Direct Biofiltration as a Pretreatment to Control Fouling in Ceramic Membranes in Drinking Water Treatment

by

Jangchuk Tashi

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Ceramic membranes have been widely and successfully used in the food and beverage processing industry. Despite their success, ceramic membranes are not commonly employed in drinking water treatment due to their high initial capital cost. Polymeric membranes, on the other hand, have gained widespread use in drinking water treatment in the last few decades due to their ability to meet stringent water quality regulations. Ceramic membranes have a number of advantages over polymeric membranes, which include high chemical and thermal stability, higher fluxes and longer operational life. Advances in membrane technology in recent years coupled with innovative design have made the life cycle cost of implementing ceramic membranes competitive with that of polymeric membranes. This has resulted in a number of drinking water treatment plant installing ceramic membranes as part of the treatment process, especially in Japan.

The biggest challenge facing membrane filtration (polymeric or ceramic) is fouling. To control fouling, coagulation prior to ceramic membrane filtration is often implemented and has been shown to be effective in controlling both hydraulically reversible and irreversible fouling. Direct biofiltration without pretreatment (BF_{WP}) (coined by Huck *et al.*, 2015) has been shown to be another effective "green" pretreatment to control fouling in polymeric membranes. High molecular weight natural organic matter (NOM) such as biopolymers have been found to be directly related to the hydraulically reversible fouling and to play a key role in hydraulically irreversible fouling of polymeric membranes and biofiltration is able to reduce the concentration of this NOM fraction.

Given the effectiveness of BF_{WP} in controlling fouling in polymeric membranes, there is an opportunity to investigate its applicability to ceramic membranes. Therefore, the goals of this study were to investigate the efficacy of BF_{WP} as a pretreatment to control fouling in ceramic membranes and characterize the fouling of the membranes over time. The effects of Empty Bed Contact Time (EBCT) of the biofilters, membrane materials and pore sizes (Microfiltration (MF) vs. Ultrafiltration (UF)) on the fouling rates were also investigated in the study.

For the study, a direct biofiltration pilot plant was set up at the Mannheim Water Treatment Plant (WTP) in Kitchener, Ontario, Canada. Two dual-media biofilters – one with 8 minutes and the other with 16 minutes EBCT, were fed with roughing filter (RF) effluent, which in turn draws its influent from the raw water main line which feeds the WTP. The Mannheim WTP treats Grand River water which is impacted by agricultural and wastewater effluent upstream. The effluents from the biofilters were then used as influent to the ceramic membrane test units for the membrane fouling experiments.

Fouling experiments were conducted using two parallel test units to compare the efficacy of different pretreatments (RF effluent and biofilter effluents) on MF and UF ceramic membranes. The study found that direct biofiltration is able to substantially remove turbidity and biopolymers from the feed water, thereby reducing both reversible and irreversible fouling rates in both MF and UF ceramic membranes. A higher EBCT biofilter also performed significantly better in terms of turbidity and biopolymer removal, corresponding to lower irreversible and reversible fouling in ceramic membranes. MF ceramic membranes were also found to foul at a much lower rate compared to UF ceramic membranes.

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Table of Contents

List of Figures

List of Tables

List of Acronyms

AOC: Assimilable organic carbon

ATP: Adenosine triphosphate

BB: Building Blocks

BDOC: Biodegradable dissolved organic carbon

BF: Biofilter

BF$_{WP}$: Direct biofiltration without pretreatment

BOM: Biodegradable organic matter

BP: Biopolymer

B8: Biofilter with 8 minutes EBCT

B16: Biofilter with 16 minutes EBCT

CA: Cellulose acetate

CEB: Chemically enhanced backwash

CIP: Clean in place

DOC: Dissolved Organic Carbon

DBP: Disinfection by-products

EBCT: Empty bed contact time

EfOM: Effluent Organic Matter

FA: Fulvic acid

FEEM: Fluorescence excitation-emission matrix

GAC: Granular activated carbon

HS: Humic substances

IEP: Iso-electric point

LC-OCD: Liquid chromatography organic carbon detection

LMH: Liter per membrane area per hour

LMW: Low molecular weight

LPM: Low-pressure membrane

MF: Microfiltration

MWCO: Molecular weight cut off

NF: Nanofiltration

NOM: Natural organic matter

PA: Polyamide
PAC: Powdered activated carbon
PES: Polyethersulfone
PP: Polypropylene
PS: Polysulfone
PVDF: Polyvinyl fluoride
RF: Roughing filter
SUVA: Specific ultraviolet absorbance
TMP: Transmembrane pressure
TOC: Total organic carbon
UF: Ultrafiltration
UV_{254}: Absorbance of ultraviolet (UV) light at a wavelength of 254 nm
WTP: Water Treatment Plant

Chapter 1

Introduction

1.1 Problem Statement

The United Nations have explicitly recognized access to clean drinking water as a human right and acknowledge its fulfillment as a prerequisite for the realization of all other human rights. Humans have been treating water for consumption since ancient times, with Hippocrates, the father of medicine, advising to boil and sieve water before drinking (Crittenden *et al*., 2005). In 1854, John Snow highlighted the importance of clean drinking water when he traced the terrible cholera epidemic in London to a water well contaminated by a cesspool. With advancement in science and technology over the years, the water treatment processes have seen improvement but have become more complex at the same time.

In the last few decades, the application of membranes in water treatment has dramatically increased due to a reduction in membrane cost and an increase in membrane quality (Jacangelo *et al*., 1997; Atkinson, 2002; Furukawa, 2008). As the water treatment industry is faced with new challenges with the emergence of new contaminants and poorer water quality, membrane filtration is often the technology of choice due to its ability to produce consistent high water quality. However, membrane fouling remains one of the biggest challenges in membrane operation today. Therefore, integrating pretreatment with membrane filtration to control fouling has been developed as it can improve productivity and reduce the overall operating cost.

Recent studies have identified natural organic matter (NOM) as a membrane foulant, with the biopolymer (Peldszus *et al*., 2011; Amy, 2008; Kimura *et al*., 2004) and humic substances (Yuan & Zydney, 1999) fractions of NOM playing a major role in both reversible and irreversible fouling. A pretreatment which has shown promise in recent years is biofiltration. Biofiltration without prior coagulation is a "green" pretreatment that has been demonstrated to help reduce fouling in polymeric membranes by removing biopolymers and particulate matter (Hallé *et al*., 2009).

Today, the dominant membranes used in water treatment are polymeric membranes due to their lower cost and greater operational experience (Guerra & Pellegrino, 2013). Nevertheless, ceramic membranes are gaining interest due to advantages such as higher mechanical strength, better thermal and chemical stability and longer operational life compared to polymeric membranes. However, the bulk of the studies on pretreatment technologies are mainly for polymeric membranes with no studies yet on the efficacy of biofiltration for ceramic membranes. Therefore, there is an opportunity to study the fouling reduction capacity of biofiltration for ceramic membranes. In addition, the effects of biofilter Empty Bed Contact Time (EBCT) and membrane characteristics such as membrane material and pore size (UF/MF) on fouling behaviour following biofiltration pretreatment would produce valuable information for its application in treatment plants.

1.2 Objectives

The objectives of the research study were to -

- Investigate the efficacy of direct biofiltration without prior coagulation (BF_{WP}) as a pretreatment to control fouling in MF ceramic membranes.
- Study the impact of different biofilter EBCTs on the fouling of ceramic membrane as well as the difference in fouling potential of MF and UF ceramic membranes.
- Study the influence of membrane materials on the fouling of MF ceramic membranes with BF_{WP} pretreatment.
- Study the long term performance of MF ceramic membranes using BF_{WP} pretreatment.

1.3 Approach

The study was conducted at the Mannheim Water Treatment Plant (WTP) located in Kitchener, in the Region of Waterloo, Ontario, Canada. The source of raw water for the Mannheim WTP is the Grand River, which is impacted by agricultural run-off and wastewater effluents upstream. At the plant, a biofiltration pilot plant was set up consisting of two biologically active dual media filters (anthracite over sand) – one with 8 minutes EBCT and the other with 16 minutes EBCT. Raw water was drawn from the main line feeding the treatment plant and fed to four parallel roughing filters. The combined effluent from the roughing filters (RF) was then pumped to the top of the biofilters.

Membrane fouling experiments were conducted from March to August 2015 using two membrane test pilots operating in parallel. The test pilots were operated with different influents and/or membranes to study the effects of pretreatment on different membranes. Each membrane fouling experiment was performed in constant flux mode and change in transmembrane pressure (TMP) was used to assess the performance of the membrane. Water samples were also collected 24 hours into the permeation cycle and analysed for water quality parameters such as total organic carbon (TOC), dissolved organic carbon (DOC), and ultraviolet absorbance at 254 nm (UV_{254}). To gain insight into the impact of different fractions of NOM on membrane fouling, liquid chromatography – organic carbon detection (LC-OCD) and fluorescence excitation emission matrix (FEEM) measurements were made.

1.4 Thesis Structure

The thesis is divided into six chapters with Chapter 1 providing the overall objectives and approach of the research study. Chapter 2 provides the general background and literature review of the current state of membrane pretreatment technologies as well as the motivation for the study. Chapters 3, 4 and 5 were written in paper format with separate experimental methods section. However, there was significant overlap on the experimental methods and materials among the three chapters, so only the experimental methods and materials that were not covered in previous chapters but were relevant in the later chapters were included.

Chapter 3 summarizes the preliminary proof of concept experiment where the efficacy of BF_{WP} was investigated. The chapter also includes studies performed to examine the effect of different biofilter EBCTs on the fouling of MF ceramic membrane. In addition, fouling of UF and MF ceramic membranes were compared under similar BF_{WP} pretreatment. Chapter 4 discusses the fouling potential of MF ceramic membranes made of different material under the same BF_{WP} pretreatment.

Chapter 5 discusses the fouling behaviour of MF ceramic membrane over a period of ten weeks under BF_{WP} pretreatment. During the first three weeks, membrane fouling experiments were operated with effluent from a biofilter with an EBCT of 8 minutes while the later seven weeks were operated with effluent from a biofilter with an EBCT of 16 minutes. Changes in raw water quality, biofilter effluent, and permeate were also studied to elucidate trends and potential correlations to membrane performance. Finally, Chapter 6 presents a synthesis of the overall findings of the research study and provides recommendations for the water industry and future studies.

Chapter 2

Literature Review

2.1 Membrane Filtration in Drinking Water Treatment

2.1.1 General overview

The primary objective in drinking water treatment is to provide a clean, safe and aesthetically pleasing water to the general public. Stringent provincial and federal regulations have to be met in order to achieve a high-quality drinking water. Fundamental to achieving these goals is the removal of suspended particulate matter and different kinds of pathogens and chemical contaminants (including odour-causing chemicals) from the source water. One of the treatment technologies that have gained widespread use in recent decades is membrane filtration.

Membranes provide an absolute barrier to suspended particles and contaminants that are larger than the pore size of the membrane while letting water pass through. The filtering layer of the membrane is composed of highly uniform pores, which reject any particles that are larger than the pore size; these particles then remain on the feed side. The bulk carrier fluid, water, together with the finer particles and/or dissolved substances smaller than the pore size, pass through the membrane as permeate. The ability of membranes to provide an absolute barrier to particles larger than the pore size makes them an ideal technology where stringent provincial and federal standards need to be met. In comparison to conventional granular media filters, membrane filtration requires less chemicals, can be more easily automated with supervisory control and data acquisition (SCADA) system and is more compact (Pearce, 2011).

Membranes were first used in the 1950s for the sterilization of pharmaceuticals (Crittenden *et al.*, 2005) and had since been used successfully in the food and beverage processing industry. Membranes are now widely used in municipal drinking water treatment plants, with the first large-scale membrane process installed in 1988 (Pearce, 2007).

2.1.2 Membrane classification

Four different kinds of membranes are used in drinking water treatment – microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The membranes are classified based on the nominal pore size and operating pressure. The nominal pore size of MF membranes are typically around 0.5 to 0.1 μm while UF membranes have an order of magnitude smaller pore size in the range of 0.01 to 0.02 μm. Another approach called molecular weight cut off (MWCO) is sometimes used instead of pore sizes to characterize UF and NF membranes. In the MWCO classification, the membrane is rated by the lowest molecule size at 90 percent rejection. The MWCO for UF membrane can range from 1000 Daltons (Da) to 500 kDa (Crittenden, *et al*., 2005).

MF and UF membranes are classified as low-pressure membranes (LPM) and operate in the pressure range of 0 to 5 bar while NF and RO membranes are classified as high-pressure membranes and require pressure in excess of 5 bars to operate. MF membranes can effectively reject particles, colloids, protozoa, most bacteria and algae (Figure 2-1). Viruses, which are much smaller than the pore size of MF, are removed to some extent by MF membranes due to their ability to act as a depth filter, but MF does not provide a complete barrier to viruses. A UF membrane with a MWCO of 1 kDa to 500 kDa corresponds to 1 to 30 nm in the hydrodynamic diameter of the molecule, which suggests that some of the tighter membranes can completely retain viruses while the looser membranes would be pervious to viruses.

In addition to the materials rejected by MF and UF membranes, NF membranes are able to reject dissolved organic matter and divalent ions to at least some extent, while RO membranes are able to reject monovalent ions. Due to lower operating costs and their ability to meet particle removal goals, MF and UF are the predominant membranes used in drinking water treatment. NF and RO membranes are used respectively where organics and/or hardness removal is required and where a desalination process is required for treating brackish water or seawater.

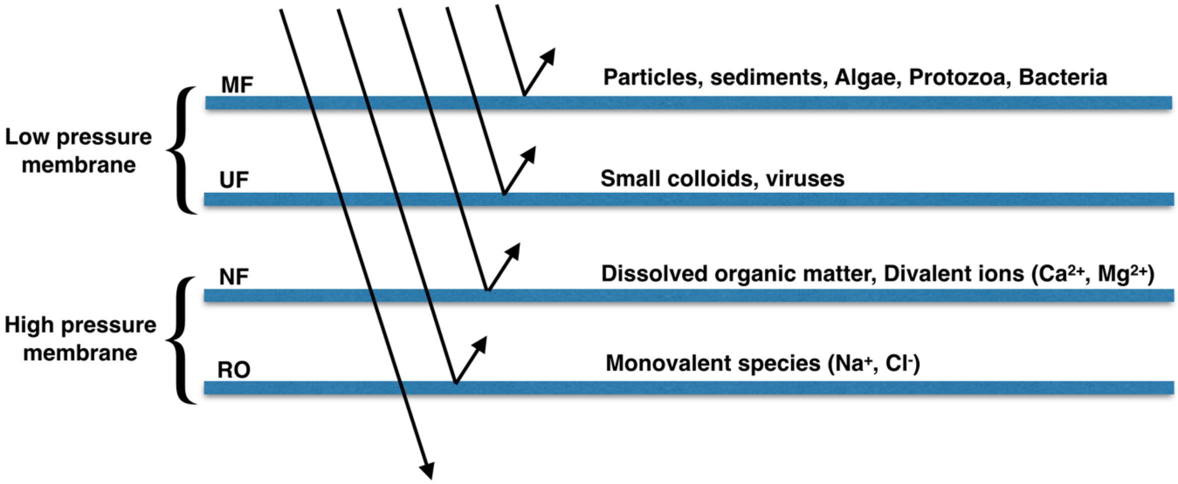


Figure 2-1 - Membrane classification based on material rejection and membrane operating pressure (Adapted from Crittenden *et al.*, 2005)

2.1.3 Membrane materials and properties

The performance of a membrane is mainly dependent on the material's chemical and physical properties, and also on operating conditions. The ideal material is one that can operate at high flux without fouling, physically strong, durable and non-biodegradable, chemically stable and resistant while being inexpensive (Crittenden *et al.*, 2005). Currently, two distinct kinds of materials are used in fabricating membranes– polymeric and ceramic materials. Polymeric membranes are fabricated using polymers such as cellulose acetate (CA), polysulfone (PS), polyethersulfone (PES), polyamide (PA), polyvinylidene fluoride (PVDF) and polypropylene (PP) while ceramic membrane are manufactured using metal oxides such as aluminum oxide (Al_2O_3), titanium dioxide (TiO_2), zirconium oxide (ZrO_2), etc.

The hydrophobicity, surface charge and surface morphology such as surface roughness play a key role in the membrane performance. Depending on the material used, a membrane can be either hydrophilic or hydrophobic. Polymeric membranes exhibit a wide range of hydrophobicity, from completely hydrophilic CA membrane to completely hydrophobic PP membrane. Other polymeric membranes – PS, PES, PA and PVDF exhibit hydrophobicity between that of the CA and PP membranes (Pearce, 2011). All ceramic membranes, in general, are hydrophilic as they are made of metal oxides. The hydrophobicity of a membrane is quantified by measuring the contact angle between a droplet of water and the membrane surface as shown in Figure 2-2. A hydrophobic membrane has a low wettability and forms beads like water droplets on a good rain jacket whereas a hydrophilic membrane is completely wetted by the water like a cotton jacket.

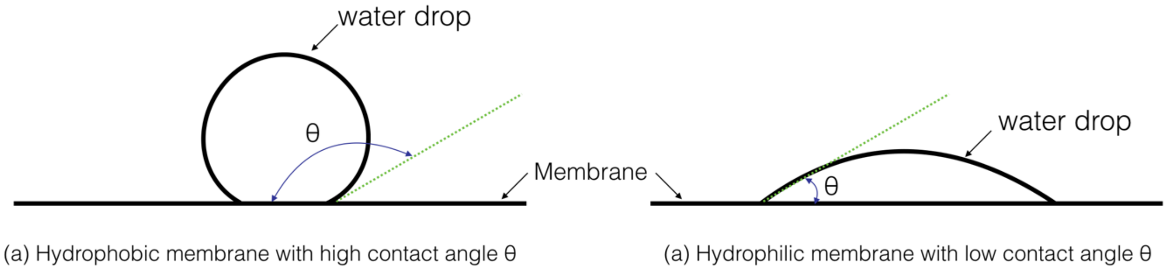


Figure 2-2 - Contact angles of hydrophobic and hydrophilic membrane (adapted from Pearce, 2011)

Hydrophobicity is an important property as it has a big influence on the performance of a membrane. A hydrophilic membrane is easily wetted by water and results in high permeability. NOM in drinking water is generally negatively charged and has the tendency to attach and adsorb to a hydrophobic membrane which exacerbates membrane fouling. Hence, a hydrophilic material is desirable for membrane performance.

Surface charge is another property that affects membrane performance. The charge on the membrane surface is a function of pH of the feed water. The pH at which the surface charge is neutral is known as the isoelectric point (IEP) (Vrijenhoek *et al*., 2001). At pH values lower than the IEP, the membrane surface is positively charged while at pH higher than the IEP, the membrane surface is negatively charged. Polymeric membranes are generally negatively charged (Elimelech *et al*., 1994) at neutral pH. Negatively charged NOM could bond tightly to a positively charged surface and exacerbate fouling by making the NOM harder to dislodge during backwashing. On the other hand, negatively charged NOM would be repelled by the negatively charged membrane, reducing membrane fouling (Cho *et al*., 2000). However, the presence of ionic species (total dissolved solids) in the feed water and their interaction with NOM makes it hard to truly assess the significance of a negatively charged membrane surface. Therefore, a desirable surface charge for a membrane is one that is neutral at the pH of the feed water, as it reduces the risk of fouling by minimizing interactions between the charged molecules and membrane surface (Pearce, 2011).

Membrane morphology such as surface roughness plays an important role in membrane performance. Smooth membrane surface provides better performance as foulants are not easily attached to the membrane surface and are easier to remove during the backwashing procedure. A rough membrane surface is suitable for some application as it can help create turbulent conditions near the membrane in cross-flow mode operation (Pearce, 2011). However, membrane operations in drinking water treatment are mostly carried out in dead-end mode making smooth membrane surface the membrane of choice.

2.1.4 Ceramic membranes

The predominant type of membrane used in drinking water treatment today is mostly made of polymeric materials. This has largely been due to advances in membrane technology achieved over the past few decades in polymeric membranes that have led to a lower capital and operational costs (Singh, 2015).

However, polymeric membranes have a shorter life span and a higher risk of membrane integrity breach that are undesirable in drinking water treatment. These shortcomings are overcome by ceramic membranes that are robust and durable. In addition, ceramic membranes have the following advantages over polymeric membranes (Pearce, 2011; Finley, 2005; Ciora & Liu, 2003).

- Ceramic membranes possess high chemical and mechanical strength. Harsh chemicals such as sodium hypochlorite, a strong oxidizing agent, can be used to recover the membrane once it has been completely fouled.
- Ceramic membranes can be operated at a much higher flux compared to polymeric membranes.
- Ceramic membranes have a high thermal stability which allows the use of elevated temperature during cleaning processes to recover the membrane permeability once it has been exhausted.
- Ceramic membranes also have a longer operational life compared to polymeric membranes. Ceramic membranes have a lower risk of breakage and guarantee a higher level of membrane integrity compared to polymeric membranes.

Despite these advantages, the biggest limitation of ceramic membranes remains with their high capital cost. Ceramic membranes are much more expensive compared to polymeric membranes. Even though the raw materials used in manufacturing ceramic membranes are relatively cheap, the manufacturing procedure is much more expensive (Pearce, 2011). Nevertheless, economies of scale and developments in new technologies such as CeraMac® (Galjaard *et al.*, 2012) have lowered the life cycle cost of ceramic membranes so that it is becoming competitive with that of polymeric membranes.

2.1.5 Separation mechanisms

The removal/rejection of particles through the membrane process differs significantly from a conventional granular media filtration process. In a granular media filter, the grain sizes are in excess of 100 µm and this creates similar pore sizes in the filter media. However, due to the depth of the filter, particles much smaller than the pore sizes (media grain sizes) are effectively captured and removed from the filtrate. This phenomenon is known as depth filtration. In membranes, four distinct mechanisms are involved in the rejection of particles (Huang *et al*., 2009; Bruggen *et al*., 2003)

- The most important mechanism by which particles are removed through the membrane is via physical straining (aka steric exclusion). The membrane resembles a fine screen/sieve with sub-micron sized meshes (Huang *et al*., 2009). Any particles that are smaller than the mesh size (pore size) can pass through the membrane with the bulk carrier fluid (water) while any particles that are bigger are retained on the membrane.

- Adsorption is another mechanism by which particles/contaminants present in the feed water are removed. NOM and other contaminants present in natural water are easily adsorbed to the surface and pores of the membrane and are removed even though their physical dimensions are much smaller than the pore size of the membrane. This mechanism is especially important during the initial phase of the filtration process after installing a clean membrane. As the adsorption sites are slowly exhausted after repeated filtration cycles, adsorption is not an important mechanism in a long-term operation of a membrane. However, adsorption of NOM and contaminants have a significant impact on the membrane process as the adsorption of organics can reduce the pore size which exacerbates membrane fouling.

- Electrostatic interaction between the particles and colloids in the feed water with the charged membrane surface can also aid with the removal/rejection of particles and colloids present in the feed water (Zydney & Pujar, 1998). In membranes that are negatively charged, greater rejection of negatively charged NOM and colloids can be expected due to repulsive electrostatic interaction. As the surface charge of the membrane is a function of the pH of the bulk carrier fluid, electrostatic interaction becomes an important filtration mechanism when the membrane surface is charged, either positive or negative.

- Cake layer formation on the surface of the membrane is another mechanism by which particles are removed. During the course of filtration, the membrane surface can quickly accumulate particles and form a layer of cake. This dynamic layer on the surface of the membrane can act as a secondary filtration media and help remove particles from the feed water (Crittenden *et al*., 2005). Cake layer formation is especially important in dead-end filtration mode where the feed is forced on the membrane surface at 90 degrees and particles and contaminants quickly accumulate on the membrane surface (Figure 2-3). In a cross-flow filtration operation, the feed flows parallel to the membrane surface creating a shear stress on the surface that helps reduce cake layer formation.

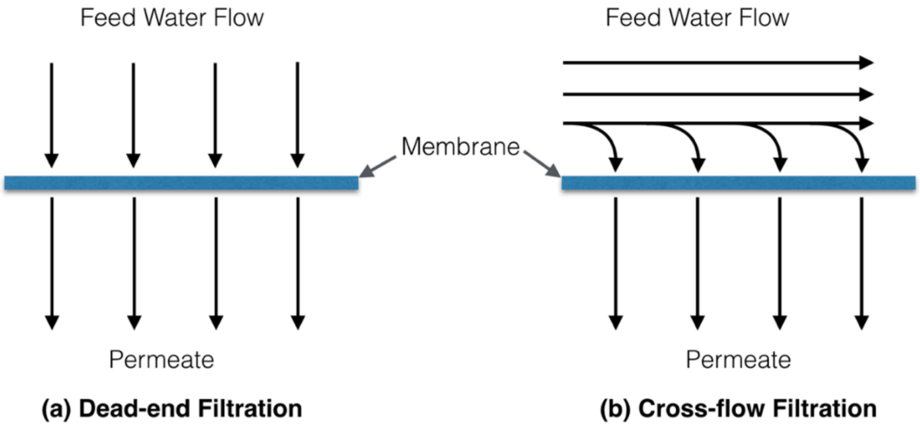


Figure 2-3 - Flow regimes in Dead-end and Cross-flow filtration mode (adapted from Crittenden *et al*., 2005)

2.2 Membrane Fouling Phenomena

The biggest challenge in membrane operation is fouling. Fouling is defined as the loss of performance due to the deposition of suspended particulate matter and dissolved substances on the surface, the pore opening and within the pores of the membrane (Crittenden *et al*., 2005). Flux (J), which is the flow per unit area per unit time, can be modeled using a modified form of Darcy's law (Cheryan, 1998) where the flux is directly proportional to the transmembrane pressure (TMP) and inversely proportional to the absolute viscosity of the water.

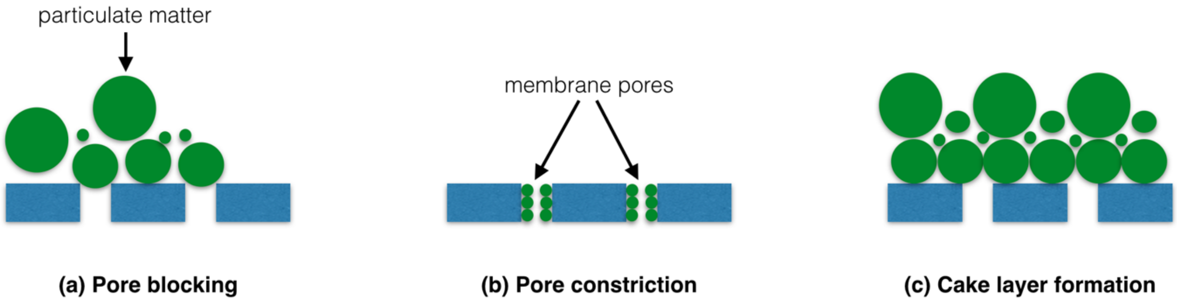
$$J = \frac{Q}{A} = \frac{\Delta P}{\mu \times R_m} \qquad \textbf{Equation 2-1}$$

where $J =$ flux
$Q =$ filtrate flow
$A =$ membrane area
$\mu =$ viscosity
$\Delta P =$ transmembrane pressure
$R_m =$ hydraulic resistance of clean membrane to water permeability

In a constant flux mode, membrane fouling manifests itself as an increase in transmembrane pressure. In declining flux mode, where the transmembrane pressure is held constant, membrane fouling manifests itself as a decline in flux over a filtration cycle. In both cases, membrane fouling leads to an increase in operation cost, loss of productivity, and shorter membrane life.

2.2.1 Mechanisms of fouling

Membrane fouls via three very distinct mechanisms known as pore blocking, pore constriction and cake formation as shown in Figure 2-4 (Crittenden *et al*., 2005).



(a) Pore blocking (b) Pore constriction (c) Cake layer formation

Figure 2-4 - Diagram of the mechanism of membrane fouling (adapted from Crittenden *et al*., 2005)

In pore constriction, NOM and other dissolved contaminants present in the feed water get adsorbed to the inside of the pores, reducing the effective pore size of the membrane. In pore blocking, the pores of the membrane are completely blocked by particles that are of similar and larger size than the pores. Once the pores are blocked, other particulate (both small and large size) matter accumulate on the surface of the membrane, forming a cake layer. In all cases, the end result is an increase in resistance to the flow of water through the membrane reducing productivity.

2.2.2 Types of fouling

Membranes are typically operated in a dead-end mode in drinking water treatment as they have a lower cost of operation in terms of electrical energy usage. In this mode, all the suspended particulate matter removed from the feed water due to permeation accumulates on the membrane surface over the course of the filtration cycle. For a successful long-term operation, a regular cleaning process is employed after each filtration cycle known as hydraulic backwashing.

During backwashing, the direction of water (permeate) is reversed, which helps dislodge particulate matter from the membrane pores and surface. Based on the reversibility, membrane fouling is classified as either hydraulically reversible fouling or hydraulically irreversible fouling (Figure 2-5). The flux or the TMP that is recovered after a backwash is known as hydraulically reversible fouling while the remaining flux or the TMP that cannot be recovered is known as irreversible fouling.

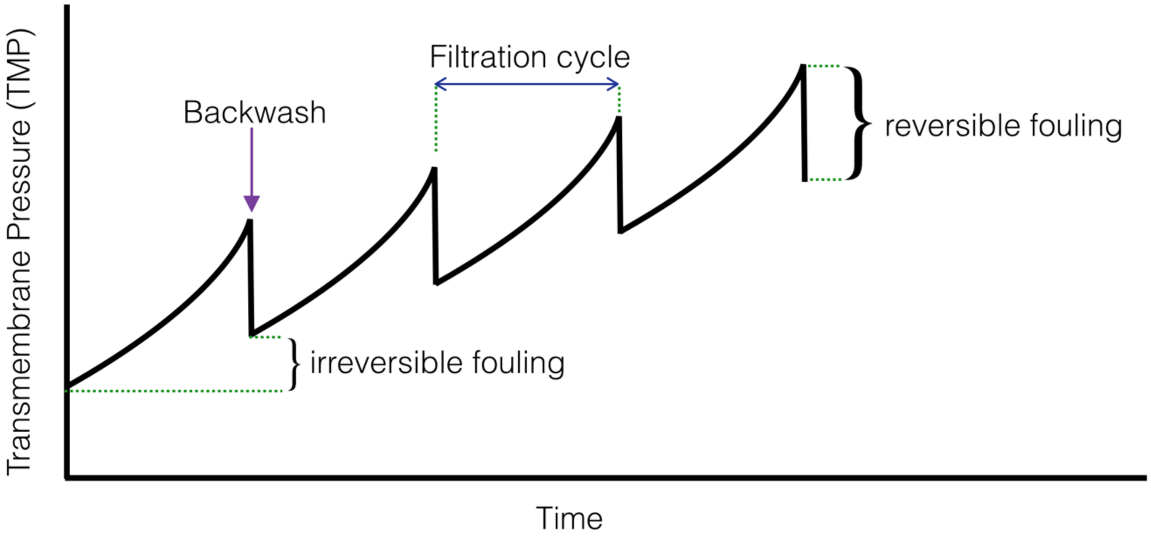


Figure 2-5 - Reversible and irreversible fouling during a constant flux mode operation

Fouling can also be classified based on the type of foulants as follows (Mosqueda-Jimenez & Huck, 2006; Pearce, 2011):

- Particulate fouling
- Organic fouling
- Inorganic fouling
- Microbiological organisms or biofouling.

Particulate fouling is caused by suspended particles blocking the pores as well as forming a cake layer on the surface of the membrane. Hydraulic backwashing is an effective means to control particulate fouling, especially the removal of cake layer from the membrane surface (Howe & Clark, 2002). However, particles lodged in the pores can be harder to remove and contribute to hydraulically irreversible fouling. Organic fouling is caused by the NOM or Effluent Organic Matter (EfOM) present in the incoming water. NOM is an important constituent of natural water and its constituents have been largely reported to be responsible for hydraulically irreversible fouling. Biopolymer (Peldszus *et al*., 2011; Kimura *et al*., 2004) and humic (Yuan & Zydney, 1999) fractions of NOM have been shown to be responsible for irreversible fouling in both polymeric and ceramic membranes. EfOM can also contribute to fouling when it is present.

Inorganic fouling is the formation of scale on the membrane surface due to precipitation of inorganic salts from the feed water. Inorganic fouling is common in high-pressure membranes since they are able to reject multivalent ions (Her *et al*., 2007) but is uncommon in low-pressure UF and MF membranes. Biofouling is caused by the accumulation and growth of microorganisms on the membrane surface, which in turn increases the resistance to the flow of water. Biofouling is an issue in high-pressure spiral wound membranes since a backwash cleaning procedure is not used. In low-pressure membranes, use of chlorine (Baker & Dudley, 1998) and the backwashing procedure is normally able to effectively control biofouling.

2.2.3 Composition and characterization of NOM

Natural organic matter is a complex mixture of organic chemicals present in all water bodies. The source of NOM in water bodies is mainly from the remains of plants and animals and their waste, although some can be generated within the water body, for example by algae. NOM in the raw water is undesirable as it can cause taste and odour, increase coagulant dose, and produce disinfection by-products (DBP) with chlorine during conventional water treatment process. In membrane processes, dissolved organic matter has been shown to adsorb to the membrane surface (Jucker and Clark, 1994) which leads to loss of membrane performance.

NOM is primarily composed of carbohydrates, lipids, amino acids, nucleic acids as well as in combination with other inorganic chemicals. Thousands of different organic compounds are produced due to the wide range of biological activity, local soil conditions, climate and hydrologic conditions (Crittenden *et al*., 2005). Therefore, characterization of NOM is difficult and NOM from different water bodies exhibits different effects when it undergoes water treatment. Total organic carbon (TOC), dissolved organic carbon (DOC), and ultraviolet absorbance at 254 nm wavelength (UV_{254}) are some bulk methods used to measure and quantify NOM. TOC provides an overall concentration of NOM while DOC presents the dissolved fraction which passes through a 0.45 μm filter. UV_{254} gives an indication of the presence of unsaturated bonds present in NOM. These bulk parameters give an aggregate value of NOM but do not present any insight into the different fractions of NOM. For example, these bulk measurements do not give any information on the varying molecular weights, charge densities and hydrophobicity of the different fractions of NOM.

Liquid chromatography with online carbon detection (LC-OCD) is a relatively new method which can be used to gain insight into the different fractions of NOM, although without revealing the exact nature of NOM. Using LC-OCD, NOM can be subdivided into the following 6 major sub-fractions: (Huber *et al*., 2011):

- Biopolymers (BP) – are the first NOM fraction to elute and have a molecular weight (MW) of 10 kDa or higher. The biopolymer fraction is hydrophilic and doesn't absorb UV. The fraction is composed of polysaccharides, protein and amino sugars (Huber *et al*., 2011).
- Humic Substances (HS) – are the second NOM fraction to elute with humic acids eluting at 43.4 minutes and fulvic acid eluting at 46.7 minutes (Huber *et al*., 2011). The humic substance fraction is normally the largest and most dominant peak in the OCD chromatogram and responds to UV due to the presence of unsaturated bonds (Figure 2-6).

- Building Blocks (BB) – are the third fraction to elute after humic substances and have a variable response to UV. The fraction is mainly composed of lower molecular weight humic substances which originate from the breakdown of HS, thus the name - building blocks (Huber *et al*., 2011).

- LMW acids – this fraction are anions at neutral buffer pH and elutes as the peak next to the shoulder of BB (Huber *et al*., 2011).

- LMW neutrals – the last fraction to elute and composed mainly of LMW alcohols, aldehydes, ketones, sugars and have no response to UV.

- Hydrophobic Organic Carbon (OC) – this fraction represents the difference in DOC value as measured by the bypass column from the sum of all fractions calculated from the chromatogram (Huber *et al*., 2011). The reason for the difference is the hydrophobic interaction between the column and water sample. Therefore, the term hydrophobic OC is given.

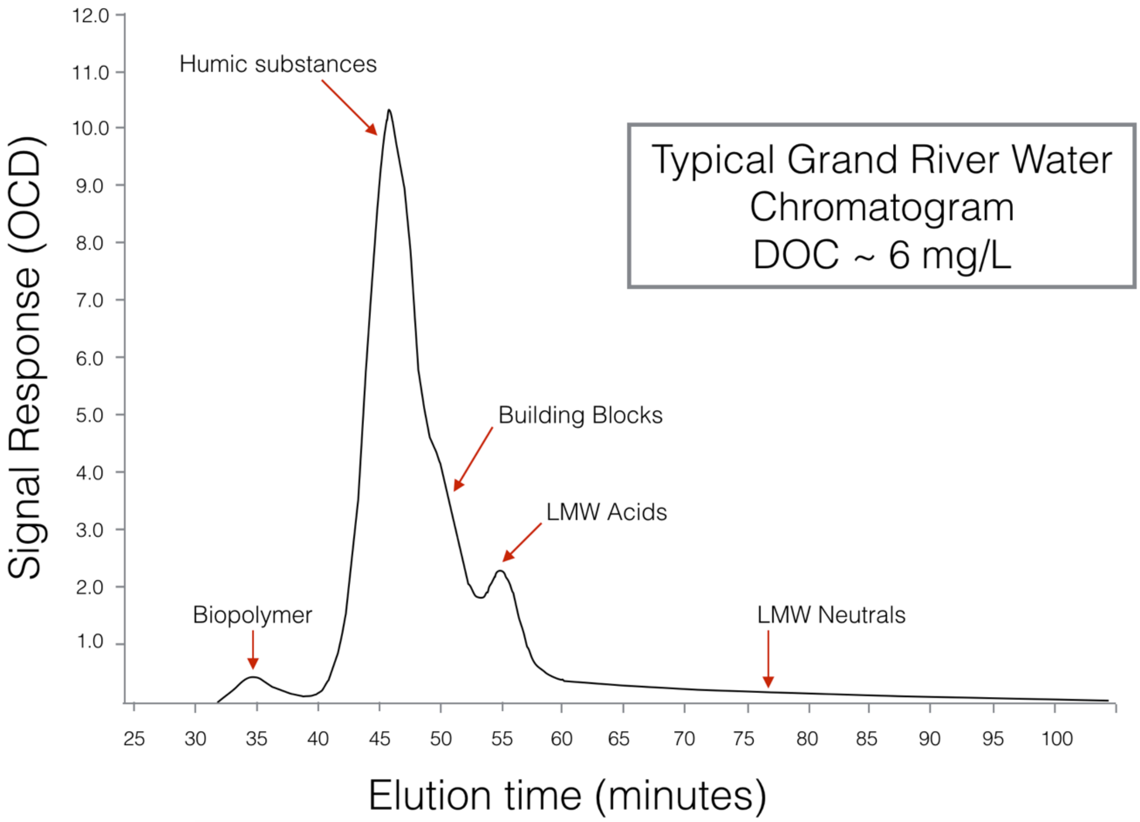


Figure 2-6 - A typical Grand River water LC-OCD chromatogram showing the five different NOM fractions

NOM has been widely acknowledged as a membrane foulant; however, it is only recently with the use of LC-OCD that specific fractions of NOM such as biopolymer (Peldszus *et al*., 2011; Amy, 2008; Kimura *et al*., 2004) and humic substances (Yuan & Zydney, 1999; Mueller *et al*., 2010) have been identified to play a major role in both reversible and irreversible fouling. Therefore, the goal of an effective pretreatment process is to remove the NOM fractions such as biopolymer from the membrane feed.

Another method that can provide insight into the different fraction of NOM is fluorescence excitation emission matrix (FEEM). The fluorescence spectra from the different NOM in water can be used to determine NOM subcomponents of different composition and functional properties (Chen *et al*., 2003) and detect protein like content, humic and fulvic acids with high sensitivity (Peldszus *et al*., 2011).

2.3 Membrane Pretreatment Technologies

Membrane pretreatment processes are employed before membrane filtration as they can help reduce cost by improving specific flux, membrane performance and finished water quality regardless of source water quality (Adham *et al*., 2005). Pretreatment can influence membrane operation by altering the contaminant size distribution, altering mutual affinities of the contaminants towards each other and to the membrane surface and removing biodegradable organic matter (Huang *et al*., 2009).

Pretreatment can help membrane performance by improving the feed water quality by altering its physical, chemical and biological properties. The size of contaminants can be increased by pretreatment processes so that they can be removed by the membrane. Increasing the size of contaminants also helps shift the mode of fouling from pore blocking and pore constriction to cake formation which can be controlled by hydraulic backwashing (Huang *et al*., 2009). Pretreatment processes with chemical addition can help alter the chemistry of foulants and reduce their affinity to the membrane. Some pretreatment can help reduce easily biodegradable organic matter such as biopolymers and help control hydraulically reversible and irreversible fouling. The following are some of the pretreatment processes for membranes used in water treatment.

2.3.1 Coagulation

Coagulation pretreatment is one of the most common and successful pretreatments for LPM (Gao *et al*., 2011; Crittenden *et al*., 2005). Coagulation improves membrane performance by not only removing 15 to 50 percent of the NOM (Crittenden *et al*., 2005) present in the feed water but also removing contaminants which are smaller than the pore size of the membrane (Meyn *et al*., 2008; Huang *et al*., 2008; Loi-Brügger *et al*., 2006). Removal of contaminants smaller than the pore size of the membrane helps alleviate membrane fouling by the pore blocking mechanism that leads to mainly hydraulically irreversible fouling. However, it is important to understand coagulation chemistry and factors that affect the coagulation process as it has been reported that coagulation can sometimes exacerbate fouling (Huang *et al*., 2009; Schäfer *et al*., 2001)

Two types of coagulants are commonly used in water treatment: inorganic metal salts (Al(III) and Fe(III)) and organic macromolecules (polymers). Inorganic salts are the most commonly used coagulant in water treatment plants (Huang *et al*., 2009). Salts of Al(III) and Fe(III) form numerous destabilizing cationic species which can react with a wide array of particles, including turbidity, particulates, and NOM in water (O'Melia, 1998). The coagulation process occurs by adsorption and a combination of charge neutralization which is highly dependent on pH and by "sweep flocculation" (Huang *et al*., 2009; O'Melia, 1998). Negatively charged particles in the water are neutralized by the positively charged cationic species (coagulant) and the particles flocculate which increases their size. At the same time, the negatively charged dissolved contaminants and NOM are also attracted to the positively charged species due to electrostatic forces. The charged contaminants and NOM may also adsorb on the flocs and get removed from the feed water before membrane filtration.

Coagulation pretreatment can be implemented as either standard coagulation or inline coagulation (Gao *et al*., 2011). In standard coagulation, the coagulation is followed by sedimentation which removes part of the flocs by settling, by conventional gravity or plate settlers. Therefore, turbidity and some of the NOM and contaminants adsorbed to the coagulants are separated and removed before membrane filtration. As a result, the membrane fouls less in comparison to a membrane operated with no pretreatment (Huang *et al*., 2009). However, irreversible fouling can still be a problem as not all foulants, such as uncharged polymeric substances, are removed during the coagulation process (Carroll *et al*., 2000).

In inline coagulation, the coagulated water is directly applied to the membrane. Therefore, the size and the affinity of the flocs towards the membrane surface is an important factor in membrane fouling. Flocs which are the same size or smaller than the membrane pores causes fouling by pore blocking mechanism while flocs with affinity to the membrane surface can be harder to remove during hydraulic backwash. To develop the most effective inline coagulation pretreatment, it is important to select membranes that are made of materials with less affinity and smaller pore size than the floc (Huang *et al*., 2009). Inline coagulation pretreatment can be an attractive option where lowering the footprint of the LPM filtration facility is important (Choi & Dempsey, 2004).

2.3.2 Adsorption

Adsorption pretreatment is another process where adsorbents are used before LPM filtration. Adsorbents, such as powdered activated carbon (PAC), have huge specific surface area which is thermodynamically unstable and can adsorb dissolved contaminants from the water (Huang *et al*., 2009). Adsorption pretreatment can remove dissolved contaminants in the size range of a few nanometers which cannot be removed by LPM (Schäfer *et al*., 2001).

Adsorption pretreatment has been reported to have mixed results in controlling fouling in membranes (Campinas & Rosa, 2010; Xia *et al*., 2007; Mozia & Tomaszewska, 2004). PAC, which is the most commonly used adsorbent, is used in water treatment to remove trace contaminants, taste and odour compounds and DBP precursors. These compounds, once they are adsorbed by PAC, can be effectively removed by LPM as the pore size of LPM is much smaller than PAC (Zhang *et al*., 2003). However, Mozia *et al*. (2004) reported that using PAC has minimal to an adverse effect on controlling fouling in polymeric membranes. Similar results were observed in MF ceramic membrane by Zhao *et al*. (2005).

The impact of PAC fines on both polymeric and ceramic membrane fouling in a hybrid membrane process was reported by Oligny *et al*. (2016). They noted that an increase in the transport of PAC fines from the pretreatment contactors to the membrane increased fouling in the polymeric membrane. However, the effect on the ceramic membrane fouling was not significant.

Studies with granular activated carbon (GAC) filters have shown that they are a better system to utilize the adsorption capacity while improving the performance of membranes (Schideman *et al*., 2007; Tsujimoto *et al*., 1998; Yuasa, 1998). Improvements in membrane performance in such studies have been attributed to the biological activity in GAC contactors which can break down biodegradable organics (Wend *et al*., 2003).

2.3.3 Preoxidation

Ozone, permanganate, and chlorine are the most common oxidants used in conventional water treatment plants (Gao *et al*., 2011). Oxidants can be used in feed water to suppress microbial growth and maintain an oxidative condition in water (Huang *et al*., 2009). Oxidants are also used to aid coagulation and flocculation with ozone preferred over chlorine due to the formation of chlorine DBP (Farahbakhsh *et al*., 2004).

Of the oxidants, ozone is commonly studied for membrane pretreatment while limited research is available on chlorine and permanganate with LPM process (Gao *et al*., 2011). As ozone is a strong oxidant, it is not compatible with most polymeric membranes. Therefore, most research available is for ceramic MF and UF membranes. However, studies with ozone-resistant PVDF membranes by Hashino *et al*. (2000) found that application of ozone (dose - 3 mg/L) achieved a three to four times increase in flux compared to no pretreatment. Similar results were obtained by Schlichter *et al*. (2004) who studied a hybrid process which combined ozone with MF/UF membrane.

Since ozone reacts with NOM to produce assimilable organic compounds (AOC) which are readily biodegradable (Crittenden *et al*., 2005), it can be combined with biological filtration to remove easily biodegradable organics from the feed water. The performance of ozone-biofiltration process as a pretreatment is dependent on the removal of BOM before membrane filtration, especially the fraction of BOM responsible for organic fouling. Studies by Hozalski *et al*. (1999) showed that the removal of total organic carbon through ozone-biofiltration process increased as ozone dose increased but the effects were dependent on NOM characteristics. Higher molecular weight NOM saw greater removal due to its amenability to breakdown by ozone.

2.3.4 Biofiltration

Biofiltration is a “green” pretreatment used to control fouling in LPM. Biofiltration is commonly implemented as a pretreatment in two ways – direct biofiltration without prior coagulation or ozonation or integrated ozone-biofiltration process. Biofiltration is discussed in detail in section 2.4

2.3.5 Other

Other membrane pretreatment includes prefiltration and magnetic anion exchange resin (MIEX$^{®}$). Removal of particles and LPM foulants can be achieved by using coarse membrane filters and/or granular media filters. Granular media filter can achieve particle removal in the size range of 0.1 μm to a few μm (Huang *et al*., 2009) which can help control fouling due to cake layer formation. However, organic foulants can pass through granular media uninhibited and cause irreversible fouling. In a MIEX$^{®}$ process, the negatively charged organic foulants in the water are exchanged with anions and removed before membrane filtration to control membrane fouling. Studies by Kabsch-Korbutowicz *et al*., (2008) on an integrated process of MIEX®DOC with ultrafiltration found MIEX® to be an effective process for removing NOM from the studied water.

2.4 Biofiltration

2.4.1 Overview

Biologically active filtration or biofiltration is a process where rapid granular media filters are operated without disinfectant residual in the feed and backwash water. Biofilters are operated with the goal of achieving particle as well as biodegradable organic matter (BOM) removal (Hozalski & Bouwer, 2001). Traditional biological processes such as slow sand filtration, bank filtration, and ground passage have been successfully used in drinking water treatment for years (Urfer *et al*., 1997).

Naturally occurring species such as BOM, NH^{4+}, Fe^{+2}, NO^{-2}, Mn^{2+}, and S in surface water are electron donors and cause biological instability (Urfer *et al*., 1997) by promoting regrowth of microbial mass in the distribution system. These species, especially BOM, serve as energy sources for heterotrophic bacteria by donating electrons (Hozalski *et al*., 1999).

The removal of easily biodegradable organic matter by biofiltration helps decrease bacterial regrowth in the distribution system, reduce both chlorine demand (during disinfection) and the amount of DBP precursors, and reduce taste and odour in finished water (Hozalski *et al*., 1999; Urfer *et al*., 1997; Rittmann *et al*., 1995; Bouwer & Crowe, 1988; Huck *et al*., 2013). Biofiltration is also an effective membrane pretreatment to control fouling in LPMs (e.g. Peldszus *et al*., 2011) due to the removal of biopolymers. In addition, Biofiltration also has the potential to remove micropollutants and biodegradable trace contaminants such as endocrine disrupting compounds and pharmaceuticals (Huck and Sozański, 2008).

2.4.2 Biofiltration process

Any granular media filter in drinking water treatment will operate biologically in the absence of a disinfectant residual in the filter influent and backwash water (Huck and Sozański, 2008). In the absence of a disinfectant residual, such as chlorine, the native bacteria present in natural water can slowly colonize the filter media grains as shown in Figure 2-7. As surface water rich in BOM, nutrients, bacteria and dissolved oxygen flow through the filter, a thin slimy film known as a biological film (or biofilm) starts to develop. The development of biofilm may take anywhere from a few days to months depending on factors such as influent organic matter (Chaudhary *et al*., 2003), water temperature, and bacterial community composition (Velten *et al*., 2011). Transport of substrate (energy and carbon source) to the biofilm occurs via bulk and surface transport phenomena (Chaudhary *et al*., 2003). The substrate is transported from the bulk liquid to the surface of the biofilm and eventually diffuses into the biofilm for biodegradation.

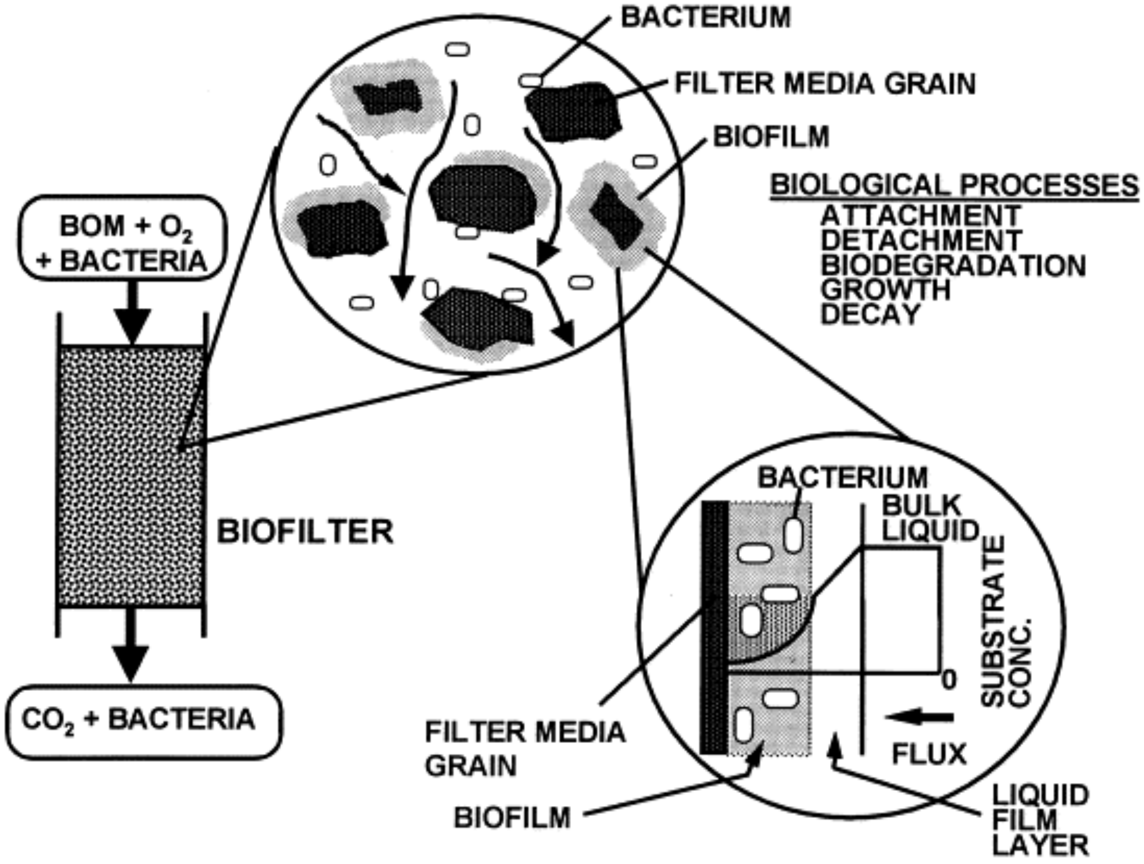


Figure 2-7: Schematic of the processes in a drinking water biofilter (From Hozalski & Bouwer, 2001)

The biological processes that occur in a biofilter are attachment, growth, decay and detachment of bacteria (Hozalski & Bouwer, 2001). As the primary goal of a biofilter is the removal of BOM, the success of a biofilter largely depends on the attachment and sustained growth of bacteria on the media. For this to happen, a constant source of nutrients and organics is required in the filter influent (Chaudhary *et al*., 2003). Detachment of the biomass from the media can take place due to decay, fluid shear and backwashing (Hozalski & Bouwer, 2001). Backwashing is an important process for a successful operation of a filter and therefore, requires careful management to prevent undue biomass loss. Despite the loss of some bacteria and biomass during backwash, the loss of biomass which is responsible for the biodegradation and removal of BOM during the normal backwashing process is not sufficient to compromise the effectiveness of the biofilter (Chaudhary *et al*., 2003; Ahmad & Amirtharajah, 1998).

An increased acknowledgement of biofiltration as an important treatment process in drinking water has led to the development of numerous physical–chemical, biochemical and microbiological methods to characterize biological activity in a biofilter. Biofilm activity can be characterized by estimating the relative biomass quantity by measuring total cell count, biofilm thickness, and total dry weight (Lazarova & Manem, 1995). However, these methods are unable to provide sufficient description of biofilm activity (Lazarova *et al*., 1994). A knowledge of the physiological behaviour of the biofilm is necessary in order to accurately characterize biological activity. Proteins and lipids can be used to characterize biological activity using the phospholipid analytical technique and have shown good correlation with substrate removal rates (Wang *et al*., 1995). Another indicator used is adenosine triphosphate (ATP), the currency of energy transfers in cells. The quantity of ATP in a biofilm represents bacterial activity in biofilms and have shown good correlation with oxygen uptake rate (Velten *et al*., 2011; Lazarova *et al*., 1994). However, a review of the published ATP data by Pharand *et al*. (2014) saw no quantitative correlation between ATP levels on the surface of the biofilter to biofilter performances in terms of DOC removal.

2.4.3 Factors affecting biofilter performance

The removal of BOM and particles through a rapid biofilter is affected by numerous factors. Discussed below are some of the important factors which affect biofilter performance (Chaudhary *et al*., 2003; Urfer *et al*., 1997):

- Contact time – The contact time, usually expressed as empty bed contact time (EBCT), represents the amount of time the water is in contact with the filter media in a filter, assuming the velocity of the water is same throughout the filter. Contact time has a significant impact on the removal of BOM through a biofilter (Urfer *et al*., 1997; Huck *et al*., 1994). A short contact time can severely affect the removal of BOM with longer contact time leading to better removal (Servais *et al*., 1991). Though the removal of BOM increases with longer contact time, the removal follows a diminishing return. Once an optimal BOM removal is achieved, increasing contact time will no longer increase BOM removal (Zhang & Huck, 1996).

- Filter media – The choice of adsorptive media (GAC) and non-adsorptive media (sand and anthracite) is primarily dependent on treatment goals and cost. Adsorptive media such as GAC are able to remove micropollutants by physical adsorption in addition to biodegradation of BOM. For biological activity, the important characteristics of media are surface area and texture. A media with a larger specific surface area would provide better BOM removal due to increased area for biofilm formation (Chaudhary *et al*., 2003). The irregular and rougher nature of GAC surface also provide a better opportunity for bacteria to attach to the media surface while preventing the loss of biomass during backwash (Servais *et al*., 1991).

- Backwashing – Backwashing is a critical process in the functioning of the filters where the particles and colloids cumulated over the filtration cycle are removed. As biofilters rely on the biomass for the biodegradation of the BOM, it is important that too much of the biomass on the media grains is not lost during backwash (Ahmad *et al*., 1998; Bouwer & Crowe, 1988). The loss of biomass also depends on the techniques of backwashing employed, although Servais *et al*. (1991) found no significant loss of biomass with the air scouring backwash of GAC filters. BOM removal through the biofilter was also found to be insensitive to backwashing conditions (Emelko *et al*., 2007; Huck *et al*., 2001).

- Temperature – Another operational parameter important in the performance of a biofilter is temperature. The biological activity of microbes is temperature dependent and found to increase with increase in temperature (e.g. Chaudhary *et al*., 2003). However, Emelko *et al*. (2007) found that temperature did not affect total organic carbon (TOC) removal, although a GAC biofilter performed better than an anthracite biofilter at lower temperatures.

- Other factors of importance are nature and composition of BOM, pH and toxic substances present in the bulk water. The nature and composition of BOM can be altered by treatment processes before biofilter such as ozonation (Urfer *et al*., 1997) with significant removal of more readily degradable substrate achieved, even at lower temperature once pseudo-state is achieved (Hozalski *et al*., 2001).

2.4.4 Biofiltration as a LPM pretreatment

The impetus for the implementation of biofiltration as a LPM pretreatment has been largely due to the acknowledgement of NOM as a major membrane foulant (Her *et al*., 2007; Kimura *et al*., 2004; Kaiya *et al*., 2000; Cho *et al*., 1998). Recent studies have shown that biopolymers play a significant role in reversible and irreversible fouling of polymeric membrane (Haberkamp *et al*., 2011; Peldszus *et al*., 2011; Hallé *et al*., 2009). Since biopolymers are biodegradable, a biofiltration process can be an effective pretreatment to reduce membrane fouling by reducing the concentration of the biopolymer fraction in the membrane influent.

Although the factors which affect the performance of biofilters have been mostly studied and reported, the factors on biofiltration as a membrane pretreatment is largely lacking. Studies by Hallé *et al*. (2009) showed that direct biofiltration without prior coagulation or ozonation was an effective pretreatment to control fouling in a polymeric membrane. They also showed that biopolymer removal through the biofilter was directly correlated to the EBCT with longer EBCT performing better as a membrane pretreatment.

Application of ozone prior to filtration have also been shown to reduce membrane fouling (Bhavana *et al*., 2005). However, Yavich *et al*. 2004 showed that the effect of ozone on NOM is largely dependent on source water. Application of ozone can produce both rapidly and slowly biodegradable fractions of NOM. Therefore, ozone-biofiltration pretreatment would be suitable for a source water with NOM which is more amenable to ozone.

2.5 Research Motivation

Direct biofiltration has been demonstrated as an effective pretreatment to control fouling in polymeric LPM (Haberkamp *et al*., 2011; Peldszus *et al*., 2011; Hallé *et al*., 2009). The identification of biopolymers (Peldszus *et al*., 2011; Kimura *et al*., 2004) and humic substances (Yuan & Zydney, 1999) as major membrane foulants have made biofiltration an attractive option to remove these NOM fractions before membrane filtration. Polymeric membranes are the dominant type of membrane used in water treatment today due greater operational experience and lower capital cost compared to ceramic membranes (Guerra & Pellegrino, 2013). Therefore, almost all studies on the efficacy of biofiltration as a pretreatment have largely focused on polymeric membranes.

However, ceramic MF and UF membrane have numerous advantages over polymeric membranes including physical strength, thermal and chemical stability, long operation life (Guerra & Pellegrino, 2013; Finley, 2005; Weber *et al*., 2003) and high flux (Loi-Brügger *et al*. 2006). The higher cost of a ceramic membrane can be offset by operating it at higher flux while controlling membrane fouling (Meyn *et al*., 2008). Furthermore, innovation in newer design such as CeraMac® (Galjaard *et al*., 2012) have lowered the operational cost, making ceramic membranes competitive with polymeric membranes.

Although there are numerous studies on different pretreatments for ceramic membranes, little is known about the efficacy of direct biofiltration without prior coagulation as a pretreatment to control fouling. Therefore, a proof of concept study of BF_{WP} as a pretreatment would provide much-needed information on the efficacy of this process to control fouling in ceramic membranes. An important finding from the Hallé *et al*. (2009) study was that the biopolymer removal increased with longer EBCT, thereby reducing both reversible and irreversible fouling rates in polymeric membranes. Hence, a study of the effects of EBCT on fouling of ceramic membranes would provide information on whether that parameter has similar effects as for polymeric membranes. Ceramic membranes also come in different materials such as TiO_2, $Al_2O_{3,}$ and ZrO_2. The material cost of the three different membranes is similar, and therefore, information on which material provides the best performance with BF_{WP} pretreatment will be of interest to treatment plants who are interested in implementing ceramic membranes.

Chapter 3

Impact of Biofilter EBCT and Membrane Pore Size on the Fouling of Ceramic Membranes

3.1 Introduction

The invention of synthetic membranes in the middle of last century has been seen as a major development in water treatment due to the membrane's ability to produce consistently high-quality water (Wiesner & Chellam, 1999). The use of membrane filtration in drinking water treatment has grown significantly in the last couple of decades due to improvement in membrane quality and a decrease in membrane cost (Huang *et al*., 2009). In a 2008 report, Furukawa states that the cost of installing LPMs systems has dropped below the cost of conventional treatment fueling further growth in the installation of membranes. The LPM used in drinking water treatment today have been largely made of polymeric materials due to their lower cost and greater operational experience in the water treatment industry. Yet, there are other membranes made out of inorganic materials (ceramic membranes) that have a much higher mechanical strength, can be operated at a higher flux and are more resilient against chemicals used for cleaning compared to polymeric membranes (Finley, 2005; Guerra & Pellegrino, 2013). Despite these advantages, the adoption of ceramic membranes in drinking water treatment has been largely slow due to their high initial capital cost. Nevertheless, this trend is slowly changing as the advances in technology, economies of scale and development of new systems such as CeraMac® (Galjaard *et al.*, 2012) has made the life cycle cost of installing ceramic membranes competitive with that of polymeric membranes.

As with all membrane operations, the biggest challenge remaining is membrane fouling. Membrane fouling refers to the loss of performance due to the deposition of materials such as particles, colloids and organic matter from the feed water on the membrane surface and pores, thereby increasing the resistance to the flow of water through it. Depending on the mode of membrane operation, membrane fouling can be quantified by measuring the increase in resistance. When the membrane is operated in a constant flux mode, fouling can be observed by the gradual increase in pressure across the membrane (TMP) over the course of the filtration cycle. The increase in pressure required to maintain the flux over time requires additional use of electrical energy to power the pumps. In a system where the TMP is kept constant, fouling is observed by a gradual decrease in flux over the course of the filtration cycle. The decrease in flux represents a loss of productivity that increases production cost. In both scenarios, membrane fouling leads to an increased operational cost as well as reduced membrane life.

Membrane fouling can be classified as either hydraulically reversible or irreversible fouling. In a constant flux mode operation, the gradual rise in TMP over a permeation cycle can be recovered by hydraulically backwashing the membrane, and it is known as hydraulically reversible fouling. However, over multiple permeation cycles, the starting TMP after a hydraulic backwash gradually increases due to slow adsorption and clogging of the membrane pores (Crittenden *et al*., 2012). The rise in TMP over multiple permeation cycles can only be recovered by using chemical cleaning and is known as hydraulically irreversible fouling. To keep operational cost low, it is essential to control membrane fouling, in particular, hydraulic irreversible fouling as it determines the frequency of chemical cleaning. Numerous studies have reported that coagulation prior to membrane filtration is an effective pretreatment for ceramic membrane operation (Huang *et al*., 2009; Loi-Brügger *et al*., 2006; Meyn *et al*., 2008; Shirasaki *et al*., 2014). They noted coagulation is effective in removing colloids, higher molecular weight NOM and more hydrophobic components of the NOM which have been attributed to cause fouling in both polymeric and ceramic membranes. Another novel pretreatment that has gained attention recently is the application of direct biofiltration without pretreatment (BF_{WP} - without prior coagulation or ozone addition) to control fouling in polymeric membranes. This chemical-free pretreatment can remove the biopolymer fraction of NOM (proteins, polysaccharides, and amino acids) as well as particulate matters which are widely acknowledged as membrane foulants for polymeric membrane (e.g. Hallé *et al*., 2009). Hallé et al., (2009) also reported that a biofilter with longer empty bed contact time (EBCT) led to a greater reduction in both hydraulically reversible and irreversible fouling. Although recent studies on the efficacy of direct biofiltration as pretreatment to control fouling in polymeric membranes (Hallé *et al*., 2009; Huck *et al*., 2011; Peldszus *et al*., 2012) has shown promise, its efficacy as a pretreatment in ceramic membranes is largely unknown.

In this study, the efficacy of direct biofiltration as a pretreatment to control fouling in ceramic membranes was investigated. The investigation was carried out using biofiltration pilot plant at Mannheim Water Treatment Plant which treats the Grand River water. The effluent of the biofilters was then used as influent to the membrane fouling experiments. The focus of the research was to establish whether BF_{WP} would provide the same benefits for ceramic membranes as it has been shown to provide for polymeric membranes. In addition, the impact of biofilter EBCT and membrane pore size on membrane fouling was examined. The study looked at whether a biofilter with a longer EBCT performed better than a biofilter with a shorter EBCT with regards to fouling control in ceramic membranes. This chapter also looked at how membranes of different pore size (MF vs. UF) fouled under identical pretreatment conditions to gain insights into their fouling behavior and evaluate the impact of natural water constituents on fouling.

3.2 Materials and Methods

3.2.1 Biofiltration pilot plant

A biofiltration pilot plant located at the Mannheim Water Treatment Plant in Kitchener, Ontario, Canada was used. The Mannheim WTP treats Grand River water which is heavily impacted by wastewater effluent and agricultural runoff. Raw water, which is drawn from the main raw water line feeding the treatment plant, is used as influent to the roughing filters.

The pilot plant consisted of two biofilters running in parallel (Figure 3.1). The biofilters were constructed from two 8-inch diameter schedule 40 PVC pipes connected in the middle with a slip flange. Both biofilters were comprised of dual media – anthracite over sand which was biologically active. The biofiltration pilot plant had been in operation over a year before the start of this study. The biofilters were monitored for biological activity during the time and have been reported by both Wilson (2015) and El-Hadidy (2016) to be biologically active.

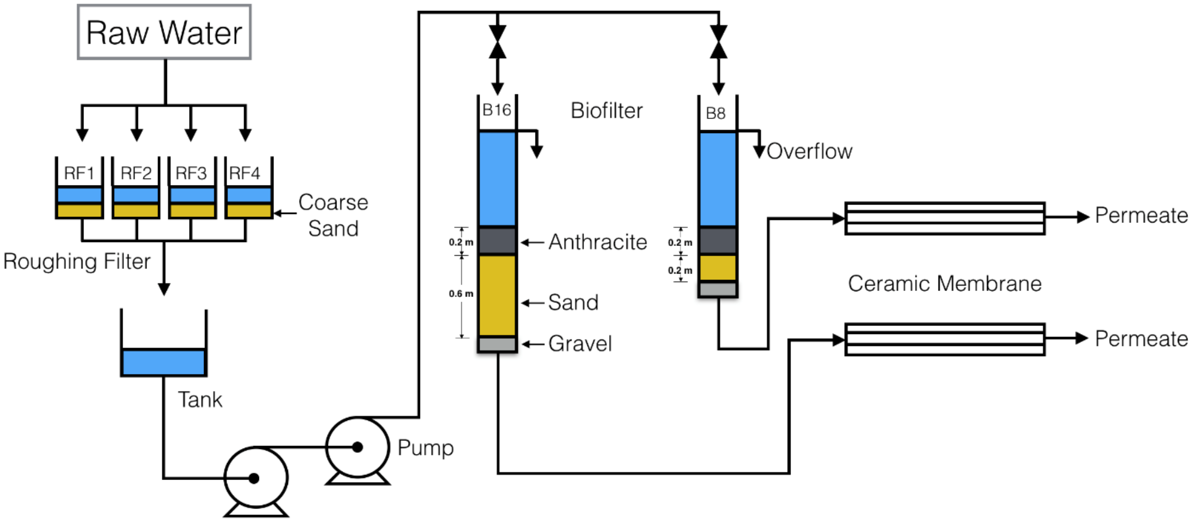


Figure 3.1 – Schematic of the Biofiltration Pilot Plant Set-up

Biofilter B8 featured 0.2 m of anthracite over 0.2 m of sand that was supported by 0.15 m of coarse gravel. Biofilter B16 featured 0.2 m of anthracite over 0.60 m of sand that was also supported by 0.15 m of coarse gravel. Both biofilters (B8 and B16) were operated at a constant flow mode at a rate of 100 L/h, which corresponds to a loading rate of 3.08 m/h. As the volume of media differed in the two biofilters, the EBCT of biofilter B8 was 7.8 minutes while the EBCT of biofilter B16 was 15.6 minutes. Preceding the biofilters were four independent roughing filters. The roughing filters could be cleaned independently and allowed for a continuous supply of effluent to the biofilters. Each roughing filter was constructed from two opaque 8-inch PVC pipe stacked on top of each other containing very coarse sand with very low EBCT. The effluents from all four roughing filters were collected centrally in a tank located directly underneath. Two low shear pumps pumped the water from the tank to the top of the biofilters. An overflow at the top of the biofilters maintains a constant water level in the biofilter throughout the filter run.

To achieve a constant flow rate through the biofilters, and thus maintain the same EBCT throughout a filter run, an automatic flow controller was installed on both the biofilter effluent line. This system mirrors the full-scale operation where the filters are also operated at a constant flow mode as opposed to a declining flow mode where a constant head is maintained but the flow decrease due to headloss through the filter. Effluents from both biofilters were collected in a common backwash tank. The backwash tank was also fitted with an overflow to help drain the effluent as the tank fills up.

The biofilter effluent collected in the backwash tank was used for backwashing the biofilters. The filters were backwashed every Monday, Wednesday, and Friday to remove the particles that have been accumulating in the filter during the filtration run. During backwash, biofilter effluent from the backwash tank was pumped using a centrifugal pump via the bottom of the biofilter and the dirty water exited via the overflow located at the top of the biofilter. The flow during the backwash was measured using a variable area flow meter and controlled via a global valve upstream of the flow meter. The addition of pressurized air to the biofilter was also possible via an external connection to a compressed air cylinder.

The biofilters were backwashed by first draining the water in the biofilter to a level which was slightly above the media. This step prevented the loss of media during the air scouring process that followed. During the air scouring process, pressurized air was provided together with a low water flow (at subfluidization velocity) to the bottom of the biofilter. The process, known as collapse pulsing, was run for 3 minutes. After the air scouring process, the air was shut off, and the flow rate was increased to achieve 50% bed expansion. This process was run for nine and half minutes, after which the flow to the bottom of the biofilter was slowly reduced until it reached zero in the next 30 seconds. After the backwash, the biofilter was put back in service by closing the backwash valve and opening the effluent valve.

3.2.2 Membrane test unit description

The MF and UF ceramic membranes were operated using a membrane test unit manufactured by Convergence Industry B.V in Enschede, Netherlands. The membrane test unit consisted of a fully programmable membrane system that could be automated to run membrane fouling experiments i.e. long term constant flux filtration including hydraulic backwashing, clean water permeability (CWP) test and online chemical cleaning tests.

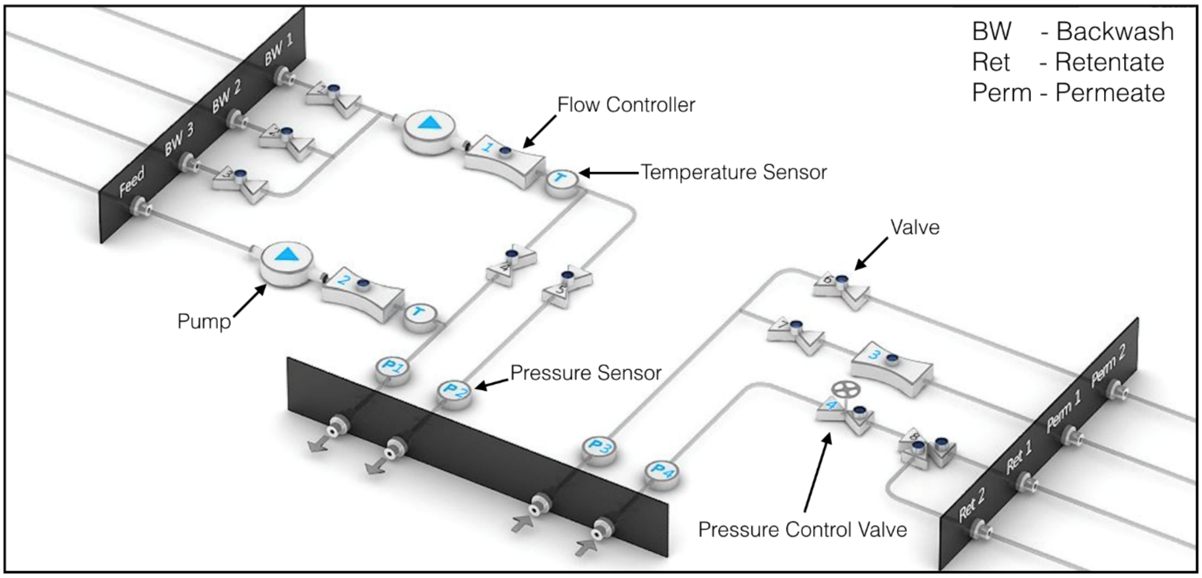


Figure 3.2 - Flow diagram of the membrane test unit showing the valves and flow meters that could be manually controlled via the custom-built software

The test unit was comprised of two pumps, one on the feed line and another one the backwash line. The pumps had the capacity to drive feed and backwash water through the membrane up to a flow rate of

100 L/h. Coriolis mass flow meters on the feed and backwash line measured the flow through the feed and backwash line. The system was equipped with a proportional-integral-derivative controller (PID controller) to maintain the set flow through the system during the permeation and backwashing cycles. Online temperature sensors were located on the feed, backwash and permeate line to measure the temperature at those points in the system (Figure 3.2). The teflon tubing inside the system was fitted with valves which could be switched on and off using the custom-built software for the system.

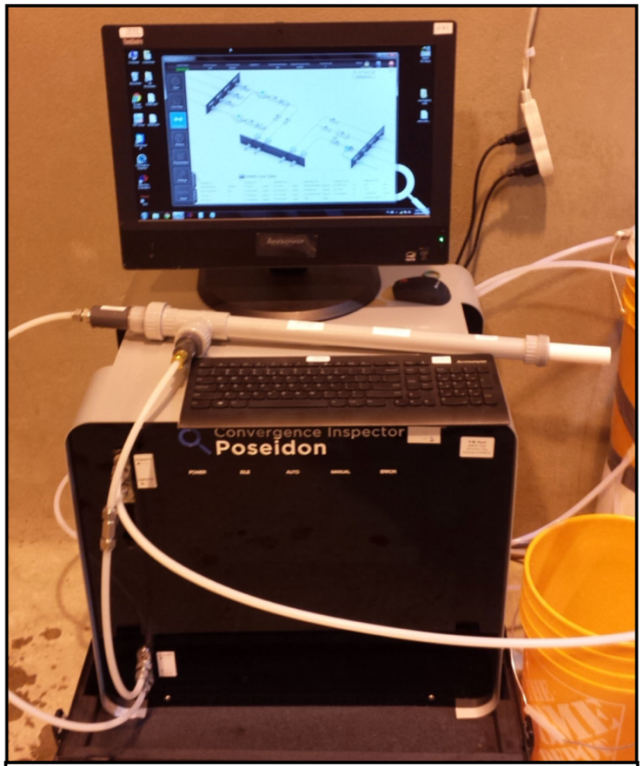


Figure 3.1 - Membrane test unit

The membrane test unit (Figure 3.3) was operated via a computer that was connected to it via an Ethernet cable. All operations, whether it was to switch on and off the valves and pumps or set a flow rate through the system, were carried out via the software. The system could be operated in either manual mode or automated mode. In the manual mode, the system continues running in the current state until it is interrupted by input from the user. While, in the automated mode, the system executes a set of instructions from a loaded program that has been written and saved as a program. The software offers the user the ability to custom write programs for operating the system. A set of programs written for the membrane fouling experiment is given in Appendix A.

Ceramic membranes of different pore sizes and materials manufactured by Atech Innovations (Germany) were used for this study. The ceramic membranes were composed of a highly porous supporting layer and a thin separation layer. The supporting porous layer (made of alumina) was sinter-fused with the separation layer (made of zirconia) of a defined mean pore size manufactured by tightly controlling temperature and moisture (atech, 2014). Two different types of membranes, an MF membrane with a nominal pore size of 0.1 μm and a UF membrane with a MWCO of 500 kDa were used for this study. Both membranes were tubular in structure with 7 channels, 600 mm long and had a nominal surface area of 0.08 m^2. All membrane used in the study were 1200 mm long during the manufacturing process and were subsequently cut into two 600 mm module.

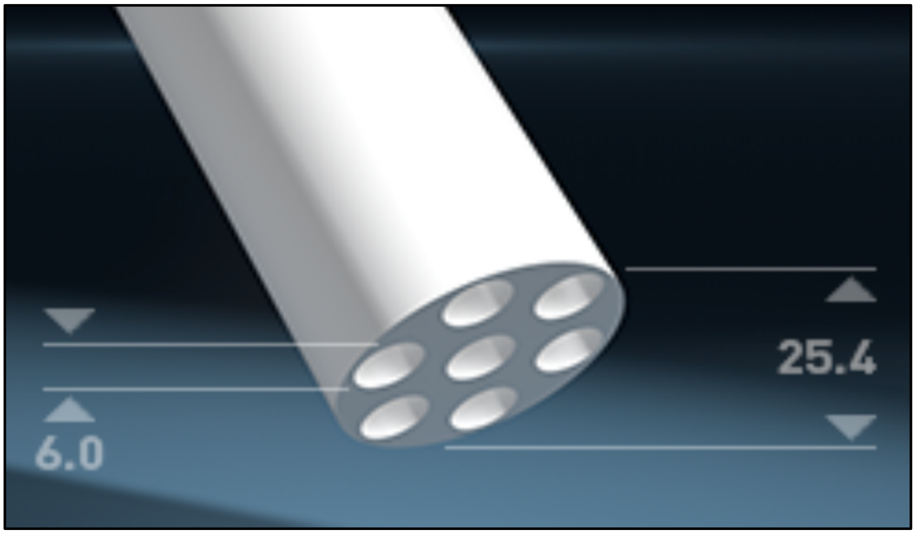


Figure 3.4 - Atech 7 channels tubular ceramic membrane *(photo credit: www.atech-innovations.com)*

3.2.3 Membrane fouling experiments

To assess the efficacy of direct biofiltration as a pretreatment, a membrane fouling experiment was conducted using biofilter effluent and roughing filter effluent as the membrane influent. Two membrane test units were operated in parallel using MF zirconia ceramic membrane modules, one fed with biofilter effluent and the other with roughing filter effluent. The membranes were operated in constant flux mode in dead-end configuration. The membrane filtration process included membrane permeation for 30 minutes followed by a forward flush of the membrane lumens using permeate water at a flow rate of 20 L/h for 30 seconds. After the forward flush, the membranes were backwashed using permeate water for 3 minutes at twice the permeation flux, and the filtration cycle was repeated. The ceramic membranes were housed inside PVC housing which sat horizontally on the membrane test unit as shown in Figure 3.3.

To make them comparable, experiments were run at a temperature-corrected flux corresponding to an equivalent flux of 85 L/m^{2}h (LMH) corrected to 20°C which was maintained during the permeation cycle, while an equivalent flux of 170 LMH corrected to 20°C was maintained during the backwash cycle. To calculate the temperature-corrected membrane fluxes, Equation 3-1 (Crittenden *et al.*, 2005) was used.

$$\boldsymbol{J_s = J_m(1.03)^{T_s - T_m}} \qquad \textbf{Equation 3-1}$$

where J_s = Standard flux (85 LMH)
J_m = Measured flux
T_s = Standard temperature (°C)
T_m = Measured Temperature (°C)

Operating the membranes at temperature-corrected fluxes accounts for the effect of a change in viscosity of water due to changes in temperature. The viscosity of the water increases as the temperature decreases which in turn increases the resistance to flow through the membrane. To compare the membrane performance at different temperatures, it is important to run at temperature-corrected fluxes so that an increase in resistance at a lower temperature is not incorrectly inferred to as membrane fouling. The temperature at the start of each experiment as measured by the online sensor (on the feed line in the membrane test unit) was used for establishing the temperature-corrected flux for each experiment. The membrane fouling experiment was terminated at the end of four days or when the TMP reached 3 bars, whichever occurred first. To account for deviation in the feed water temperature from the temperature used for determining the temperature-corrected flux during the experiment, a correction to the measured TMP was applied during the data analysis process as given by Equation 3-2

$$\boldsymbol{TMP_c = TMP_m \times 1.025^{T-T_{set}}} \qquad \textbf{Equation 3-2}$$

where TMP_c = Corrected TMP (bar)
TMP_m = Measured TMP (bar)
T_c = Corrected Temperature (°C)
T_{set} = Set Temperature (°C)

The ceramic membranes were chemically cleaned before the start of every experiment using commercially available sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH). The membranes were soaked in a 3.0% NaOCl solution for two to three days, after which they were rinsed with tap water and soaked in 2.5% NaOH for a further 30 minutes. After the 30 minutes, the membranes were cleaned with permeate water and installed in the membrane housing. The membranes were soaked in 3.0% NaOCl for two to three days because the membrane experiments were run from Monday to Friday and fouled membranes were left soaking over the weekend. Since the objective of the study was not to optimize the membrane cleaning procedure but rather to test the membrane performance, it was imperative that a comparable baseline with clean membranes at the start of every experiment was achieved. By soaking the membrane for a longer duration, greater recovery of the fouled membrane is expected.

A clean CWP test was performed before the start of every experiment to test the membrane recovery after the chemical cleaning. During the CWP test, permeate water was used as feed to the membrane.

The membrane was operated in dead-end configuration at three different flow rates, 2 L/h, 4 L/h, and 6 L/h, for five minutes each. TMP data was recorded every five seconds during the CWP test. To compute the clean water permeability in terms of LMH/bar, the flow was converted into flux and corrected to 20°C using Equation 3-1 and plotted against the measured average TMP for each flux. CWP test was also performed at the end of each experiment to measure the loss of the permeability as a measure of fouling accumulated during the experiment. Before the start of each experiment, the biofilter used as feed for the membrane experiment was backwashed.

The pressure on the influent and backwash line of the membrane was measured and recorded every 5 seconds during the fouling experiments. The pressure on the influent line represents the TMP as the effluent line is open to atmosphere. TMP data from the permeation cycle was used for calculating the hydraulically reversible and irreversible fouling rates. The irreversible fouling represents the fouling which cannot be removed by backwashing and were calculated using the TMP readings at the start of each permeation cycle after a backwash cycle. A linear trend line was plotted on the starting TMP readings to generate a single irreversible fouling rate for each experiment. Reversible fouling, however, represents the fouling that can be recovered by backwashing and was calculated using the TMP readings of two consecutive permeation cycles. The reversible fouling rates were calculated by taking the difference in TMP reading at the end of one permeation cycle to the starting of the next permeation cycle and dividing by the permeation time (30 minutes). A single reversible fouling rate for the experiment was calculated by taking the average of all reversible fouling rates for each permeation cycle.

A 2x2 2-level factorial experiment was designed to test the impact of biofilter EBCT (8 min vs. 16 min) and membrane pore size (MF vs. UF) on membrane fouling. The design included running a control membrane test unit in parallel to the experimental membrane test unit to account for any changes in raw water quality. The ceramic membrane and biofilter effluent for the control test unit were the same for each run while the ceramic membranes (UF and MF) and biofilter effluent (B8 and B16) for the experimental test unit changed from week to week as shown in Table 3-1.

Table 3-1 - 2x2 factorial experiment design with levels for experimental and control membrane test unit

Run Number	Experimental Membrane Test Unit				Control Membrane Test Unit			
	Membrane		Biofilter Effluent		Membrane		Biofilter Effluent	
	Level	Value	Level	Value	Level	Value	Level	Value
1	-	MF	-	B8	-	MF	-	B8
2	+	UF	-	B8	-	MF	-	B8
3	-	MF	+	B16	-	MF	-	B8
4	+	UF	+	B16	-	MF	-	B8

The levels of the membrane (MF and UF) and biofilter effluent (B8 and B16) for each run was randomized using a random number generator in Excel®. Since the levels of the independent variables were discrete, centre points could not be used to obtain an independent estimate of error. To obtain an independent estimate of error, a replicate of the entire factorial design needed to be performed. As will be discussed in the Section 3.3.1, there were many challenges while running the factorial design experiments and not all data points from every run of the factorial design could be used.

3.2.4 Sample collection and analysis

Water samples for various water quality parameters were collected 24 hours into every membrane fouling experiment. This time frame was chosen to allow sufficient time to pass to avoid the influence of adsorption of organic matter on the clean membrane that is predominant during the initial phases of membrane filtration. The water samples from roughing filter effluent, biofilter effluent, and membrane permeate were collected and analyzed for TOC/DOC, pH, UV_{254} absorbance, turbidity, LC-OCD, and FEEM.

A TOC analyzer from OI-Analytical (model 1010, College Station, TX, USA) was used to measure TOC and DOC using standard methods 5310D that employed a wet oxidation method. FEEM was analyzed using a Cary Eclipse fluorescence spectrophotometer from Agilent Technologies. The excitation (Ex) wavelengths ranged from 250 to 380 nm with an increment of 10 nm while the emission (Em) wavelengths ranged from 300 to 600 nm with a scan rate of 600 nm/min. A quartz cuvette with four optical windows was used with photomultiplier tube voltage set at 650 V. Peak picking technique was used to evaluate the FEEMs with the intensity at Ex/Em = 320 nm/415 nm corresponding to humic acids (Sierra *et al*, 2005) and the intensity at Ex/Em = 280 nm/330 nm corresponding to fulvic acids, and the intensity at Ex/Em = 270 nm/460 nm corresponding to protein-like material (Peiris *et al*., 2010; Sierra *et al*., 2005).

Different NOM fractions – biopolymers, humic substances, building blocks, low molecular weight (LMW) acids, and LMW neutrals, as described by Huber *et al*., (2011) were analyzed using LC-OCD (DOC-Labor Dr. Huber, Karlsruhe, Germany). A turbidimeter (Model -2100N, HACH, Loveland, Colorado, USA) was used to measure turbidity at the pilot plant immediately after sample collection. Except for turbidity which was measured at the site, all samples were transported from the pilot plant to the University of Waterloo laboratory and analyzed within 24 hours.

All water samples were filtered through a 0.45 μm polyethersulfone (PES) filter (PALL, Port Washington, New York) before analysis except for TOC and FEEM water samples. Before filtration, the set-up was rinsed with ultrapure water. After installing the PES 0.45 μm filter, roughly 150 mL of ultrapure water was filtered, and the filtered ultrapure water was discarded. Then 20 – 30 mL of the sample was filtered and discard. The next 100 mL of the filtered sample was used for all water quality analysis mentioned above except for FEEM and TOC. Phosphoric acid is used to acidify TOC and DOC backup samples to pH of 2 and stored at 4°C.

3.3 Results and Discussion

3.3.1 Challenges faced in running the membrane fouling experiments

The proof of concept and the 2x2 factorial design experiments were performed with two identical membrane test units running in parallel. One of the test units acted as the control unit while the other acted as the experimental unit. The inclusion of a control unit was meant to account for any changes in raw water quality, which were expected since natural water was used in this study. This approach necessitates that the variability between the two membrane test units be ideally negligible, or at least smaller than any differences in the effects of the factors under study.

To establish the variability between the two parallel membrane test units, a preliminary membrane fouling experiment was conducted. The two membrane test units were operated using the same biofilter effluent and under identical settings for membrane filtration. Results from the initial experiment revealed that the two test units performed similarly as can be seen in the TMP profile shown in the insert in Figure 3.9. However, it was observed during the factorial experiments that the TMP profile between the control unit and the experimental unit, when run under identical settings showed significant differences (Figure 3.5). During the first factorial experiment, the MF membrane module in the control test units was not tracked over the experiments as it was assumed that the variability in the membranes would be negligible as the membranes were manufactured in one piece and cut in half afterward. Therefore, the variability in the fouling was hypothesized to be due to the membrane inherent variability and a second factorial experiment was conducted with the same membrane module in the control test unit over all the experiment runs.

However, the differences in the TMP profile observed between the two units when run under identical settings were comparable to the differences observed for other runs where the effects of the different factors were studied. As a result, it was imperative to investigate whether the variability was due to the inherent variability in the ceramic membrane module or with the membrane test units.

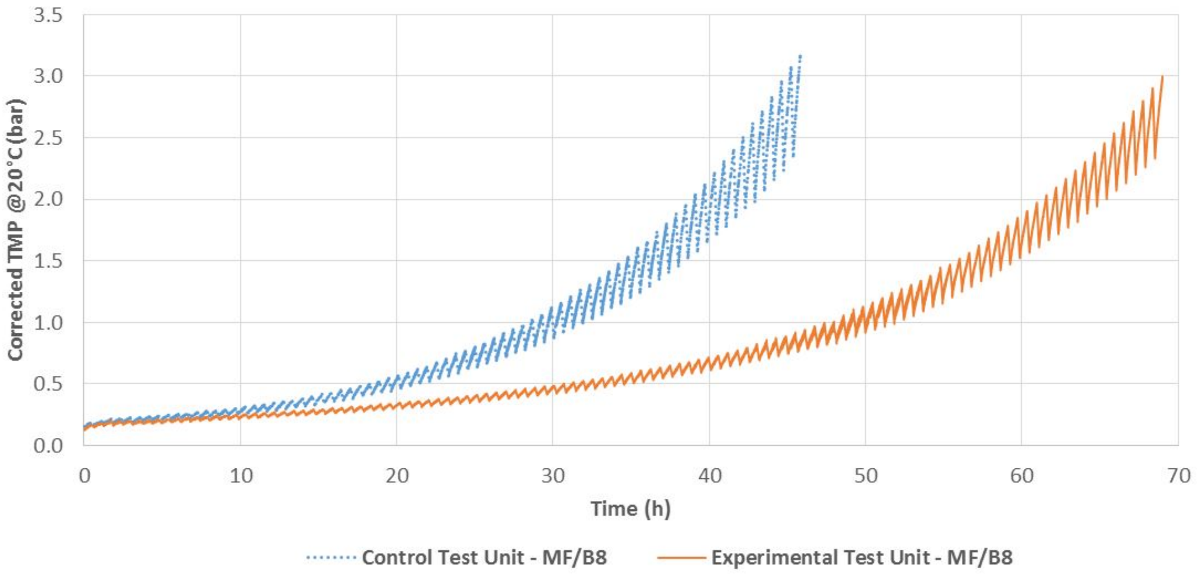
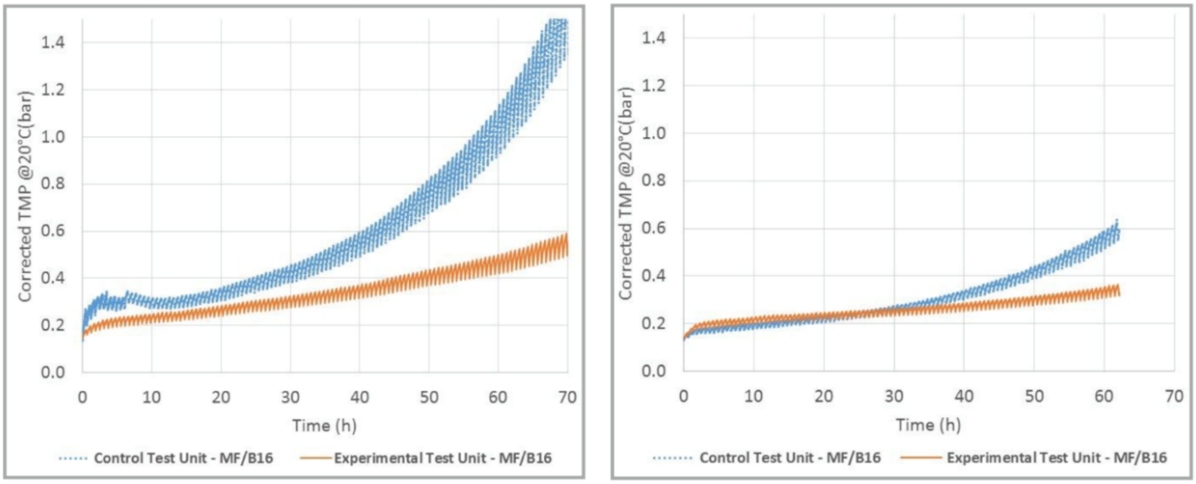


Figure 3.5 - TMP profile of control and experimental unit with MF zirconia ceramic membrane run identically with effluent from biofilter B8 *(MF – Microfiltration ceramic membrane)*

To investigate this further, two membrane fouling experiments were conducted. In the first membrane fouling experiment, the two test units were run under identical settings using biofilter effluent as feed. In the second membrane fouling experiment, the experiment was repeated with the membrane modules swapped. The membrane module from the control unit was installed in the experimental unit and vice versa. The TMP profile from the two experiments showed that the membrane in the control test unit fouled much faster in both experiments compared to the experimental test units (Figure 3.6). It should be noted that the two experiments were done after the factorial experiments and are discussed here to provide context for interpreting the data.

This result provides strong evidence that the difference in the fouling behavior of the two membrane systems was due to the inherent variability in the membrane test units rather than the variability between membrane modules. The ceramic membrane modules used in these experiments were from the same single 1200 mm long membrane module which was cut in half at our request. As a result, it was reasonable to expect that the variability between the membrane modules was low.



a) Experiment 1

b) Experiment 2

Figure 3.6 - TMP profile of MF ceramic membrane in Control and Experimental Test Units. *(B16 – biofilter B16 effluent was used as feed to the membrane fouling experiment)*

Since the first preliminary experiment showed that the two membrane systems seemed to perform identically, it could be reasoned that the variability between the membrane systems increased over time. However, a closer look at the results from the first preliminary comparison experiment suggests otherwise. The preliminary experiment was conducted at the end of March 2015 when the raw water quality was poor due to spring run-off. As a result, that particular membrane fouling experiment lasted less than 15 hours to reach 3 bars, the criterion for the end of an experiment, whereas it consistently took 3 to 4 days to reach 3 bars if at all in the subsequent experiments as water quality improved. Therefore, it is likely that the duration of the initial comparison experiment was not long enough to expose the inherent variability between the two membrane test units, which becomes more apparent at longer run times.

Table 3-2 - Membrane fouling experiments conducted for the research study

		Control Train		Experimental Train		
	Experiment Date	**Pretreatment TU1**	**Membrane in TU1**	**Pretreatment TU2**	**Membrane in TU2**	**Experiment Number**
Proof of concept	April 4-6, 2015	Roughing Filter	MF - ZrO_2	Biofilter B16	MF - ZrO_2	1
Factorial experiment 1	May 18-21, 2015	Biofilter B8	MF - ZrO_2	Biofilter B8	UF - ZrO_2	2
	May 25-28, 2015	Biofilter B8	MF - ZrO_2	Biofilter B16	MF - ZrO_2	3
	June 1-4, 2015	Biofilter B8	MF - ZrO_2	Biofilter B16	UF - ZrO_2	4
	June 8-12, 2015	Biofilter B8	MF - ZrO_2	Biofilter B8	MF - ZrO_2	5
Factorial Experiment 2	July 1-4, 2015	Biofilter B16	MF - ZrO_2	Biofilter B16	MF - ZrO_2	6
	July 15-18, 2015	Biofilter B16	MF - ZrO_2	Biofilter B8	MF - ZrO_2	7
	July 20-23, 2015	Biofilter B16	MF - ZrO_2	Biofilter B8	UF - ZrO_2	8
	July 27 - 30, 2015	Biofilter B16	MF - ZrO_2	Biofilter B16	UF - ZrO_2	9
Membrane comparison Experiment	Aug 3 - 6, 2015	Biofilter B16	MF - ZrO_2	Biofilter B16	MF - ZrO_2	10
	Aug 10-13, 2015	Biofilter B16	MF - ZrO_2	Biofilter B16	MF - Al_2O_3	11
	Aug 17-20, 2015	Biofilter B16	MF - ZrO_2	Biofilter B16	MF - TiO_2	12

Even with extensive troubleshooting, the intrinsic difference between the two membrane test units could not be eliminated, and the standard factorial experiment analysis could not be performed on the data collected. Therefore, an alternate approach to data analyses had to be employed. The TMP profile data set collected over the two sets of the factorial design experiments (Table 3-2) was closely examined to determine the control membrane runs for which the observed fouling was similar from week to week. For these runs where the control fouling was similar (Table 3-3), fouling results from the corresponding experimental train could be compared and therefore the factors which were different in the experimental train could be assessed. In such a way, the effects of EBCT and pore size on the membrane fouling were evaluated.

Table 3-3 - Membrane fouling experiments which are referred to in each chapter with the corresponding names used. *(* refer to Table 3-2 for experiment details; ** only the control train experiments were discussed in chapter 5)*

	Name of experiment as referred to in Chapter		
Experiment Number*	**chapter 3**	**Chapter 4**	**Chapter 5****
1	POC	-	-
2	-	-	E1
3	Exp 1	-	-
4	-	-	E2
5	Exp 2	-	E3
6	Exp 3	-	E4
7	-	-	E5
8	-	-	E6
9	Exp 4	-	E7
10	-	MC1	E8
11	-	MC2	E9
12	-	MC3	E10

3.3.2 Proof of concept – Efficacy of biofiltration as a pretreatment

Studies by Hallé *et.al*., (2009) showed that direct biofiltration was an effective "green" pretreatment to control fouling in polymeric UF membranes. However, its efficacy is largely unknown for ceramic membranes. Therefore, a proof of concept experiment was conducted to assess the efficacy of direct biofiltration to control fouling in ceramic membranes.

Two identical membrane test units with MF zirconia ceramic membrane were used for the membrane fouling experiment. Membrane test unit 1 (TU1) was fed with effluent from the roughing filter while membrane test unit 2 (TU2) was fed with effluent from biofilter B16. Both membrane test units were operated under identical conditions at a corrected flux of 85 LMH (refer to Section 3.2.3 for experiment details).

The Grand River water, which is impacted by agricultural runoff and input of wastewater effluent, was used as influent to the biofiltration pilot plant. The raw water was fed through four roughing filters in parallel before being pumped to the top of the biofilters.

Impact of biofiltration on water quality

The turbidity of the roughing filter effluent and biofilter effluent during the proof of concept (POC) experiment was 7.61 NTU and 0.573 NTU respectively. The turbidity of the effluent from the MF ceramic membrane (M1) fed with effluent from the roughing filter was 0.053 NTU. Similarly, the turbidity of the effluent from the MF ceramic membrane (M2) fed with biofilter effluent was 0.060 NTU.

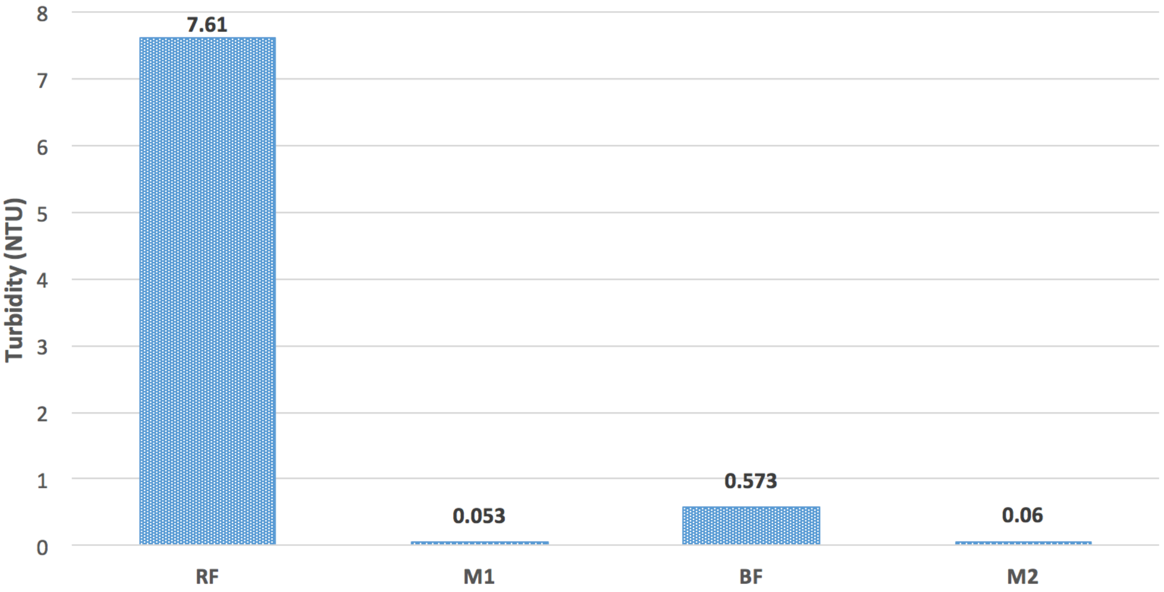


Figure 3.7 - Turbidity of water samples from the proof of concept experiment. *(RF – roughing filter; M1 – ceramic membrane in test unit 1; BF – Biofilter; M2 – ceramic membrane in test unit 2*)

The turbidity removal through the biofilter was 92.4% while the turbidity removal through the membrane M1 and M2 (based on membrane influent) was 99.3% and 89% respectively. The overall turbidity removal for the biofilter and membrane (M2) process together was 99.2%. The turbidity removals through the membrane with pretreatment and without pretreatment were identical. This is expected, as membrane filtration is a size exclusion process and able to produce consistent water quality in terms of particulate matter irrespective of the influent water quality. However, the turbidity of the biofilter effluent was much lower (0.573 NTU) compared to roughing filter effluent (7.61 NTU), which drastically reduces the particle loading on the membrane with pretreatment.

The concentration of TOC and DOC in the roughing filter effluent was 6.3 mgC/L and 6.2 mgC/L respectively (Figure 3.8). The TOC and DOC concentration in the biofilter effluent was 5.1 mgC/L and 5.0 mgC/L respectively. The DOC concentration of M1 membrane permeate was 5.6 mgC/L while that of M2 membrane permeate was 5.0 mgC/L. In the biofilter-membrane process train, the biofilter achieved a DOC percent removal of 17.7% with a further 1.9% through the membrane for a total overall DOC removal of 19.6%. In the process train with no pretreatment, the DOC removal through the membrane was 9.6%.

The percentage removal of biopolymers through the biofilter (51%) was substantially higher than for the other NOM fractions (humics – 8%, building blocks – 10%, LMW neutrals – 24%). This is consistent with a study by Hallé *et al.*, (2009) who used a similar biofiltration setup with the same source water. A study by Maeng *et al.* (2008) also showed the preferential removal of non-humics substances (i.e. biopolymers) by riverbank filtration which is also a biological filtration process.

The percentage removal of biopolymers through membranes M1 and M2 was also substantially higher than for the other NOM fractions (Figure 3.8). The percent removal of biopolymers through membrane M1 and M2 were 34% and 47% of respectively, while the percent removal of all other NOM fractions combined (humics, building blocks, LMW neutrals) were less than 9% and 0.5% for membrane M1 and M2 respectively. The molecular weight of biopolymers as quantified by LC-OCD (Huber *et al*., 2011) is 10 kDa or higher while the molecular weight of humics and other NOM fractions are less than 10 kDa. The pore size of the MF ceramic membrane used in this study was 0.1 µm and was therefore much bigger than the molecular weight of humic substances. Consequently, insignificant removal of humics and other smaller NOM fractions through the membrane were consistent with what was expected.

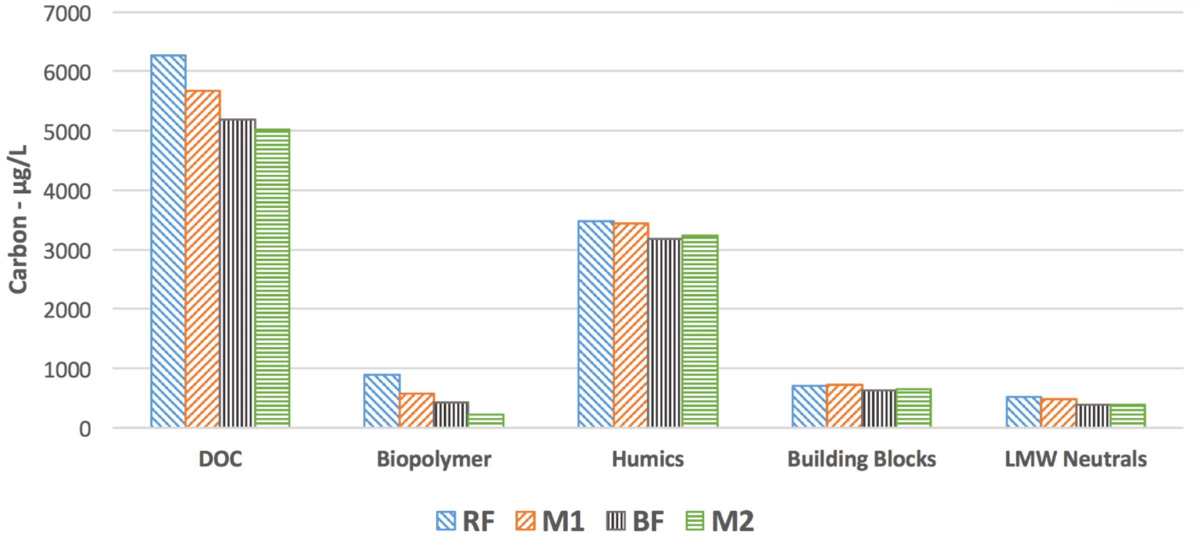


Figure 3.8 - DOC and NOM fraction concentration from LC-OCD analysis for the proof of concept experiment *(RF – roughing filter; M1 – ceramic membrane in test unit 1; BF – Biofilter; M2 – ceramic membrane in test unit 2)*

3.3.2.1 Impact of biofiltration pretreatment on the fouling of a ceramic membrane

A preliminary membrane fouling experiment conducted immediately before the proof of concept experiment indicated that the fouling behavior of the two MF ceramic membranes in the control and experimental membrane test units was similar as indicated by the TMP profiles shown as an insert in Figure 3-8 (refer to Section 3.3.1 for more details). Therefore, the difference in fouling behavior observed between the two membranes in the proof of concept experiment when fed with roughing filter effluent vs. biofilter effluent was directly related to the quality of the feed water.

The TMP profiles shown in Figure 3.9 of the two MF ceramic membranes fed with roughing filter and biofilter effluent provide clear evidence of the efficacy of the direct biofiltration as a pretreatment to control membrane fouling (experiment 1 in Table 3-3). Although the rise in TMP during the first few filtration cycles was comparable, the rise in the membrane fed with roughing filter effluent was substantially higher in the later cycles. In fact, the TMP in the membrane fed with roughing filter effluent reached the setpoint of 3 bars in less than 33 hours (50 permeation cycles). In the membrane fed with biofilter effluent, the TMP did not exceed 0.37 bars even after 51 hours of membrane permeation (83 permeation cycles).

Turbidity loading on the membrane supports the TMP profiles of the two membranes. The turbidity of roughing filter effluent was 7.61 NTU compared to 0.573 NTU for the biofilter effluent. The high turbidity loading on the membrane may have exacerbated fouling as the pores of the membranes can be blocked which manifests itself in the form of increased resistance to the flow of water. The biopolymer loading on the membrane from roughing filter was much higher at 889 μgC/L compared to 432 μgC/L in biofilter effluent. This corresponds to biopolymer concentration rejection of 308 μgC/L by the membrane fed with roughing filter effluent while it was 205 μgC/L by the membrane fed with biofilter effluent. Therefore, higher rejection of biopolymers (47%) in the membrane fed with roughing filter effluent was observed compared to the membrane fed with biofilter effluent (34%). A higher rejection of biopolymers is consistent with the fouling behavior observed as a higher percentage of biopolymers retained by the membrane surface and pore would increase the resistance to the flow of water and therefore increase the TMP across the membrane.

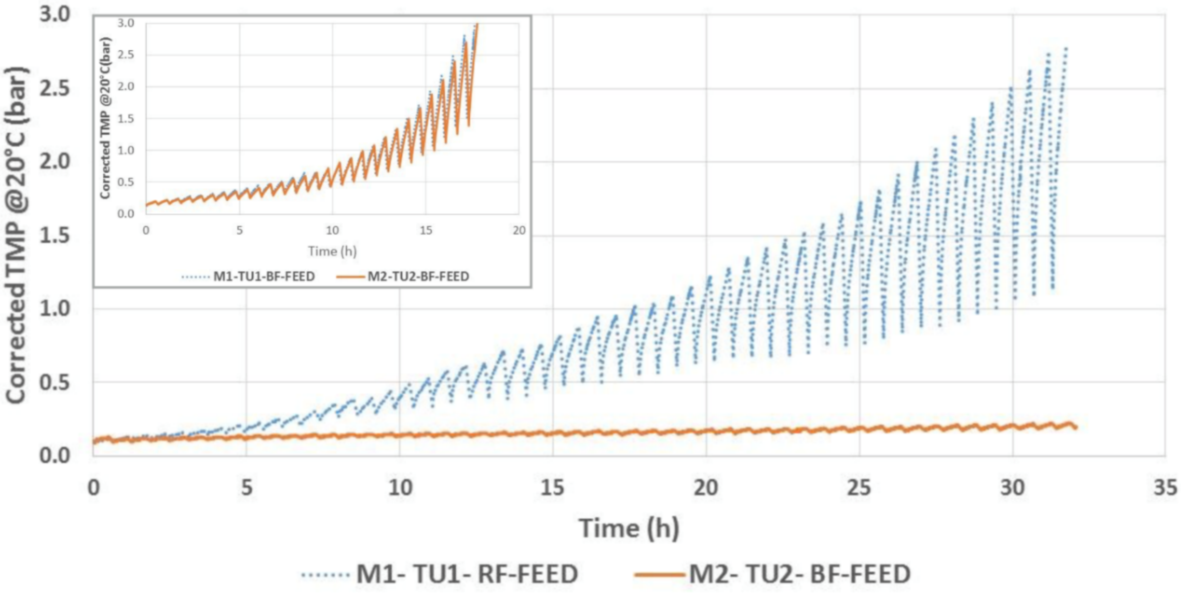


Figure 3.9 - TMP profile for ceramic membrane fed with Roughing Filter effluent and Biofilter effluent over a 32 hours filtration period. The insert in the figure shows the TMP profile of the parallel run of membranes in TU1 and TU2 respectively where the membranes were operated identically using the same biofilter effluent. *(TU1- Membrane Test Unit 1; M1- MF ceramic membrane in TU1; BF- Biofilter effluent; TU2- Membrane Test Unit 2; M2- MF ceramic membrane in TU2)*

A major portion of membrane permeability at the end of a permeation cycle can be recovered by hydraulic backwashing of the membrane and is known as reversible fouling. The difference in the TMP at the end of a permeation cycle and the starting TMP of the next permeation cycle represents the TMP which has been recovered, and this can be expressed as pressure recovered over time.

The reversible fouling rate of the two membranes starts off at the same value initially but gradually diverges after 4 to 5 filtration cycles (Figure 3.10) The membrane fed with biofilter effluent showed a gradual increase in reversible fouling rate, starting at 0.048 bar/h and ending at 0.062 bar/h, which represents an increase of around 30% in reversible fouling rate over 50 filtration cycles. However, in the membrane fed with roughing filter effluent, we see a very drastic increase in the reversible fouling rate which follows a non-linear trend. The reversible fouling rate starts off at 0.037 bar/h and ends at 2.60 bar/h, which represents an increase of about 6900% over 50 filtration cycles. Contrasting the two reversible fouling rates, it is clear that biofiltration pretreatment substantially reduces the reversible fouling rate.

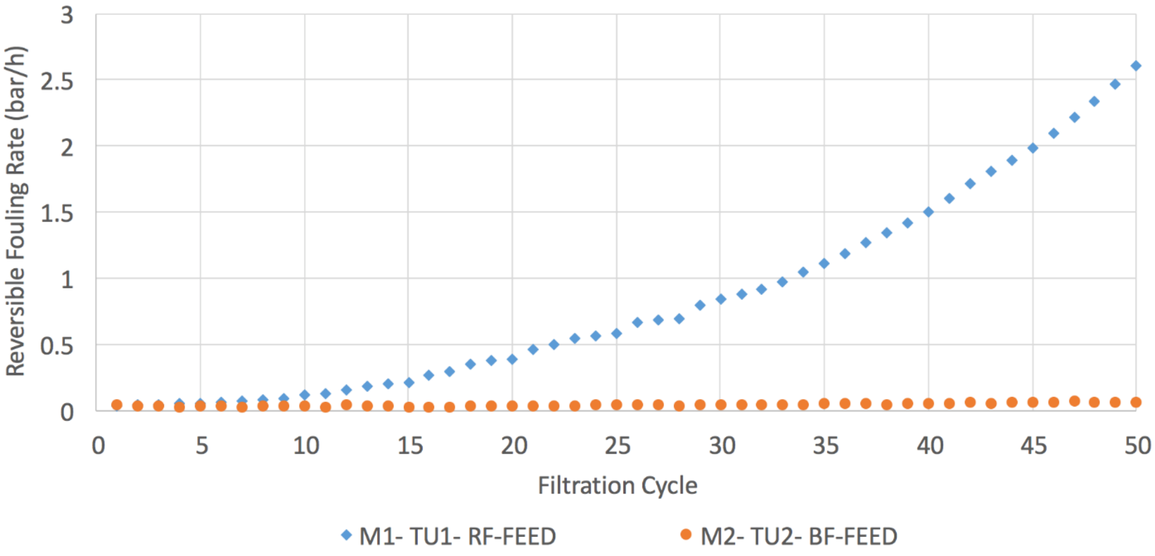


Figure 3.10 - Reversible fouling rate for membrane feed with roughing filter effluent and biofilter effluent. *(TU1- Membrane Test Unit 1; M1- MF ceramic membrane in TU1; BF- Biofilter effluent; TU2- Membrane Test Unit 2; M2- MF ceramic membrane in TU2)*

Materials that are deposited on the surface and in the pores of the membrane during permeation but are not removed during the hydraulic backwash cause irreversible fouling. Irreversible fouling manifests itself as an increase in the starting TMP from one filtration cycle to the next and can only be recovered by chemically cleaning the membrane.

To provide approximate quantitation, a simple linear regression is employed to calculate the irreversible fouling rates, even though the results for M1 do show some departure from linearity (Figure 3.11). The slope of the linear trend line represents the irreversible fouling rate for that membrane. A simple linear regression fits the data set for the membrane fed with biofilter effluent; however as noted above, the data set for the membrane fed with roughing filter effluent does not. Nevertheless, a linear regression is fitted for the sole purpose of making a comparison between the two membranes.

The irreversible fouling rate for the membrane fed with biofilter effluent is 0.0027 bar/h while the irreversible fouling rate of the membrane fed with roughing filter effluent of 0.032 bar/h. The membrane without pretreatment thus fouls approximately ten times fasters than the membrane with pretreatment. Despite the shortcomings of using linear regression to capture the irreversible fouling rate for the membrane without pretreatment, the method is useful in illustrating the difference between the two irreversible fouling rates.

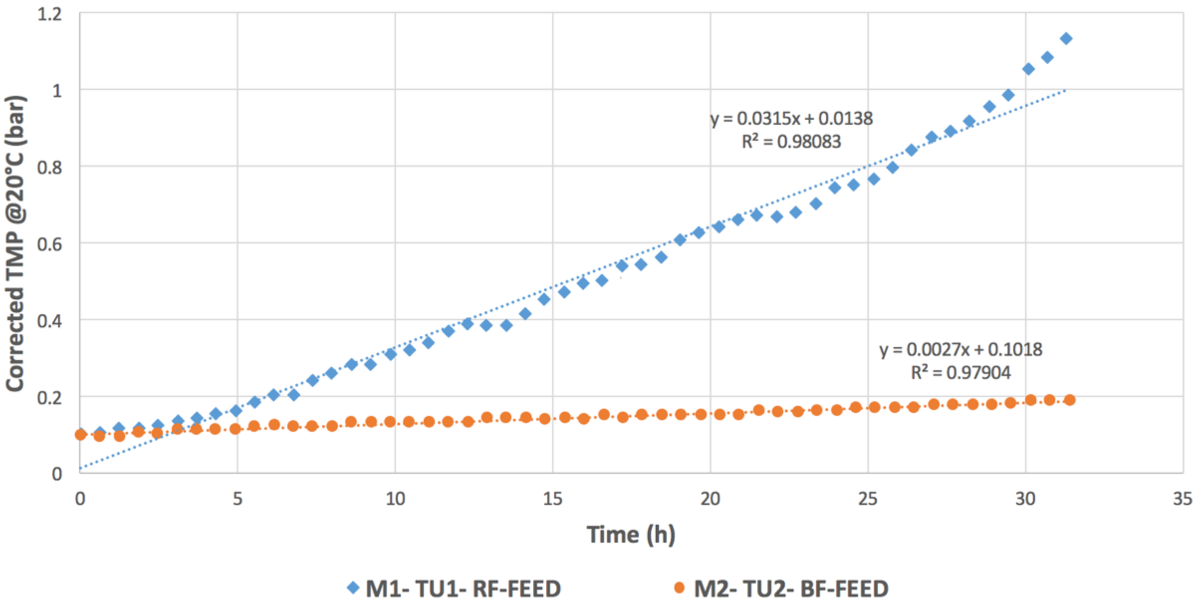


Figure 3.11 - Irreversible fouling rate for membrane feed with Roughing Filter effluent and Biofilter effluent. *(TU1- Membrane Test Unit 1; M1- MF ceramic membrane in TU1; BF- Biofilter effluent; TU2- Membrane Test Unit 2; M2- MF ceramic membrane in TU2)*

3.3.3 Effect of biofilter EBCT on membrane fouling

The removal of biodegradable organics through the biofilter is affected by contact time with longer contact time achieving higher removals. Hallé *et al*., (2009) reported that biofilters with longer EBCT were able to remove a greater fraction of biopolymers, which in turn reduced both hydraulically reversible and irreversible fouling in polymeric membranes. Therefore, a factorial membrane fouling experiment was conducted to assess the effects of EBCT and pore size on controlling fouling in ceramic membranes. However, a described in Section 3.3.1, due to the challenges and problems faced while running the full factorial design experiments, a full factorial analysis could not be carried out on the data collected to study the effects of EBCT on membrane fouling.

Therefore, an alternate approach to draw some information from the experimental data was utilized. As described previously, the control test unit fouling experiments were analyzed to find experiments where the membrane fouling was consistent. As the control test unit was operated identically during all experiments, any control experiments where the fouling was similar could be used to evaluate the corresponding differences in fouling in the experimental test unit in that particular experiment. The reasoning being that a consistent fouling in the control test unit suggests a similar water quality during the experiments (as all other parameters are the same) and can be used to evaluate the other factors which differed between the control unit and the experimental test unit.

In such a way, two experiments were selected from the first factorial experiment where the control test units had similar membrane fouling and the only other factor that was different in the experimental test units was the membrane feed. The experiments were the second and fourth factorial runs and are referred to as Exp1 and Exp 2 (refer to Table 3-3 for details). The test unit membrane feed in Exp 1 was biofilter B8 effluent while the membrane feed in Exp 2 was biofilter B16 effluent. Therefore, the fouling difference between the two experiments can be used to expound the significance of EBCT on membrane fouling.

The fouling experiments were performed using an MF ceramic membrane operated in dead-end mode at a constant flux of 90 LMH (corrected to 20°C). The filter layer of the membrane was made of zirconium dioxide while the supporting layer was made of aluminum oxide.

3.3.3.1 Impact of biofilter EBCT on Water Quality

Water quality analyses were performed on roughing filter effluent, biofilters B8 and B16 effluent and the membrane permeate. All water samples were collected 24 hours after the start of a membrane fouling experiment.

The roughing filter effluent turbidity during the two experiments was 2.25 NTU and 2.49 NTU. Biofilter B8 effluent turbidity was 0.184 NTU while biofilter B16 effluent turbidity was 0.147 NTU. The turbidity percent removal through biofilter B8 and B16 were 92.6% and 93.5% respectively. At just a 0.9% difference in percent removal, both biofilters performed similarly in terms of turbidity removal.

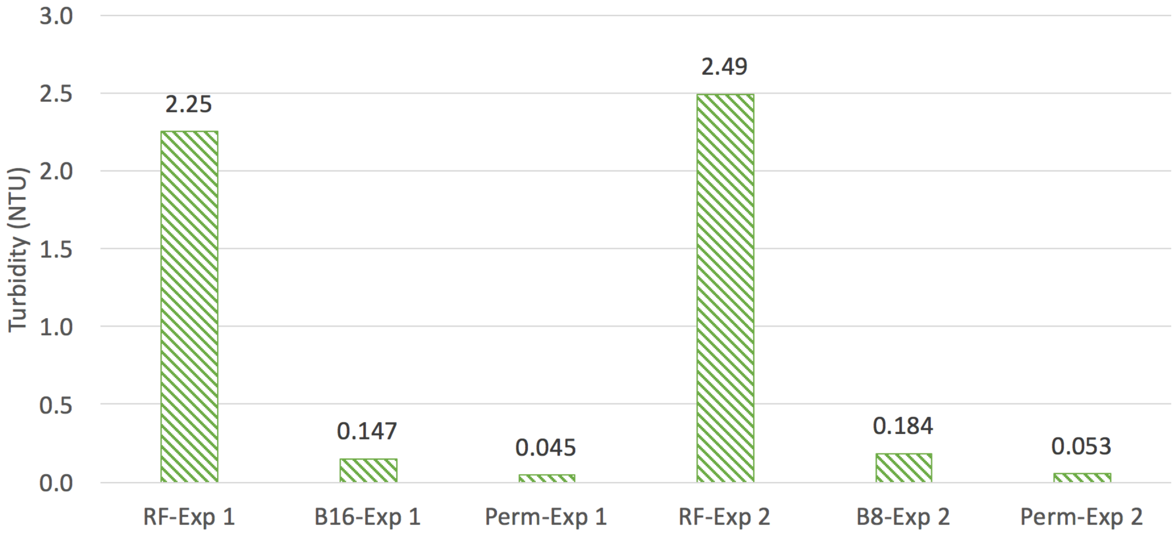


Figure 3.12 - Turbidity of roughing filter effluent, biofilter effluent and membrane permeate from experiment Exp 1 and Exp 2. *(RF – roughing filter effluent; B8 – Biofilter B8 effluent; B16 – Biofilter B16 effluent; Perm – MF ceramic membrane permeate)*

In the membrane fed with B8 effluent, the permeate turbidity was 0.053 NTU for a percent removal (based on membrane influent) of 71% while the membrane fed with B16 effluent, the turbidity was 0.045 NTU for a percent removal of 69%. The overall turbidity removal through the treatment train with B8 biofilter was 97.8% while for the treatment train with B16 biofilter it was 98%.

A similar overall turbidity removal through both trains is consistent with expected results. This is because membrane filtration is a size exclusion process and any particles or molecules larger than the pore size of the membrane are rejected irrespective of the influent water quality. As the raw water turbidity was similar during the two experiments and the membranes achieved similar permeate turbidity, the overall turbidity removal through the two trains was basically identical.

NOM characterization by LC-OCD analyses

The concentration of DOC in the roughing filter effluent was 6.5 mgC/L and 6.4 mgC/L during experiments Exp 1 and Exp 2 respectively (Figure 3.13). The main fraction of DOC as identified by

LC-OCD was humics and the concentration in the roughing filter effluent was 3.38 mgC/L during both experiments Exp 1 and Exp 2 respectively. Similarly, the concentration of biopolymers in the roughing filter effluent was 706 µgC/L and 616 µgC/L during experiments Exp 1 and Exp 2 respectively (refer to Figure 3.13 for other fraction concentrations).

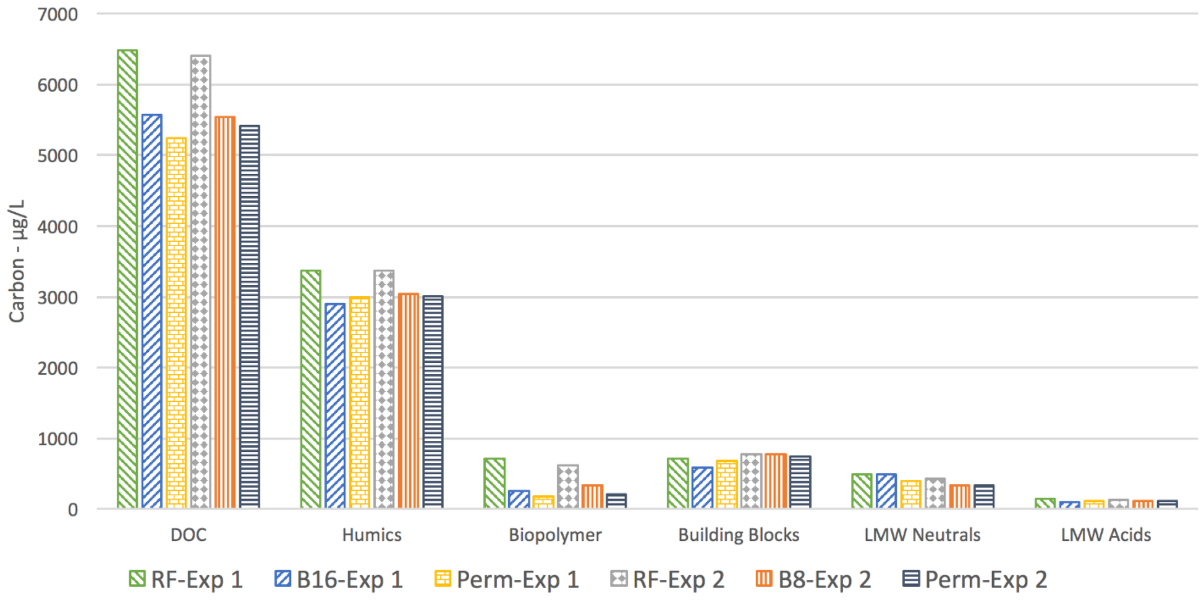


Figure 3.13 – DOC and NOM fraction concentration of roughing filter effluent, biofilters B8 and B16 effluent and membrane permeate from experiment Exp 1 and Exp 2. *(RF – roughing filter effluent; Perm – MF ceramic membrane permeate; LMW – Low molecular weight)*

In a similar fashion to the results presented in Section 3.3.2, despite humics being the main fraction, its removal through the biofilter was not as efficient compared to the biopolymer fraction removal. Only 10% of humics were removed through biofilter B8 while the percent removal of biopolymers was 46%. In biofilter B16, the percent removal of humics was 14% while the biopolymer percent removal was 64%. Clearly, biopolymers were selectively removed at a higher rate than humics. This is consistent with studies carried out by Hallé *et al*., (2009) using water from the same river, which saw similar biofilter performance in terms of biopolymer and humics removal. Biopolymers fractions as identified by LC-OCD are principally made of polysaccharides-like material as well as proteinaceous materials (Huber *et al*., 2011) and are more easily biodegradable than humics.

In terms of the difference between the two biofilters, biofilter B16 outperformed biofilter B8 in both percent humics and biopolymer removal. Biofilter B16 outperformed biofilter B8 in percent removal of humics by 4 percentage points and percent removal of biopolymers by 18 percentage points. The better performance of the biofilter with a higher EBCT is consistent with studies done by others for example LeChevallier *et al*., (1992), Hallé *et al*., (2009) and Huck *et al*., (2013) showed that longer contact time achieved better organic removals. However, S Zhang and Huck, (1996) noted that once an optimal EBCT is achieved, increasing EBCT does not lead to higher organics removal (assimilable organic carbon).

Fluorescence Excitation Emission Matrix Results

Another tool to characterize different fractions of NOM is FEEM (Figure 3.14). Using the peak picking technique, the relative amount of protein-like material, humic and fulvic acids in the sample is represented by intensity values at key FEEM coordinates. When used in combination with LC-OCD data, FEEM analysis can be used to complement the quantification of NOM fractions.

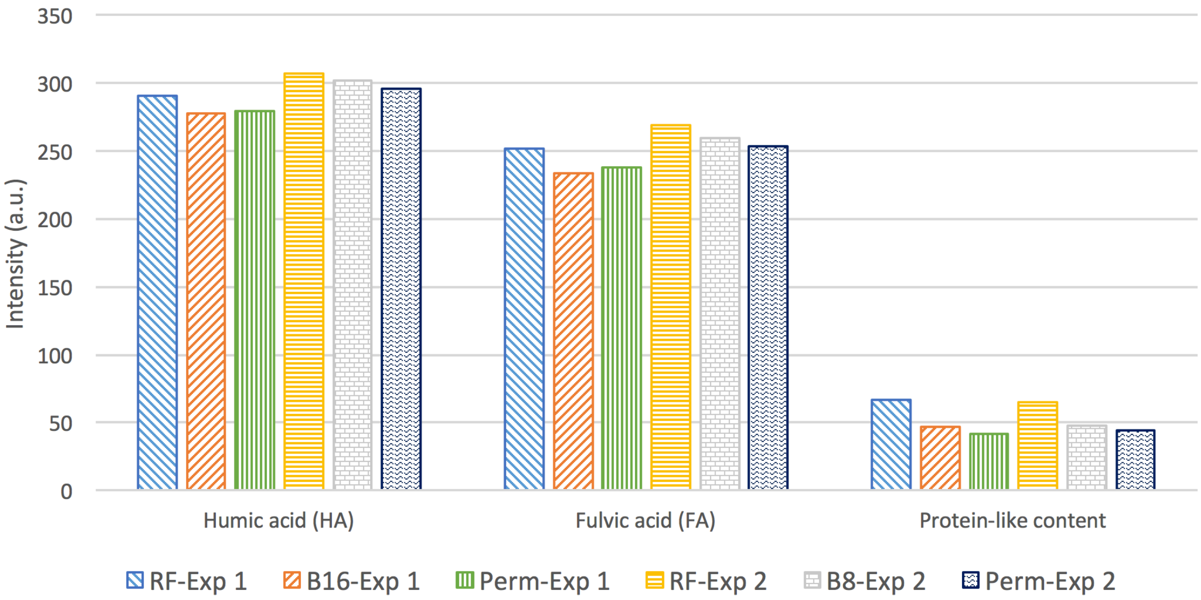


Figure 3.14 – FEEM analysis results – Humic acid, fulvic acid, and protein-like material concentration of roughing filter effluent, biofilter B8 and B16 effluent and membrane permeate from experiment Exp 1 and Exp 2. *(RF – roughing filter effluent; Perm – MF ceramic membrane permeate)*

The percent removal of humic acid, fulvic acid, and protein-like material through biofilter B8 was 1.8%, 3.5%, and 26.2% respectively. Similarly, the percent removal of humic acid, fulvic acid, and protein-like material through biofilter B16 was 4.5%, 7.2%, and 29.8% respectively. The higher removal of protein-like material, which is part of the biopolymer fraction in LC-OCD analysis, is consistent with the LC-OCD results shown in Figure 3.13. However, FEEM analysis showed that the percent removal of protein-like material through the two biofilters was similar at 26% and 30% whereas the biopolymer removals were higher and differed between the filters (46% through B8 and 64% through B16). These results were expected as FEEM analysis semi-quantifies protein-like material while the biopolymers as identified by LC-OCD include both proteins as well as polysaccharides. An inference that can be drawn from these results is that the protein component of the biopolymers is less biodegradable than the polysaccharides.

3.3.3.2 Impact of EBCT on membrane fouling

The MF ceramic membranes in the control test unit during experiments Exp 1 and Exp 2 fouled similarly, and this is shown as an insert in Figure 3.15. As the corresponding influent to the MF ceramic membrane during Exp1 and Exp 2 in the experimental test unit were biofilter B16 and B8 respectively, the effects of EBCT on membrane fouling can be evaluated from these two experiments.

The two membranes fed with different EBCT biofilter effluent starts off with the same rise in TMP for roughly 12 hours. After the 12 hour mark, the rise in the TMP is greater for the membrane fed with effluent from biofilter B8 (EBCT = 7.8 minutes) and gradually follows a non-linear trend. The experiment for the membrane fed with biofilter B8 effluent was terminated after it reached the set TMP of 3 bars around 69 hours into the experiment. However, the TMP for the membrane fed with biofilter B16 effluent was only a third (0.9 bars) as high at the end of the first experiment (69 hours). The experiment for the membrane fed with biofilter B16 effluent was terminated after reaching the end of the experiment period of 96 hours at a TMP of 1.52 bars.

It is evident from Figure 3.15 that the membranes fed with effluent from biofilter B16 and biofilter B8 performed similarly during the initial 12 hours. However, the membrane fed with biofilter B16 effluent performed much better in the later stages compared to the membrane fed with biofilter B8 effluent. The difference is particularly noticeable after 24 h of operation with B8 effluent causing an exponential rise in TMP while B16 effluent had a more gradual rise in TMP, being essentially linear up to about 40 hours.

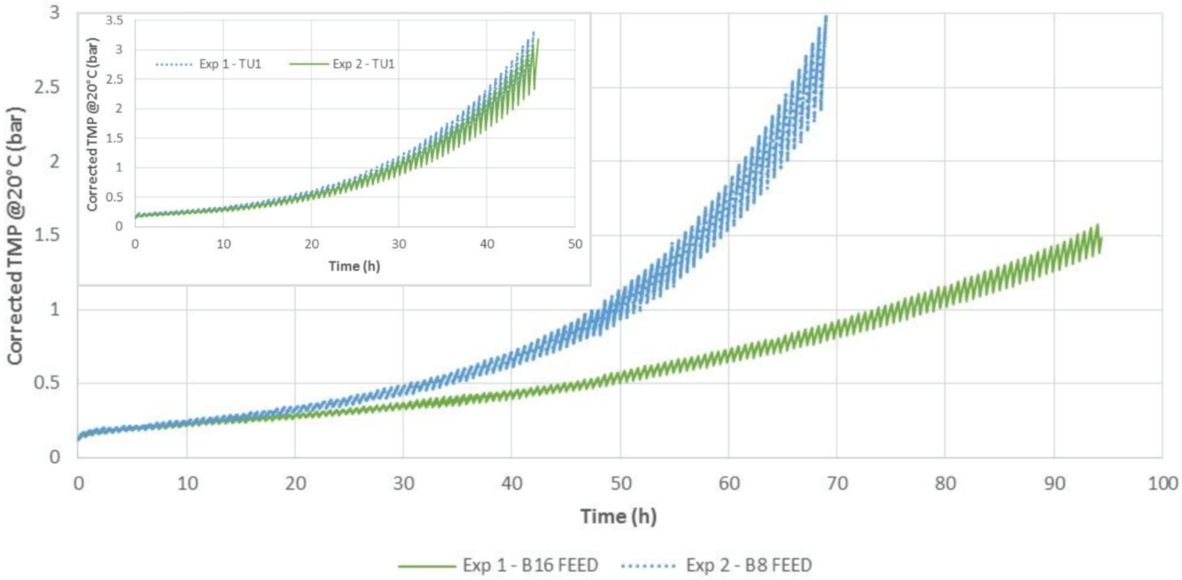


Figure 3.15 - TMP profile of MF ceramic membrane during experiment Exp 1 (fed with biofilter B16 effluent) and experiment Exp 2 (fed with biofilter B8 effluent) - Both experiments were run on Test Unit 2, two weeks apart (refer to Table 3-3 for details). *The insert in the figure shows the TMP profile of the corresponding MF ceramic membrane in Control Test Unit 1.*

The better performance of the membrane fed with a longer EBCT biofilter can be attributed to a higher water quality. Biopolymers have been widely acknowledged as a major membrane foulant (Hallé *et al*., 2009; Kimura *et al*., 2004; Peldszus *et al*., 2012), and direct biofiltration was able to efficiently remove a large percentage of the biopolymers. Although both biofilters (B8 and B16) achieved quite good biopolymer removals (46% and 64% respectively), the biofilter with the longer EBCT (B16) outperformed the biofilter with the shorter EBCT (B8) by 18 percentage points. Therefore, the biopolymer loading on the membrane receiving biofilter B16 effluent was much lower than the membrane receiving biofilter B8 effluent. As a result, the membrane fed with biofilter B16 effluent performed much better in the longer term compared to the membrane fed with biofilter B8 effluent.

Both biofilters achieved excellent turbidity removal and as a result, the particle loading on the membranes was similar. As a result, the substantial difference in performance observed between the two experiments is not likely to be due to differences in particle loading on the membranes.

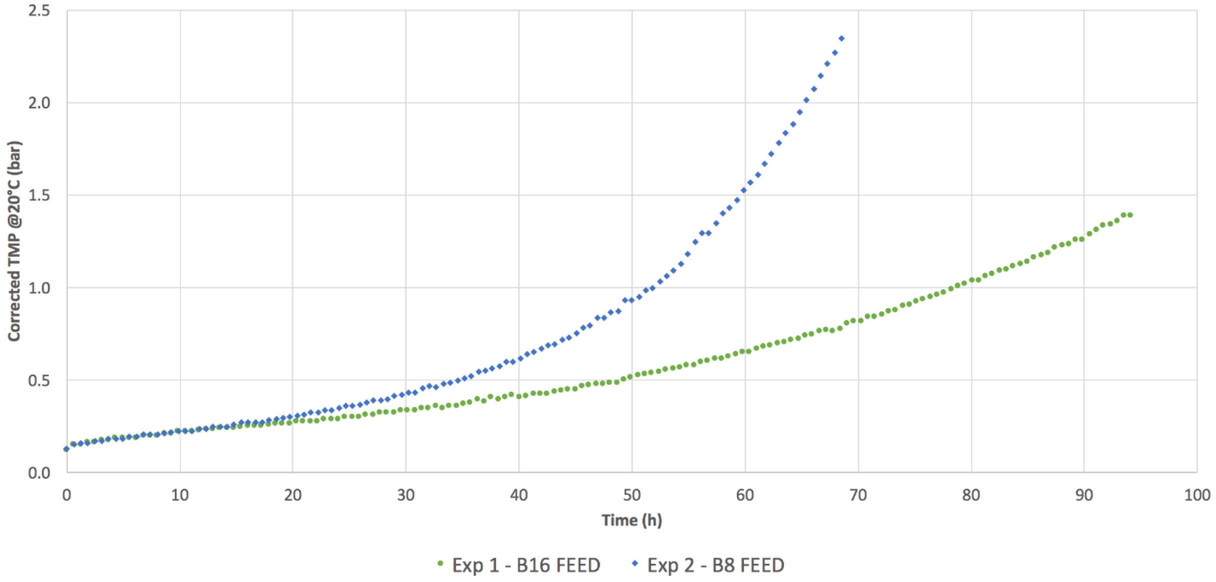


Figure 3.16 - Irreversible fouling - TMP at the start of each permeation cycle for MF ceramic membrane fed with biofilter B8 effluent (experiment Exp 2) and biofilter B16 effluent (experiment Exp 1). *Both experiments were run on Test Unit 2, two weeks apart (refer to Table 3-3 for details).*

The starting TMP for both membranes after a hydraulic backwash was the same for the first 12 hours and diverged thereafter (Figure 3.16). The trend for irreversible fouling here is similar to the TMP profile (Figure 3.15) as Figure 3.16 is plotted with the first TMP point at the beginning of each filtration cycle. The membrane fed with biofilter B16 has a lower irreversible fouling compared to the membrane fed with biofilter B8. This is likely due to lower biopolymer loading on the membrane in biofilter B16 effluent compared to a higher biopolymer loading on the membrane from biofilter B8.

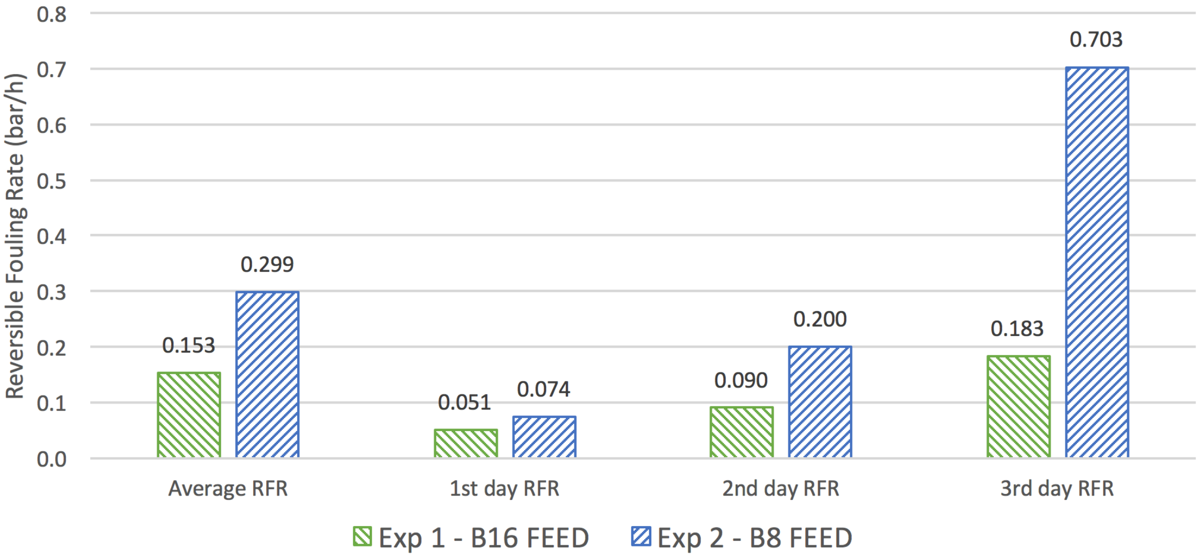


Figure 3.17 – Reversible fouling rate - MF ceramic membrane fed with biofilter B8 effluent (experiment Exp 2) and biofilter B16 effluent (experiment Exp 1). *Both experiments were run on Test Unit 2, two weeks apart (refer to Table 3-3 for details). (RFR – Reversible fouling rate)*

The reversible fouling as indicated by the amplitude of the recovered TMP gradually increased over time. The reversible fouling rate averages for each day of operation as well as the overall average reversible fouling rate are shown in Figure 3.17. It is evident that the reversible fouling rate is lower in all cases for the membrane fed with effluent from biofilter B16. The lower reversible fouling rate represents cost saving as higher reversible fouling represents a higher pressure requirement for producing the same quantity of water.

The experimental results provide strong evidence to support the conclusion that the membrane fed with effluent from the biofilter with the longer EBCT performs substantially better than the membrane fed from the biofilter with a shorter EBCT, and it will make a big difference in terms of energy saving if the membrane is operated without chemical cleaning for longer than a day. However, most membrane operation using ceramic membranes uses chemically enhanced backwash (CEB) frequently to control irreversible fouling. If a CEB were to be used after every 12 hours, it can be reasoned that both pretreatments would perform similarly under the conditions employed in this study as the TMP profile and the fouling rates are similar during this time. Therefore, using a higher 16 minutes EBCT would not necessarily provide an advantage over a lower 8 minutes EBCT. Nevertheless, use of CEB involves loss of production time as well as the cost associated with chemicals. Therefore, it is desirable to optimize and increase the time between consecutive CEB. In such a scenario, pretreatment with a longer 16 minutes EBCT would provide better overall performance, not just from an economical point of view, but also keep the usage of chemicals lower, which is environmentally friendly.

3.3.4 Effect of membrane pore size (UF vs. MF) on membrane fouling

To analyze the effect of membrane pore size on the membrane fouling, two experiments from the second factorial experiment were identified where the MF ceramic membrane in the control test unit fouled similarly. The corresponding membrane in the experimental test unit was of different pore sizes with the same pretreatment (biofilter B16 effluent) and therefore, the experiments could be used to elucidate the difference in fouling of a membrane of different pore sizes. The experiments were the first and the third factorial runs from the second factorial experiment and is referred to as Exp 3 and Exp 4 (refer to Table 3-3 for details).

An MF ceramic membrane with a pore size of 0.1 μm was used in experiment Exp 3 while a UF ceramic membrane with an MWCO of 150 kDa was used in experiment Exp 4. Both ceramic membranes were made of the same material – filtering layer made of ZrO_2 over a supporting layer made from Al_2O_3. The ceramic membranes were operated in dead-end mode at a constant flux of 90 LMH (corrected to 20°C). For details on the fouling experiment, refer to Section 3.2.3 and Section 3.3.3.

3.3.4.1 Water quality

The roughing filter effluent turbidity was 4.65 NTU and 2.05 NTU while the biofilter B16 effluent turbidity was 0.235 NTU and 0.135 NTU during experiment Exp 3 and Exp 4 respectively (Figure 3-18). Despite the roughing filter effluent turbidity being more than twice as high during experiment Exp 3 compared to experiment Exp 4, the biofilter performed consistently in terms of percent turbidity removal at 95% and 93.4% respectively. The MF membrane permeate turbidity was 0.048 NTU, and UF membrane permeate was 0.060 NTU.

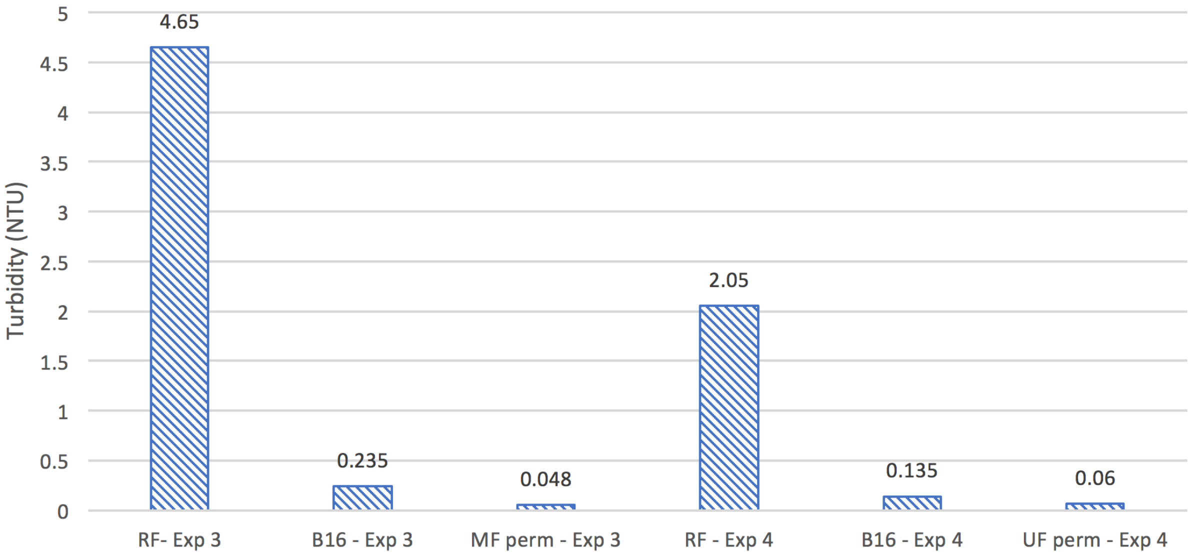


Figure 3.18 - Turbidity of roughing filter effluent, biofilter effluent and membrane permeate for experiment Exp 3 and experiment Exp 4. *(RF – roughing filter effluent; B16 – biofilter B16; MF – microfiltration ceramic membrane; UF – ultrafiltration ceramic membrane; perm – permeate)*

The DOC concentration in the roughing filter effluent was 7.8 mgC/L and 7.0 mgC/L while humics concentration was 4.4 mgC/L and 4.3 mgC/L during experiments Exp 3 and Exp 4 respectively. Similarly, the DOC concentration in biofilter effluent was 7.0 mgC/L and 5.9 mg/L while the humics concentration was 4.3 mgC/L and 4.1 mgC/L during experiment Exp 3 and Exp 4 respectively. This represents a DOC and humics percent removal of 10.8% and 4.1% respectively for experiment Exp 3 and a percent DOC and humics removal of 16.1% and 3.2% for experiment Exp 4.

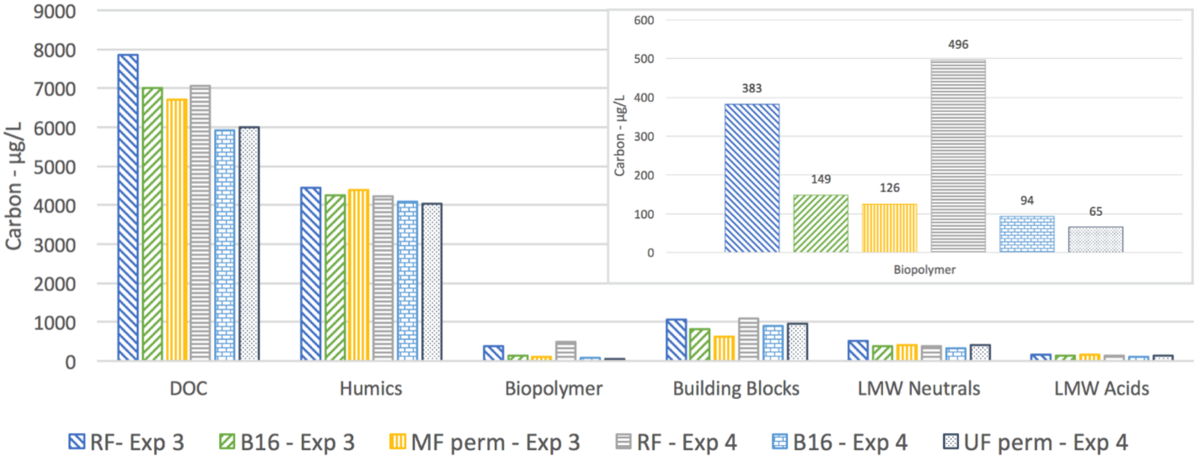


Figure 3.19 - DOC and NOM fraction concentration of roughing filter effluent, biofilter effluent and membrane permeate for experiment Exp 3 and experiment Exp 4. The insert in the figure shows the enlarged biopolymer concentration from the experiments. *(RF – roughing filter effluent; B16 – biofilter B16; MF – microfiltration ceramic membrane; UF – ultrafiltration ceramic membrane; perm – permeate*

The highest percent removal of a NOM fraction observed was for biopolymers (Figure 3.19). Analysis of water samples from experiment Exp 3 resulted in biopolymer concentration of 383 µgC/L, 149 µgC/L, and 126 µgC/L in roughing filter effluent, biofilter effluent, and MF membrane permeate respectively. This corresponds to a biopolymer percent removal of 61.1% through the biofilter and 15.4% through the MF ceramic membrane (based on membrane influent). Results from experiment Exp 4 had biopolymer concentration at 496 µgC/L, 94 µgC/L, and 65 µgC/L for roughing filter effluent, biofilter effluent, and UF membrane permeate respectively. This corresponds to a biopolymer percent removal of 81.0% through the biofilter and 30.8% through the UF membrane (based on membrane influent).

The biopolymer percent removal through the UF membrane was much higher (30.8% ~ 29 μgC/L) compared to the percent removal through the MF membrane (15.4% ~ 23 μgC/L). This is expected as the smaller pore size of the UF membrane would reject a greater fraction of biopolymers compared to the larger pore size of MF membrane. In terms of biopolymer removal through the biofilter, the biofilter performed significantly better during experiment Exp 4.

3.3.4.2 Membrane fouling

During the factorial experiment, the control train fouled similarly during two runs as shown as an insert in Figure 3.20. The corresponding pretreatment to the experimental train was biofilter B16 effluent in both the experiments but the membranes used were different. In experiment Exp 3, an MF ceramic membrane was used while a UF membrane was used in experiment Exp 4.

As the experiments were run a week apart, there was some variability in water quality parameters between the two experiments as discussed in Section 3.3.4.1. However, the fact that the membrane in the control trains fouled similarly during the two experiments suggests that the difference in water quality observed had a negligible effect on membrane fouling. As a result, the fouling difference that is observed in the experimental train is assumed to be solely attributed to the pore size of the membrane used. Therefore, the two experiments could be analyzed to elucidate the impact of pore size on membrane fouling.

The TMP for the UF membrane starts off much higher than the MF membrane (Figure 3.20). This is expected as the narrower pore size of the UF membrane (MWCO – 150 kDa) provides a greater resistance to the flow of water through it compared to the larger pores of MF membrane (pore size - 0.1μm). The UF membrane exhibit two stages of fouling with a slow linear rise in TMP during the initial 10 hours of membrane filtration followed by a higher linear rate of rise in TMP thereafter. The MF membrane, on the other hand, fouls in one linear stage throughout the experiment. Neither of the experiment reached the cut off TMP of 3 bars with the experiment terminated by reaching the end of the four-day experimental duration.

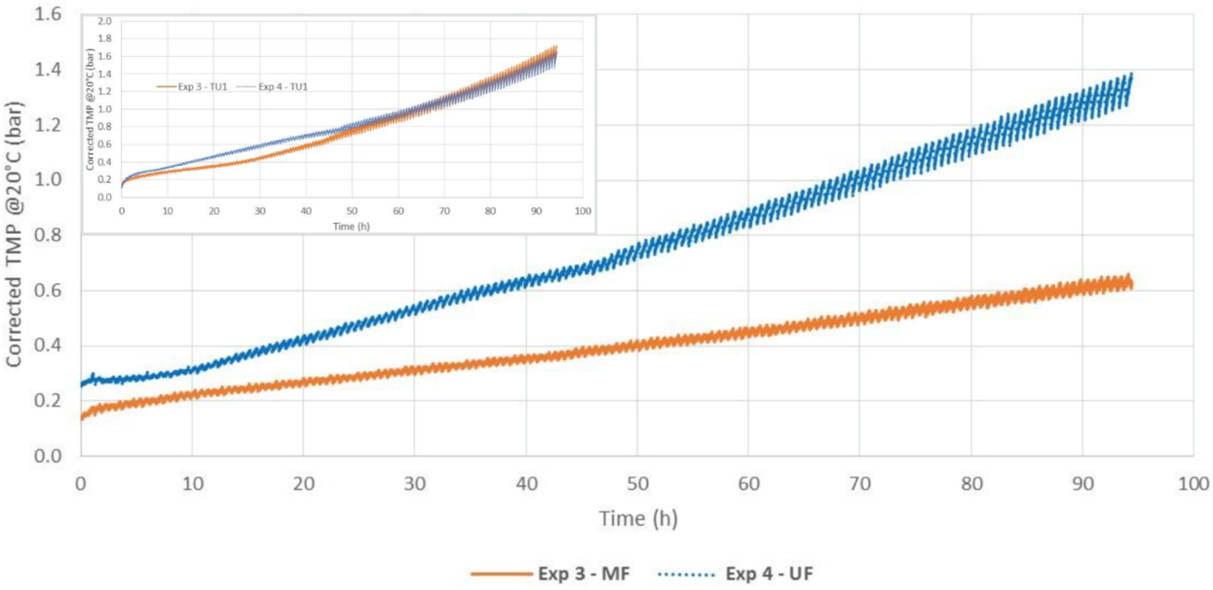


Figure 3.20 - TMP profile for experiment Exp 3 (MF membrane) and experiment Exp 4 (UF membrane). Both membranes fed with biofilter B16 effluent and operated on Experimental Test Unit 2, a week apart. *The insert in the figure shows the TMP profile for experiment Exp 3 and Exp 4 from the Control Test Unit. Both experiments were run identically with the same pretreatment (B16 effluent) and MF ceramic membrane. (MF – Microfiltration ceramic membrane; UF – Ultrafiltration ceramic membrane; TU1 – Control Test Unit)*

A simple linear regression was plotted through the TMP at the start of each permeation cycle to calculate the irreversible fouling rates (Figure 3.21). Overall, the UF membrane fouled at a rate of 0.011 bar/h, which is twice the fouling rate of MF membrane at 0.005 bar/h. Therefore, in terms of fouling, the MF membrane performed much better compared to the UF membrane.

However, the UF membrane fouled in two distinct stages. Therefore, the comparison between the two irreversible fouling rates needs to differentiate between the later higher fouling rate and the lower initial fouling rate. When comparing the irreversible fouling rate during the first ten hours for both membranes, the UF membrane outperformed the MF membrane. The UF membrane fouled at a rate of 0.004 bar/h during the first ten hours compared to 0.007 bar/h for the MF membrane. Therefore, if the membrane operation included CEB frequently to control irreversible fouling, a UF membrane would be recommended. However, in these experiments, the fact that both the particle (turbidity) and biopolymer loading to the UF membrane were lower may have played a role.

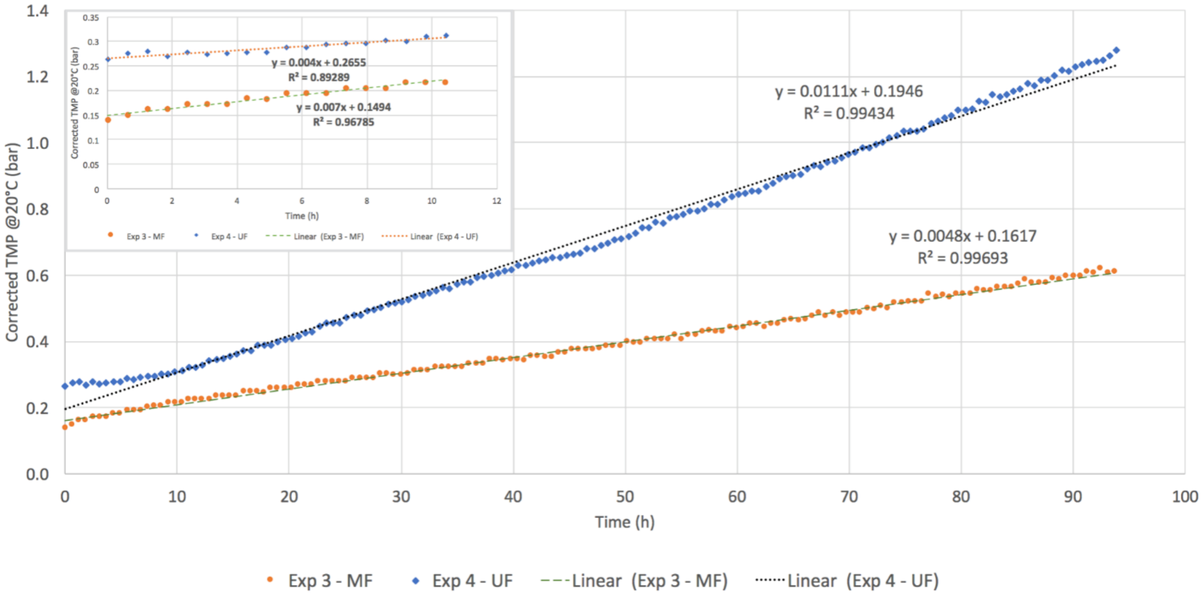


Figure 3.21 - Irreversible fouling rate of UF and MF membrane from experiment Exp 3 and Exp 4 (UF membrane – 0.011 bar/h and MF membrane – 0.0048 bar/h). Both membranes were fed with biofilter B16 effluent and operated on Test Unit 2, one week apart. *The insert in the figure shows the irreversible fouling rate during the first ten hours for experiment Exp 3 and Exp 4. (MF – Microfiltration ceramic membrane; UF – Ultrafiltration ceramic membrane)*

As the UF membrane operates at a much higher TMP and fouls at twice the rate over the course of the entire membrane operation, the MF ceramic membrane presents the better option from a fouling perspective. However, UF membranes are able to achieve a higher water quality in terms of microorganism removal. For example, the pores of UF membrane are generally small enough to be able to reject viruses (Lee *et al*., 2016; El-Hadidy *et al*., 2013) while MF membrane pores are large enough for viruses to pass through. Nevertheless, the MF membrane fouling is much smaller compared to the UF membrane when operated under similar conditions.

The average reversible fouling over the entire experiment was twice as high for the UF membrane with 0.105 bar/h compared to 0.045 bar/h for the MF membrane (Figure 3.22). The reversible fouling for the first day was comparable for the UF and MF membranes at 0.041 bar/h and 0.037 bar/h respectively. However, the reversible fouling rates for the subsequent days were much higher for the UF membrane compared to the MF membrane. This trend was similar to the irreversible fouling rate trend as expected.

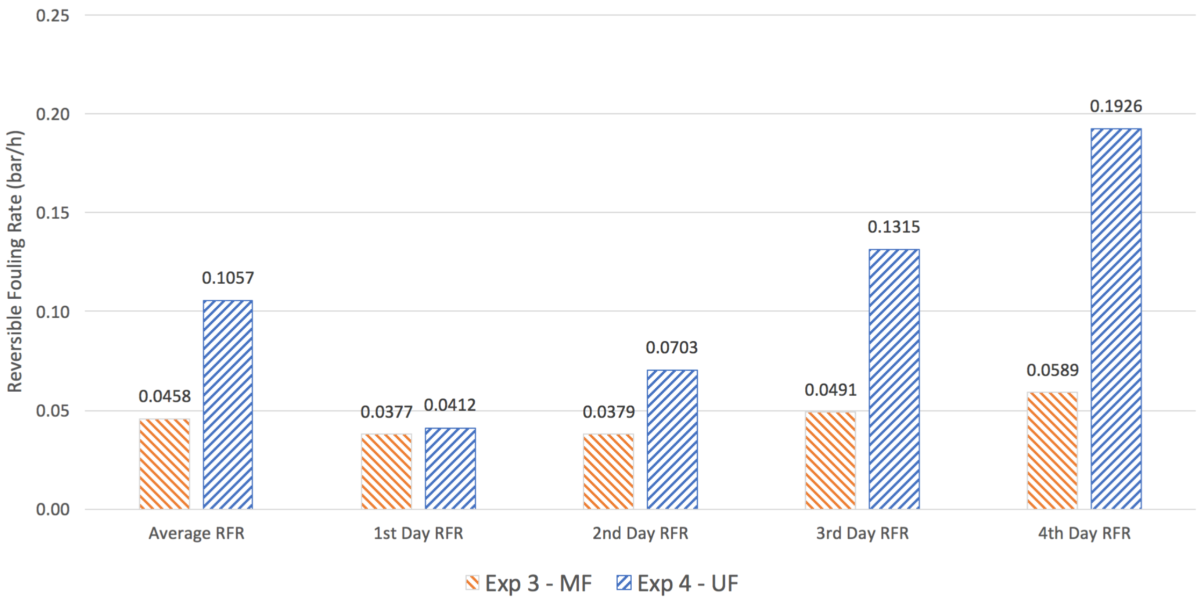


Figure 3.22 - Daily and the overall reversible fouling rate of UF and MF membrane from experiment Exp 3 and Exp 4. Both membranes were fed with biofilter B16 effluent and operated on Test Unit 2, one week apart. *(RFR- Reversible fouling rate; MF – Microfiltration ceramic membrane; UF – Ultrafiltration ceramic membrane)*

A higher reversible fouling rate suggests that the membrane is getting fouled at a higher rate and corresponds to a higher energy requirement during the permeation cycle to maintain the set flux. As such, a lower reversible fouling rate is desired in membrane operation. Both irreversible and reversible fouling rate suggest that the MF membrane performs better over the UF membrane with respect to fouling.

3.4 Conclusions

This study evaluated the efficacy of direct biofiltration as a pretreatment to control fouling in ceramic membranes. The effects of biofilter EBCT and the membrane pore size on membrane fouling control were also evaluated. From this study, the following conclusions can be drawn:

- Direct biofiltration (BF_{WP}) without prior coagulation is an effective pretreatment to control fouling of MF ceramic membranes. Both reversible and irreversible fouling rates were significantly lower in the membrane fed with biofilter effluent compared to the membrane fed with roughing filter effluent.

- Turbidity and biopolymers have a significant effect on the fouling of MF ceramic membranes. The membrane fed with influent with higher turbidity and biopolymer concentration fouled at a much higher reversible and irreversible fouling rate.

- Direct biofiltration can substantially remove turbidity and biopolymer from the feed water thereby reducing both reversible and irreversible fouling rate in both MF and UF ceramic membranes

- The biofilter with the longer EBCT performed significantly better in terms of turbidity removal and biopolymer removal compared to the biofilter with shorter EBCT.

- The membrane fed with effluent from the biofilter with a shorter EBCT fouled at a significantly higher reversible and irreversible fouling rate after the initial few hours of membrane operation compared to a membrane fed with the longer EBCT biofilter effluent.

- Irreversible fouling in MF and UF ceramic membranes were comparable during the first ten hours of operation. After the ten hours, the UF fouled at a substantially higher rate compared to the MF ceramic membrane. A similar trend was observed for the reversible fouling rate. If both UF and MF membranes meet treatment goals, MF ceramic membranes will provide cost savings as it operates at a much lower TMP.

Chapter 4

Influence of Membrane Materials on the Fouling of MF Ceramic Membranes with Direct Biofiltration Pretreatment

4.1 Introduction

The use of ceramic membranes in drinking water treatment is slowly gaining prominence due to their physical and chemical robustness over polymeric membranes (Van Der Bruggen *et al*., 2003; Ciora & Liu, 2003; Weber *et al*., 2003). The robustness of ceramic membranes allows for the use of higher pressure during filtration to increase production and control hydraulically reversible fouling during backwash. However, higher ceramic membrane cost still remains a major hurdle for wider adoption. Nevertheless, a recent study on the operating and life cycle cost of ceramic membranes and polymeric membranes shows that they are beginning to get competitive (Guerra & Pellegrino, 2013).

Ceramic membranes are made of oxides of inorganic materials such as alumina, titania, and zirconia. These are composite membranes made of a highly porous supporting structure sinter-fused to a thin separation layer to create a highly stable structure (atech, 2014). The supporting structure and the separation layer can be of the same material or different materials, and membrane properties are characterized by the material and structure of the separation layer.

The fouling behavior of a membrane is complex with factors such as membrane materials, hydrodynamic conditions, feed water quality and pretreatment affecting the extent of fouling. Most studies, therefore, employ model solutions to identify foulants for different membrane types. However, the applicability of findings from these laboratory experiments to full-scale treatment plant is limited. Pilot-scale studies with membranes of similar hydrodynamic conditions to the membranes used in full-scale operation are necessary in order to evaluate the efficacy of pretreatment and the suitability of different types of membrane for a given case specific scenario.

Studies on the comparison of the fouling of different ceramic membranes published in the scientific literature are limited. One study published is by Hofs *et al*., (2011) who reported that ceramic membranes of different materials foul differently using surface water pretreated with a 1 μm cartridge filter. They performed membrane fouling experiments in a laboratory setting using single lumen membranes manufactured by Atech Innovations, Germany. The membranes were operated in a constant flux mode up to 5 hours. They noted that the titania membrane they investigated showed a lower TMP rise due to lower irreversible and reversible fouling compared to the alumina and zirconia membrane.

In the present study, three different MF ceramic membranes made of alumina, zirconia and titania were used in membrane fouling experiments after BF_{WP} pretreatment. The objectives of this study were to investigate the fouling behavior of different MF ceramic membranes made from different materials under identical experimental conditions. The experiments were operated at a constant flux mode with full-size membranes to achieve similar hydrodynamic conditions to the full-scale operation to deduce findings that would be meaningful to the water industry.

To achieve these goals, fouling experiments with MF ceramic membranes of different materials were operated with effluent from a biofilter with an EBCT of 16 minutes located at the Mannheim WTP over a period of three weeks. The rise in TMP during the experimental period was recorded to quantify membrane fouling. Water samples were also collected 24 hours into each experiment to characterize water quality and the removal efficiency of particles and NOM through the membrane. In addition, backwash water was collected during the sampling period to elucidate information on membrane foulants.

4.2 Materials and Methods

4.2.1 Feed water

The effluent from biofilter B16 (i.e. having a 16 minute Empty Bed Contact Time) was used for the membrane fouling experiment in this study. Both the control test unit and experimental test unit were operated with the same influent (Figure 4-1). The biofilter was operated and maintained as described in Chapter 3.

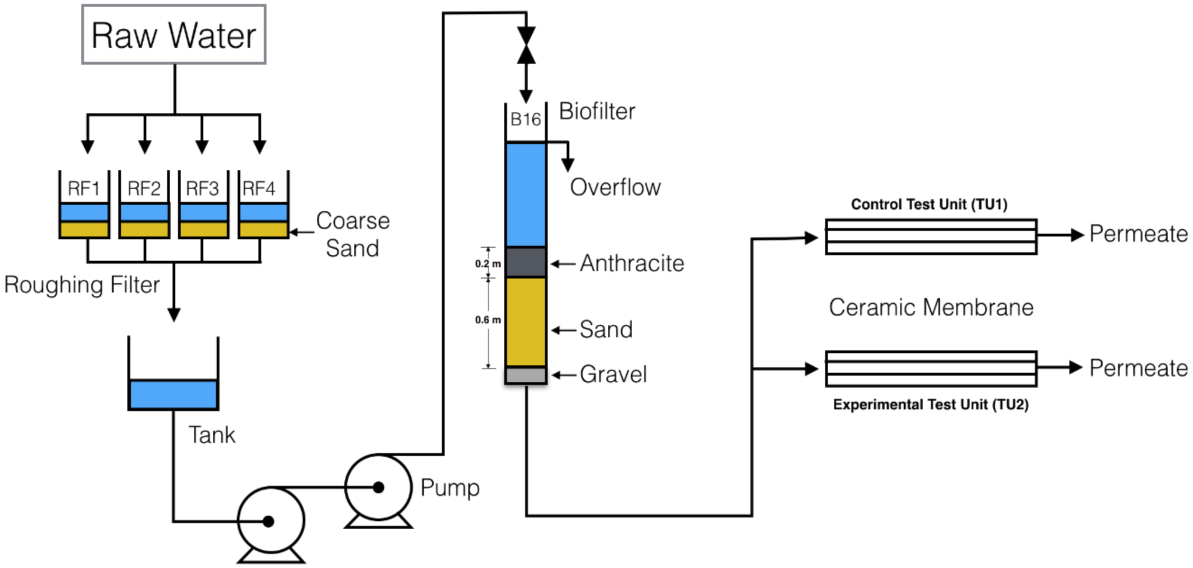


Figure 4-1 - Experimental setup. Biofilter B16 effluent was used for both the control and experimental test unit in the membrane fouling experiments

4.2.2 Membranes

The MF ceramic membranes used in this study were described in Chapter 3. The material and properties of the MF ceramic membranes are given in Table 4-1.

Table 4-1 - Material and properties of the ceramic membranes used. [a] supplier information, D_{int} = internal diameter. All membranes manufactured and supplied by Atech Innovations GmbH, Germany.

Membrane Material	Pore	Surface Area[a]	Configuration		
			Length	D_{int}	# of channels
ZrO_2	0.1 μm	0.079 m^2	600 mm	6 mm	7
Al_2O_3	0.1 μm	0.079 m^2	600 mm	6 mm	7
TiO_2	0.1 μm	0.079 m^2	600 mm	6 mm	7

4.2.3 Sampling and data analysis

Water samples were collected 24 hours into the fouling experiment and analyzed for water quality parameter as described in Chapter 3. Analysis of TMP data also followed the same procedure as stated in Chapter 3.

4.3 Results and Discussion

To assess the difference in fouling of MF ceramic membranes made of different materials, three membrane fouling experiments were conducted over a period of three weeks from August 3rd to 21st 2015. For the study, three tubular membranes made of ZrO_2, Al_2O_3, and TiO_2 with a supporting structure made of Al_2O_3 manufactured by Atech Innovations GmbH (Gladbeck, Germany) were used. Two membrane test units were operated in parallel with test unit 1 (TU1) operating as the control train and test unit 2 (TU2) operating as the experimental train. TU1 was operated with the same ZrO_2 membrane over the three experiments while the membrane in TU2 was changed as shown in Table 4-2.

Table 4-2: Membrane used in different fouling experiments *(MC – membrane comparison experiment)*

Fouling experiment	Experiment date	Membrane in	Membrane in	Pretreatment
MC1	Aug 3 – 6, 2015	ZrO_2	ZrO_2	Biofilter B16
MC2	Aug 10-13, 2015	ZrO_2	Al_2O_3	Biofilter B16
MC3	Aug 17-20, 2015	ZrO_2	TiO_2	Biofilter B16

The membranes were operated at a temperature-corrected flux of 90 LMH and fed with effluent from biofilter B16. As described in Section 3.3.1, there were challenges associated with operating the two test units identically. Therefore, the difference in the fouling between the control and experimental train could not be used to study the effects of membrane materials. However, as TU1 was operated under identical conditions over the three fouling experiments, the fouling trend of the ZrO_2 membrane could be observed over time. This allows for the capture of effects of changes in water quality on membrane fouling and can be used to distinguish between changes in membrane fouling due to changes in water quality or differing membrane materials. This would not have been possible if only a single train had been used.

4.3.1 TMP profiles

As the membranes were operated in constant flux mode, the TMP increased due to reversible and irreversible fouling of the membrane over the course of the fouling experiment. For the control ZrO_2 membrane in TU1, the TMP increase was much higher during the first experiment MC-1 compared to experiments MC-2 and MC-3 as shown in Figure 4-2.

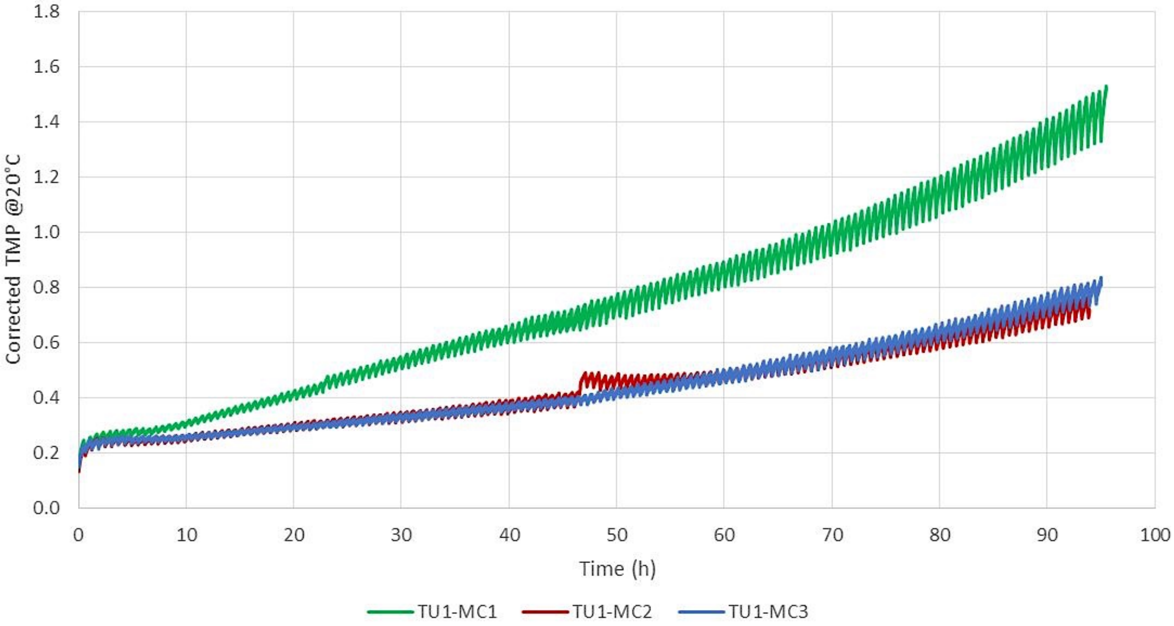


Figure 4-2 - TMP profile of control ZrO_2 membrane in TU1 during fouling experiments MC1, MC2, and MC3. *(TU1 – Membrane (Control) Test Unit 1, MC – membrane comparison experiment)*

However, fouling experiments MC-2 and MC-3 in TU1 saw very similar increases in TMP. As the only difference between the two experiments was the variability in the feed water quality (operated a week apart), it can be reasoned that similar water quality prevailed during the course of the two experiments. Therefore, any difference in TMP rise observed in membranes in TU2 during these two experiments can be attributed to the effects of membrane material only.

As discussed above, the control membrane fouled differently during fouling experiment MC1 compared to experiments MC2 and MC3 (Figure 4-2). Consequently, the ZrO_2 membrane fouling in TU2 during MC1 could not be directly compared to the Al_2O_3 and TiO_2 membrane fouling from experiment MC2 and MC3 respectively. Therefore, as discussed later, a transformation of the TMP data for the ZrO_2 membrane from experiment MC1 was carried out to glean some information on the difference in fouling of ZrO_2 membrane compared to Al_2O_3 and TiO_2 membranes. The transformation could only be applied to the irreversible fouling data (i.e. the TMP at the start of each permeation cycle) due to the simplified nature of the analysis.

The TMP increase for ZrO_2, Al_2O_3 and TiO_2 membrane in TU2 were different over the three fouling experiments. However, only the TMP profiles of Al_2O_3 and TiO_2 from experiments MC2 and MC3 are presented in Figure 4-3 (Refer to Appendix B for all three TMP profiles). Since the control membrane in TU1 fouled similarly during MC2 and MC3 and the only factor which was different in TU2 was the membrane material, the difference in TMP observed can be attributed solely to the effects of membrane material.

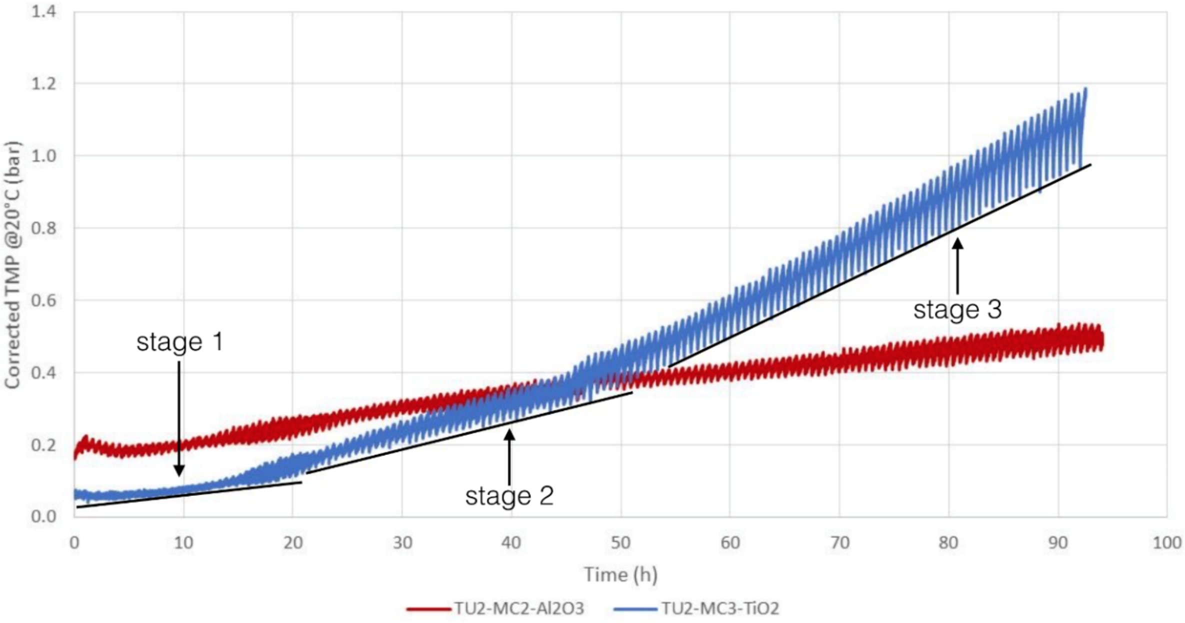


Figure 4-3 - TMP profile of Al_2O_3 and TiO_2 membrane in TU2 during fouling experiment MC2 and MC3 respectively. The figure also shows three distinct linear sections in TMP for the TiO_2 membrane during experiment MC3.

The TMP increased gradually for the Al_2O_3 membrane and followed an almost linear trend until the experiment was terminated at the end of four days. However, the TMP increase for the TiO_2 membrane followed three distinct stages which were mostly linear as shown in Figure 4-3. During stage 1, the rise in TMP is similar to the rise in TMP in the Al_2O_3 membrane, but the rise during stage 2 and 3 are substantially higher. Even though the rise in TMP was more gradual for the Al_2O_3 membrane, the TMP required to maintain the flux was much lower for the TiO_2 membrane during the initial stages of the experiment, especially stage 1. The TMP of the TiO_2 membrane only surpassed the TMP of the Al_2O_3 membrane around 45 hours into the experiment. This has important implications on the production cost of water as lower pressures translate into lower energy cost for treatment plants.

4.3.2 Fouling rates

Both hydraulically reversible and irreversible fouling rates were calculated from the operational data. The reversible fouling rate for each permeation cycle was calculated by dividing the reduction in TMP after each backwash by permeation time (30 minutes). To calculate the irreversible fouling rate, the TMP at the start of each permeation cycle after a backwash was plotted vs the experiment time. The slope of the linear fit to these TMP data yielded the irreversible fouling rate.

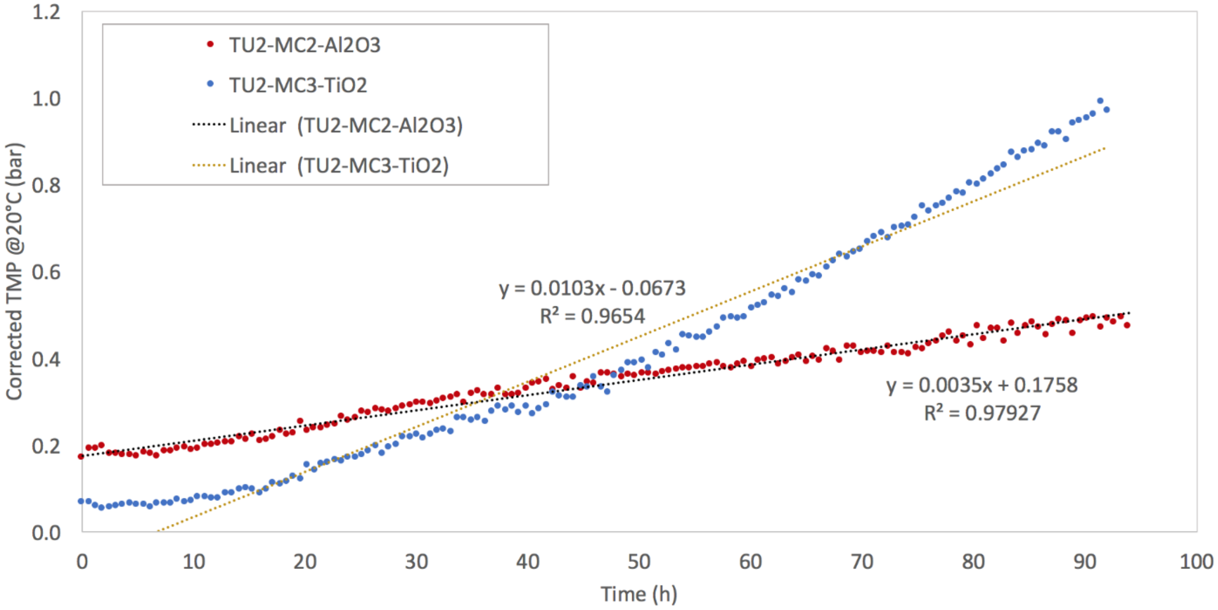


Figure 4-4 – The starting TMP after each backwash is plotted vs. experiment time. The slope represents the irreversible fouling rate of the Al_2O_3 and TiO_2 membranes over the entire experiment period. (TU2- Test Unit 2; MC2 – Membrane Comparison Experiment 2)

The slope of the linear fit to the TMP data of the Al_2O_3 membrane yields a good fit with an R^2 of 0.9793 as shown in Figure 4-4. Analysis of the residuals shows that, although there is some trending, they are fairly randomly distributed suggesting that a linear fit is appropriate (refer to Appendix B for residual plots). However, the linear fit to the TMP data of the TiO_2 membrane shows a U-shaped residual plot suggesting that a linear fit is inappropriate despite showing high R^2 value (refer to Appendix B for residual plots). Therefore, a linear fit to the TMP data was fitted on a daily basis, and the daily irreversible fouling rates of the two membranes were calculated (Figure 4-5). Based on a daily irreversible fouling rate calculation, the fouling rate of the TiO_2 membrane was slightly higher during the first day followed by substantially higher fouling rates in the latter days of the experiment compared to the Al_2O_3 membrane.

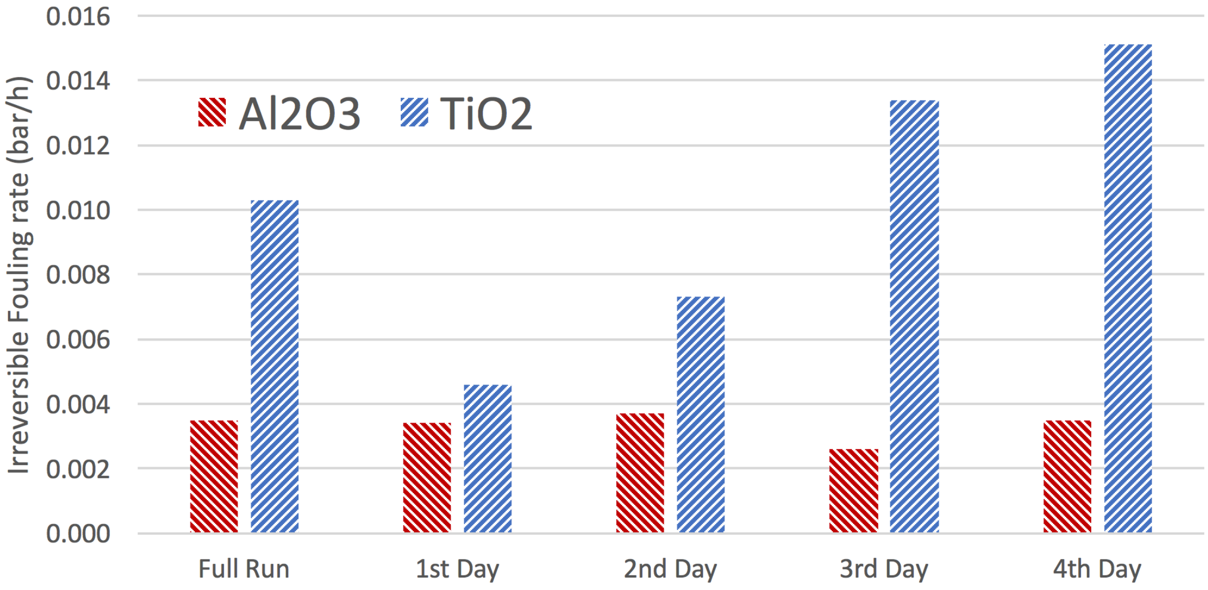


Figure 4-5 - Daily irreversible fouling rates of Al_2O_3 and TiO_2 membrane. A linear regression was fitted to the TMP data on a daily basis and the slope, which represents the irreversible fouling rate, is plotted above

To extract the effects of membrane materials only between the Al_2O_3 and ZrO_2 membrane, a transformation was carried out on the starting TMP ($TMP_{t=0}$) data of each permeation cycle after a backwash. The difference (Δ) of the starting TMPs of each permeation cycle between fouling experiments MC1 and MC2 in the control train (TU1) was computed. This difference was then used to adjust the starting TMP of the ZrO_2 membrane in TU2 of MC1. Adjusting the difference of the starting TMP data in MC1 normalizes its fouling to be similar to MC2, thereby allowing a simple comparison between the ZrO_2 membrane and Al_2O_3 membrane (refer to Figure 4-6)

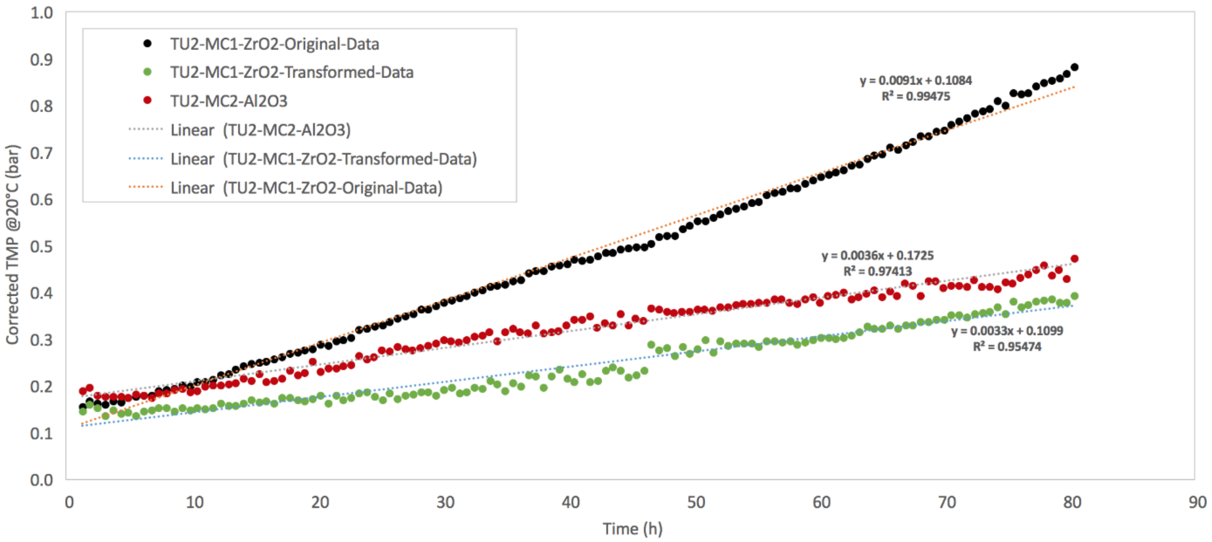


Figure 4-6 - TMP at the start of each permeation cycle after a backwash for ZrO_2 and Al_2O_3 membrane in the experimental train (TU2) from experiment MC1 and MC2. *The transformed TMP data was adjusted by the difference in TMP observed between the control membrane during MC1 and MC2 fouling experiment.*

The transformed irreversible fouling rate of the ZrO_2 membrane was 0.0033 bar/h compared to the irreversible fouling rate of the Al_2O_3 membrane of 0.0036 bar/h. This suggests that if we control for the effects of water quality changes during the two experiments, the two membranes fouled similarly. This result is supported by findings of Hofs *et al*., (2011) who observed similar fouling of Al_2O_3 and ZrO_2 membranes made by the same manufacturer. Al_2O_3 and ZrO_2 also operated at a similar TMP during the initial stages of the experiment for a given flux compared to a substantially lower TMP for the TiO_2 membrane as shown in Figure 4-3. The irreversible fouling rates of the original data for Al_2O_3 and ZrO_2 were also similar if only the first 8 hours of the experiment are included in the calculation (Figure 4-6). Therefore, there is strong evidence to suggest that Al_2O_3 and ZrO_2 membranes foul similarly.

The trends observed for the reversible fouling rates for the Al_2O_3 and TiO_2 membrane were similar to the irreversible fouling rates (compare Figure 4-5 to Figure 4-7). The only difference observed was the reversible fouling rate during the first day, where the rate for the TiO_2 membrane was lower than for the Al_2O_3 membrane. Data transformation analysis could not be used for calculating reversible fouling rates due to the simplistic nature of the analysis.

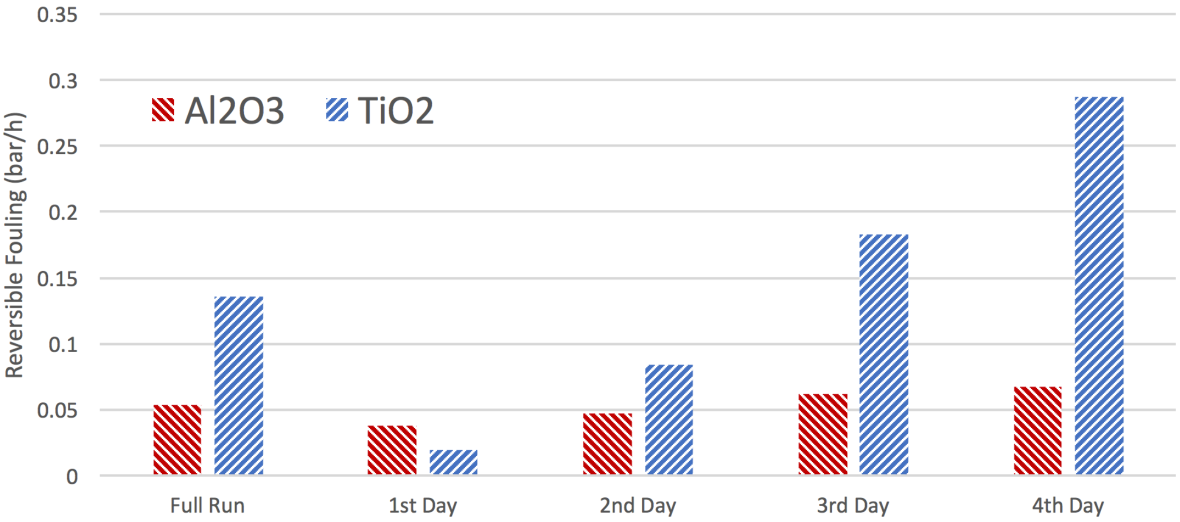


Figure 4-7 – Daily reversible fouling rates of Al_2O_3 and TiO_2 membranes. *The reversible fouling rates were calculated for each permeation cycle and averaged over the entire duration or the experiment periods. The reversible fouling rates were also averaged on a daily basis to produce daily fouling rates.*

Membrane structure (average pore size and porosity), membrane geometry, surface morphology and properties play a vital role in membrane performance and membrane fouling (Vrijenhoek *et al*., 2001; Elimelech *et al*., 1997). Therefore, to perform a membrane materials comparison study, it is important that the geometry of the membranes be the same so that the hydrodynamic conditions are similar. As the membranes used in the study have identical geometries and were manufactured by the same manufacturer, it is reasonable to assume that overall membrane structure and geometry did not play a role in the fouling difference observed during this study. The only factors which differed were the membrane material's properties and related surface morphology.

An important property of any membrane material is its surface charge, which can be measured by zeta-potential as a function of pH (Pearce, 2011). The iso-electric point (IEP), which is the pH at which the membrane surface carries no charge, is given in Table 4-3. The IEP of the membranes used in the study could not be measured to confirm the values given in Table 4-3 as the membranes would have had to be destroyed in order to measure the zeta-potential. The membrane surface is positively charged at a pH below the IEP while the membrane surface is negatively charged at a pH above the IEP. A desirable IEP for a membrane surface is one which is at the pH of the source water (Pearce, 2011). A membrane surface with no charge would provide the least resistance to the flow of charged dissolved molecules present in the feed water, increasing permeability. The pH of the Grand River water, which was used in the study, fluctuated between 7.34 – 7.88 during the course of the study (refer to Table 5.1 for more water quality detail). Therefore, at the pH of the influent water, the TiO_2 and ZrO_2 membrane are negatively charged while Al_2O_3 membrane is positively charged.

Table 4-3 – Iso-electric point of different membrane materials from literature. ([a] – Kosmulski, 2009; [b] – Mullet *et al.*, 1997; [c] – Minghua *et al.*, 1994)

Material	Iso-electric point
ZrO_2	6.3-7.1 [a,b,c]
Al_2O_3	8-9.4 [a,b]
TiO_2	5.1-6.4 [a,b]

Studies by Baroña *et al*., (2007) on the sulfonation of a PVDF membrane found that the membrane became more hydrophilic and negatively charged, and led to an increase in flux and rejection while the fouling decreased. Therefore, they hypothesized that a negatively charged membrane fouls less due to electrostatic repulsion between the negatively charged membrane surface and negatively charged solutes. This suggests that the TiO_2 membrane which is negatively charged at the pH of the feed water should perform better compared to the positively charged Al_2O_3 membrane. However, the results of the fouling rates suggest otherwise, with the only exception being the reversible fouling rate during the first day.

Hofs *et al*., (2011) who studied the fouling of different ceramic and polymeric membranes also found that Al_2O_3 and ZrO_2 membranes fouled similarly while lower reversible and irreversible fouling was observed for a TiO_2 membrane. Therefore, there is disagreement between the fouling result obtained in this study and the results of Hofs *et al*., (2011) and this is likely due to the length of the experiments. Both Baroña *et al*., (2007) and Hofs *et al*., (2011) used data from a few hours of membrane filtration while data from four days of membrane filtration were used in this study. For example, if only a few hours of membrane filtration data from this study were used in calculating the fouling rates of the TiO_2 and Al_2O_3 membrane, we find that both reversible and irreversible fouling rates were similar.

As the TMP at the start of the experiment and the subsequent increase in the TiO_2 membrane during the first day of the experiment were substantially lower than the TMP of Al_2O_3 membrane, higher flux could have been achieved if the TiO_2 membrane were operated at the same TMP as Al_2O_3 membrane. This supports the result of Baroña et al., (2007) who found increased flux for a negatively charged membrane. Zhang *et al*., (2009) also found similar results where higher flux was observed in a TiO_2 composite membrane compared to the Al_2O_3 membrane. The finding has an important implication for the water industry as a higher production of permeate can be achieved using a TiO_2 membrane compared to Al_2O_3 and ZrO_2 membranes when operated at the same TMP. This could represent a significant saving in operational cost for the treatment plant.

Another factor which is important in fouling control is surface roughness. Physical roughness plays an important role in colloidal fouling, with a rough membrane surface prone to fouling at a faster rate compared to a smoother membrane surface (Vrijenhoek *et al*., 2001). However, the determination of the surface roughness was not possible due to the geometry of the modules and there was no literature that studied the surface roughness of the membranes used in this study.

Single channel ceramic membranes composed of ZrO_2, TiO_2, and Al_2O_3 manufactured by Atech Innovations were used by Hofs *et al*., (2011) in a comparison study. In the study, they measured the pore sizes of the membrane and found that there were significant differences from values supplied by the manufacturer as shown in Table 4-4.

Table 4-4 - Difference in measured pore size compared to the pore size supplied by the manufacturer (Atech Innovations, Germany). ([a] mean flow pore size; [b] nominal pore size) (Adapted from Hofs *et al*., 2011)

Membrane Material	Pore Size (μm)	
	Measured[a]	Supplier[b]
Al_2O_3	0.24	0.1
TiO_2	0.51	0.1
ZrO_2	0.16	0.1

As the membrane used in the present study were from the same manufacturer as those used by Hofs *et al*., (2011) and differed only in configuration i.e. one channel for Hofs *et al*., (2011) and 7 channels in this study, it can be hypothesized that similar differences in the pore sizes of the membranes used in this study can be expected. Consequently, the lower TMP observed in the TiO_2 membrane can be hypothesized to be due to the larger pore size. However, determination of the pore sizes of the actual membranes used in the study would be required to confirm this hypothesis, and this was beyond the scope of the research program.

4.3.3 Turbidity and NOM removal efficiency

Turbidity removal through the treatment train

Water samples were collected 24 hours into all experiments and analyzed for turbidity and NOM concentrations. During the study period, the average turbidity of the roughing filter effluent was 2.35 NTU with a standard deviation of 0.410 NTU while the average biofilter effluent turbidity was 0.165 NTU with a standard deviation of 0.037 NTU. The average membrane permeate turbidity from all three membranes was 0.050 NTU with a standard deviation of 0.008 NTU. The individual turbidity data during the experiments are summarized in Figure 4-8.

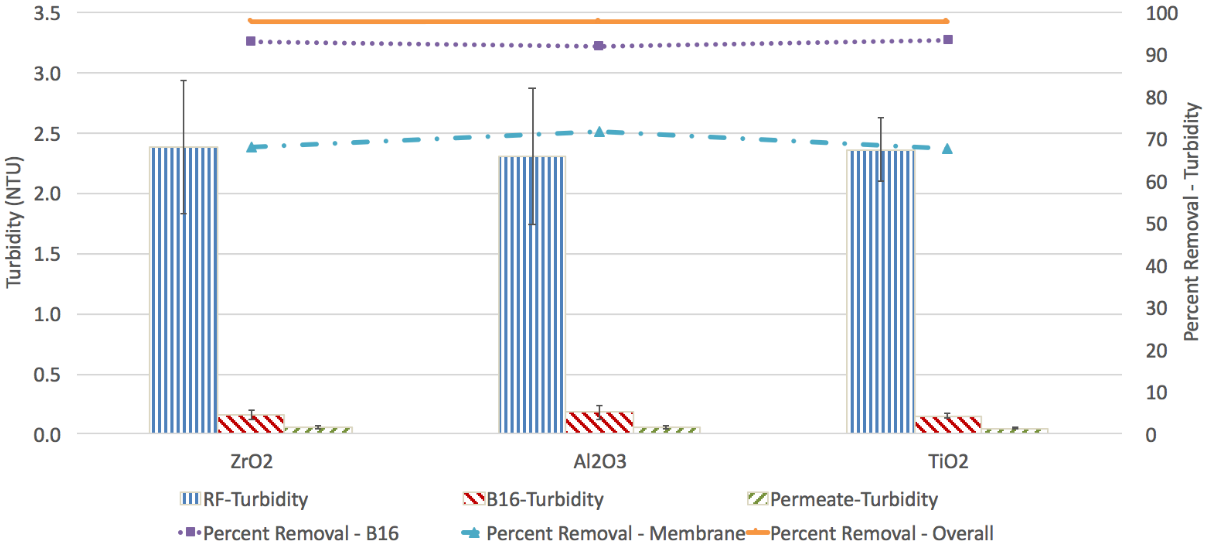


Figure 4-8 – Turbidity of roughing filter effluent, biofilter effluent, and membrane permeate. The percent removal through the treatment train during fouling experiments MC1, MC2 and MC3 where ZrO_2, Al_2O_3, and TiO_2 membranes were used, respectively. *Error bars indicate standard deviation (n = 3 for RF and B16, n = 2 for membrane permeates). RF: roughing filter; B16: Biofilter B16*

The percent turbidity removal through the treatment train is consistent for all three membranes at more than 97%. Similar turbidity removals through the membranes (based on membrane influent) used in the study were reported in the literature (Hofs *et al*., 2011). The percent turbidity removal observed was also similar to those observed in the previous membrane fouling experiments from Chapter 3. The particulate matter represented by this turbidity would contribute to fouling of the membranes.

NOM removal through the treatment train

The water samples were also analyzed for NOM fractions using LC-OCD and FEEM. The DOC concentrations and their percent removal through the biofilter and the membranes are shown in Figure

4-9. The percent removal of DOC through the biofilter was consistent throughout the study at 16.9% with a standard deviation of 0.5%. Similar DOC removals were observed by Hallé *et al*., (2009) for water from the same river through biofilters (with similar EBCT) operated without pretreatment. The DOC percent removal (based on membrane influent) through all three membranes were less than 2%. These results are consistent with previous membrane fouling experiments using MF ceramic membranes (Chapter 3). However, when pretreatment wasn't used, relatively high DOC removal of 30% through the MF ceramic membrane was observed (Hofs *et al*., 2011). The low removal observed in this study is likely due to the efficient removal of larger DOC molecules by biofiltration pretreatment before membrane filtration while they were likely present in the influent with no pretreatment. This is supported by low DOC (measured as NPOC) removal by Al_2O_3 MF ceramic membrane when pretreatment (coagulation and anion exchange) was used (Hofs *et al*., 2012).

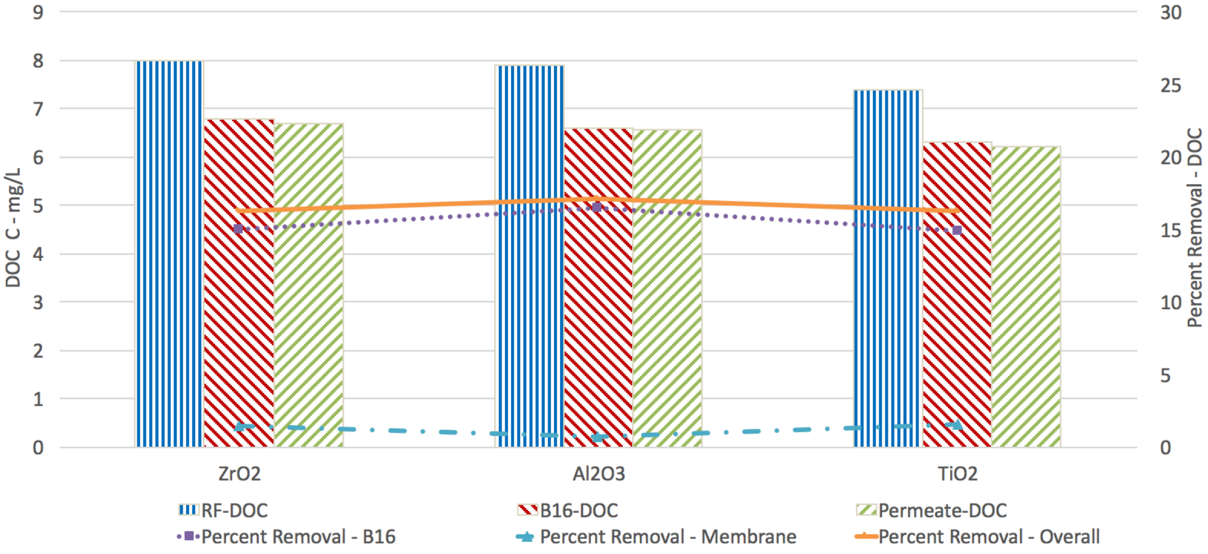


Figure 4-9 - DOC concentration of roughing filter effluent, biofilter effluent, and membrane permeate. The DOC percent removal through the treatment train during fouling experiments MC1, MC2 and MC3 where ZrO_2, Al_2O_3, and TiO_2 membranes were used respectively.

Biopolymers saw the highest percentage removal through the biofilters with 73% (standard deviation of 4%) followed by humic substances with 9.5% (standard deviation of 1.8%). Other NOM fraction saw negligible removal through the biofilters (Figure 4-10).

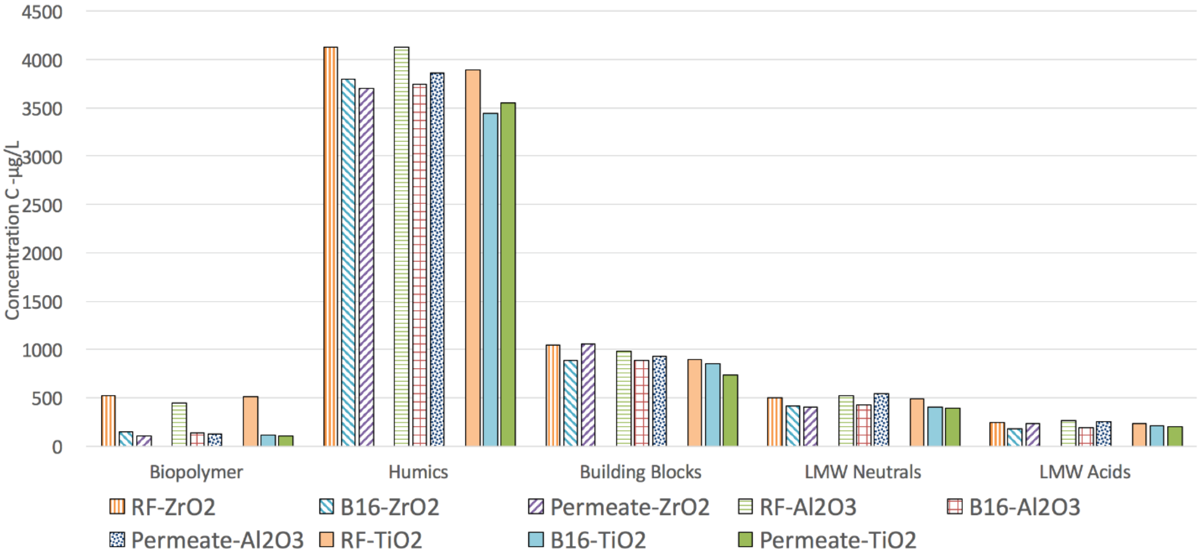


Figure 4-10 - NOM fraction concentration of roughing filter effluent, biofilter effluent and membrane permeate from the three membrane fouling experiments.

(RF: roughing filter; B16: Biofilter B16; LMW: Low molecular weight)

The only NOM fraction to see substantial removal through the membranes in all three experiments was biopolymers with an average removal of 20% with a standard deviation of 2%. Biopolymer percent removal through the ZrO_2, Al_2O_3, and TiO_2 membranes (based on membrane influent) was 22%, 19% and 18% respectively (Figure 4-11). Biopolymers have been acknowledged as a foulant in LPMs (Her *et al*., 2007; Hallé *et al*., 2009, Peldszus *et al*., 2012) and their high removal through all the MF ceramic membranes during experiment MC1 likely contributed to the high fouling rate observed.

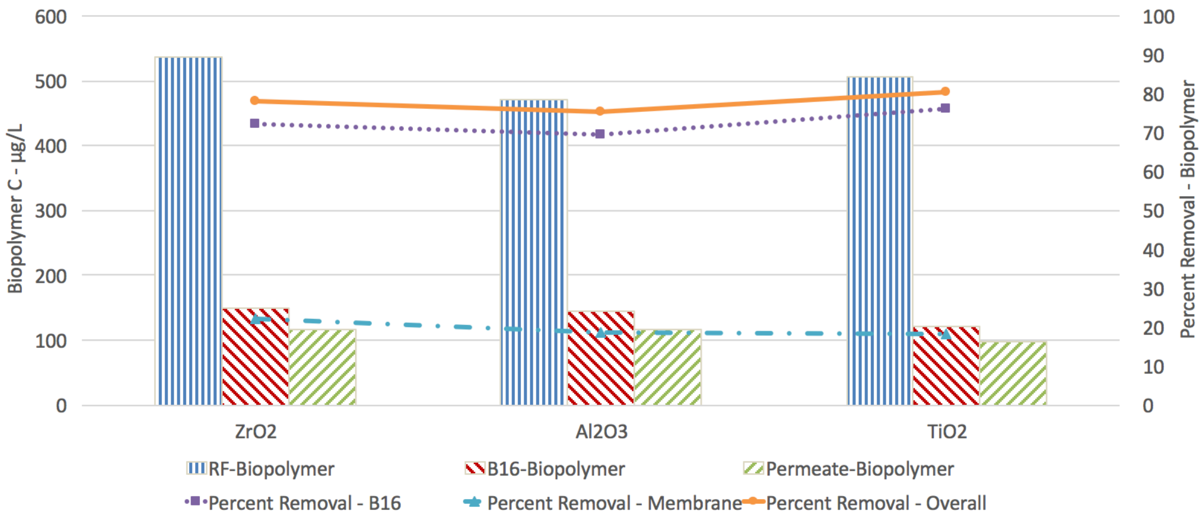


Figure 4-11 – Biopolymer concentration of roughing filter effluent, biofilter effluent, and membrane permeate. The biopolymer percent removals are through the treatment train during fouling experiments MC1, MC2 and MC3 where ZrO_2, Al_2O_3, and TiO_2 membranes were used respectively.

NOM fractions were also characterized using the FEEM peak picking technique. The relative amounts of humic acid, fulvic acid and protein-like content from the fouling experiments are shown in Figure 4-12. These results are consistent with the LC-OCD results. Although the results shown are measured values, the comparisons in the next several sentences refer to relatives or percentage removals. For the biofilter, substantial removal of protein-like content (analogous to biopolymers from LC-OCD) was observed while the removal of humic acid and fulvic acid was small. Some removal of protein-like content was observed through all three membranes, whereas negligible removals of humic and fulvic acid were observed.

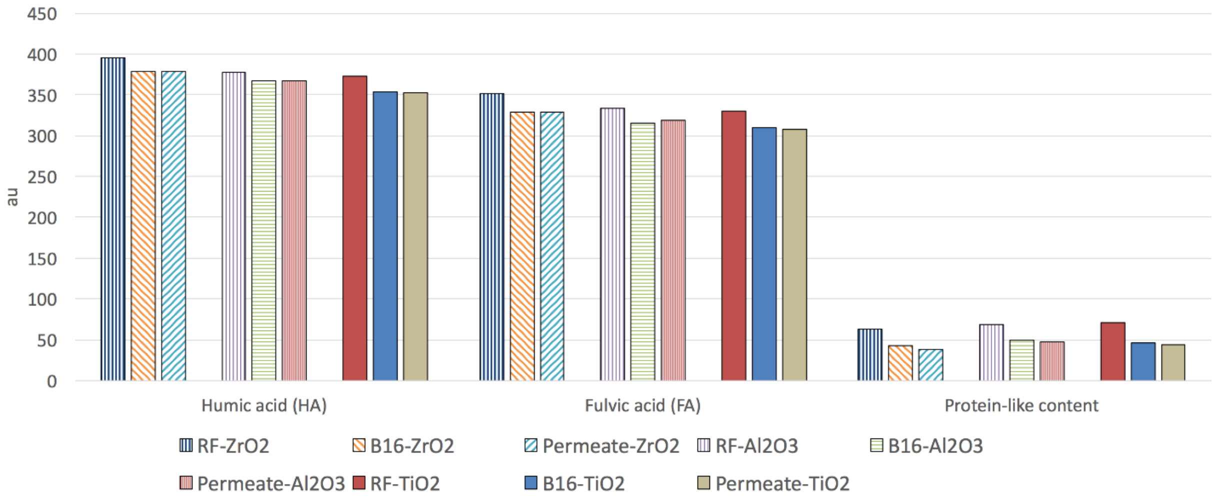


Figure 4-12 – NOM fraction as measured by FEEM peak picking from water samples collected during fouling experiments MC1, MC2 and MC3 where ZrO_2, Al_2O_3, and TiO_2 membranes were used respectively.

4.3.4 NOM in backwash water

During the sampling of experiments MC1, MC2, and MC3, backwash water was also collected from three consecutive backwash cycles to glean insight into the membrane foulants for each membrane type. Permeate water was collected in a tank during the permeation cycles and used to backwash the membranes. In addition to the values for permeate water already discussed, backwash water from the tank was also analyzed for turbidity, LC-OCD, FEEM, and UV_{254}.

A comparison of the turbidities of the permeate water and backwash water is given in Figure 4-13. The turbidity of the backwash water was 3 to 5 times higher than the permeate water turbidity. Higher turbidities in the backwash water were expected as colloids and particles that are larger than the membrane pore size are rejected during the permeation cycle and washed away from the membrane during the backwash process.

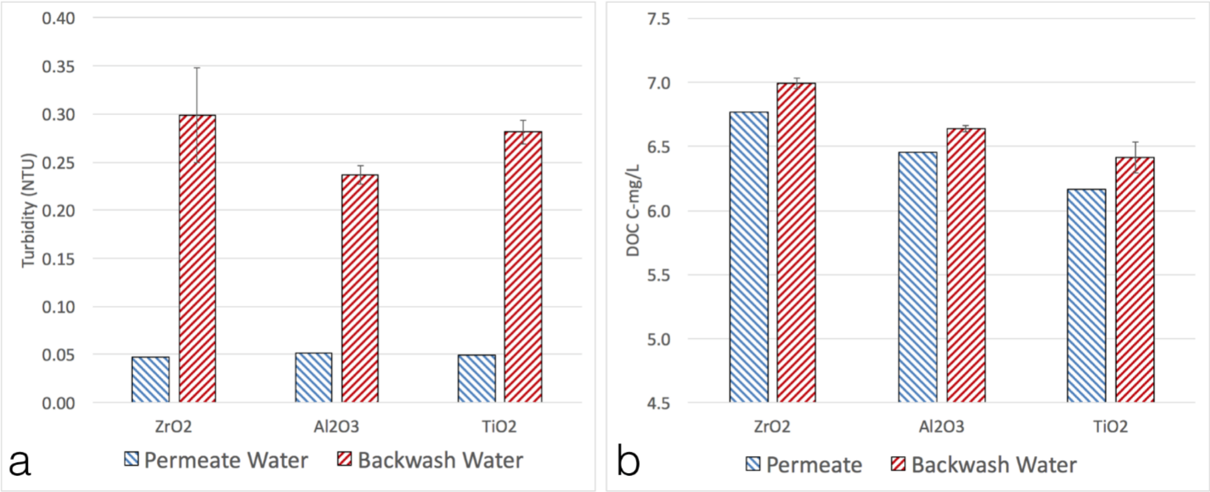


Figure 4-13 – Turbidities[a] and DOC concentrations[b] of permeate water and backwash water. The error bars on the backwash water represents the standard deviation (n = 3)

The percent increase in DOC concentration in the backwash water was 3.2%, 2.8%, and 4.0% for the ZrO_2, Al_2O_3, and TiO_2 membranes respectively. Although a relatively low percent increase in DOC is observed, almost all of the DOC increase is due to the biopolymer fraction of DOC (Figure 4-14). A negligible increase in other NOM fractions was observed in the backwash water. A 192% increase in biopolymer concentration was observed for the ZrO_2 membrane while 54% and 69% increases were observed for the Al_2O_3 and TiO_2 membrane respectively. The presence of higher biopolymer concentrations in the backwash water indicates that measurable amounts of biopolymer were rejected by the membrane and removed from the membrane during the backwashing process.

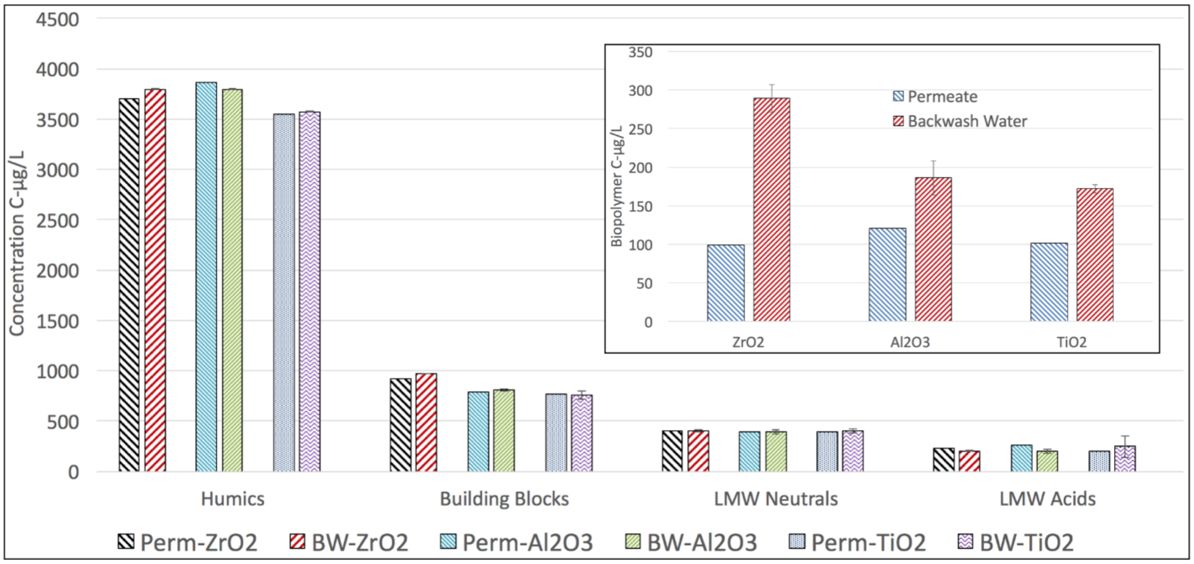


Figure 4-14 – NOM fraction of permeate water and backwash water. The error bars on the backwash water represents the standard deviation (n = 3). The biopolymer fraction in permeate and backwash water is shown as an insert on the figure to reflect the substantial increase in backwash water compared to other NOM fractions.

A substantial percent increase in the concentration of biopolymer in the backwash water can be seen as a confirmation of biopolymer as a major reversible foulant in MF ceramic membranes. Although humic substances have been acknowledged as a foulant for MF ceramic membranes (Jucker & Clark, 1994; Yuan & Zydney, 1999; Mueller *et al*., 2010), there was no evidence in the present study to show that humic substances as characterized by LC-OCD play a role in MF ceramic membrane fouling. Shang *et al*., 2015 also found similar results and noted that biopolymers were the major foulant for an MF ceramic membrane while humic substances played a role in the fouling of UF ceramic membranes. However, it is important to note that the backwash water samples in the present study were collected 24 hours into the filtration process, and the absence of humics in the water sample only suggest that humics didn't play a role at that stage of the filtration process. It is likely and highly probable that during the initial filtration process, humics may interact with the membrane pores/surface and get deposited on the membrane. Results from FEEM peak picking also support the finding from LC-OCD and have been included in Appendix B.

4.4 Conclusions

In this study, direct biofiltration was used as a pretreatment to investigate the influence of membrane materials on the fouling of tubular MF ceramic membranes operated at a constant flux in dead-end configuration. The experiments were intended to determine differences in fouling between membranes made of different materials but with identical hydrodynamic conditions and operating conditions. From this study, the following conclusions could be drawn:

- Although the TMP for the TiO_2membrane was initially lower, a higher irreversible fouling rate was observed for that membrane compared to the Al_2O_3 membrane. A ZrO_2 membrane and an Al_2O_3 membrane exhibited similar irreversible fouling, though this conclusion would need to be confirmed as the transformation of data was required to reach the latter conclusion.

- The reversible fouling rate was lower for the TiO_2 membrane during the first day of operation than for the Al_2O_3 membrane. However, the reversible fouling rate during the latter three days of the experiments was much higher for the TiO_2 membrane than for the Al_2O_3 membrane.

- Both ZrO_2 and Al_2O_3 membranes operated at similar TMPs at the start of the experiment while the TiO_2 membrane displayed a much lower starting TMP to maintain the same constant flux. Therefore, there is an opportunity for considerable energy saving by adopting membranes made of TiO_2, if they are to be operated for shorter cycles.

- Excellent turbidity removal through all three MF ceramic membranes was observed with more than 97% removed through the treatment train. The final membrane effluent turbidities were consistently below 0.060 NTU for all membranes.

- Among the different NOM fractions, substantially higher rejection and removal of the biopolymer fraction was observed, suggesting that it plays an important role in fouling of MF ceramic membranes. This was likely due to the interaction between the relatively large molecule size of biopolymers with the fouling layer and pores of the membrane which causes it to be retained on the membrane and removed during the backwash process.
- Negligible removal of humic substances was observed through all three MF membranes. Analysis of backwash water also saw a negligible increase in humic substances (through both LC-OCD and FEEM analysis) suggesting that humic substances are not an important foulant for MF ceramic membranes.

Chapter 5

Long Term Performance of MF Ceramic Membranes Using Direct Biofiltration Pretreatment

5.1 Introduction

The use of ceramic membranes in drinking water treatment has slowly gained momentum due to their numerous advantages over polymeric membranes. Ceramic membranes can be operated at a much higher flux, can be cleaned much more efficiently using harsh chemicals and have a long operational life (Ciora & Liu, 2003; Finley, 2005; Guerra & Pellegrino, 2013). Despite the numerous advantages of ceramic over polymeric membranes, one major disadvantage remains the high initial capital cost. However, the economic of scale and development of new systems such as CeraMac® (Galjaard *et al.,* 2012) has lowered the life cycle cost of ceramic membranes to the level that it is now competitive to that of polymeric membranes.

Membrane filtration removes contaminants and pathogens in the feed water by the process of size exclusion. Any contaminants in the feed water that are bigger than the nominal pore size of the membrane are rejected and remain on the feed side. Build up of rejected material on the feed side results in a loss of permeability of water across the membrane known as membrane fouling. Membrane fouling remains the biggest challenge facing membrane operation today as it represents a loss of productivity and an increase in production cost. Development of different pretreatment approaches in order to control membrane fouling remains a major area for research today.

Numerous studies have shown that different fractions of NOM such as biopolymers (Kimura *et al*., 2004; Peldszus *et al*., 2011a) and humic substances (Yuan & Zydney, 1999; Zhang *et al*., 2009) present in surface water are responsible for hydraulically reversible and irreversible fouling in LPM membranes. These results suggest that the composition and size distribution of organic matter in the surface water are far more important than a simple aggregate measure of NOM (concentration) when it comes to measuring the impact of NOM on membrane fouling. Inorganic particles in the size range of the membrane pore size have also been found to aggravate membrane fouling by obstructing the back diffusion of organic matter during backwashing (Zhang *et al.*, 2009).

Numerous studies on coagulation prior to membrane filtration have shown this to be an effective pretreatment in controlling fouling in ceramic membranes (Huang *et al.*, 2009; Loi-Brügger *et al.*, 2006; Meyn *et al.*, 2008; Shirasaki *et al.*, 2014). Another pretreatment for membrane filtration is direct biofiltration without prior coagulation or ozone addition, also known as biofiltration without pretreatment (BF_{WP}). This novel membrane pretreatment has been found to be effective to control fouling in polymeric membranes (Hallé *et al.*, 2009; Peldszus *et al.*, 2012), although its efficacy for ceramic membranes is yet to be reported.

In this chapter, the fouling behavior of an MF ceramic membrane with BF_{WP} as a pretreatment was investigated over an extended period of time. In addition, the study assessed the impact of changing raw water quality on the performance of an MF ceramic membrane. Membrane fouling experiments were conducted consecutively with effluents from two different biofilters with 8 minutes and 16 minutes EBCT over periods of 3 weeks and 7 weeks, respectively. The biofilters were continuously fed with Grand River water and assessed for NOM and particle removal throughout the study. LC-OCD and FEEM analysis were used to characterize organic matter present in the membrane influent and permeate to discern the NOM fractions responsible for reversible and irreversible fouling of the ceramic membrane. Changes in raw water quality, biofilter effluent and permeates were studied to elucidate trends and potential correlations to membrane performance. The backwash water from the ceramic membrane was also collected during the last experiment to obtain information on the composition of membrane foulant.

5.2 Materials and Methods

The membrane fouling experiments conducted on the control test units from the first and second factorial experiments (Chapter 3) and membrane materials comparison experiment (Chapter 4) were used in this study. The control test unit during the first factorial experiment was operated with effluent from biofilter B8 while it was operated with B16 effluent in the second factorial and the membrane materials comparison experiment. Three experiments from the first factorial experiments and seven experiments from the second factorial experiment and the membrane comparison experiment was used for the study. The detail of experiments and the label used in this chapter is given in Table 5-1

Table 5-1 – Membrane fouling experiments used in this study. *(* the experiment was not used due to water sample contamination during that experiment)*

		Control Train		
	Experiment Date	**Pretreatment**	**Membrane**	**Experiment Label**
Factorial experiment 1	May 18-21, 2015	Biofilter B8	MF - ZrO_2	E1
	May 25-28, 2015	Biofilter B8	MF - ZrO_2	-*
	June 1-4, 2015	Biofilter B8	MF - ZrO_2	E2
	June 8-12, 2015	Biofilter B8	MF - ZrO_2	E3
Factorial Experiment 2	July 1-4, 2015	Biofilter B16	MF - ZrO_2	E4
	July 15-18, 2015	Biofilter B16	MF - ZrO_2	E5
	July 20-23, 2015	Biofilter B16	MF - ZrO_2	E6
	July 27 - 30, 2015	Biofilter B16	MF - ZrO_2	E7
Membrane Materials Comparison Experiment	Aug 3 - 6, 2015	Biofilter B16	MF - ZrO_2	E8
	Aug 10-13, 2015	Biofilter B16	MF - ZrO_2	E9
	Aug 17-20, 2015	Biofilter B16	MF - ZrO_2	E10

For details on the experimental setup, sampling, and analysis, please refer to materials and methods section in Chapter 3.

5.3 Results and Discussion

5.3.1 Raw water quality

The fouling of MF ceramic membranes (ZrO_2 with 0.1 µm pore size) fed with effluents from two biofilters, 8 minutes EBCT (B8) and 16 minutes EBCT (B16), was monitored over a ten week period. For the first three weeks, the ceramic membrane unit was fed with effluent from biofilter B8 followed by 7 weeks of operation with effluent from biofilter B16. A summary of Grand River water quality during the experiment period conducted from May to August 2015 is shown in Table 5-2 below.

Table 5-2 - Biofilter feed water quality (= RF effluent) during the membrane fouling experiments.

Parameters		Unit	Average	Maximum	Minimum	Data points
Temperature		°C	19	24.0	16.1	29
pH		-	7.66	7.88	7.34	100
Turbidity		NTU	2.87	6.15	1.14	50
TOC		mg/L	6.7	7.7	5.9	10
DOC		mg/L	6.7	7.7	5.8	10
SUVA		L/(mg C·m)	4.04	4.34	3.76	10
LC-OCD	Biopolymers	µg/L	519	706	383	10
	Humics	µg/L	3915	4450	3300	10
	Building Blocks	µg/L	919	1108	628	10
	LMW Acids	µg/L	180	264	130	10
	LMW Neutrals	µg/L	489	540	389	10
FEEM	Humic Acid	au	374	440	291	10
	Fulvic Acid	au	332	389	252	10
	Protein-Like	au	65	71	58	10

A generally consistent raw water quality was observed during the experiments with some variability in turbidity and temperature. The raw water feeding the biofilter has a hydraulic retention time of a few days in raw water storage basins after being drawn from the Grand River. Therefore, spikes in turbidity of the raw water were usually observed at the treatment plant a few days after a rain event. As the experiments were conducted during the summer months, the temperature of the raw water did not change significantly throughout even though the Grand River temperature fluctuates from a low of 0°C in the winter to a high of 24°C in the summer.

5.3.2 Turbidity and NOM removal through the treatment trains

As a pretreatment to control fouling in ceramic membrane, the goal of the biofilter is the removal of turbidity and organic matter which have been widely acknowledged as major membrane foulants (Yuan & Zydney, 1999; Her *et al*., 2007; Hallé *et al*., 2009; Peldszus *et al*., 2011a). Both biofilter B8 and B16 achieved high turbidity removal throughout the experiments. On average, 92.4% turbidity removal was achieved through biofilter B8 (Figure 5.1**)** with a further 66% of the turbidity removal through the membrane (based on membrane influent) to yield an overall turbidity removal of 97.5%. Similarly, the average turbidity removal through biofilter B16 was 94.5% (Figure 5.2) followed by a further 59.6% turbidity removal through the membrane to yield an overall turbidity removal of 97.7%. The average turbidity of the biofilter effluents was 0.20 NTU and ranged from 0.16 – 0.27 NTU suggesting very efficient particle removal through both biofilters. The biofilter effluent turbidities were consistently well below the guideline values of 0.3 NTU for conventional and direct filtration as outlined in the Canadian Drinking Water Guidelines. (It should be noted that higher effluent turbidities might be expected if the biofilter influent turbidities were higher, because no chemical addition is practiced. However, because the biofilters are followed by a membrane, the biofilters themselves would not have to meet regulatory turbidity values.) The average turbidity of the membrane permeate was 0.051 NTU and ranged from 0.047 - 0.056 NTU, which meets the guidelines for the Canadian Drinking Water Quality recommendation limits of 0.1 NTU or less.

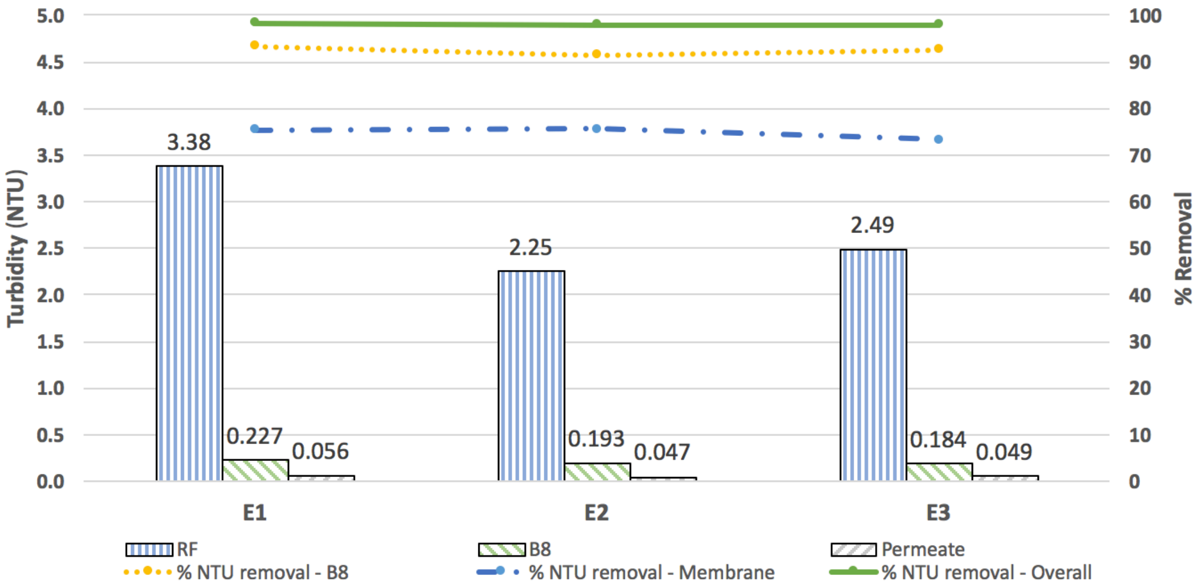


Figure 5.1 – Turbidity data for roughing filter (RF) effluent, biofilter B8 effluent, and MF membrane permeate from fouling experiments E1-E3. *(The percent removal is calculated in reference to the influent to the unit process with the overall percent removal calculated in reference to the influent to the biofilter)*

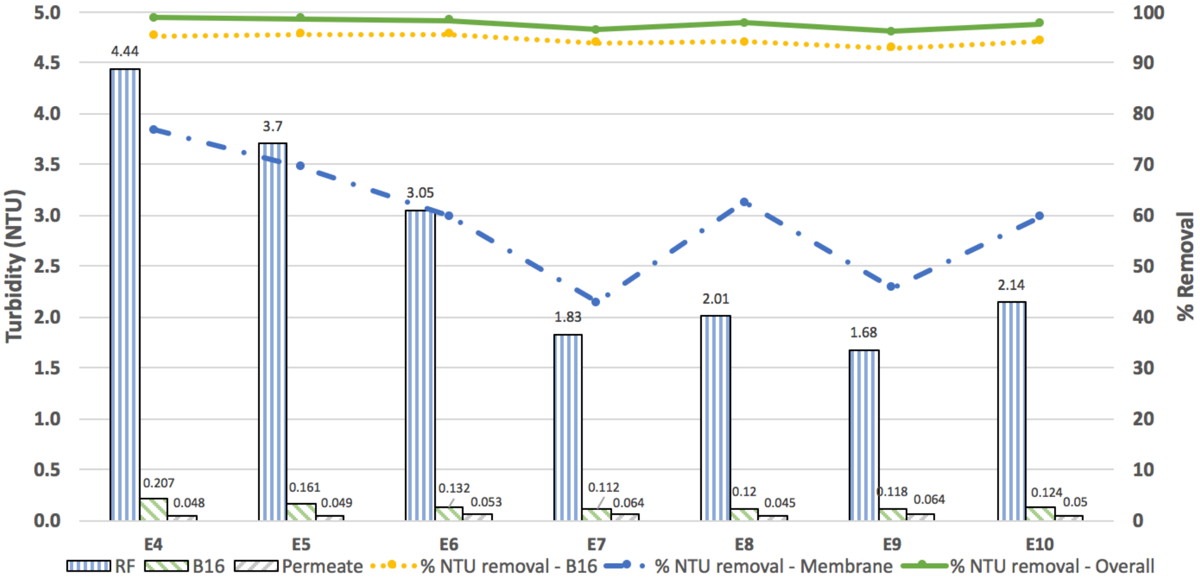


Figure 5.2 – Turbidity data for roughing filter (RF) effluent, biofilter B16 effluent and MF membrane permeate from fouling experiments E4-E10. *(The percent removal is calculated in*

reference to the influent to the unit process with the overall percent removal calculated in reference to the influent to the biofilter)

In comparison to turbidity removal, relatively low removal of TOC (14.3% - 16.8% through B8 and 9.8% - 19.6% through B16) and DOC (9.5% - 16% through B8 and 12.7% - 17.5% through B16) was observed. However, this is expected as only a portion of the organic matter is biodegradable and adsorptive capacity of these filters has been exhausted. As is evident from Table 5-2, essentially all of the TOC is present in the dissolved form, so there is essentially no particulate organic carbon to be removed by the filters. Hallé *et al*., (2009) observed similar DOC removal through biofilters fed with Grand River water during warmer periods.

The biopolymer percent removal through biofilter B8 (Figure 5.3) ranges from 41.9% to 46.1% while the humics percent removal (Figure 5.5) ranges from 9.6% to 10.1%. Similarly, the biopolymer percent removal through biofilter B16 (Figure 5.4) ranges from 61.1% to 81% while the humics percent removal (Figure 5.6) ranges from 4.2% to 11.5%. Both biofilters achieved substantially higher percent removal of biopolymers compared to humics. Studies by Hallé *et al*., (2009) also showed similar biopolymer and humics removal through biofilters (5 minutes and 14 minutes EBCT) without pretreatment during warmer temperature but also saw a significant drop in removal during the colder winter temperature. The high removal of biopolymers observed is likely due to warmer temperatures and well-acclimated biofilters. Although both biofilters achieved high biopolymer removal, biofilter B16 outperformed biofilter B8 by almost 1.5 times in terms of biopolymer removal. This is consistent with studies which showed longer EBCT can improve organic removals (LeChevallier *et al*., 1992; Hallé *et al*., 2009), although once an optimal EBCT is reached, increasing EBCT does not improve organic removal (Zhang & Huck, 1996).

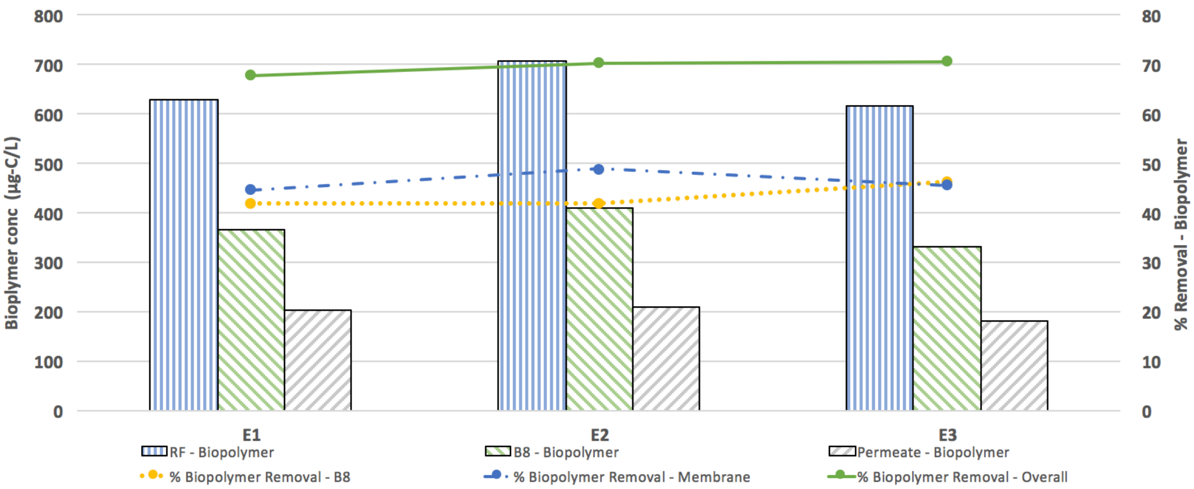


Figure 5.3 - Biopolymer concentration data for roughing filter (RF) effluent, B8 effluent, MF membrane permeate and their removal through the treatment train from fouling experiments E1-E3. *(The percent removal is calculated in reference to the influent to the unit process with the overall percent removal calculated in reference to the influent to the biofilter)*

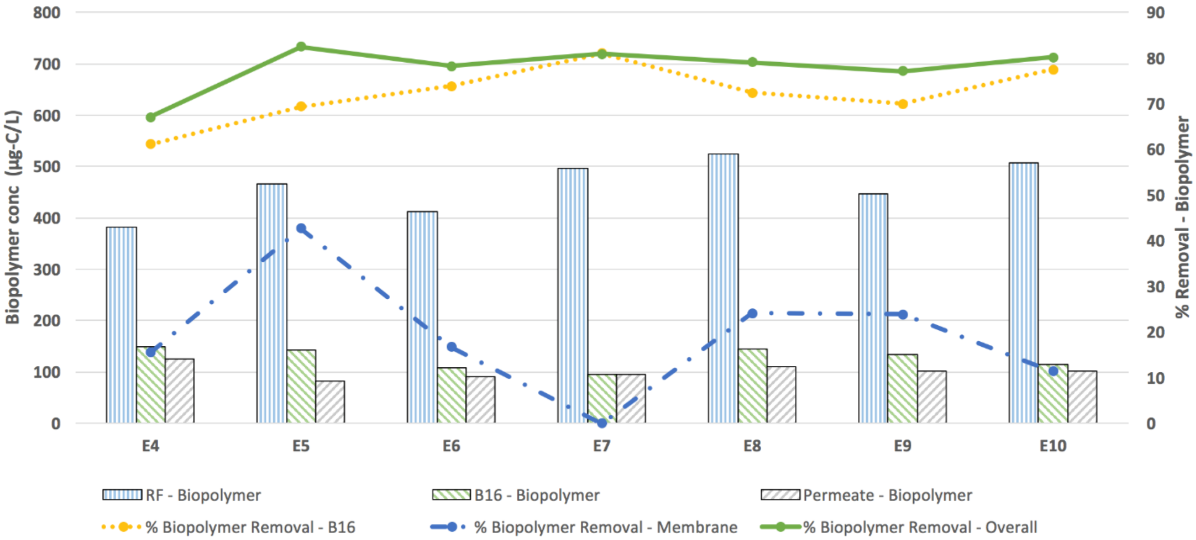


Figure 5.4 - Biopolymer concentration data for roughing filter (RF) effluent, B16 effluent, and MF membrane permeate and their removal through the treatment train from fouling experiments E4-E10. *(The percent removal is calculated in reference to the influent to the unit process with the overall percent removal calculated in reference to the influent to the biofilter)*

However, both biofilters achieved similar humics percent removal, albeit much lower than biopolymer percent removal (refer to Figure 5.5 and Figure 5.6). The consistency in humics percent removal through the two biofilters can be explained due to their slow biodegradation rates. NOM removal through biofilter are mostly due to biodegradation but humic substances, in general, are recalcitrant to biodegradation. However lower molecular weight humic substances may be removed by biodegradation in a biofilter (Basu & Huck, 2003). In contrast, biopolymers are mainly composed of polysaccharides, proteins, and amino acids which are biodegradable and thus, higher percent removal is observed through the biofilter.

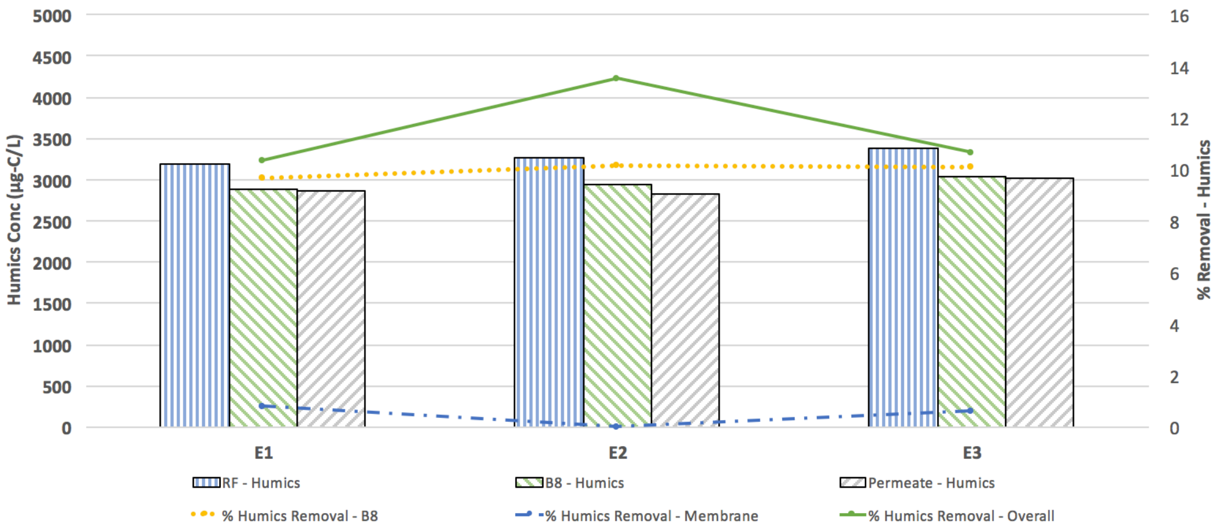


Figure 5.5 - Humics concentration data for roughing filter (RF) effluent, B8 effluent, and MF membrane permeate and their removal through the treatment train from fouling experiments E1-E3. *(The percent removal is calculated in reference to the influent to the unit process with the overall percent removal calculated in reference to the influent to the biofilter)*

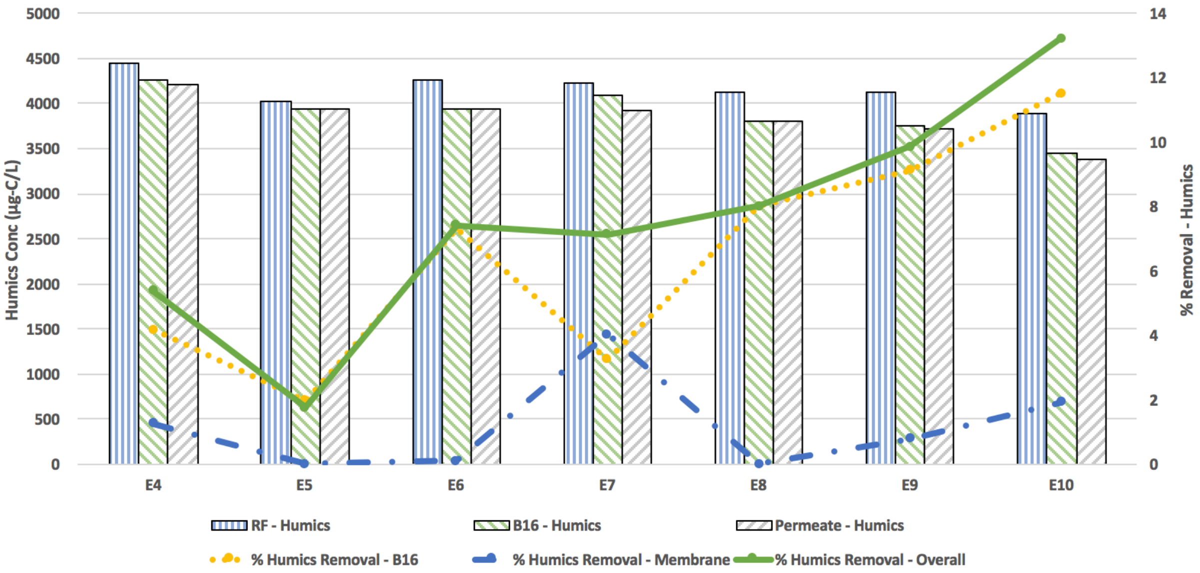


Figure 5.6 - Humics concentration data for roughing filter (RF) effluent, biofilter B16 effluent, and MF membrane permeate and their removal through the treatment train from fouling experiments E4-E10. *(The percent removal is calculated in reference to the influent to the unit process with the overall percent removal calculated in reference to the influent to the biofilter)*

Another analytical tool to characterize NOM is FEEM, and it can be used to detect protein-like content, and humic and fulvic acids with high sensitivity (Peldszus *et al*., 2011). Using the peak peaking technique, the x and y coordinates corresponding to the emission and excitation values of the relative amounts of protein-like content, humic and fulvic acid can be determined. Figure 5.7 shows the relative amount of protein-like content, humic and fulvic acid for the first three experiments (E1-E3) where biofilter B8 effluent was used as a pretreatment. It is evident from the figure that a very small fraction of humic acid and fulvic acid are removed through the biofilters while hardly any removal is seen through the membrane. However, the protein-like content saw a substantially higher removal compared to humic acid and fulvic acid through the biofilter as well as through the membrane. This is consistent with the finding from the LC-OCD analysis where substantial removal of biopolymers was observed while low removals of humic substances were observed. Similar results for protein-like content, and humic acids and fulvic acid removal through the biofilter B16 and membrane for experiments E4-E10 were observed. See appendix C for the FEEM data on the fouling experiments fed with biofilter B16 effluent.

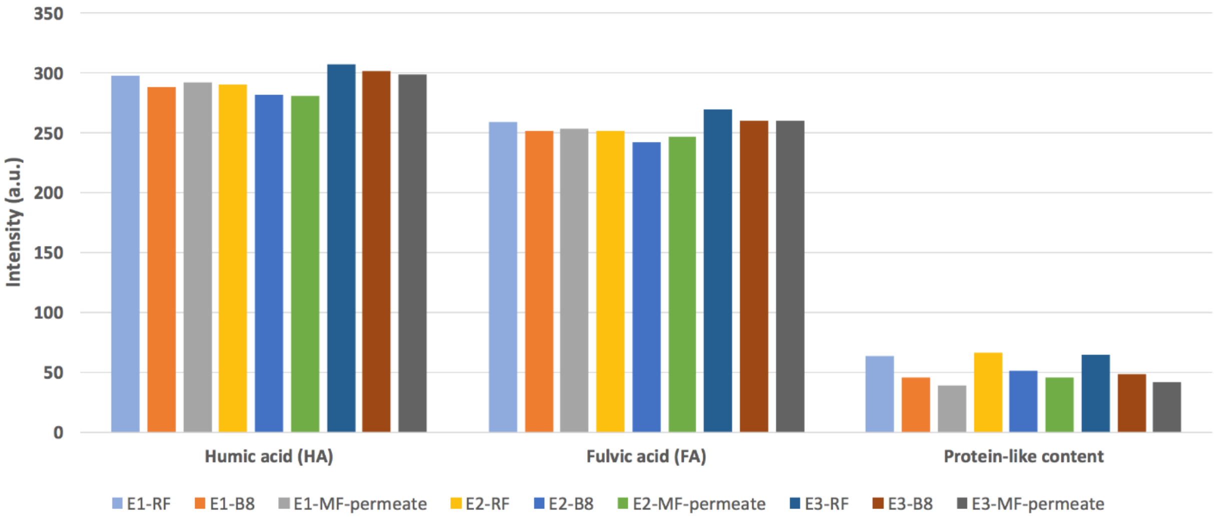


Figure 5.7 - NOM fraction as measured by FEEM peak picking for experiments E1-E3 operated with biofilter B8 effluent as pretreatment *(RF – roughing filter; MF – microfiltration)*

5.3.3 TMP profile for membrane fouling experiments

The fouling experiments were performed using an MF ceramic membrane operated in dead-end mode at a temperature corrected constant flux of 90 LMH using biofilter effluent from B8 and from B16 as feed. As the membrane was operated in constant flux mode, the TMP across the membrane gradually increased due to the increase in resistance from the deposition of particles and NOM on the membrane surface and in the pores. At the beginning of the experiment, the rise in TMP is very small as the membrane was clean and it took a few permeation cycles for the irreversible fouling of the membrane to increase. Gradually, the membrane got irreversibly fouled by repeated particle and organic loading which accelerated the rise in TMP over each permeation cycle. This trend is clearly visible in Figure 5.8 and Figure 5.9 which show the TMP data for the two sets of experiments run with effluents from biofilter B8 and from biofilter B16 respectively.

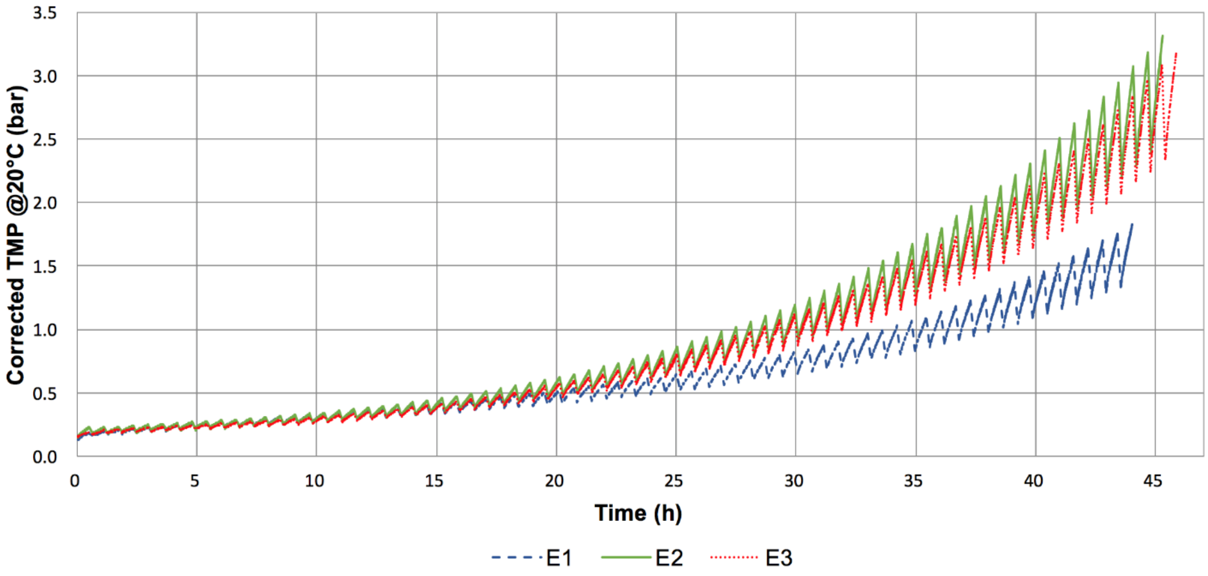


Figure 5.8 - TMP profile for fouling experiments E1- E3 when the membrane was fed with biofilter B8 effluent *(Note: There was a disruption in the power supply which terminated experiment E1 before it reached the criterion for run termination of 3 bars)*

It can be seen from Figure 5.8 that the experiments E2 and E3 showed a very similar rise in TMP over the course of the experiment. However, the first experiment (E1) showed a milder rise in TMP after about 20 h compared to the other two experiments. The milder rise in TMP in experiment E1 suggests that the membrane performed much better during the latter part of this experiment compared to experiments E2 and E3.

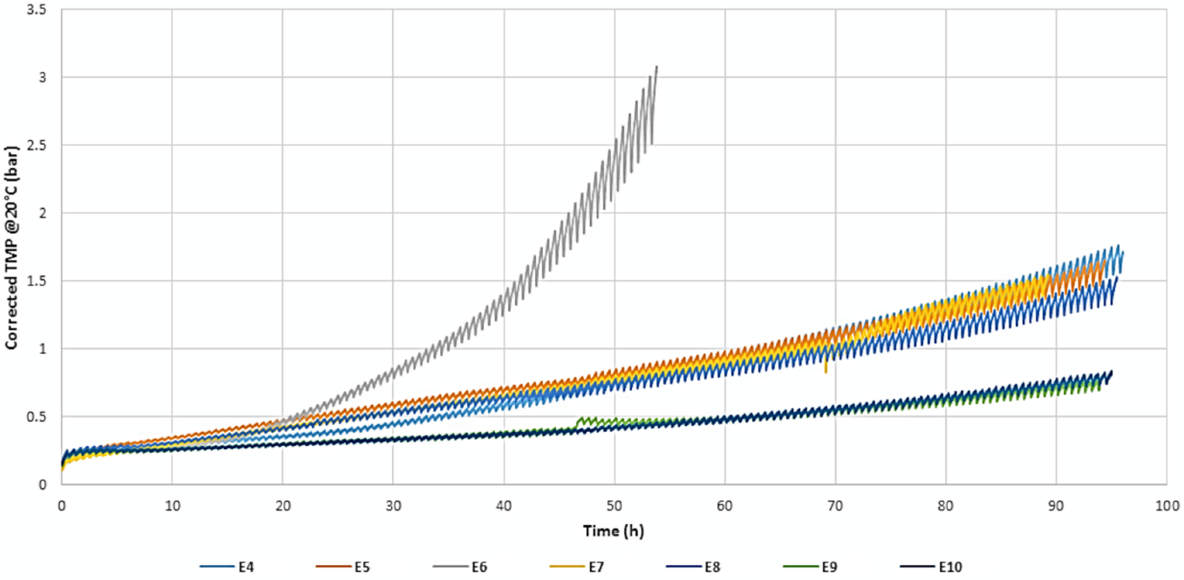


Figure 5.9 - TMP profile for fouling experiments E4-E10 when the membrane was fed with biofilter B16 effluent

Figure 5.9 shows the TMP profile for the fouling experiments when the membrane was fed with effluent from biofilter B16. Except for experiment E6, we see a much lower increase in TMP profiles in the experiments E4 to E10 which were fed with biofilter B16 effluent compared to experiments E1 to E3 which were fed with biofilter B8 effluents. This resulted in longer experiment run times in all but experiment (E6), which was mentioned above. Except for the experiment E6 that terminated by reaching the set TMP of 3 bars, the rest of the experiments were terminated at the end of 4 days. The rise in TMP over the course of the experiments was also almost linear for experiments operated with biofilter B16 effluent while it was non-linear for the experiments operated with biofilter B8 effluent (Figure 5-8).

5.3.4 Irreversible fouling

Figure 5.10 represents the TMP at the start of each permeation cycle for experiments E1 to E3 which was fed with biofilter B8 effluent. The TMP at the start of each permeation cycle after a hydraulic backwash gradually increases linearly during the first 20 hours of membrane operation (about 30 permeation cycles) for all three experiments, after which the rise in TMP takes on a non-linear trend.

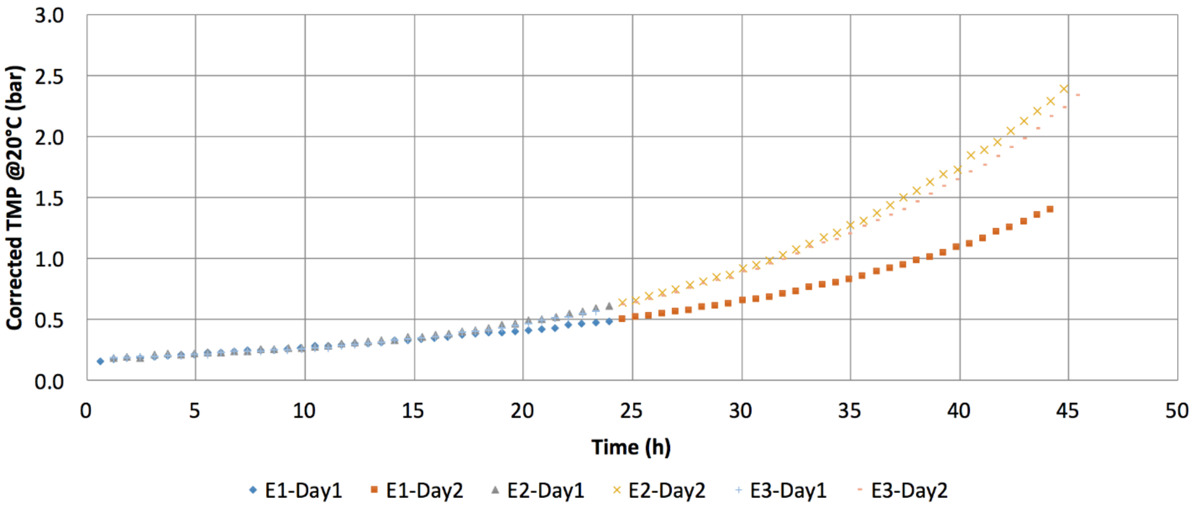


Figure 5.10 – TMP at the start of each permeation cycle after a hydraulic backwash of MF ceramic membrane fed with biofilter B8 effluent

A simple linear regression was used to calculate the irreversible fouling rate. The slope of the linear trend line using all starting TMP of each permeation cycle represents the irreversible fouling rate. However, the trend of the irreversible fouling was not linear over the entire run for all experiments (Figure 5.10). Therefore, irreversible fouling rates were calculated on a daily basis, as the rise in TMP was linear during the initial stage of the experiment followed by a non-linear trend towards the end of the of the experiment. The rise in TMP during the first day of experiment followed an almost linear trend in all three experiments. Analysis of the simple linear regression used for calculating the irreversible fouling rates for the first day showed a very high R-squared value (< 0.94) for all three experiments showing that the model fits the data very well (refer to appendix C for daily fouling rates and the corresponding R-squared values). However, examination of the residual plots shows that there is a missing higher order term in the model to explain a slight curvature at the beginning of the experiments i.e in the first few permeation cycles and towards the end of the first day. However for simplicity a linear model was used to make the semi-quantitative comparisons discussed below. The reason for the curvature in the initial permeation cycles is due to an initial high irreversible fouling observed at the beginning of the experiment and a non-linear increase towards the end of the day (refer to Figure 5.10). After a few permeation cycles, the irreversible fouling stabilizes and a steady linear rise in starting TMP is observed until around 20 hours into the experiment.

At the start of the experiment, a rapid increase in irreversible fouling was observed. This initial high irreversible fouling at the start of the experiment can likely be attributed to an adsorption fouling mechanism (Howe & Clark, 2002). As the membrane permeation continued, fewer sites were available on the membrane for adsorption (Jucker & Clark, 1994). After a number of sustainable permeation cycles (depending on the water quality and pretreatment), the starting TMP increased approximately nonlinearly i.e. after 20 h in Figure 5.10. This is possibly due to repeated fouling of the membrane by a pore narrowing mechanism which is mainly irreversible (Shang *et al*., 2015) and can lead to rapid increase in the TMP.

Although the second day starting TMP followed a non-linear trend, a simple linear trend line was fitted for the second day TMP data to capture the change in irreversible fouling rates as illustrated in Figure 5.11. Refer to Appendix C for linear regression data for irreversible fouling rates of experiment E1-E3. Similar to the TMP profiles shown in Figure 5.8, the irreversible fouling rates of the first experiment (E1) are much lower than the later two experiments (E2 & E3) for both the first and second day (Figure 5.11). As mentioned before, the value of the irreversible fouling rates for the second day for all three experiments shown in Figure 5.11 represents an estimation of the true irreversible fouling rates.

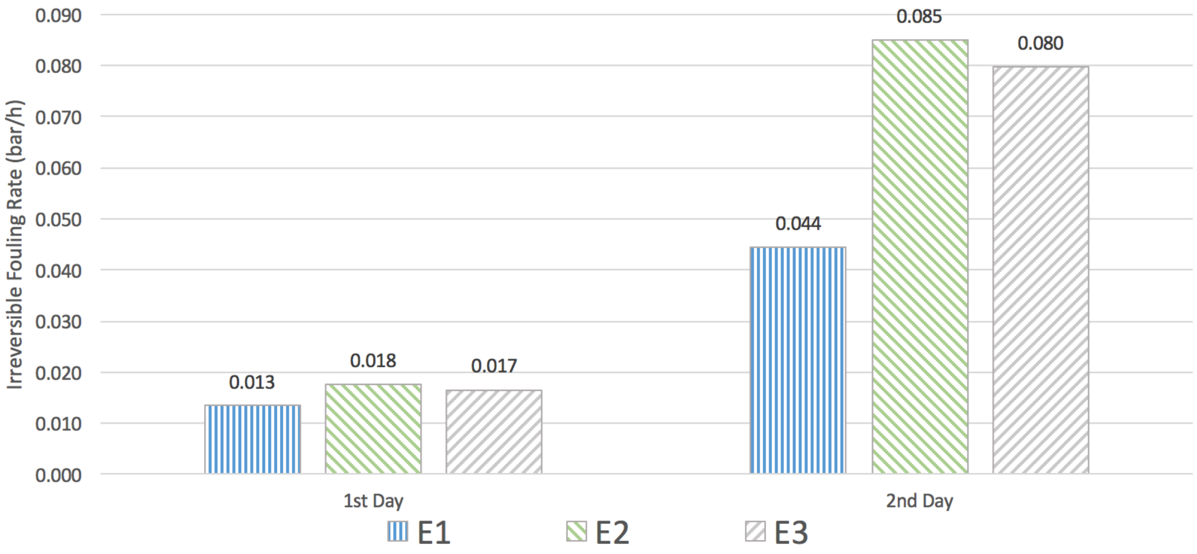


Figure 5.11- Daily irreversible fouling rates of MF ceramic membrane fed with biofilter B8 effluent

Figure 5.12 represents the TMP at the start of each permeation cycle for experiments E4-E10 where the membrane was fed with biofilter B16 effluent. Except for experiment E6, which saw an nonlinear rise in the starting TMP over the course of the experiment, all other experiments saw a gradual, essentially linear rise in starting TMP.

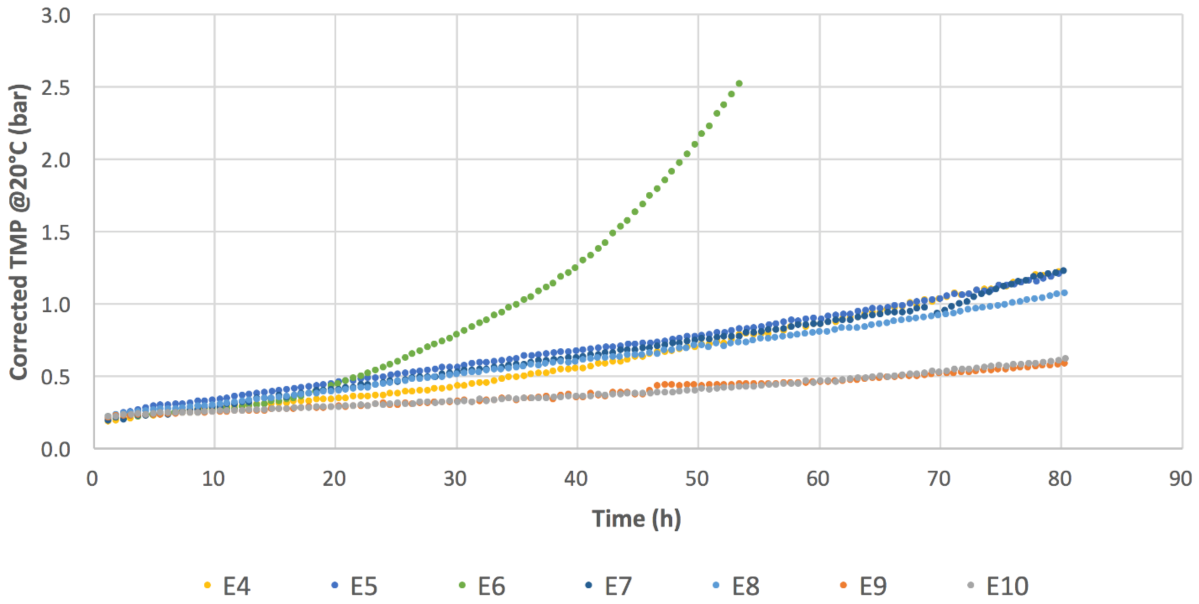


Figure 5.12 – TMP at the start of each permeation cycle after a hydraulic backwash of MF ceramic membrane fed with biofilter B16 effluent

In the experiments where the pretreatment was biofilter B8 effluent, experiments E2 and E3 terminated by reaching the set TMP of 3 bars in less than two days while E1 was terminated at a TMP of 1.90 bar due to power failure. In contrast, all experiments (except E6) fed with biofilter B16 effluent terminated by reaching the end of the study period of four days with the TMP well below 2 bars. In addition, the starting TMP of each permeation cycle seemed to follow a linear trend (except E6), and a simple linear regression was used to calculate the irreversible fouling rates for each of the four days which was consistent with calculations for experiments E1-E3.

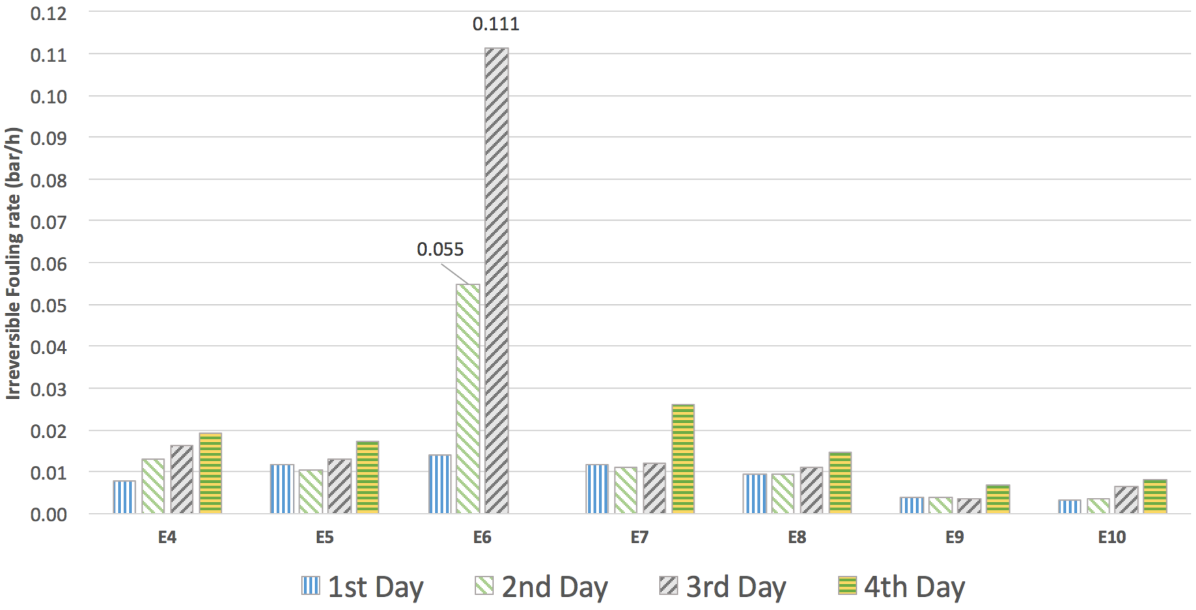


Figure 5.13 - Daily irreversible fouling rates of MF ceramic membrane fed with biofilter B16 effluent

In the experiment E6, the irreversible fouling followed a non-linear trend similar to the trend observed on the second day in the experiments fed with biofilter B8 effluent. Nevertheless, the irreversible fouling rates for experiment E6 were computed using a simple linear regression for the purpose of comparing the irreversible fouling rates with the other experiments.

Once the rise in TMP begins to follow a non-linear trend, it is uneconomical in terms of production cost to continue operating the membrane. Therefore, in practice, the membrane would typically be chemically cleaned in place (CIP) or a chemically enhanced backwash (CEB) would be commenced to recover irreversible fouling. However, neither CIP nor CEB was performed in this study as the goal was to study and compare fouling trends over a longer time period without the influence of chemical cleaning. The effects of chemical cleaning on the fouling rates were beyond of the scope of this chapter.

5.3.5 Reversible fouling

The reversible fouling rates for experiments fed with biofilter B8 effluent (Figure 5.14) follow a trend similar to the starting TMP of each permeation cycle (Figure 5.8). The general trend for all three experiments (E1 – E3) is non-linear, and a rapid increase in the reversible fouling rate later in the permeation cycle is observed. For experiments E1, the reversible fouling rate is smaller than for the other two experiments (E2 & E3), which is consistent with the irreversible fouling rates.

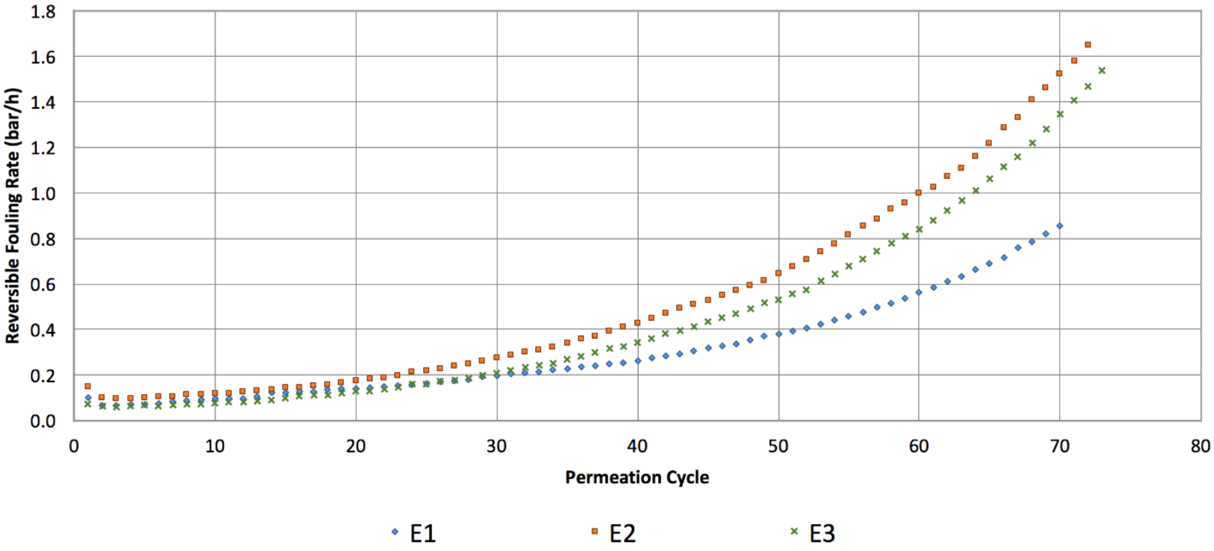


Figure 5.14 - Reversible fouling rate of MF ceramic membrane fed with biofilter B8 effluent

In contrast to the experiments operated with biofilter B8 effluent, the experiments operated with biofilter B16 revealed a different trend at the beginning of each experiment. At the start of the experiment, a higher reversible fouling rate is observed, which gradually decreases and then gradually increases again. This trend is barely noticeable in the experiments with B8 effluent as pretreatment, but it is distinctly clear in all experiments with biofilter B16 effluent as a pretreatment (Figure 5.15).

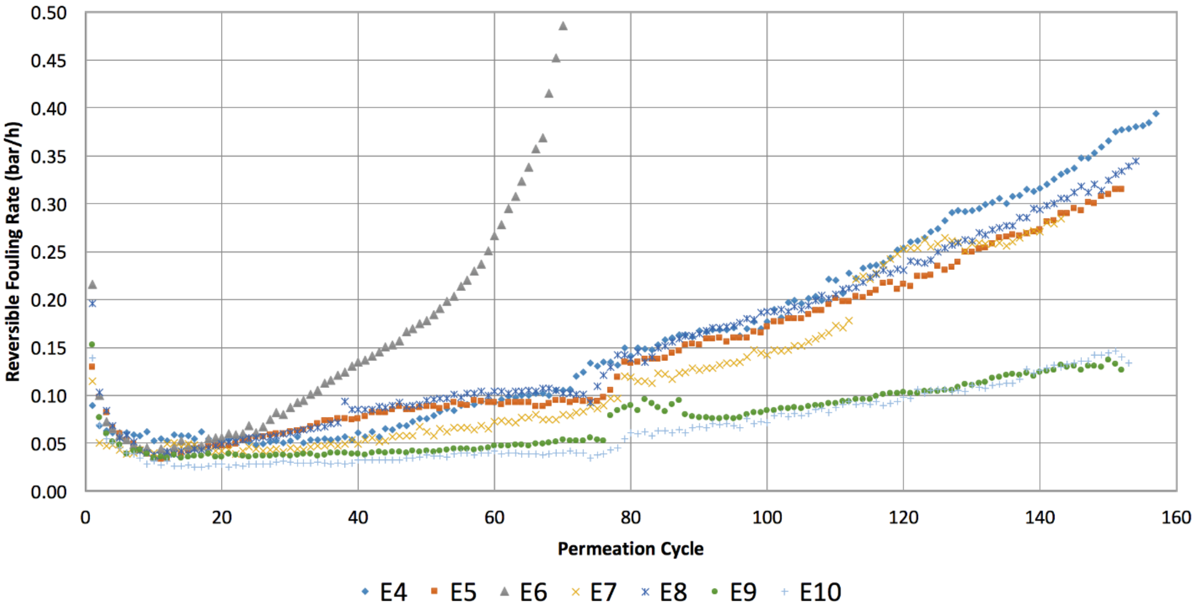


Figure 5.15 - Reversible fouling rate of ceramic MF membrane fed with biofilter B16 effluent

This might be due to an adsorptive fouling mechanism that is more evident at the start of membrane operation as has been reported for polymeric membranes (Howe & Clark, 2002; Koh *et al*., 2005) and ceramic membranes (Shang *et al*., 2015). Before the start of each experiment, the membrane is chemically cleaned to remove foulant materials attached/adsorbed to the membrane surfaces and pores from previous experiments. Therefore, at the start of a membrane experiment, the foulants present in the feed have more surface area available for adsorption leading to a higher reversible fouling rate. A steady state is quickly reached after a few cycles (5 - 7 cycles) into the membrane operation as the adsorption sites available on the membrane gradually decrease (Jucker & Clark, 1994; Koh *et al*., 2005). The reversible fouling rate slowly rises again as pore blocking and cake layer fouling mechanism typically take over during the later cycles of the membrane operation, a behavior which is consistent with trends in Figure 5.15.

5.3.6 Water quality and membrane fouling

All membrane fouling experiments were operated under similar conditions, with variability only in the influent water quality. Significantly higher reversible and irreversible fouling rates were observed during experiments (E1-E3) fed with biofilter B8 effluent compared to experiments (E4-E10) fed with biofilter B16 effluent. This suggests that turbidity and NOM concentration have a significant effect since it has been shown that B8 and B16 remove turbidity and biopolymers to different degrees (Figure 5-1 – Figure 5-4). Better water quality in terms of turbidity from biofilter B16 was observed with an average turbidity of 0.139 NTU (standard deviation of 0.04 NTU) compared to biofilter B8 effluent average turbidity of 0.20 NTU (standard deviation of 0.02 NTU). A consistently lower irreversible and reversible fouling observed in membrane fed with effluent from biofilter B16 suggests that lower turbidity of biofilter B16 effluent has some positive effect on membrane performance.

Similar results were observed in terms of biopolymer concentration in biofilter effluents. The average biopolymer loading on the membrane from biofilter B8 effluent was 369 μg/L (standard deviation 39 μg/L) while the average biopolymer loading from biofilter B16 effluent was 127 μg/L (standard deviation 21 μg/L). Higher biopolymer percent removal through the membrane was also observed for membrane fed with biofilter B8 effluent at 46.3% (standard deviation = 1.8%) compared to biopolymer percent removal of 22.1% (standard deviation = 11.1%) when fed with biofilter B16 effluent. The absolute removal of biopolymers is also higher by the membrane during experiments fed with biofilter B8 effluent which saw higher biopolymer loading.

A higher biopolymer loading and percent removal/rejection correlate well with the higher rate of both reversible and irreversible membrane fouling. This is likely due to the constricting of membrane pores as more biopolymers are retained by the membrane. The biopolymers which are removed during backwash contribute to reversible fouling while those which are not removed contribute to irreversible fouling. This result is consistent with observations by numerous studies which have noted that biopolymers have a high propensity to foul both polymeric membranes (Hallé *et al*., 2009; Lee *et al*., 2004, Peldszus *et al*., 2012) and ceramic membranes (Shang *et al*., 2015, Zhang *et al*., 2013). In addition, the biopolymer concentration in the membrane feed remained relatively constant through the weeks, which corresponds well with the consistent fouling rates observed for most experiments.

In terms of humics loading on the membrane, the average humics concentration from biofilter B8 effluent was 2.95 mg/L (standard deviation = 0.08 mg/L) while the average concentration from biofilter B16 effluent was 3.89 mg/L (standard deviation = 0.26 mg/L). Despite the high loading rate, negligible percent removal through the membrane was observed in experiments. The percent removal through the membrane when fed with biofilter B8 effluent was 0.5% (standard deviation = 0.3%) while it was 1.2% (standard deviation = 1.4%) when fed with biofilter B16. The observation suggests that humics are not retained by MF ceramic membrane and therefore, does not play a role in membrane fouling. This is consistent with expectation as the average molecular weight of humics is around 1000 Da (Huber *et al*., 2011) and is considerably smaller than the pore size (0.1μm) of the MF membrane used in the study. This makes it unlikely that humics would be retained by the membrane.

However, this is in contrast to studies by Mueller *et al*., (2010) where an elevated concentration of humic substances was removed during MF ceramic membrane filtration of spent filter backwash water. The difference between the two studies is likely due to the difference in the quality of the feed water and the way humic substances were measured. For this study, LC-OCD was used to quantify humic substances while Mueller et al., (2010) used DOC concentration and UV absorption to quantify humic substances.

Turbidity and biopolymer are the two main constituents which are substantially retained by the membrane. The other NOM fractions pass through the membrane since negligible differences were observed between the membrane influent and effluent. In this study, the turbidity and biopolymer concentration were consistently lower in the biofilter B16 effluent compared to the biofilter B8 effluent. As lower reversible and irreversible fouling were observed in membrane fed with biofilter B16, it is evident that biofilter B16 provides a superior pretreatment. This is consistent with the finding of Chapter 3 where effluent from a longer EBCT biofilter saw substantially lower reversible and irreversible fouling.

5.3.7 NOM Characterization in backwash water

To elucidate further information on the composition of membrane foulants, the backwash water after three consecutive permeation cycles was collected during the sampling (i.e. after 24 h) in experiments E8 to E10, which were fed with biofilter B16 effluent. The backwash water samples were analyzed for various water quality parameters including turbidity, UV_{254} absorbance, TOC, DOC, LC-OCD, and FEEM. As the permeate water produced during the permeation cycle was used for backwashing the membrane, a comparison between the permeate water and backwash water sheds light on the composition of the reversible foulants which are removed during a backwash cycle.

A forward flush using the permeate water preceded the backwash cycle so that the materials which had built up inside the lumens of the membrane during the permeation cycle could be removed. Therefore, the backwash water would only contain materials that were not removed during the forward flush but are removed during the backwash cycle. Consequently, the composition of the backwash water represents the foulants (responsible for reversible fouling) that were removed from the surface and pores of the membrane.

The forward flush was not collected due to logistical difficulties. There was no valve outlet immediately following the membrane to collect the forward flush water. The only way was to collect the forward flush water after it passes through the tubing of the membrane test unit. As the tubing following the membrane is primed with permeate water and materials from the previous forward flush, it was not possible to collect the forward flush without contaminating the sample. Therefore, a detailed mass balance analysis could not be done. However, comparison of the relative concentration of the backwash water and permeate water sheds light on reversible membrane foulants.

A comparison of the turbidity of the permeate water and backwash water from experiment E8-E10 is illustrated in Figure 5.16. The turbidities of the backwash water are 3 to 6 times higher than the permeate water. The high turbidity of backwash water suggests the presence of colloids that have been shown to cause reversible membrane fouling (Fan *et al*., 2001; Howe & Clark, 2002).

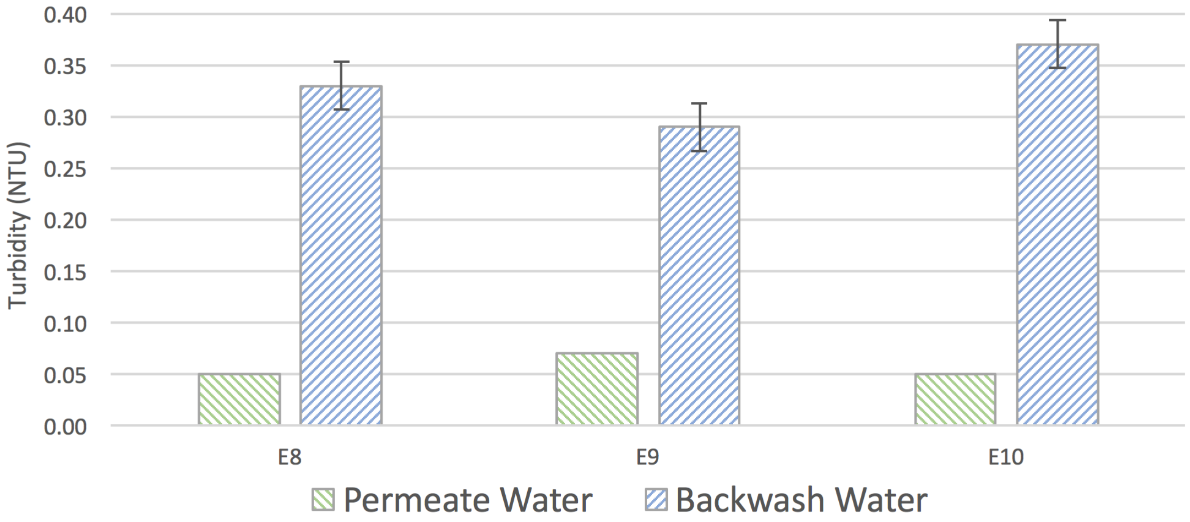


Figure 5.16 – Turbidities of permeate water and backwash water for experiments E8-E10. *The error bars on the backwash water represents the standard deviation of three turbidity measurements from three backwash water samples.*

Humic substances (Jucker & Clark, 1994; Yuan & Zydney, 1999, Mueller *et al*., 2010) and especially biopolymers (Hallé *et al*., 2009; Her *et al*., 2007; Peldszus *et al*., 2012) have been acknowledged as major foulants in both ceramic and polymeric membranes. Comparisons of different NOM fractions of membrane feed (both biofilter B8 and B16 effluent) vs. the corresponding permeate water (Figure 5.3

- Figure 5.6) showed that mainly biopolymers were retained by the membrane used in this study. Humics, building blocks, LMW neutrals and LWM acids of the NOM fraction saw negligible removal through the membrane indicating that they basically passed through (Figure 5.17). Since a significant fraction of the biopolymers is removed/retained by the membrane, they can act as reversible and/or irreversible foulants. Hallé *et al*., (2009) also observed similar results where higher removal of biopolymers by the biofilters achieved a reduction in both reversible and irreversible fouling in UF polymeric membranes.

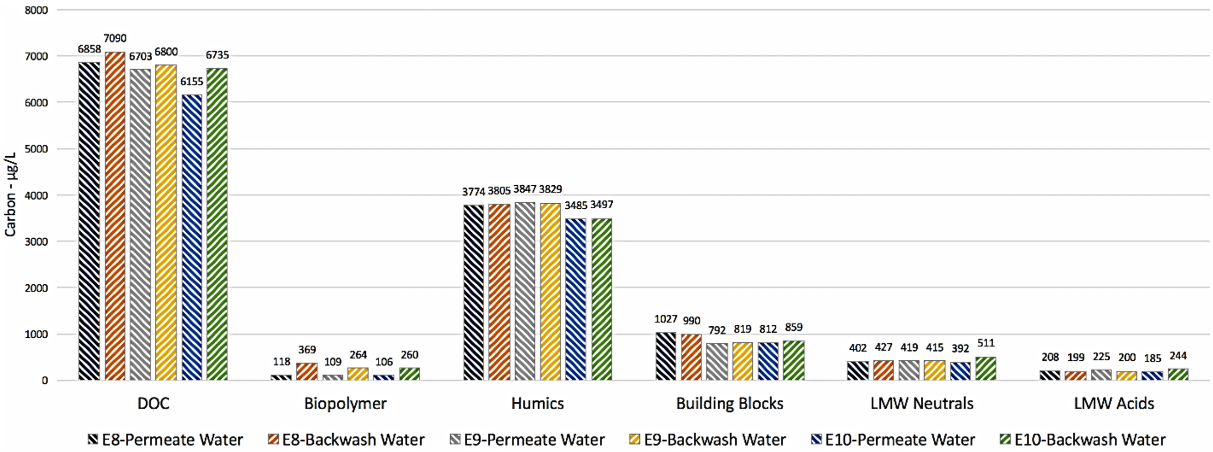


Figure 5.17 - NOM fraction concentration of permeate water (used in backwashing the membrane) and backwash water *(LMW – Low molecular weight)*

The backwash water showed an average increase of 167% (143% - 214%) in the concentration of biopolymers compared to less than 1% for humic substances. This is consistent with the observation of Shang *et al*., (2015) where they noted that fouling of an MF ceramic membrane was predominately from biopolymer adsorption while the fouling of UF ceramic membrane was mainly due to adsorption of humic substances. The negligible increase in the concentration of humics in the backwash water in all three experiments corresponds well with the insignificant removal of humics during the permeation cycle. NOM fraction analysis using FEEM peak peaking showed similar results (refer to appendix C for FEEM figure).

5.3.8 Clean water permeability

A clean water permeability (CWP) test was conducted on the MF ceramic membrane at the start and end of every experiment. The CWP at the start of the experiment was carried out to establish that the membrane was clean while the CWP at the end of the experiment was carried after a backwash to assess the extent of irreversible fouling. The clean water permeability at the start of the experiment showed a range of permeability after chemical cleaning with an average permeability of 800 LMH/bar and a standard deviation of 94 LMH/bar. The variability in the permeability of the clean membrane is partly due to the method employed to compute the permeability as well as the resolution of the TMP recorded during the test.

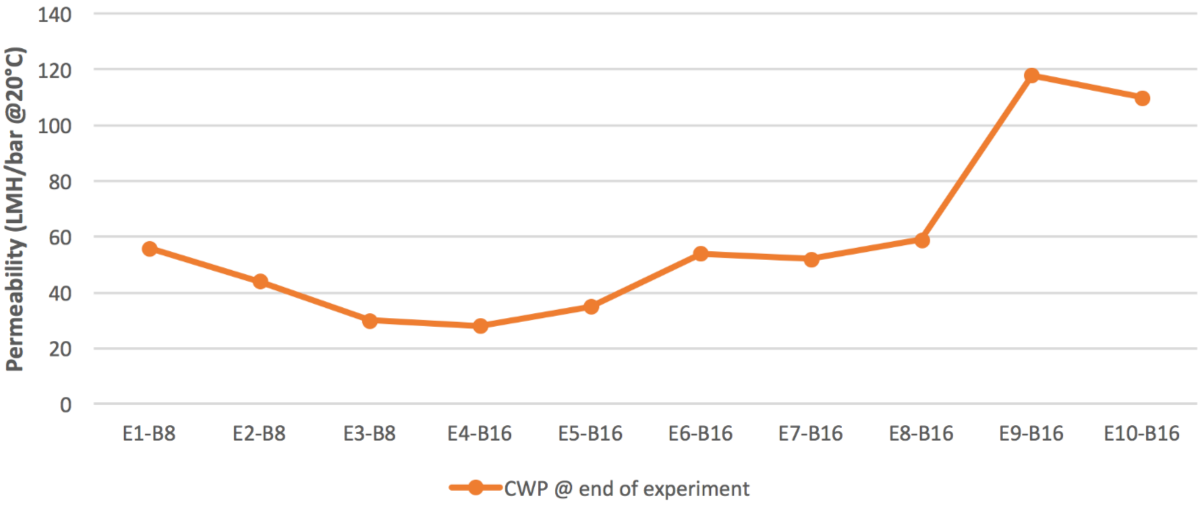


Figure 5.18 - Clean water permeability test results at the start and end of experiment. *(Experiment E1 was terminated at a TMP of 1.85 bar due to power failure while the rest of the experiment terminated by reaching TMP of 3 bars or reaching the end of 4 day experiment period ; B8 – Biofilter B8; B16 – Biofilter B16)*

Similarly, the clean water permeability of the membrane at the end of the experiment was on average 56 LHM/bar with a standard deviation of 32 LHM/bar. The variability in the permeability of the membrane at the end of the experiment largely depended on how the experiment was terminated. For experiments that terminated by reaching the set TMP of 3 bars i.e. complete fouling of the membrane, the clean water permeability was 41 LMH/bar on average with a standard deviation of 16 LMH/bar. These were experiments which experienced high fouling rates. For the experiments that terminated by reaching the four days period, the average clean water permeability was 67 LMH/bar with a standard deviation of 38 LMH/bar.

5.4 Conclusion

This study on the performance of MF ceramic membranes after BF_{WP} pretreatment over time shows that biological filtration can be an effective pretreatment to control membrane fouling, with the biofilter with a longer EBCT performing significantly better. In addition, the following conclusions can be drawn from this study:

- Biofiltration without pretreatment (BF_{WP}) independently and especially in combination with a ceramic membrane is able to achieve excellent turbidity removal. Biofilter B8 and B16 had an average turbidity removal of over 92% and 94% while the overall biofilter membrane treatment process achieved over 97% for both biofilter combinations. The ceramic membrane effluent turbidity was consistently below 0.07 NTU, which demonstrates the reliability and ability of the system to meet stringent regulations in the future.
- The irreversible fouling was substantially lower in the experiments operated with biofilter B16 effluent compared to the experiments operated with biofilter B8. Using biofilter B16 effluent was able to control irreversible fouling for at least 4 days in all experiments (except one experiment E6) compared to less than two days using biofilter B8.

- The reversible fouling also followed a similar trend to irreversible fouling with lower reversible fouling observed in experiments fed with biofilter B16 effluent compared to experiments fed with biofilter B8 effluent.

- At the start of experiments when the membrane was membrane fed with biofilter B16 effluent, the reversible fouling rates gradually decrease for a few filtration cycles (5 – 7 cycles) after which the fouling rates gradually increases again. The gradual decrease in fouling rates is mostly likely due to the initial conditioning of the membrane.

- Among the NOM fractions, only the biopolymer removal across the two biofilters differed significantly. The biofilter with higher EBCT (B16) had a significantly higher biopolymer removal compared to the biofilter with the lower EBCT (B8). The removal of other NOM fractions such as humics, building LMW acids and LMW neutrals was negligible. Since a significant fraction of biopolymer was removed/rejected by the membrane, it is likely that biopolymers have a significant influence on the reversible and irreversible fouling of the membrane. During the experiments when the membrane was fed with biofilter B16 effluent, the Grand River raw water quality saw an improvement in terms of turbidity in the later weeks of the experiment. The biopolymer concentration remained relatively constant through the weeks, which corresponds well with the consistent fouling rates observed for most experiments.

- The backwash water had a significantly higher turbidity (5 – 7 times as much) compared to the permeate water (used for backwashing) suggesting an effective process to recover hydraulically reversible fouling.

- The concentration of biopolymers in backwash water was also significantly higher (143% - 214%) compared to the biopolymer concentration in permeate water used for backwashing the membrane. This further confirms that the biopolymers are related to reversible fouling of ceramic membranes.

- The clean water permeability test conducted after chemical cleaning over time shows a consistent high recovery of membrane permeability. This in turn indicates that the chemical cleaning approach used (high concentrations of NaOCl (3% w/w) and NaOH (2.5% w/w)) can be safely and effectively employed to recover ceramic membrane permeability after the membrane has been completely fouled

Chapter 6

Conclusions and Recommendations

The objectives of the research presented in this thesis were to:

- Assess the efficacy of direct biofiltration as a pretreatment to control fouling in ceramic membranes in drinking water treatment.
- Evaluate the effects of biofilter EBCT and membrane pore size on ceramic membrane fouling.
- Investigate the influence of membrane material on the fouling of MF ceramic membranes following direct biofiltration pretreatment.
- Evaluate the long term performance of MF ceramic membranes following direct biofiltration pretreatment.

To achieve these goals, a biofiltration pilot plant set-up at the Mannheim Water Treatment Plant in Kitchener, Ontario, Canada was used. Grand River water, which is heavily impacted by treated wastewater effluents and agricultural runoff, was used as source water for the biofilters. The biofiltration pilot plant consisted of two dual-media biofilters with an EBCT of 7.8 minutes and 15.6 minutes each which were preceded by a roughing filter. Two custom built membrane tests unit were used to run membrane fouling experiments using effluent from the biofilters and roughing filter. MF and UF tubular ceramic membranes manufactured by Atech Innovations were used for the study. LC-OCD and FEEM were used to characterize NOM and elucidate ceramic membrane foulants.

6.1 Summary of Conclusions

The experiments were conducted from April to August 2015. A proof of concept experiment (i.e. with and without biofiltration pretreatment), two sets of factorial experiments (i.e. investigating the effects of biofilter contact time and membrane pore size), and a membrane materials comparison experiment were conducted for this study. Due to the challenges faced in operating the two membrane test units identically, a full factorial analysis could not be performed. Nevertheless, alternative data analysis approaches were used to evaluate the effects of the factors under study. The control test unit, which was operated using the same operating conditions throughout the experiments, was monitored to evaluate the long-term performance of a MF ceramic membrane under varying water conditions. The most significant conclusions from the research study are presented below:

- Direct biofiltration without pretreatment (BF_{WP}) is an effective pretreatment to control fouling in MF ceramic membranes. This is a new finding that has not previously been reported in the literature. The MF membrane operated with pretreatment fouled significantly less than the MF membrane operated without pretreatment.
- Humic substances which are a major fraction of the NOM were poorly removed through both biofilters with EBCTs of 8 min (B8) and 16 min (B16). However, this is consistent with results reported in the literature for humic substance removal by biological processes.
- BF_{WP} was able to substantially reduce both turbidity and biopolymer concentration in the feed water. Both biofilters (B8 and B16) consistently achieved over 92% turbidity removal during the course of the study. However, biofilter B16 with a longer EBCT removed substantially higher biopolymer concentration from the feed water compared to biofilter B8 with a shorter EBCT.
- The biofilter with the longer EBCT (B16) performed substantially better in terms of controlling fouling of a MF ceramic membrane compared to the biofilter with the shorter EBCT (B8). The membrane operated with effluent from B16 fouled at substantially lower reversible and irreversible fouling rates than the membrane operated with B8 effluent, especially in the later stages of the experiments after more than 1 or 2 days of operation.

- The irreversible and reversible fouling rates of UF and MF membranes were comparable during the initial ten hours of operation, however, in the later stages, the UF membrane fouled at a substantially higher rate. The TMP of the UF membrane was also substantially higher than the TMP of the MF membrane when maintaining the same flux.

- An MF TiO_2 membrane fouled irreversibly at a much higher rate compared to an MF Al_2O_3 membrane, whereas MF ZrO_2 and Al_2O_3 membranes exhibited similar irreversible fouling. However, further experiments would need to be performed to confirm the findings for the ZrO_2 membrane as a direct comparison was not possible for this membrane and a data transformation technique had to be applied to come to the latter conclusion.

- Lower reversible fouling was observed for the TiO_2 membrane compared to the Al_2O_3 membrane during the first day of operation. However, the reversible fouling rate for the TiO_2 membrane was substantially higher during the latter stages of the experiment compared to Al_2O_3 membrane.

- The TMP at the start of the experiments for Al_2O_3 and ZrO_2 membrane was similar while it was substantially lower for the TiO_2 membrane when operated at the same temperature corrected flux. Therefore, there is an opportunity for considerable energy saving when using a TiO_2 membrane instead of Al_2O_3 and ZrO_2 membranes, if the membranes are operated for relatively short times between cleaning cycles.

- Biopolymers were the only NOM fraction that saw substantial rejection through the MF ceramic membrane. On average, 46% of biopolymers were rejected with biofilter B8 pretreatment while 22% of biopolymers were rejected with biofilter B16 pretreatment. Other NOM fractions saw negligible rejection through the MF ceramic membrane. Since a substantial fraction of biopolymers is rejected by the membrane, it is highly likely that biopolymers play a significant role in the fouling of ceramic membranes.

- The concentration of biopolymers in backwash water was also substantially higher (143% - 214%) compared to the biopolymer concentration in the permeate water used for backwashing the membrane. This provides further evidence to support the hypothesis that biopolymers are involved in the reversible fouling of MF ceramic membranes.
- The turbidity of the backwash water was substantially higher than in the permeate water used for backwashing the membrane suggesting a role of colloids/particulates in the reversible fouling of MF ceramic membrane.
- Concentrated bleach (3% w/w NaOCl) and NaOH (2.5% w/w) were safely used to chemically clean the ceramic membranes after each experiment when the membranes were fouled. Clean water permeability tests of the membranes after chemical cleaning showed high and consistent recoveries of permeability.

6.2 Recommendations for the Water Industry

The results from this study show that direct biofiltration without pretreatment (BF_{WP}) is an effective pretreatment to control fouling in ceramic membranes. Although the efficacy of BF_{WP} to control fouling has been largely established for polymeric membranes, its efficacy for ceramic membranes had not been previously studied. BF_{WP} is considered a “green” pretreatment, as no chemicals are required for operating the biofilters. Furthermore, the reduction in fouling of the ceramic membranes means that less chemicals will be required for cleaning the membranes once irreversible fouling reached unsustainable levels. Therefore, the combination of BF_{WP} with ceramic membrane filtration provides an environmentally friendly process and is very well suited for small communities where chemical cost and transportation are major hurdles.

Although BF_{WP} showed promise as a pretreatment, it should be noted that the study was conducted during warmer temperatures during the summer. Numerous studies reported observing decrease in biofilter performance during colder winter temperatures. Therefore, it is recommended that the process is implemented in places experiencing warmer temperatures until further studies can be performed to confirm the efficacy of the pretreatment at colder temperatures.

DOC and especially humic substances were not effectively removed through the combination of BF_{WP} with ceramic membrane filtration. Although the high level of humics observed in this study was not detrimental to membrane performance, other pretreatment steps might be necessary for utilities treating surface water with high humics level whose treatment goal include substantial removal of humics and other NOM fraction for disinfection by-product control.

An improvement in performance in terms of turbidity and biopolymer removal was observed for the biofilter with the longer EBCT compared to the biofilter with the shorter EBCT. This improvement translated into reduced fouling of the ceramic membranes and is important information for utilities when making decisions regarding biofilter design, operation and optimization as a membrane pretreatment.

The MF membrane made from TiO_2 operated at a much lower TMP at the same temperature corrected flux compared to the membranes made from Al_2O_3 and ZrO_2. Therefore, less energy is required to produce the same amount of water using the TiO_2 membrane compared to the Al_2O_3 and ZrO_2 membranes. This represents an opportunity for substantial savings in operating costs for the utilities. However, as the TiO_2 membrane fouled faster over the long term this has to be balanced by potentially higher chemical costs due to more frequent chemical cleaning to control irreversible fouling.

6.3 Future Work

The attempt to conduct a factorial experiment to study the main effects and interaction of EBCT and membrane pore size was unsuccessful due to the inherent variability of the two membrane test units when run in parallel. The membrane test units were custom built and required considerable technical expertise and experience for operation. Therefore, for any future work with these membrane test units, a comprehensive optimization of the units is necessary to reduce this variability between the two units before the start of any study. Despite the challenges with the membrane test units, the study provided valuable information on BF_{WP} pretreatment for ceramic membrane and the following can be recommended for future studies:

- Ascertain the efficacy of BF_{WP} pretreatment for ceramic membranes using different water sources.
- Investigate and confirm the efficacy of BF_{WP} pretreatment during the colder winter temperatures and determine if BF_{WP} pretreatment provides a robust alternative to other pretreatments which are unaffected by temperature fluctuations.
- Perform research on the composition and nature of biopolymers rather than the concentration effects on the irreversible fouling of the ceramic membranes.
- Determine the characteristics and composition of the membrane materials. Measure pore sizes and other properties of the membranes to confirm the manufacture's ratings of the membranes.
- Compare BF_{WP} with other pretreatments such as coagulation using the same water to understand the limitation and advantages of each pretreatment over the other.
- Investigate the fouling mechanism of biopolymers on the ceramic membranes.

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Appendix A

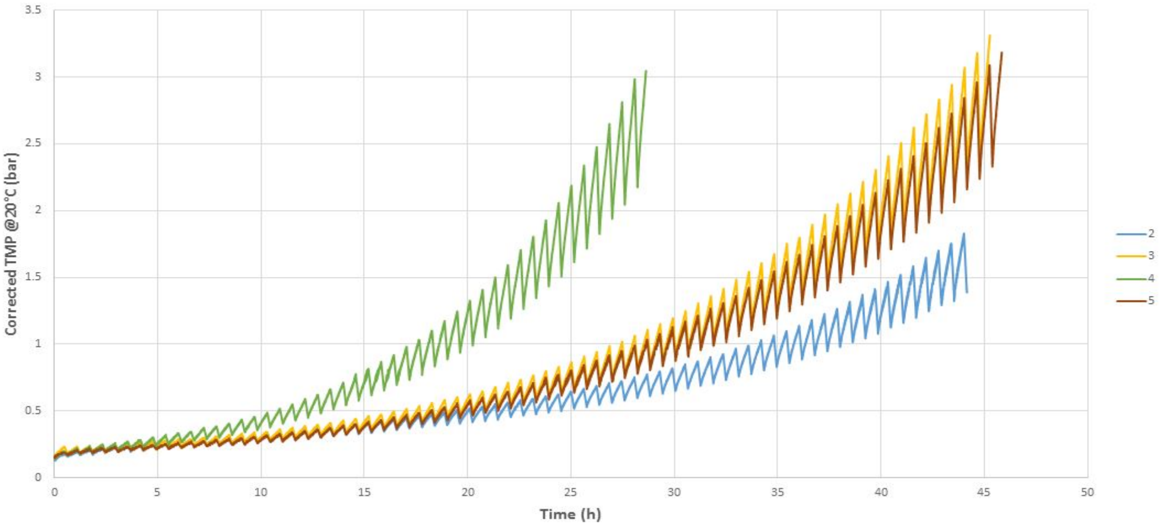

Figure A-1 – Factorial Experiment 1 – TMP profile of MF membrane in the control test unit. The experiments were operated with biofilter B8 effluent. For experiment number details, refer to table 3-3 in Chapter 3

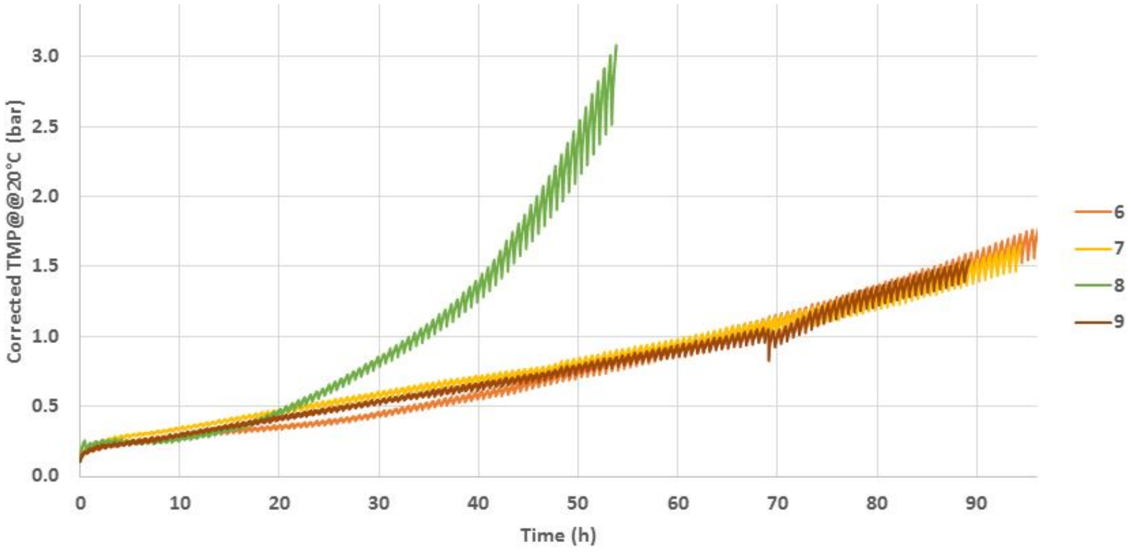

Figure A-2 – Factorial Experiment 2 - TMP profile of membrane in the control test unit. The experiments were operated with biofilter B16 effluent. For experiment number details, refer to table 3-3 in Chapter 3

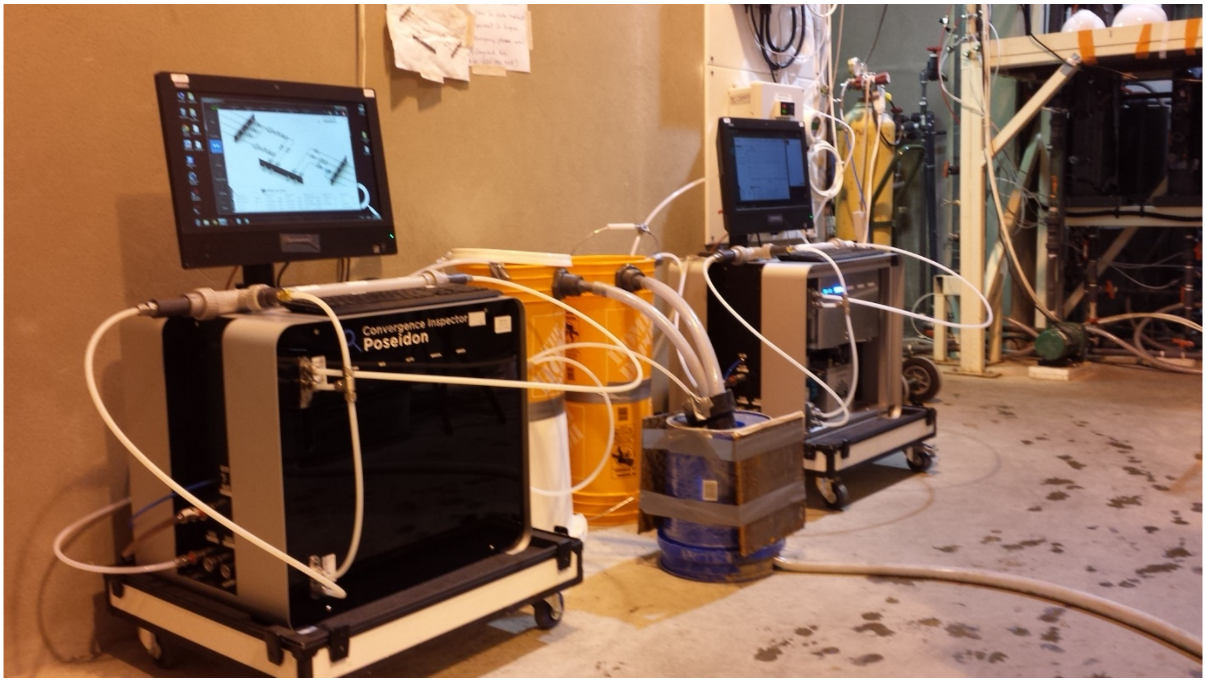

Figure A-3 – Membrane test units used for the membrane fouling experiments.

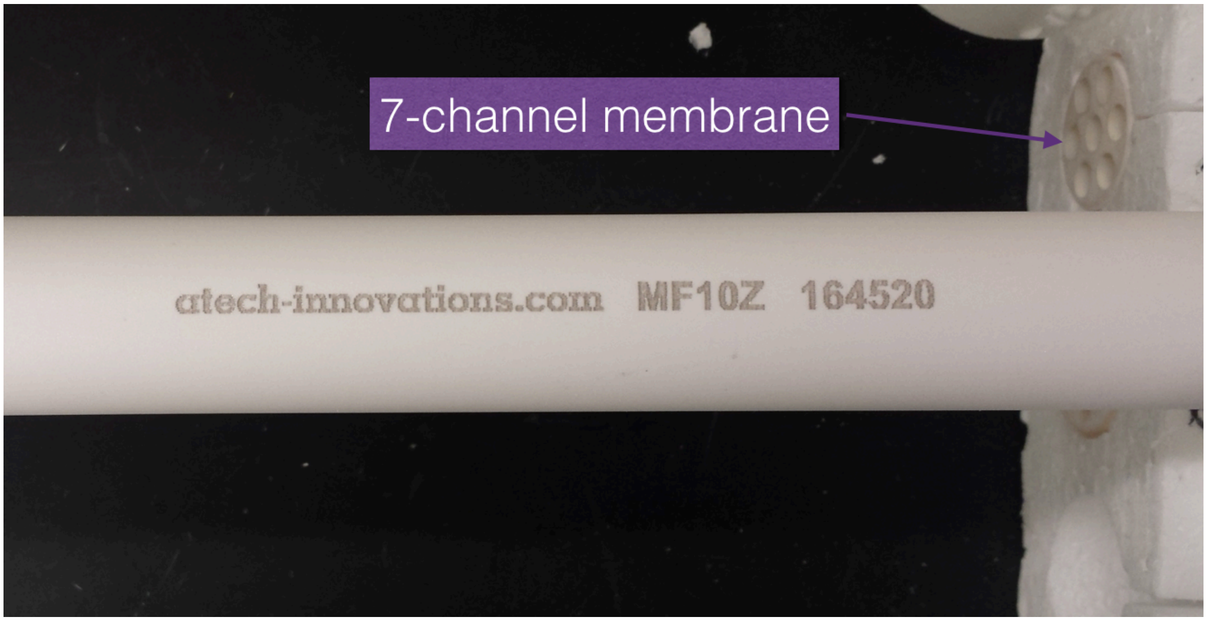

Figure A-4 – MF ceramic membrane manufactured by Atech-innovations, Germany.

Figure A-5 – Biofiltration pilot plant set up at the Mannheim Water Treatment plant in Kitchener, Waterloo, Ontario.

Filtration Program (Filtration.OSMO)

0	Set Status To	Filtration
1	*Comment Line*	*Turn on the permeate valve with flow meter and*
2	Valve Number 6	OFF
3	Valve Number 7	ON
4	Valve Number 8	ON
5	Wait	0.500000s
6	*Comment Line*	*Turn off backwash valves - Just as a precaution*
7	Valve Number 4	OFF
8	Valve Number 1	OFF
9	Valve Number 5	OFF
10	Wait	0.500000s
11	Channel 28-Hold Value	OFF
12	*Comment Line*	*Start of Filtration cycle*
13	Set Status To	Filtration
14	Output 1-Control At Constant Channel 5	7.30000000Kg/hr
15	Wait Until Channel 5 Reaches	6.80000000Kg/hr
16	Comment Line	hold the time of the start of filtration cycle
17	Channel 28-Hold Value	ON
18	Stop Program When Channel 16 Reaches	3.000000barg
19	Stop Program When Channel 9 Reaches	4.500000barg
20	Wait Until Channel 29 Reaches	1800.000000s
21	Output 1-Control At Constant Channel 5	0.000000Kg/hr
22	Wait	30.000000s
23	Channel 28-Hold Value	OFF
24	Valve Number 7	OFF
25	Wait	0.500000s
26	Run Program From Path	C:Programs\Backwash.OSMO

Backwash Program (Backwasho.OSMO)

```
 0  Set Status To                           Backwash-START
 1  Output 1-Control At Constant Channel 5  0.000000Kg/hr
 2  Wait                                    10.000000s
 3  Valve Number 1                          ON
 4  Valve Number 4                          ON
 5  Valve Number 5                          OFF
 6  Wait                                    0.500000s
 7  Valve Number 7                          OFF
 8  Valve Number 6                          OFF
 9  Valve Number 8                          OFF
10  Output 3-Integer Constant               0
11  Wait                                    0.500000s
12  Set Status To                           Forward Flush
13  Output 0-Control At Constant Channel 6  20.000000Kg/hr     Forward flush at 20 kg/l
14  Wait Until Channel 6 Reaches            19.000000Kg/hr
15  Wait                                    30.000000s
16  Output 0-Control At Constant Channel 6  0.000000Kg/hr
17  Wait                                    30.000000s
18  Valve Number 4                          OFF
19  Valve Number 5                          ON
20  Wait                                    0.500000s
21  Set Status To                           BackWash
22  Output 0-Control At Constant Channel 6  14.600000Kg/hr
23  Wait Until Channel 6 Reaches            14.100000Kg/hr
24  Wait                                    180.000000s        hydraulic backwash for 3
25  Output 0-Control At Constant Channel 6  0.000000Kg/hr
26  Valve Number 5                          OFF
27  Wait Until Channel 6 Drops To           1.000000Kg/hr
28  Valve Number 1                          OFF
29  Wait Until Channel 6 Drops To           0.500000Kg/hr
30  Wait                                    0.500000s
31  Run Program From Path                   C:\Programs\Filtration.OSMO
```

Appendix B

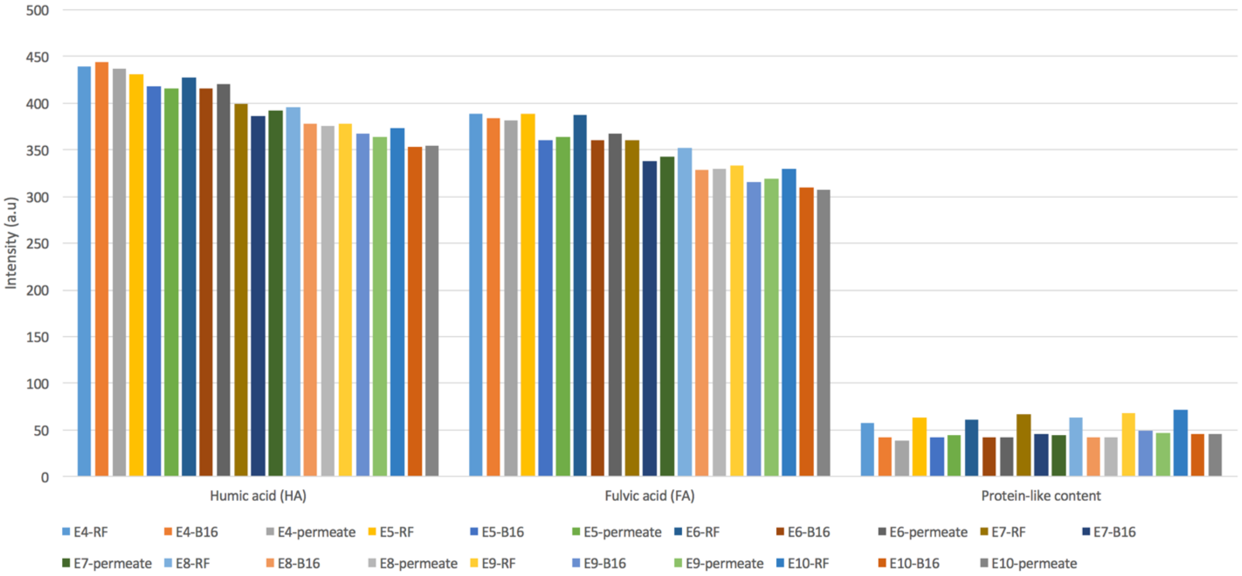

Figure B-1 - NOM fraction as measured by FEEM peak picking for experiments E4-E10 operated with biofilter B16 effluent as pretreatment

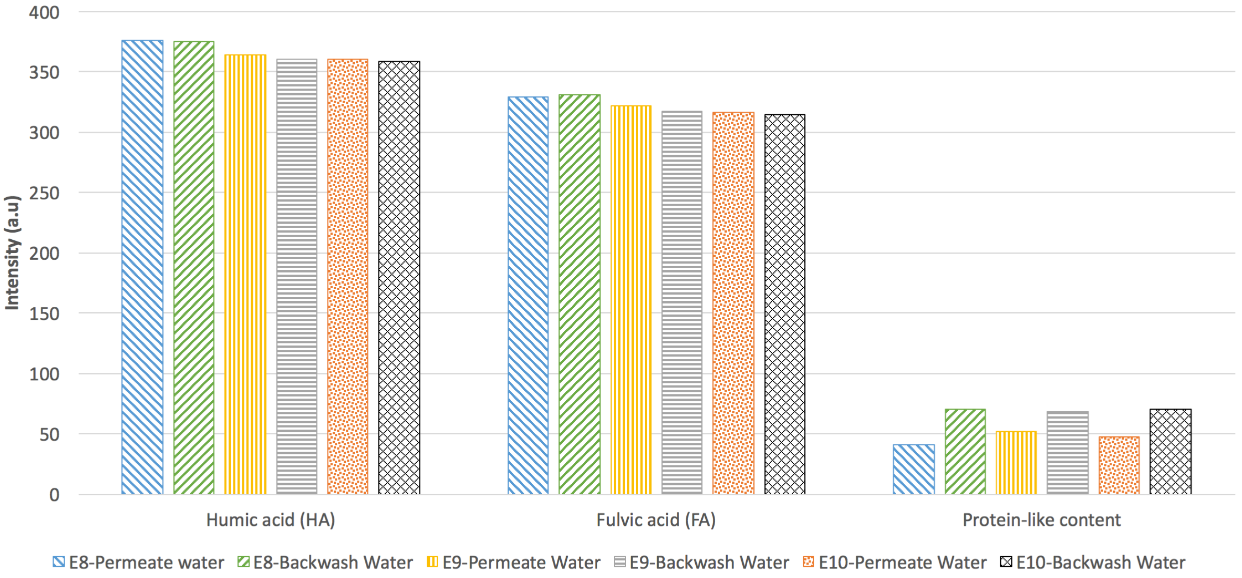

Figure B-2 - NOM fraction as measured by FEEM peak picking for permeate water (used in backwashing the membrane) and backwash water

Table B-1 - Daily irreversible fouling rates for experiments E1-E3 with the corresponding R-squared value from regression analysis

	Irreversible fouling rates			
	1st Day	**R^2**	**2nd Day**	**R^2**
E1	0.013	0.9889	0.044	0.9682
E2	0.018	0.9442	0.085	0.9733
E3	0.017	0.9440	0.080	0.9772

Table B-2 - Daily irreversible fouling rates for experiments E4-E10 with the corresponding R-squared value from regression analysis. *(* Linear regression plotted on a non-linear data of experiment E6; results included for qualitative comparison purpose only; ** experiment terminated early)*

	Irreversible fouling rates							
	1st Day	**R^2**	**2nd Day**	**R^2**	**3rd Day**	**R^2**	**4th Day**	**R^2**
E4	0.0076	0.982	0.0129	0.9926	0.0161	0.9911	0.0191	0.9507
E5	0.0116	0.9943	0.0105	0.9961	0.0129	0.9961	0.0171	0.9693
E6	**0.0141***	**0.8921***	**0.0547***	**0.972***	**0.1114***	**0.9989***	**-****	**-****
E7	0.0116	0.9932	0.011	0.9967	0.0119	0.9956	0.0262	0.9844
E8	0.0093	0.9962	0.0095	0.995	0.011	0.9924	0.0146	0.9927
E9	0.0037	0.9825	0.004	0.9258	0.0036	0.9201	0.0069	0.9967
E10	0.0033	0.9866	0.0036	0.98116	0.0063	0.9871	0.00811	0.9598

Appendix C

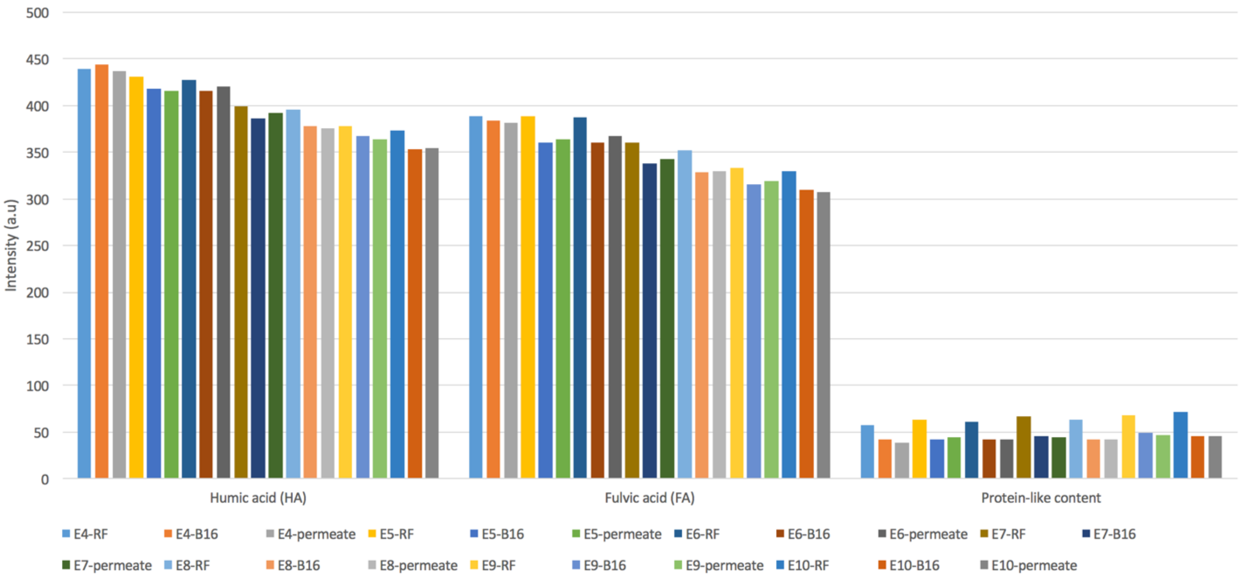

Figure C-1 - NOM fraction as measured by FEEM peak picking for experiments E4-E10 operated with biofilter B16 effluent as pretreatment

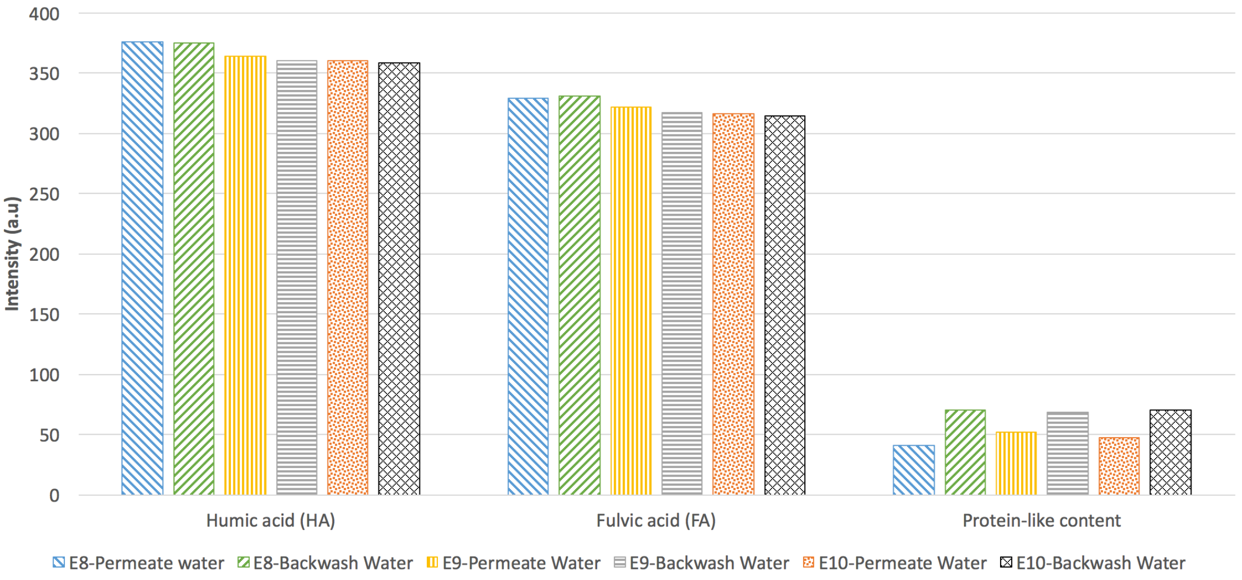

Figure C-2 - NOM fraction as measured by FEEM peak picking for permeate water (used in backwashing the membrane) and backwash water

Table C-1 - Daily irreversible fouling rates for experiments E1-E3 with the corresponding R-squared value from regression analysis

	Irreversible fouling rates			
	1st Day	R^2	2nd Day	R^2
E1	0.013	0.9889	0.044	0.9682
E2	0.018	0.9442	0.085	0.9733
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Table C-2 - Daily irreversible fouling rates for experiments E4-E10 with the corresponding R-squared value from regression analysis. *(* Linear regression plotted on a non-linear data of experiment E6; results included for qualitative comparison purpose only; ** experiment terminated early)*

	Irreversible fouling rates							
	1st Day	R^2	2nd Day	R^2	3rd Day	R^2	4th Day	R^2
E4	0.0076	0.982	0.0129	0.9926	0.0161	0.9911	0.0191	0.9507
E5	0.0116	0.9943	0.0105	0.9961	0.0129	0.9961	0.0171	0.9693
E6	**0.0141***	**0.8921***	**0.0547***	**0.972***	**0.1114***	**0.9989***	**-****	**-****
E7	0.0116	0.9932	0.011	0.9967	0.0119	0.9956	0.0262	0.9844
E8	0.0093	0.9962	0.0095	0.995	0.011	0.9924	0.0146	0.9927
E9	0.0037	0.9825	0.004	0.9258	0.0036	0.9201	0.0069	0.9967
E10	0.0033	0.9866	0.0036	0.98116	0.0063	0.9871	0.00811	0.9598