophilic charged to study the effects on membrane fouling.

(6) The cleaning procedure with 0.1N NaOH was only effective for Raw ORW. Research cleaning methods used on membranes subjected to pre-treated waters (coagulation/flocculation).

(7) The UF system must be given time to reach the pure water TMP with RO water prior to introducing the feed water to the membrane. Doing this will allow each experiment to start at the same pressure and thus making comparisons easier and fouling indices analysis possible.

(8) Conduct a pure water test for every new membrane module and find the critical flux for every type of water used.

(9) As the water treatment plant using floatation used a different coagulant aid than the plant using sedimentation, experiments need conducted to establish to what extent the observed improved performance was due to the coagulant aid and due to floatation.

(10) As the fouling resistance of the Alum floated water seemed to reach a pseudo-steady state, two types of experiments are recommended. First, experiments with longer periods between chemical cleans. Second, experiments with both shorter and longer filtration periods between backwashes.

(11) As membrane characteristics greatly impact performance, similar experiments should be conducted with other membrane types.

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APPENDIX A: XAD8/XAD4 Resin and Sample Preparation

The procedure which was used for NOM characterization in this study was adapted from Thurman and Malcolm (1981):

XAD8/XAD4 Column/Resin Preparation:

1) The resin was cleaned as per manufacturers recommendations.

2) Rinse column for 1-3 hours with 0.1 N NaOH

3) Rinse column with hot RO water. Take column from stand, seal with stopper and shake vigorously

4) Rinse column with 10% 1M HCL acid once

5) Pass RO water through the column. Analyse the RO water before and after the column with a TOC analyser. If the effluent has a higher concentration than the influent, repeat steps 3 and 4. Do this until effluent and influent have the same TOC concentration.

Sample Preparation:

1) Filter sample with a 0.45 μm membrane filter. This removes precipitates.

2) Lower pH of sample to below 2 with 10% HCL.

3) Pass the sample through the column of XAD8 and/or XAD4 resin.

4) Allow the first 100mL of column effluent to go to waste.

5) Collect remaining effluent from column. Pass the collected effluent twice more through the column - the sample should pass through the column a total of three times.

6) Conduct desired analysis on effluent.

APPENDIX B: Total Iron Stock Solution and Calibration

Total iron concentrations were determined. Below is the instructions for producing the stock solution required to make standards for calibration.

The stock solution was made as follows:

(1) Add 20 mL of concentration H_2SO_4 to 50 mL of RO water

(2) Dissolve 1.404 g of ferrous ammonium sulfate hexahydrate

(3) Add 0.1 M of potassium permanganate dropwise until a faint pink colour persists

(4) Dilute to the 1000 mL mark and mix

(5) 1.00 mL of stock iron solution = 200 μg Fe

The 200 ppm Fe stock solution was diluted to a 10 ppm Fe solution, which was used as the injection solution for calibration purposes. The spectrophotometer was calibrated by injecting a known volume of 10 ppm Fe solution into the 10 mL sample cells and then filled with RO water. The table below shows the injection volumes, actual concentrations of the standards, and the concentrations returned by the spectrophotometer.

Table B.1. Injection volumes with corresponding iron concentrations

Injection Volume (mL)	Actual Iron Concentration (mg/L)	Iron Concentration from Spectrophotometer (mg/L)
0.0	0.0	0.0000
0.1	0.1	0.0367
0.3	0.3	0.0103
0.5	0.5	0.0173
1.0	1.0	0.0330
1.5	1.5	0.0473
1.7	1.7	0.0500
2.0	2.0	0.0580
2.5	2.5	0.0660
3.0	3.0	0.0783
5.0	5.0	0.1300
10.0	10.0	0.1950

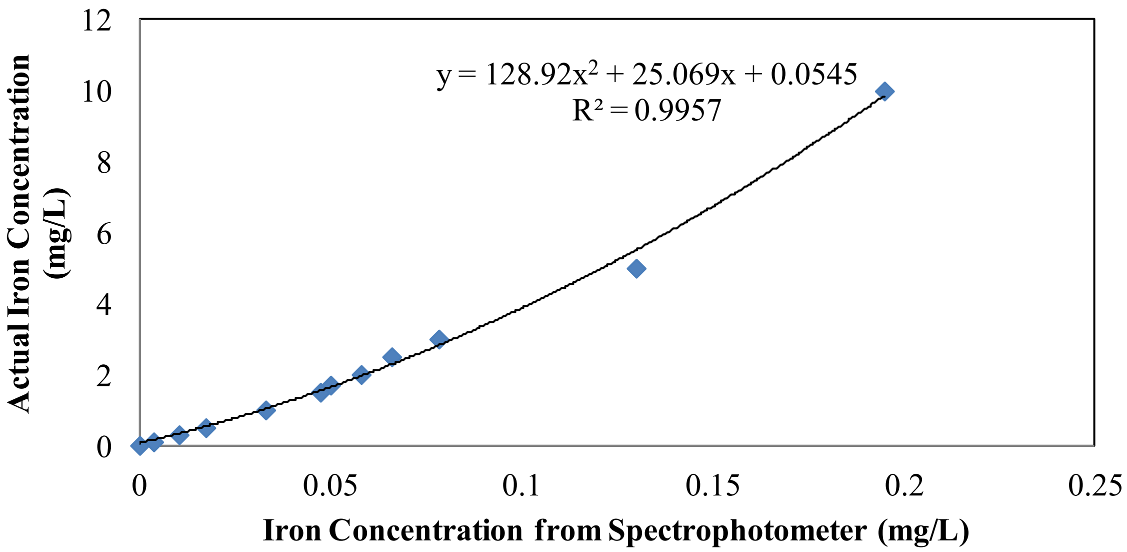

Figure B.1. Relationship between actual and measured iron concentrations

APPENDIX C: TOC-UV Relationship

A UV-TOC correlation was made for Raw ORW and its permeates, Alum S and its permeate and Alum F and its permeates. The UV-TOC correlation cannot be used for Iron water or its permeates because they contain iron flocs/particles which interfere with the UV measurements.

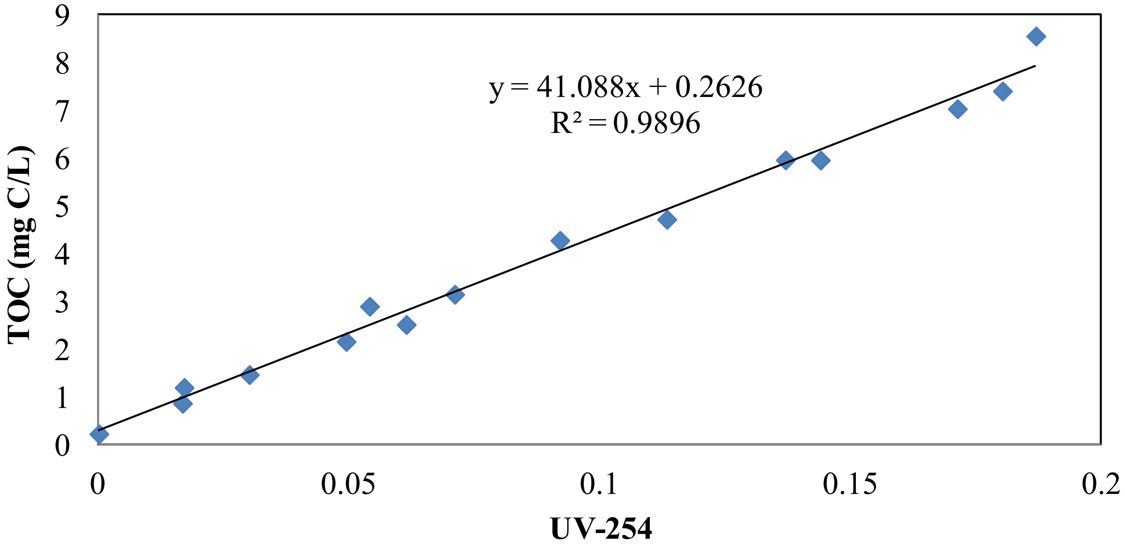

Figure C.1. UV-TOC correlation

The UV-TOC relationship was used if the TOC or UV machine were unavailable.

APPENDIX D: Pure Water Flux Results

The pure water flux was determined by running RO water through the membrane at a low flux. After recording the TMP for 15 minutes the flux was increased. This procedure continued in a step-wise fashion. The results of the pure water flux can be seen below.

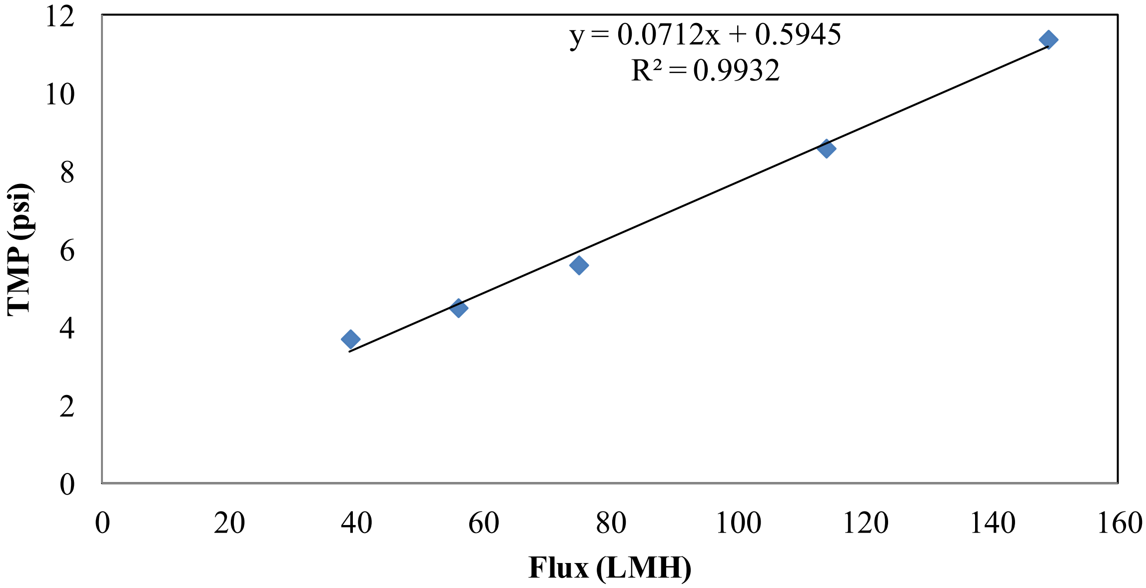

Figure D.1. Pure Water Flux

The pure water flux results were used to determine the resistance of a virgin membrane K_m (m^{-1}). From the above relationship:

$$TMP = 0.0712\, x\, J\ +\ 0.5945 \tag{D.1}$$

where TMP is in units PSI and flux is in units LMH.

$$K_m = \frac{TMP}{\mu J} \tag{D.2}$$

where TMP is in units kg $m^{-1}s^{-2}$, viscosity (μ) is in units kg m^{-1} s^{-1} and flux is in units $m^3m^{-2}s^{-1}$.

APPENDIX E: Raw Data from TOC Analyzer versus TOC Concentration (ppm) Relationship

The TOC analyzer counts the carbon particles that are oxidized from the samples. These carbon particles are expressed as Raw Data. When the TOC analyzer is blanked with the persulfate reagent, the Raw Data can then be expressed in terms of ppm Carbon.

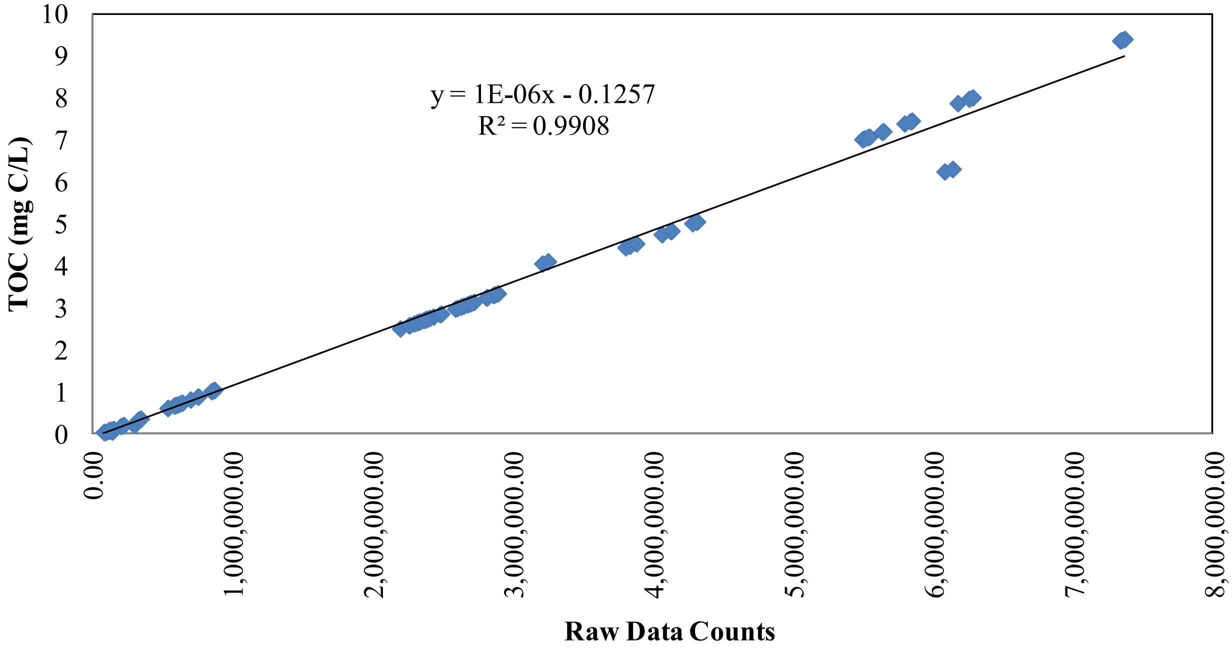

Figure E.1. Relationship between Raw Data and ppm Carbon

If the TOC machine could not be blanked, the above relationship could be used to determine the ppm of Carbon in the sample based on the Raw Data count.

APPENDIX F: Membrane Permeate Concentrations 50 LMH Multi-Day Experiments

Due to low permeate production, permeate samples were collected every 2 hours for analysis. Figure F.1 shows the permeate TOC concentrations over 72 hours of filtration time for the multi-day 50 LMH experiments. Oddly, the permeate TOC concentration prior to 27 hours is higher than the TOC concentration in the feed water. The same trend was found for the 8-hour experiments. Since glycerol is the membrane preservative, membrane permeate samples were analyzed to determine if glycerol was leaching from the membrane. It was found that glycerol was not leaching from the membrane as glycerol concentrations were zero. It is hypothesized that another organic is leaching from the membrane.

Aside from high NOM concentrations during the first day of operation, NOM concentrations become consistent between 27 - 72 hours. It can be seen that the Raw ORW produced the highest NOM concentration while Alum F produced the lowest.

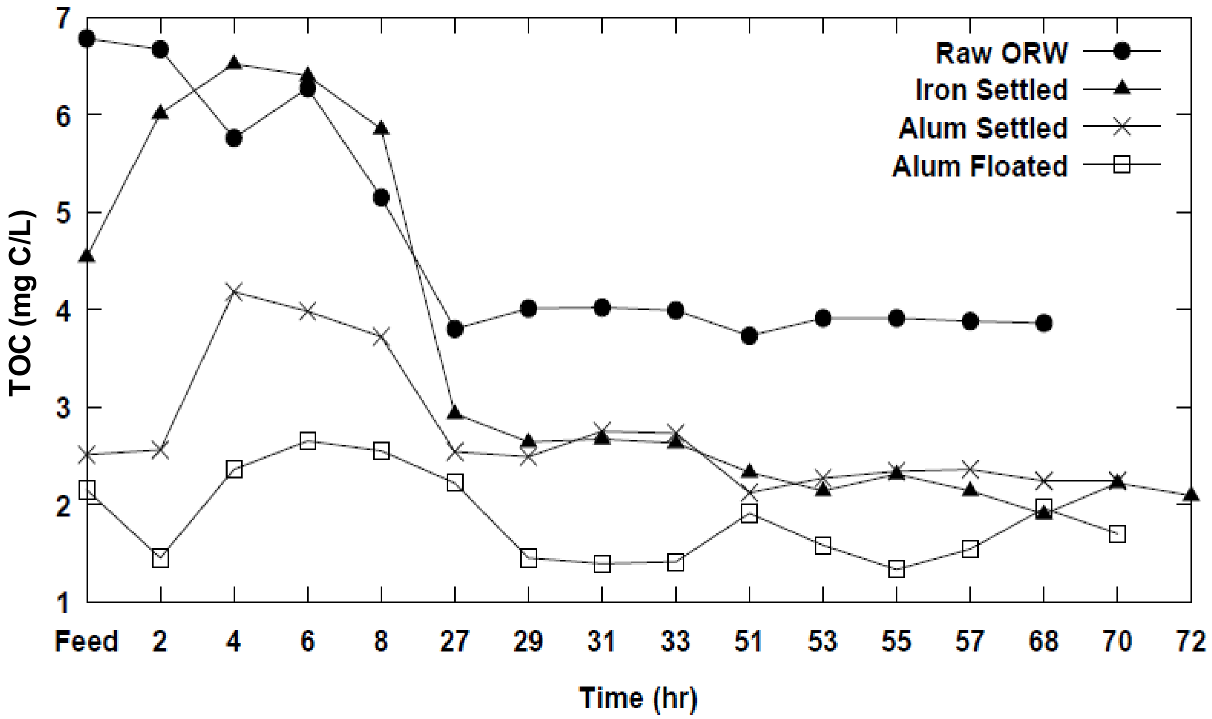

Figure F.1. Membrane permeate concentrations for the multi-day experiments at 50 LMH

APPENDIX G: Fouling Resistance Example Calculation for Raw ORW Multi-Day Experiment

From the pure water flux test (Appendix D):

$$TMP = 0.0712\, x\, J \;+\; 0.5945 \tag{D.1}$$

Using a flux of:

$$J = 50\ \frac{L}{m^2 hr}$$

$$TMP = 4.15 \text{ PSI}$$

Convert PSI to $\frac{kg}{ms^2}$:

$$TMP = 4.15\ PSI\ x\ \frac{6894.76\,\frac{kg\,m}{s^2 m^2}}{1\ PSI} = 28613.3\,\frac{kg}{ms^2}$$

<u>Calculating membrane resistance (K_m):</u>

$$J = 50\ \frac{L}{m^2 hr} = 0.0000139\ \frac{m^3}{m^2 s}$$

$$J = \frac{TMP}{\mu \cdot (K_m)} \Rightarrow \tag{G.1}$$

$$K_m = \frac{TMP}{\mu \cdot J} = \frac{28613.3\ \frac{kg}{ms^2}}{\left(0.001\ \frac{kg}{m \cdot s}\right) \cdot \left(0.0000139\ \frac{m^3}{m^2 \cdot s}\right)} = 2.06\ x\ 10^{12}\ m^{-1}$$

<u>For calculating total fouling resistance (K_F) at 1 hour of operation:</u>

$$TMP\ before\ hydraulic\ backwash = TMP\ before = 10.75\ PSI = 74118.67\ \frac{kg}{ms^2}$$

$$J = \frac{TMP}{\mu \cdot (K_m + K_F)}\ \Rightarrow \tag{G.2}$$

$$K_F = \frac{TMP\ before}{\mu \cdot J} - K_m = \frac{74118.67\,\frac{kg}{ms^2}}{\left(0.001\,\frac{kg}{ms}\right) \cdot \left(0.0000139\,\frac{m^3}{m^2 s}\right)} - 2.06 x 10^{12}\ \ m^{-1}$$

$$K_F = 3.27 x 10^{12} m^{-1}$$

For calculating hydraulically irreversible (K_{HIR}) and reversible (K_{HR}) fouling resistance at 1 hour of operation:

$$TMP\ after\ hydraulic\ backwash = TMP\ after = 9.097\ PSI = 62721.6\ \frac{kg}{ms^2}$$

$$J = \frac{TMP}{\mu \cdot (K_m + K_{HIR} + K_{HR})} \tag{G.3}$$

After a hydraulic backwash the hydraulically reversible fouling resistance should be zero, so $K_{HR} = 0$. Substituting this into eq. Eq G.3 above obtains:

$$J = \frac{TMP}{\mu \cdot (K_m + K_{HIR})} \Rightarrow \tag{G.4}$$

$$K_{HIR} = \frac{TMP\ after}{\mu \cdot J} - K_m = \frac{62721.6\ \frac{kg}{ms^2}}{\left(0.001\ \frac{kg}{ms}\right) \cdot \left(0.0000139\ \frac{m^3}{m^2 s}\right)} - 2.06x10^{12}\ \ m^{-1}$$

$$K_{HIR} = 2.45x10^{12}\ m^{-1}$$

Before a hydraulic backwash, $K_{HR} \neq 0$:

$$J = \frac{TMP}{\mu \cdot (K_m + K_{HIR} + K_{HR})} \Rightarrow \tag{G.5}$$

$$K_{HR} = \frac{TMP\ before}{\mu J} - K_m - K_{HIR} = \frac{62721.6\ \frac{kg}{ms^2}}{\left(0.001\ \frac{kg}{ms}\right)\left(0.0000139\ \frac{m^3}{m^2 s}\right)} - 2.06x10^{12}\ \ m^{-1} - 2.45x10^{12}\ m^{-1}$$

$$K_{HR} = 8.20x10^{11}\ m^{-1}$$

Calculating chemically irreversible (K_{CIR}) and reversible (K_{CR}) fouling resistance for the NaOH chemical soak:

$$TMP\ before\ the\ NaOH\ chemical\ clean = TMP\ before = 21\ PSI = 144795\ \frac{kg}{ms^2}$$

$$TMP\ after\ the\ NaOH\ chemical\ clean = TMP\ after = 12.8\ PSI = 88256\ \frac{kg}{ms^2}$$

$$J = \frac{TMP}{\mu \cdot (K_m + K_{CIR} + K_{CR})} \tag{G.6}$$

After a chemical clean, K$_{CR}$ = 0 and equation Eq G.6 becomes:

$$J = \frac{TMP}{\mu \cdot (K_m + K_{CIR})} \Rightarrow \tag{G.7}$$

$$K_{CIR} = \frac{TMP\ after}{\mu \cdot J} - K_m = \frac{88256\,\frac{kg}{ms^2}}{\left(0.001\,\frac{kg}{ms}\right)\cdot\left(0.0000139\,\frac{m^3}{m^2 s}\right)} - 2.06x10^{12}\ m^{-1}$$

$$K_{CIR} = 2.11x10^{12}\,m^{-1}$$

Before a chemical clean, K$_{CR}$ ≠ 0:

$$J = \frac{TMP}{\mu \cdot (K_m + K_{CIR} + K_{CR})} \Rightarrow$$

$$K_{CR} = \frac{TMP\ before}{\mu \cdot J} - K_m - K_{CIR} = \frac{144795\,\frac{kg}{ms^2}}{\left(0.001\,\frac{kg}{ms}\right)\cdot\left(0.0000139\,\frac{m^3}{m^2 s}\right)} - 2.06x10^{12}\ m^{-1} - 2.11x10^{12}\,m^{-1}$$

$$K_{CR} = 4.07x10^{12}\,m^{-1}$$

APPENDIX H: Membrane Filtration versus Media Filtration

To compare the performance of Alum F coupled with the membrane (Alum F + Mem. Filt) used in these experiments versus a full-scale (currently in use) media filter (Alum F + Media Filt), effluent from the media filters at the Aylmer plant was also collected for NOM quantification and fractionation (table H.1). As can be seen in table H.1 Alum F + Mem. Filt produces slightly better NOM removal than Alum F + Media Filt (i.e., % versus %). This result is not surprising based on the size of the media voids and the membrane pores. The NOM fractionation results for the Alum F + media filter versus Alum F + membrane can also be seen in table H.1. NOM fractionations were not performed for the Iron and Alum S waters due to a lack of water samples, the pilot plant runs had been completed. Overall, the membrane's performance was slightly better than that of the media filter. The membrane was able to remove more total NOM, more HPO NOM, and TPI NOM than the media filter. The media filter was only capable of removing more HPI NOM than the membrane. Zularisam et al. (2007) also found the membrane filtration removed greater percentages of HPO and TPI than HPI.

Table H.1. TOC, DOC and NOM fraction removal for Alum F pre-treatment coupled with membrane filtration and media filtration for the multi-day 50 LMH experiments

Treatment	TOC Removal (%)	DOC Removal (%)	HPO Removal (%)	TPI Removal (%)	HPI Removal (%)
Alum F + Mem Filt	72	69	69	94	23
Alum F + Media Filt	70	66	68	82	29