Pre-Treatment Evaluation Prior to Ultrafiltration in Secondary Effluent Treatment for Water Reuse

by

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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

Reusing wastewater can assist in solving water shortage problems, reduce the amount of wastewater discharged to surface water bodies and, by extension, alleviate its adverse effects on humans and the environment. Organics found in wastewater can be removed through biological treatment, however, if secondary effluent is to be reused for potable or some nonpotable applications, some form of advanced treatment is required. Membranes are often used to further treat these effluents for water reuse as they require only a small footprint and can provide a high quality treated water. They are also robust as is relates to dealing with feed waters of varying composition. However, due to the accumulation of rejected contaminants and certain natural organic matter (NOM) constituents on membrane surfaces and within pores, fouling can be an important shortcoming of this technology. Small improvements in the reduction of foulants can translate into substantial improvements in production quantity and cost savings. As such, it is worth the investment of time and research into common pre-treatment methods to identify technologies that can reduce foulant accumulation on membranes.

The primary objective of this study was to extend previous research which investigated the use of ultrafiltration (UF) membranes for secondary effluent treatment for water reuse purposes. The most appropriate UF pre-treatment method was identified by comparing three different pre-treatment process modes (biofiltration, in-line coagulation, and a combination of the two processes). In parallel, the primary UF membrane foulant types found in a secondary effluent with high biopolymer content were identified, as well as those removed by the pre-treatment methods used in this research.

In this study, aerobic biofilters typically used in drinking water treatment, were investigated for improving the characteristics of Waterloo Wastewater Treatment Plant treated secondary effluent for reuse. Two biofilters, one containing sand and the other containing anthracite, were operated under identical conditions (empty bed contact time [EBCT] of 60 min & hydraulic loading rate [HLR] of 0.75 m/h). Four different coagulants (alum, polyaluminum chloride [PACl], ferric chloride, and ferric sulfate) with a no coagulant control and two different dosages (0.5 and 5.0 mg/L) of each were investigated for their potential to remove UF foulants. To investigate the effect of combining in-line coagulation prior to biofiltration for improving UF performance, one biofilter (containing anthracite media) and one coagulant (1.0 mg/L ferric sulfate) were selected.

The organic compound fractions found in secondary effluent, were quantified by Liquid Chromatography-Organic Carbon Detection (LC-OCD) analyses in all water samples before and after each treatment step. Data revealed that both biofilters reduced dissolved organic carbon (DOC), especially the high molecular weight biopolymer fraction, which was reduced by 25-30%. However, the biopolymer concentrations in the biofiltered secondary effluent were somewhat higher than in river and lake water sources, so even with these reductions the biopolymer levels in the effluent of the biofilters were higher than would typically be seen using those sources as biofilter feed. The reduction of organic compounds attributable to biodegradation occurred in the upper layer of the biofilter as confirmed by the highest consumption of dissolved oxygen and biomass concentrations at that location. The higher removals of different DOC fractions achieved by sand appear to be attributable to the increased amount of attached biomass (measured as ATP). Physical properties of secondary effluent were also improved after biofiltration, and turbidity in the effluent of the biofilters did not exceed 1.0 NTU despite influent values ranging from 1.1 to 10.3 NTU.

To investigate the impact of pre-treatment methods, UF experiments were conducted with both secondary effluent (as collected from the full-scale plant) and after pre-treatment processes. To assess the development of UF fouling rates, changes in transmembrane pressure through UF runs were monitored and measured every 10 sec. Biofiltration effectively improved the performance of UF by reducing fouling development. The observed reduction in TMP was attributed to the removal of biopolymers (especially the protein component) and turbidity through biofiltration. Under the investigated conditions, sand as a biofilter media performed better than anthracite for reducing UF fouling. When the UF membrane was fed with biofilter effluents, both the reversible and irreversible fouling were correlated with biopolymer concentrations in feed water. Particulate matter was also weakly correlated with reversible fouling.

In-line coagulation experiments demonstrated a sustainable reduction in both reversible and irreversible fouling, and coagulant type and dosage had a major impact in improving the performance of UF. Fouling reduction by in-line coagulation was primarily attributed to the alteration of organic composition of secondary effluent and/or the size modification of particles that contributed to membrane pore blocking. The most substantial impact of in-line coagulation was observed for the irreversible fouling reduction, which is more important for sustainable operation of membranes. The higher of the two coagulant dosages tested improved foulant removal and additional reduction of membrane reversible and irreversible fouling rates. Under the conditions investigated, ferric-based coagulants were better for UF fouling control than the aluminum-based coagulants.

In-line coagulant provided additional removal of particles and organics through biofilter. In this instance it appears as if the negative surface charge of colloids and organics surface is reduced by charge neutralization resulting in larger compounds being produced and rejected by straining processes through the biofilter. In-line coagulation prior to biofiltration further improved membrane performance by reducing fouling and enhancing the removal of particles and DOC fractions (biopolymer and humic substances) through UF. Biofilter hydraulic performance was relatively unaffected by the upstream addition of coagulant.

This study demonstrated that biofiltration and in-line coagulation can, under the investigated conditions, remove some treated wastewater constituents which have been associated with membrane fouling, and negatively affect other advanced treatments for water reuse. The integration of the two pre-treatment processes provided additional fouling reduction and a better UF permeate water was produced than that of the individual pre-treatments.

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List of Acronyms

BAC	Biological activated carbon
BB	Building blocks
BF	Biofilter
BOM	Biodegradable organic matter
BP	Biopolymer fraction
BRP	Biomass respiration potential
CA	Cellulose acetate
DBPs	Disinfection by products
DO	Dissolved oxygen
DOC	Dissolved organic carbon
EBCT	Empty bed contact time
EfOM	Effluent organic matter
EPS	Extracellular polymeric substances
FEEM	Fluorescence excitation emission matrix
GAC	Granular activated carbon
HS	Humic substances
HLR	Hydraulic loading rate
IRF	Irreversible fouling
LMWa	Low molecular weight acids
LMWn	Low molecular weight natural
MBR	Membrane bioreactor
MF	Microfiltration

MW	Molecular weight
MWCO	Molecular weight cut off
NOM	Natural organic matter
NF	Nanofiltration
PA	Polyamide
PACl	Polyaluminum chloride
PAH	Polyamide-hydrazide
PCPs	Personal care products
PES	Polyethersulfone
PhAC	Pharmaceutically active compounds
POM	Particulate organic matter
PVDF	Polyvinyl fluoride
RF	Reversible fouling
RO	Reverse osmosis
SMPs	Soluble microbial products
SUVA	Specific ultraviolet absorbance
TKN	Total Kjeldahl Nitrogen
TMP	Trans membrane pressure
TOC	Total organic carbon
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
WWTP	Wastewater treatment plant

Chapter 1

Introduction

1.1 Problem statement

Uneven geographic distribution of water coupled with climate change and population growth are leading to water scarcity worldwide. Wastewater reuse is an important contribution to the recovery of usable water. It has been demonstrated that water of appropriate quality can be produced helping to protect the environment. Treated wastewater can be reused for potable or non-potable purposes (USEPA 2004).

While biological treatment processes are capable of substantial removal of organics found in wastewater, reusing secondary effluent for most purposes without advanced treatment is not recommended (Zhu *et al*. 2011). The main role of advanced treatment methods is to improve secondary effluent quality to conform to regulations and meet public approval. Membrane filtration is an effective process that has been demonstrated as advanced wastewater treatment. High pressure membranes such as nanofiltration (NF) and reverse osmosis (RO) are making inroads as water treatment technologies (Liu *et al.* 2011), especially in direct and indirect potable reuse applications where high quality effluents are required (Gomez *et al.* 2012 and Jacob *et al.* 2010). Although many studies have demonstrated the good performance of high pressure membranes processes, these processes should be combined with low pressure membranes (Juang *et al.* 2007 and Kent *et al.* 2011) or membrane bioreactors (MBR) (Joss *et al.* 2011 and Bolzonella *et al.* 2010) to reduce high pressure membrane fouling. Low pressure membranes combined with physical, chemical, or biological processes are capable of producing treated wastewaters that meet regulatory criteria, and are suitable for reusing in a variety of applications (Acero *et al.* 2012). Therefore, investigating low pressure membrane filtration as an advanced wastewater treatment is essential.

Despite the expansion in the use of membrane technology in water and wastewater production, fouling is still an important shortcoming that could impact the development of this technology and make it less competitive with alternatives. Fouling takes place due to the accumulation of compounds found in water on membrane surfaces and within pores (Al-Amoudi and Lovitt 2007). Fouling affects membrane filtration adversely, reducing permeate flux, increasing energy requirements, decreasing intervals between cleaning, and reducing membrane life (Hatt *et al*. 2011). Therefore, the mitigation and control of membrane fouling is important.

It is evident from previous studies that certain organic matter constituents are responsible for low pressure membrane fouling when treating surface water (Hong and Elimelech 1997). The organic constituents making up secondary effluent, effluent organic matter (EfOM), are considered to be important low pressure membrane foulants. EfOM is primarily composed of natural organic matter (NOM) which originates from surface water and soluble microbial products (SMPs) which remain following biological wastewater treatment processes (Shon *et al*. 2006b). EfOM may contain proteins, polysaccharides, humic substances, and lipids (Barker *et al*. 2000; Jarusutthirak *et al.* 2002). New developments in analytical technologies for organic matter allow for their relatively easy characterization. These include, for example, Liquid Chromatography Organic Carbon Detection (LC-OCD) (Hallé *et al.* 2009; Zheng *et al*. 2010; Peldszus *et al*. 2011; Rahman *et al*. 2014; Kimura *et al*. 2015) and Fluorescence Excitation- Emission Matrix (FEEM) (Peiris *et al*. 2010). These techniques can assist in providing important information about EfOM composition and a better understanding of the constituents responsible for membrane fouling.

It has been previously suggested that humic substances contribute more to membrane fouling (Jucker and Clark 1994; Shon *et al*. 2006b). However, most recent studies have reported that biopolymers are responsible for low pressure polymeric membrane fouling (Fan *et al.* 2008; Zheng *et al*. 2010; Peldszus *et al*. 2011; Filloux *et al*. 2012; Rahman *et al.* 2014). Due to the complex composition of EfOM which varies from location to location, complicated fouling mechanisms, and conflicting observations of the main foulants of low pressure membranes, further investigation is required.

To reduce organic foulants in treated wastewater, several pre-treatment processes have been investigated. Coagulation is one of the main processes used in water and wastewater production to destabilize particles. Some studies have demonstrated that pre-coagulation is an effective method for improving membrane performance (Zularisam *et al*. 2008; Humbert *et al*. 2007; and Dong *et al*. 2007) by reducing both turbidity and organics, while others have noticed decreasing or no effect in membrane performance (Lee *et al*. 2007; and Howe *et al*. 2006). When it is applied for this purpose it is often in the form of conventional coagulation with rapid mix and a tank to allow time for floc development (Howe *et. al* 2006; Haberkamp *et al*. 2007). As such, substantial space and energy are required. On the other hand, some studies have demonstrated the effectiveness of coagulants in reducing low pressure membranes when applied as in-line coagulation (Wang and Wang 2006; Delgado-Diaz *et al*. 2012; Zheng *et al*. 2012). The comparison of different coagulant types and dosages for pre-treating wastewater for membranes is still an area of investigation.

One of the promising low pressure membrane pre-treatments is biofiltration. It have been demonstrated to be an effective method for improving membrane performance by removing or altering foulants in surface water treatment (Peldszus *et al*. 2011; Filloux *et al*. 2012) and in treating secondary effluent (Zheng *et al*. 2010; Pramanik *et al*. 2014). The most common media types used in biofilters are granular activated carbon (GAC), sand, and anthracite. Direct biofiltration has many benefits over other processes including no chemical addition and less solids production making it more environmentally friendly. Zheng *et al*. (2009) investigated biofiltration as a pre-treatment to ultrafiltration (UF) for secondary effluent treatment. In their study biofiltration was applied at slow sand filtration hydraulic loading rates (HLRs) (0.25 and 0.5 m/h) but these loadings are relatively low. Biofiltration has also been investigated as a microfiltration (MF) pre-treatment for treating secondary effluent at higher hydraulic loading rates, compared with the Zheng study, corresponding to shorter empty bed contact times (40 min) (Pramanik *et al*. 2014). Biological active carbon (BAC) has been employed to produce higher effective surface area and provide better adsorptive capacity for EfOM. Investigating the performance of biofiltration in treating secondary effluent with different organic composition at lower EBCTs (higher HLRs) than those investigated by Zheng *et al*. (2009) is essential. Studies using non adsorbing media (sand, anthracite), could not found in the literature. There is also a need to expand the limited body of biofiltration research (direct and in association with coagulants) for improving membrane performance by fouling reduction.

As the composition of wastewater is complex and differs from location to location, findings obtained from previous studies may not be generally applicable. Thus, research using real wastewater obtained under different operating conditions to compare various pre-treatment methods is necessary to determine the appropriate technology for the treatment of secondary effluent in terms of the water reuse.

1.2 Research Objectives

This study had two primary goals. The first involved the investigation of UF membrane fouling caused by EfOM. The second involved the assessment of selected pre-treatment methods for UF membranes in terms of choosing the treatment that will most improve membrane performance in order to obtain high quality permeate water and, at the same time, reduce fouling.

The primary objectives of this work were to:

1. Identify the foulants found in secondary effluent with high content of biopolymers which are responsible for polymeric UF membrane fouling.

2. Assess biofiltration (through the identification of suitable media) as a pre-treatment for ultrafiltration and to study the factors affecting the process including media depth and empty bed contact time (EBCT) taking account seasonal effects on biofilter performance.
3. Investigate the effect of coagulant type and dosage in reducing membrane fouling and associated change in membrane performance.
4. Compare biofiltration to in-line coagulation for UF fouling reduction.
5. Study the effect of in-line coagulation prior to biofiltration on permeate water quality and the reduction of UF fouling.

1.3 Thesis Structure

This thesis consists of 7 chapters. The results chapters have been prepared in paper format for publication. The introduction and study objectives are presented in Chapter 1.

Chapter 2 is a literature review addressing wastewater reuse applications, ultrafiltration characteristics, and fouling mechanisms. Also, general information relevant to the pre-treatment methods investigated in this study is presented.

Chapter 3 describes the materials and methods used including a discussion of the feed water source and experimental set-ups.

Chapter 4 characterizes the selected secondary effluent and seasonal effects on EfOM composition. A comparison between two biofilters containing different media, in terms of improving secondary effluent quality and reducing EfOM is included. Observations related to the effect of biofilter EBCT on the reduction of organic fractions are discussed. The microbiological analysis of the two biofilters is presented in this chapter.

The effect of biofiltration as an ultrafiltration pretreatment is demonstrated in Chapter 5. The results of fouling experiments using both secondary effluent and biofilter effluent are described here. The effect of biofilter media in reducing organic and particulate foluants is also discussed. Seasonal changes in secondary effluent quality on biofilter performance and their impact on reducing UF fouling are examined.

Chapter 6 compares 4 different coagulants considered for in-line coagulation as a pretreatment for UF membranes. The ability of those coagulants to reduce reversible and irreversible fouling for UF is described.

The effect of in-line coagulation prior to biofiltration was investigated and the results are presented in Chapter 7. The performance of biofilters during in-line coagulant addition prior to the biofilters is examined. The effect of this combination for reducing UF fouling is demonstrated.

The general findings of this study and some future recommendations are provided in final chapter of this thesis (Chapter 8).

Chapter 2

Background Information

This review provides general background on water reuse concepts, applications, wastewater composition and treatment options, followed by a review of membrane filtration. The different pre-treatment method concepts used in this research are described. Additional detail is provided in each results chapter.

2.1 Wastewater Reuse

Wastewater reuse has received widespread attention from jurisdictions suffering from natural resource shortages, problems with the disposal of treated wastewater effluents, or are experiencing rapid population growth. Wastewater reuse is defined as the treatment of secondary effluent to obtain adequate quality water that could be used in applications where quality requirements are not high such as toilet flushing, agriculture, or groundwater recharge (UNEP 2005). Wastewater reuse has some benefits such as controlling the level of contaminations reaching natural water bodies by wastewater discharge. Also, wastewater contains high nutrient levels which, when extracted, and utilized appropriately can reduce eutrophication problems in receiving waters and ultimately may reduce the application of inorganic fertilizers. Furthermore, reusing treated wastewater is more economical in some applications than treating fresh water and ultimately available fresh water for drinking can be conserved. Water researchers are becoming more aware of the potential benefits associated with reusing wastewater and over the past decade or so have begun to pay more attention to this area, all the while recognizing that the production of high quality treated wastewater is key to public acceptance and environmental protection (Asano *et al.* 1996).

2.1.1 Non Potable Wastewater Reuse Applications

Wastewater reuse can be utilized for different applications. The following provides information about the non-potable options.

Agricultural and landscape irrigation

The largest amount of fresh water consumption worldwide is for agriculture (USEPA 2004). So, using reclaimed wastewater for agriculture and landscape irrigation is an important application. Potential advantages of using wastewater include the conservation of fresh water and reduction in fertilizer consumption. However, a high level of oversight is required to protect human health (i.e. to control pathogens and chemical contaminants in food) and the environment (UNEP 2005).

Urban applications

Using treated wastewater in urban applications refers to some non-potable usages that do not require high quality water such as toilet flushing, car washing, firefighting, and garden or park planting. Using secondary effluent after conventional drinking water treatment (coagulation – sedimentation - sand filtration) and appropriate disinfection methods may be suitable for this application (Üstün *et al.* 2011). While this application does not require advanced treatment after sand filtration, additional infrastructure such as dual distribution systems are required (UNEP 2005 and USEPA 2004).

Indirect potable water reuse

It could be argued that most surface water sources fall in this category having received wastewater treated to various levels. However, this term applies more specifically to highly treated wastewater which is discharged into potable water sources such as rivers, lakes, or groundwater (groundwater recharge). This type of application is gaining traction and is practiced in some Canadian provinces (e.g. Alberta and British Columbia) and US states (Venkatesan *et al.* 2011). The practice also facilitates additional natural treatment and storage ability (Wintgens *et al.* 2008). On the other hand, there are some concerns related to safety because these waters are often ultimately used for drinking. As such high quality treated wastewater and receiving body protection are required (UNEP 2005).

Water reuse in industry

Reusing wastewater for industrial systems is also known as water recycling, where effluent from a specific industry is recovered and used again in the same process (UNEP 2005; Exall *et al.* 2004). This is practiced in industries such as textile, leather, and paper processing (Liu *et al.* 2011). Domestic treated wastewater could also be reused in industries that require large amounts of water such as nuclear, hydropower, and thermal power production (UNEP 2005). Some problems associated with reusing wastewater in industrial systems include corrosion, scaling, and biological growth. Thus, the required degree of water quality influences its potential for use for given industry.

2.1.2 Wastewater Composition and Treatment Technologies

Conventional domestic wastewater treatment typically consists of two main steps. The first is primary treatment which includes screens, the grit chamber where solids larger than 0.01 mm are removed, and primary sedimentation, in which organic and inorganic particles in the size range of 35-100 µm are rejected (Jacob *et al.* 2010). Secondary treatment is an additional step which removes organic loads from wastewater by microbial degradation such as activated sludge, oxidation ditches, or trickling filters followed by secondary sedimentation to reject the excess biomass produced in the biological processes. The effluent of the final sedimentation tank, secondary effluent, needs additional treatment by more advanced methods for reuse applications (Zhu *et al.* 2011). It is important to be familiar with secondary effluent constituents to assist in choosing the appropriate advanced method.

Wastewater composition

As interest in wastewater reuse increases, the characterization of secondary effluent components, especially those of concern for human health and the environment, is also increasing. Secondary effluent composition is a reflection of the influent water usage and it contains a variety of organic compounds, inorganic substances, and some chemical constituents in dissolved or suspended form (Metcalf and Eddy 2007). One of the most important parameters is effluent organic matter (EfOM) which should be clearly characterized to identify the appropriate method for wastewater reuse. Most of the previous studies (Shon *et al.* 2006a; Filloux *et al.* 2012) classify EfOM composition as a combination of NOM which already exists in surface water, soluble microbial products (SMPs) which remain from biological treatment, and trace chemicals or micro-contaminants such as disinfection by-products, pesticides, herbicides, and pharmaceuticals.

The organic composition of secondary effluent is about 50% proteins, 40% carbohydrates, and 10% trace organics (Pandey *et al.* 2012). In terms of size, EfOM contains both particulate organic carbon (POC) and dissolved organic carbon (DOC). It is worth noting that EfOM composition differs from location to location due to changes in influent wastewater composition, and WWTP treatment processes and operating conditions. It is important to note that there is difference between EfOM and NOM found in surface water (Filloux *et al.* 2012). NOM usually contains proportionally higher concentrations of humic substance (HS) (hydrophobic with high MW), while EfOM contains proportionally higher non-humic hydrophilic compounds. Also, biologically treated wastewater is higher in protein content than surface water. Furthermore, the total organic carbon (TOC) concentration in EfOM is roughly 4 times higher than that found in surface water (Filloux *et al.* 2012).

EfOM, as well as NOM, has an adverse effect on treatment processes. These compounds are precursors for disinfection byproducts; they consume coagulants and oxidants; produce severe membrane fouling (Filloux *et al.* 2012), and support biological regrowth in treatment systems (Wang and Wang 2006). Also, increased oxygen consumption, septic conditions, and eutrophication problems can occur when inadequately treated wastewater is discharged into water bodies (Metcalf and Eddy 2007). Since conventional wastewater treatment is not sufficient, other advanced treatment processes are required. Advanced methods are also known as tertiary treatment and include an array of physical, chemical, and biological processes. Coagulation-flocculation, sand filtration, activated carbon adsorption, chemical oxidation, and membrane filtration are some examples of these technologies.

Choosing suitable scenarios for treatment processes is largely dependent on secondary effluent composition, quality requirements, as well as economics. It has been demonstrated that membrane technologies offer a good solution that meets most of the previously mentioned requirements. These separation processes are of considerable interest as a result of their high product water quality, ease of use, and relatively economical operation. While different types of membranes can be used for wastewater reuse; pressure membranes are the most common. High pressure membranes such as nanofiltration (NF) and reverse osmosis (RO) are widely used (Liu *et al.* 2011), especially in direct and indirect potable reuse applications (Gomez *et al.* 2012) where high quality effluents with low concentrations, and in some cases free, from organic micro pollutants are required (Gomez *et al.* 2012; Jacob *et al.* 2010). Although many studies have demonstrated the good performance of high pressure membranes processes, these processes should be combined with other types of low pressure membranes (Juang *et al.* 2007; Kent *et al.* 2011) or membrane bioreactors (MBR) (Joss *et al.* 2011; Bolzonella *et al.* 2010) as pre-treatment methods. On the other hand, low pressure membranes combined with physical, chemical or biological processes are capable of producing treated wastewaters that meet regulatory criteria, and are suitable for reuse in different applications (Acero *et al.* 2012).

2.2 Membranes in Water and wastewater

Membrane processes are used to produce high quality water regardless of the water source (Shirazi *et al.* 2010). In comparison with other methods, membrane filtration removes a variety of pollutants found in feed water, has a low footprint, consumes fewer chemicals, produces less sludge, and is relatively easy to operate and maintain (Juang *et al.* 2007). On the other hand, membrane fouling is the main membrane shortcoming that limits the development of this process. The following sections present some information about membrane classification and the different parameters affecting fouling.

2.2.1 Membrane Classification

Pressure driven membranes are classified into two main groups; low pressure membranes and high pressure membranes (Shirazi *et al.* 2010). Low pressure membranes are porous membranes in which the separation process depends on pore size. This group contains two different types, microfiltration and ultra-filtration. Microfiltration (MF) pore sizes range from 0.1 to 10 µm in diameter. So, they have the ability to reject micron sized particles. Ultrafiltration (UF) has a pore size around 0.01 µm where small collides and viruses are rejected. High pressure membranes include nanofiltration (NF) and reverse osmosis (RO) in which the separation process depends on the difference in solubility between the solvent and the solute in membranes (Li *et al.* 2008).

Polymeric membrane materials and properties

Membranes are composed of synthetic compounds that are less than 1.0 mm in thickness and they can be produced from a variety of materials. The ideal material is the one that can produce a membrane with less fouling, is inexpensive, and is stable under different chemical, physical, and biological conditions (MWH 2005). There are polymeric membranes where the material used in the manufacture is a natural or synthetic polymer such as polyvinyl fluoride (PVDF), cellulose acetate (CA), polyamide (PA), polyamide-hydrazide (PAH), and polyethersulfone (PES). Membrane material of construction impacts hydrophobicity, surface charge, roughness, porosity, and retention rate; which in turn impacts membrane performance and fouling behavior.

Hydrophobicity can be measured by contact angle analysis and it reflects the affinity between the membrane material and water (Zeman and Zydney 1996). It has been demonstrated that polymeric membranes are typically hydrophobic, while ceramic membranes are hydrophilic (Lee *et al.* 2013). On the other hand, polymeric membranes have a highly negative charge at neutral pH (Zeman and Zydney 1996) in comparison to ceramic membranes. This negative charge produces electrostatic repulsion with negatively charged materials such as NOM, which in turn reduces membrane fouling. Also, membranes with rough surfaces are more susceptible to fouling than smoother ones (Jin *et al.* 2010).

In low pressure membranes, pore size is important to characterize which particles will be retained. Molecular weight cut off (MWCO) is often used to define UF membrane pore size. The MWCO is demarcated as the molecular weight of a solute that the membrane could reject more than 90% of its concentration, where the rejection rate can be estimated using equation 2-1 (Acero *et al.* 2012).

$$R = 1 - \frac{Cp}{Cf} \qquad Eq.2-1$$

Where

R = rejection, dimensionless

C_P = permeate concentration, mole/L or mg/L

C_F = feed water concentration, mole/L or mg/L

The flow through low pressure membranes follows Darcy’s law for porous materials, as shown in equation 2-2 (Li *et al.* 2008).

$$v = Kp\frac{hl}{L} \qquad Eq. 2-2$$

Where

v = superficial fluid velocity, m/s

Kp = hydraulic permeability coefficient, m/s

hl = head loss across porous media, m

L = thickness of porous media, m

While flow through membranes follows Darcy’s law; it is described by volumetric flux J as opposed to superficial velocity, as shown in equation 2-3 (Ravazzini *et al.* 2005).

$$J = \frac{\Delta P}{\mu . Km} = \frac{dv}{dt} * \frac{1}{A} \qquad Eq. 2-3$$

Where

J = volumetric water flux through membrane, $L/m^2 \cdot h$ or m/s

ΔP = differential pressure across membrane, bar

μ = dynamic viscosity of water, $kg/m \cdot s$

Km = membrane resistance coefficient, m^{-1}

A = membrane area

v = the permeate volume at time t

Membrane structure, operation and configuration

Membranes are classified according to structure as being symmetric or asymmetric. Membranes with symmetric structures are those where there is no change in porosity through the depth of membrane (Li *et al.* 2008). On the other hand, asymmetric membranes consist of two layers; an active layer which is a thin layer with low porosity, and a very small void space and a supporting layer that is highly porous and produces some hydraulic resistance (Li *et al.* 2008). Both of these structures are used for low or high pressure membranes. But the configurations are somewhat different. The most common configurations used in low pressure membranes are hollow fiber, flat sheet, and tubular (Zeman and Zydney 1996). Variations in module characteristics and manufacture mainly affect the propensity for fouling (Howe *et al.* 2007). Spiral wound configurations are commonly used for high pressure membranes; where high packing density is provided to allow large volumes of water to be produced (Zeman and Zydney 1996).

Membrane operating processes are dependent on membrane modules. There are two flow regimes; dead-end and cross-flow filtration. The type of flow regime through a membrane impact permeates flux and membrane fouling (MWH 2005). In dead-end mode, flow passes perpendicularly through a membrane leaving pollutant compounds on membrane surface and producing one stream of treated water (Li *et al.* 2008). The problems associated with this flow regime are that more fouling can occur and the amount of water produced is low. On the other hand, potential fouling in cross-flow is lower and membranes can be operated at higher fluxes; where water passes parallel to the membranes reducing the accumulation of fouling compounds on membrane surfaces (Zeman and Zydney 1996). Also, the influent stream, in cross-flow, is divided into two streams; the concentrate which contains retained pollutants, and the permeate or treated water.

2.2.2 Membrane Fouling

Fouling is the accumulation of rejected materials on the surface and in the pores of membranes (Al-Amoudi and Lovitt 2007; Yang *et al.* 2010). Membrane fouling is very problematic for membrane processes, reducing permeate flux, increasing driving pressure (and associated energy requirements), and reducing membrane life. Fouling can be classified as reversible or irreversible. Reversible fouling is that which can be recovered after physical backwashing, while irreversible fouling is that which chemical cleaning can only recover a portion. It is the irreversible fouling which limits membrane life (Hatt *et al.* 2011).

Figure 2.1 illustrates the development of both reversible and irreversible fouling overs several cycles (as measured by transmembrane pressure [TMP]). Total fouling during each cycle between backwashes is represented by the red arrows. Following backwashing (i.e. the large drop on TMP), pressure loss attributable to reversible fouling can be recovered. Irreversible fouling is measured by monitoring the pressure increase from cycle to cycle.

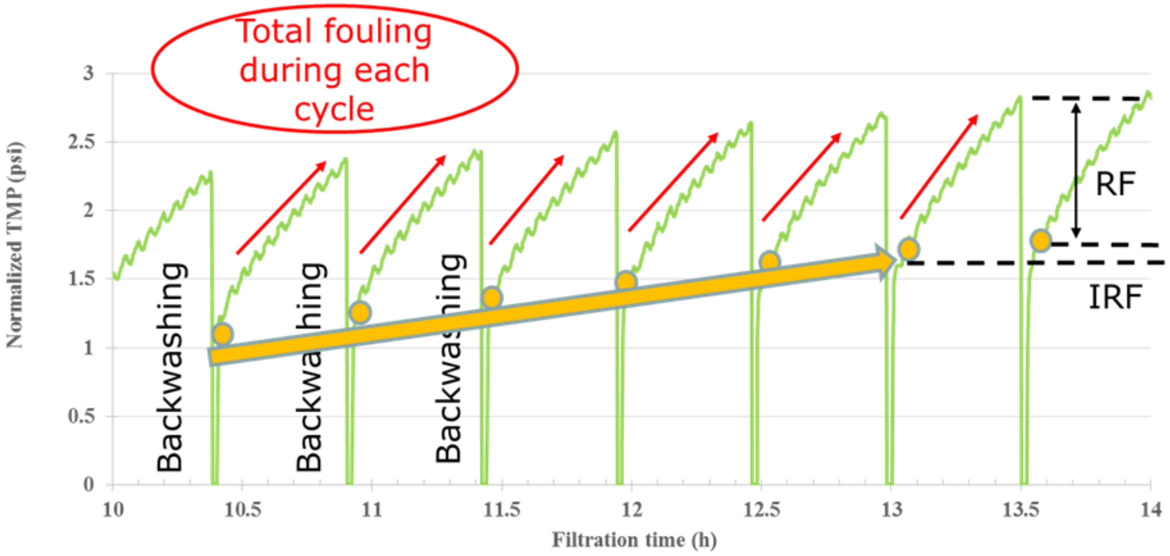


Figure 2.1 Reversible and irreversible fouling

2.2.2.1 Fouling Mechanisms

Fouling is a complex phenomenon that consists of a combination of mechanisms (Figure 2.2). Concentration polarization and cake layer formation are the expected mechanisms for reversible fouling, while pore adsorption mainly promotes irreversible fouling (Zahrim *et al.* 2011). Concentration polarization occurs as a result of permeability difference between solvent and solute which in turn increases solute or particulate concentration in the boundary layer above the membrane surface (Shirazi *et al.* 2010). Concentration polarization decreases the permeation rate and quality and promotes cake layer formation. Cake layers are formed as a result of colloid deposition on membrane surfaces by colloids larger than the membrane pores (Muthukumaran *et al.* 2011). This mechanism blocks multiple pores simultaneously. It is noteworthy that once a cake layer is formed, it works as a physical barrier between the membrane pores and feed constituents (Zahrim *et al.* 2011). As a result, hydraulic resistance through membranes increases requiring additional driving pressure to obtain the same flux (Muthukumaran *et al.* 2011). Particles smaller than membrane pores can be adsorbed within these pores and constrict the pore diameter, resulting in the minimization of area available for filtration (Juang *et al.* 2007).

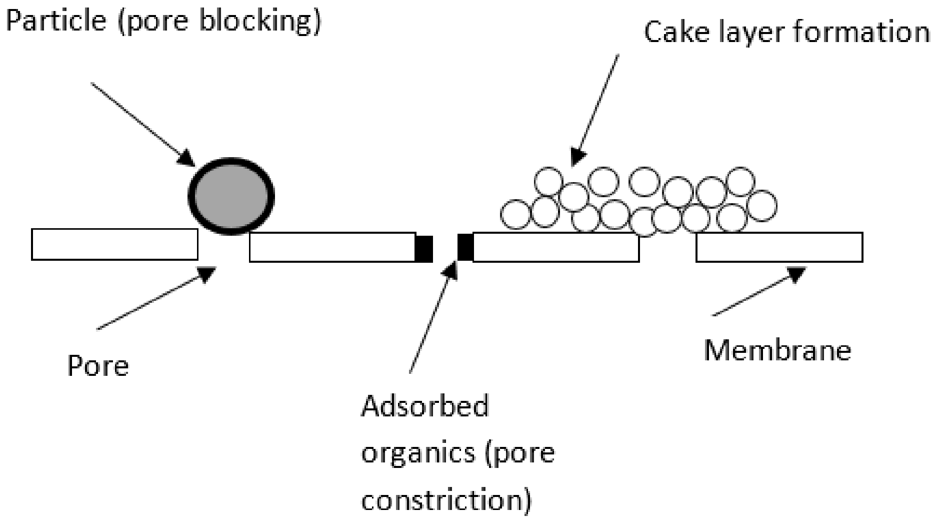


Figure 2.2 Fouling mechanisms according to the Hermia model (Hermia 1982): a) pore blocking, b) pore constriction, and c) cake layer formation

Pore blocking and organic adsorption are responsible for initial stage fouling, while cake formation takes place in the latter stage causing a slow decline in flux (Kim *et al.* 2005). Mousa and Al-Hitmi (2007) studied fouling mechanisms in sewage and concluded that pore blocking is the dominant fouling mechanism. In contrast, Ravazzini *et al.* (2005) demonstrated that the reduction in permeate flux due to fouling was primarily attributable to cake layer formation for both raw sewage and primary effluent.

2.2.2.2 Fouling Classification

Fouling can be characterized depending on its source; particulate, inorganic, organic, and biological (Matin *et al.* 2011).

Particulate fouling

This type of fouling is caused by the deposition of particulate compounds present in feed water and it is affected by small particles rather than larger ones (Juang *et al.* 2007). Accumulation of solids on membrane surfaces produces a cake layer that can reject smaller particles and promote hydraulic resistance. This type of fouling is reversible and is controlled by backwashing (Nguyen and Roddick 2013).

Inorganic fouling (scaling formation)

Inorganic fouling is the deposition of different salts on the membrane surface and pores. Salts will precipitate on the membrane when their concentration in the bulk solution exceeds their solubility limit (Antony *et al.* 2011). All types of salts precipitate in the same manner. Scale formation is affected by many factors related to membrane characteristics, chemistry of the feed flow, and operating conditions (Shirazi *et al.* 2010). Inorganic fouling is typically associated with high pressure membrane (NF, RO). Membrane characteristics dramatically affect salt rejection. The accumulation of salts at the boundary layer causes super saturation of salts on membrane surface; however, the bulk concentration is still under saturated (Zahrim *et al.* 2011). This phenomenon enhances crystallization and reduces the duration of the nucleation stage. Also, the membrane surface has a direct effect on salt rejection; where rough surfaces increase salt deposition and negatively charged surfaces improve salt rejection due to electrostatic interactions (Zhu *et al.* 2011).

Feed water properties have a direct effect on scale formation. For example, increasing water temperature reduces the solubility of salts and enhances their deposition (Zhao and Zou 2011; Jawor and Hoek 2009). Also, elevated pHs in feed water will lead to the deposition of salts (Qin *et al.* 2005). Furthermore, higher ionic strength decreases the distance between ion and salt solubility which enhances crystallization growth and participation. Finally, the presence of divalent cations such as calcium will increase calcium carbonate and calcium sulfate deposition.

Membrane operating conditions such as flow velocity (Al-Amoudi 2010; Antony *et al.* 2011), pressure (Muthukumaran *et al.* 2011), and permeate flux affect scale formation.

Organic fouling

Organic fouling occurs as a result of the rejection of organic compounds such as those making up the NOM found in surface water and EfOM found in secondary effluent. This type of fouling is formed in the first stage of membrane operation (Al-Amoudi and Lovitt 2007) by adsorption in membrane pores (Aoustin *et al.* 2001) and enhances the production of other fouling types.

There are many factors that affect the formation of organic fouling such as membrane characteristics, the chemistry of feed water, organic matter characteristics, and operating conditions.

Membrane characteristics have the potential to substantially impact organic compound rejection. For example, membrane surface charge, which is affected by the pH of solution, impacts organics removal due to electrostatic forces (Chon *et al.* 2012). Increased membrane surface roughness will accelerate fouling as a result of increasing rate of organics attachment. Moreover, membrane MWCO has a direct influence on the rejection process and fouling. With respect to organic compounds, UF can remove organic compounds in the range of 1 – 500 KDa; removal efficiency depends primarily on membrane MWCO, where higher rejection can be achieved with lower MWCO. Consequently, the higher the rejection, the more severe the fouling that is produced (Humbert *et al.* 2007). Muthukumaran *et al.* (2011) compared two different types of polymeric UF membranes in terms of MWCO and concluded that UF with a MWCO of 25 KDa did not completely reject EfOM from wastewater; most of these organics passed through membrane causing low fouling. On the other hand, a steep reduction in permeate flux due to severe fouling production was observed using UF with a MWCO of 1KDa with the same feed water. Similar observations were made by Aoustin *et al.* (2001) where UF with a 100 KDa MWCO rejected less than 7% of DOC in feed water compared with a 74% removal efficiency obtained using 10 KDa membrane. The same phenomenon has been observed in ceramic membranes. Barredo-Damas *et al.* (2010) studied the impact of MWCO on fouling rate using three ceramic membranes with different MWCO (30, 50, 150 KDa) in treating textile wastewater. They noted that the fouling rate increased with decreased MWCO. Kumar and Roy (2008) treating sewage wastewater by ceramic MF, and Jin *et al.* (2010) using ceramic membranes in membrane bioreactor as a secondary treatment, came to the same conclusion.

Feed water properties also affect organic fouling. For example, change in feed water pH will alter the behavior of organics rejection. High pH will change the surface charge of both organics and the membrane surface to be highly negative. Electrostatic repulsion will increase and the removal mechanism of organics, in this case, may be due to adsorption (Al-Amoudi 2010). On the other hand, at low pH values, membrane surface charge becomes less negative which reduces electrostatic repulsion and increases organics removal. The same mechanism can occur due to the increase in ionic strength of feed water (Al-Amoudi and Lovitt 2007). The presence of divalent cations in feed water will increase organic fouling due to the interaction between positively charged cations and negatively charged organics, enhancing accumulation on membrane surfaces. Operating conditions affect rejection process as well. Increasing both permeate flux and membrane pressure will increase organic fouling (Zularisam *et al.* 2006); however, operational impacts on organic fouling are still not as important as water source and organic compound characteristics (Huang *et al.* 2007).

Organic fouling is substantially impacted by organic characteristics. Organic foulants can be categorized in relation to molecular structure, surface charge, molecular size, and functional groups.

Many studies have been conducted to examine which part of NOM or EfOM promotes more fouling. Keeping structural analysis in mind, organic foulants can be classified as hydrophobic with high molecular weight and hydrophilic (Zularisam *et al.* 2006). It has been demonstrated that the hydrophobic fraction is the main component affecting membrane fouling (Chon *et al.* 2012). On the other hand, a study conducted by Huang *et al.* (2007) to compare water source effect on low pressure membrane fouling showed that the hydrophilic fraction of NOM produced more fouling than the hydrophobic fraction in both secondary effluent and surface water. Also, secondary effluent caused more fouling than surface water, regardless of membrane type. Furthermore, it has been observed that fouling produced from EfOM is typically reversible, while hydrophobic organics cause irreversible fouling (Aoustin *et al.* 2001). Finally, molecular weight (MW) impacts membrane fouling, where high molecular weight (e.g. biopolymers) are responsible for UF fouling (Haberkamp *et al*. 2008; Hallé *et al*. 2009; Zheng *et al.* 2010; Peldszus *et al.* 2012).

Biological fouling or biofouling

The problem of microorganism attachment and growth on membrane surfaces and pores impacts the development of membrane technology due to its deleterious effects on membrane properties and operation. Biofouling can occur at any stage of membrane operation and takes place on the membrane regardless of membrane material type or configuration (Hu *et al*. 2005). Microorganisms that adhere to and grow on membranes need not only favorable temperature and pH conditions but also an abundant food source. Therefore, biofouling is typically associated with organic fouling which provides nutrients to enhance biological growth (Kent *et al*. 2011).

Biofouling is the most difficult type of fouling to control and the most appropriate technique to limit it is disinfection, in spite of the potential adverse impacts of the disinfectant on membranes and in the environment (Matin *et al.* 2011). It is typically associated with high pressure membranes (i.e. NF and RO).

Although most current studies deal with the classification of fouling behavior and understanding its mechanisms, more research is required to investigate technologies used for reducing this problem, particularly organic and biological fouling in the case of wastewater reuse.

Improving membrane feed water quality by pre-treatment processes is one of the most promising strategies used for fouling mitigation. Different types of physical, chemical, and/or biological treatment strategies could be used for this purpose. Variation in feed water composition, operating conditions, and membrane characteristics makes the selection of the pre-treatment process and the performance predictions challenging. Thus, studying and comparing different pre-treatment processes using real water supplies is essential to predict the appropriate process that improves membrane performance and reduces fouling. In the following sections, biofiltration and coagulation are discussed as potential pre-treatment methods for membrane filtration in water and wastewater treatment.

2.3 Biofiltration

Biological filtration is defined as "the process of filtering water through a filter medium that has been allowed to develop a microbial biofilm that assists in the removal of fine particulate and dissolved organic materials" (AWWA 2010). Biological filtration processes have been used in the past couple of decades to reduce microbial regrowth in drinking water distribution systems, reduce oxidant demand, and produce less disinfection byproducts. This technology is used in wastewater treatment for microorganism reduction to improve disinfection (Metcalf and Eddy 2007). Studies have demonstrated the efficiency of biological filtration in the removal of biodegradable organic matter (BOM) and nutrients from water and wastewater (Peldszus *et al*. 2011; Filloux *et al*. 2012; Zheng *et al*. 2010; Guerdat *et al*. 2011). The main consideration in the operation of biofiltration is to maintain a healthy biomass on the filter media (Shon *et al*. 2006a).

2.3.1 General Concepts in Biofiltration

There are some important considerations such as empty bed contact time (EBCT), hydraulic loading rate (HLR), media type, and organic removal rate which should be taken into account when designing biofiltration processes (Graham 1999). One of the most vital of these is the removal rate of BOM through biofilter which depends on the amount of biomass attached to the fixed media (Rittmann *et al.* 1980). This phenomenon is controlled by factors such as the growth and decay rate of biomass, substrate diffusion inside the biofilm, substrate utilization, and biofilm thickness (Mitchell and Gu 2010).

There are some models used to estimate the rate of BOM consumption during biofiltration. Such models assist in biodegradation prediction, removal rate of specific contaminants, and biomass production (Okpokwasili and Nweke 2005). The concept of dimensionless EBCT or (X^*) has been proposed for biofiltration design (Zhang and Huck 1996). This concept includes the actual EBCT and other essential parameters that affect biodegradation such as media size, utilization rate, and substrate diffusivity (Gagnon and Huck 2001).

2.3.2 Factors Affecting Biofiltration

Many studies have been conducted with the objective of investigating the performance of a biofilter in both water and wastewater treatment. Biofilters mainly depend on microorganism behavior; the basic factors affecting this process are those related to microbe attachment and growth. Feed water characteristics such as pH, temperature, and organic concentrations impact the performance of biofilters. Factors such as media type and depth impact biodegradation processes as well as operating conditions such as contact time and backwashing procedure. The effect of these factors on biofilter operation and how it impacts membrane performance are discussed in the following sections.

Feed water characteristics

Many studies have been conducted to investigate which fractions of the organic compounds are consumed by microorganisms through biofiltration processes. These studies address two objectives; the first is to improve biofilter performance, and the second is to study the feasibility of biofiltration as a pre-treatment for membrane filtration. Peldszus *et al*. (2011) investigating the efficiency of biofiltration processes in reducing UF fouling for drinking water treatment demonstrated that biofiltration removed the protein-like substances (biopolymers) which were mainly responsible for both reversible and irreversible fouling. Additionally, these substances can interact with particles producing combined fouling layers causing severe fouling. Similar results were obtained by Filloux *et al.* (2012), where the ability of the biofiltration process to remove these compounds was confirmed as was the associated reduction of both reversible and irreversible fouling formation. It has also been observed that biofiltration is capable of not only reducing organics but also decreasing particle concentration (Graham 1999).

The effect of biofiltration processes on UF performance for secondary effluent treatment has been investigated. Zheng *et al.* (2009) reported that the biopolymer (BP) fraction is primarily responsible for UF fouling by a secondary effluent and biofiltration is capable of removing this fraction and improving UF performance.

Mosqueda-Jimenez *et al.* (2008) studied the efficiency of biofiltration processes in removing organics from surface water and the ability of this process to reduce fouling in UF membranes. They demonstrated that biofiltration removed high concentrations of both TOC and DOC. The authors also noticed that the UF used in this study without pre-treatment was able to remove more TOC and DOC due to the formation of larger cake layers that assist in removing organics but cause more severe fouling. On the other hand, using biofiltration as a UF pre-treatment slowed flux decline by reducing fouling.

It was shown by Mosqueda-Jimenez and Huck (2009) that biofiltration is capable of removing not only easily biodegradable organics but also moderately degradable organics. At the same time, biofiltration can assist in reducing both organic and biological fouling (Mosqueda-Jimenez and Huck 2009). Furthermore, this process is feasible for both low and high pressure membranes (Hu *et al.* 2005).

Some research has investigated the presence of nitrogen containing compounds in feed water on biofilters. Zheng *et al.* (2010) reported a substantial reduction in nitrogen to carbon ratio (N/C) following biofiltration reflecting the potential ability of this process to reduce nitrogen compounds as well as carbon. On the other hand, Jeong *et al*. (2006) and Guerdat *et al*. (2011) observed that this phenomenon was only achieved at low organic carbon loading, suggesting that nitrifying bacteria may only grow without extensive competition from heterotrophic bacteria.

Nutrient concentrations in feed water, especially in secondary effluent, play an important role in biofilter performance. The availability of nutrients such as nitrogen, carbon, and phosphorus, are important to good biofilter performance. A target C:N:P ratio for microbial growth was suggested to be 100:10:1 (Redfield, 1934). It is not clear to what extent this ratio applies in freshwater biofilters. It was suggested that at optimal C:N:P ratios higher removal efficiencies can potentially be achieved by both improving microorganism activity and reducing extracellular polymeric substance (EPS) production; which can occupy filter media voids and cause clogging, head loss, and underdrain problems in biofilters (Lauderdale *et al.* 2012). However, Pharand (2014) reported that drinking water biofilters substantially performed well at not optimal ratios of C:N:P. Also, Rahman (2013) investigated the impact of phosphorus addition on the performance of drinking water biofilter and reported that there was no improvement observed on biomass activity or NOM fractions removal.

It was reported by Zheng *et al.* (2010) that dissolved oxygen concentration (DO) influences biofilter performance since some bacteria consume oxygen to degrade organics. Thus, higher organics removal efficiencies can be obtained when DO in feed water is elevated. Hydrogen peroxide can provide an additional source of DO, which in turn assists in the production of enzymes that catalyze the degradation of organics and improve microorganisms' activity (Lauderdale *et al.* 2012). Although hydrogen peroxide is an oxidant and concentrations that are too high may inactivate bacteria, Urfer and Huck (1997) reported that hydrogen peroxide can be consumed through biofilters. Dissolved oxygen is not typically an issue with respect to surface water biofilters but it may impact biofilters treating secondary effluent.

Temperature plays an important role in biological activity, where increasing temperature has a positive effect in maximizing organics removal. Low removal efficiencies of biopolymers by biofiltration have been reported under winter operating conditions (Zheng *et al.* 2010). Hallé *et al.* (2009) noticed that there was no DOC removal in the winter period when temperature was less than 2°C. However, another study by Peldszus *et al.* (2012) and Azzeh *et al.* (2015) demonstrated that the biofiltration process could operate well under a wide range of temperature (1 – 25°C). Rahman (2013) reported no significant impact of temperature on biopolymer removal (all experiments were conducted above 10°C). This would expected as temperature effects would likely only begin to be apparent at temperatures a few degrees less than this (for bacteria in water).

Media type and operating conditions

Different media are used in biofiltration processes under different operating conditions. The most common biofiltration media are: granular activated carbon (GAC), sand, and anthracite, or combinations of these while some other proprietary materials are commercially available (e.g. ceramic or polyethylene-based).

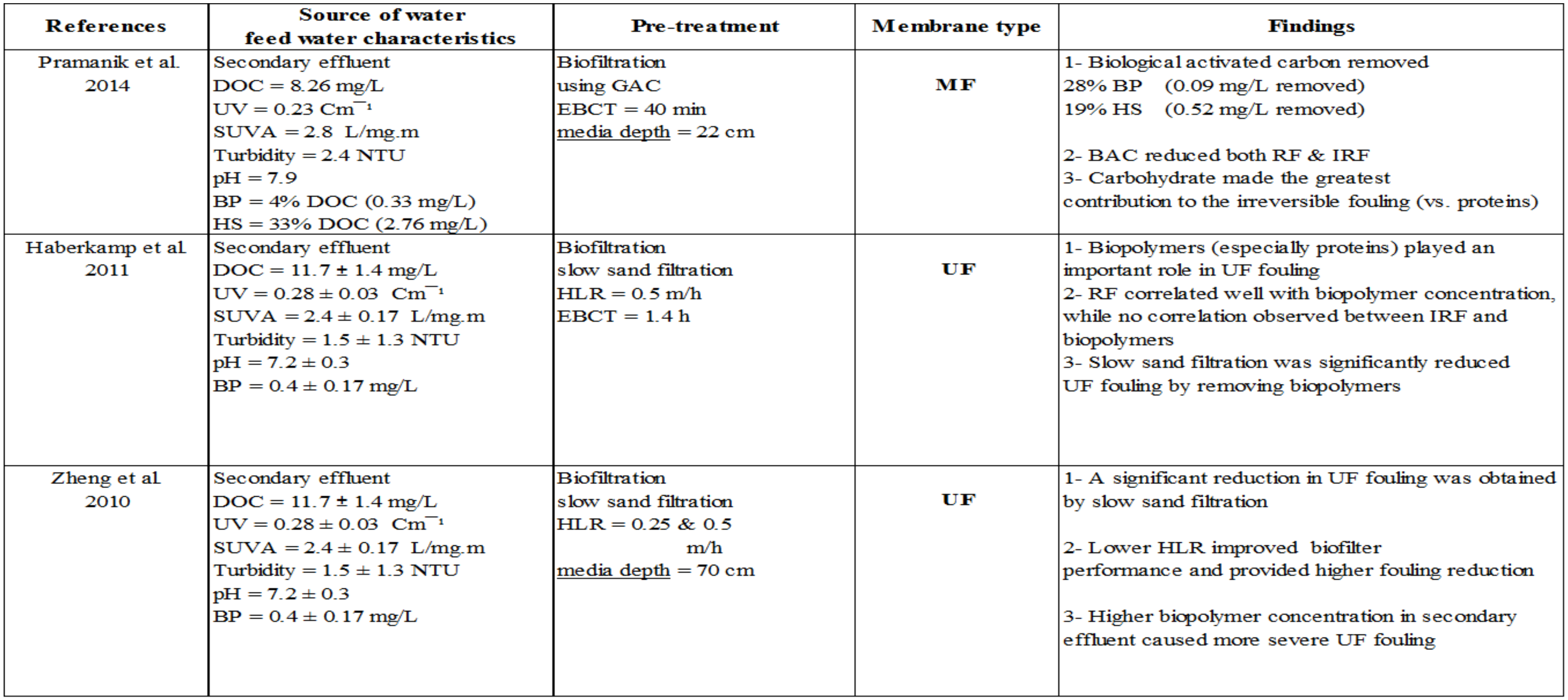
GAC biofilters/biologically active carbon (BAC) filters are relatively widely used in water and wastewater treatment (Vigneswaran *et al.* 2007; Kweon *et al.* 2009; and Yapsakli *et al.* 2010). Fresh GAC can remove both hydrophobic and hydrophilic compounds through adsorption (Vigneswaran *et al.* 2007). It provides substantial rough media surface area for microbial attachment (Yapsakli and Cecen 2010). Moreover, GAC biofilters can remove some of the more difficult to remove or non-biodegradable organics unlike those containing anthracite (Yapsakli and Cecen 2010). On the other hand, GAC is more costly and rapidly becomes loaded with background organic matter. Using sand and anthracite media, individually or in combination, has been extensively studied (Mosqueda-Jimenez and Huck 2009; Hallé *et al*. 2009; and Peldszus *et al.* 2011). Most of these investigations have demonstrated the feasibility of sand-anthracite biofilters for organics removal.

Not only do feed composition and media type affect biofiltration performance, but operating conditions, primarily empty bed contact time (EBCT) or alternatively hydraulic loading rate (HLR), also substantially impact biofilter efficiency. It has been shown in many studies (e.g. Hu *et al.* 2005; Hallé *et al*. 2009; Peldszus *et al*. 2011; Peldszus *et al*. 2012) that increasing EBCT improved the removal efficiency of organic compounds. Zheng *et al.* (2009) conducted a study to investigate the effect of HLR on slow sand filtration as a pre-treatment for UF in secondary effluent treatment. Two different HLRs were used (0.25 and 0.5 m/h). Their work demonstrated that slow sand biofiltration can remove

UF foulants found in secondary effluent and that the reduced HLRs used enhanced removal efficiency (vs. typical HLRs of 5 to about 15 m/h in drinking water biofilters). Also, it was shown that biofiltration assisted in reducing membrane fouling and allowed for longer operation of the UF membranes without a sharp TMP increase. A recent study conducted by Pramanik *et al*. (2014) to investigate biofiltration as microfiltration (MF) pre-treatment in treating secondary effluent under 0.2 m/h hydraulic loading rate that corresponding to low empty bed contact time (40 min). In their study, biological active carbon (BAC) was applied to produce higher effective surface area and provide better adsorptive capacity for EfOM removal.

Table 2.1 summarizes observations obtained from recent studies using biofiltration as membrane filtration pre-treatment applied in both water and wastewater. In general, a significant improvement in membrane performance was achieved by using biofiltration as a pre-treatment. Also, higher EBCTs are employed in operating biofilters used for wastewater treatment than those used for surface water treatment. This would not be unexpected given the higher concentrations of organic matter in wastewater effluent and the generally longer retention times in wastewater processes.

Table 2-1 Observations from recent studies using biofiltration pretreatment for membrane filtration



References	Source of water feed water characteristics	Pre-treatment	Membrane type	Findings
Pramanik et al. 2014	Secondary effluent DOC = 8.26 mg/L UV = 0.23 Cm^{-1} SUVA = 2.8 L/mg.m Turbidity = 2.4 NTU pH = 7.9 BP = 4% DOC (0.33 mg/L) HS = 33% DOC (2.76 mg/L)	Biofiltration using GAC EBCT = 40 min <u>media depth</u> = 22 cm	**MF**	1- Biological activated carbon removed 28% BP (0.09 mg/L removed) 19% HS (0.52 mg/L removed) 2- BAC reduced both RF & IRF 3- Carbohydrate made the greatest contribution to the irreversible fouling (vs. proteins)
Haberkamp et al. 2011	Secondary effluent DOC = 11.7 ± 1.4 mg/L UV = 0.28 ± 0.03 Cm^{-1} SUVA = 2.4 ± 0.17 L/mg.m Turbidity = 1.5 ± 1.3 NTU pH = 7.2 ± 0.3 BP = 0.4 ± 0.17 mg/L	Biofiltration slow sand filtration HLR = 0.5 m/h EBCT = 1.4 h	**UF**	1- Biopolymers (especially proteins) played an important role in UF fouling 2- RF correlated well with biopolymer concentration, while no correlation observed between IRF and biopolymers 3- Slow sand filtration was significantly reduced UF fouling by removing biopolymers
Zheng et al. 2010	Secondary effluent DOC = 11.7 ± 1.4 mg/L UV = 0.28 ± 0.03 Cm^{-1} SUVA = 2.4 ± 0.17 L/mg.m Turbidity = 1.5 ± 1.3 NTU pH = 7.2 ± 0.3 BP = 0.4 ± 0.17 mg/L	Biofiltration slow sand filtration HLR = 0.25 & 0.5 m/h <u>media depth</u> = 70 cm	**UF**	1- A significant reduction in UF fouling was obtained by slow sand filtration 2- Lower HLR improved biofilter performance and provided higher fouling reduction 3- Higher biopolymer concentration in secondary effluent caused more severe UF fouling

References	Source of water feed water characteristics	Pre-treatment	Membrane type	Findings
Azzeh et al. 2015	River water (Otonabee River) DOC = 5.8 - 7.3 mg/L Turbidity = 0.3 - 1.5 NTU BP = 0.41 - 0.53 mg/L Hs= 3.0 - 3.3 mg/L	Bifiltration dual media (anthracite & sand) dual media (GAC & sand) EBCT = 10 & 11 min HLR = 6.0 & 5.0 m/h media depth = 50 cm anthracite or 50 cm GAC over 50 cm sand	**UF**	1- Biofilter removed 5.0 ±2.0 % of DOC and 17 ± 6% of biopolymers 2- Biofiltration was not effective in removing HS (1.0 ± 2.0%) 3- GAC removed an additional 0.1 mg/L of DOC but no difference between GAC and anthracite in BP removal 4- Biopolymers removal through biofilters remained > 15 % even under lower temperature < 12°C 5- a reduction of 60% in IRF was achieved by Biofiltration 6- There was no impact f biofiltration in RF of UF
Rahman et al. 2014	River water (Saugeen River) DOC = 2.7 - 7.03 mg/L UV = 0.07 - .24 Cm^{-1} SUVA =2.4 - 3.7 L/mg.m Turbidity = 0.71 - 17.9 NTU pH = 7.8 - 8.4 BP = 2 - 11% of DOC (0.23 mg/L) TOC = 2.85 - 7.29	Biofiltration dual media (anthracite & sand) EBCT = 10 min HLR = 5.0 m/h media depth = 55cm anthracite over 25cm sand	**UF**	1- Low removal of DOC, TOC, and UV (0 - 12%) 2- Biofilter removed 27 - 88% of turbidity and 10 - 30% of BP (0.1 mg/L) 3- Increasing BP in feed water increased its removal through biofilter 4- At 30% removal of BP, there was a reduction in RF and IRF by 55% & 68% respectively. 5- No effective removal of humic substances
Peldszus et al. 2012	River water (Grand River) DOC = 6.2 ± 0.8 mg/L Turbidity = 0.5 - 62 NTU pH = 7.9 ± 0.24 BP = 0.1 - 0.53 mg/L HS = 3.5 - 4.9 mg/L TOC = 6.7 ± 0.9 mg/L Temp. = 1 - 25 °C	Biofiltration dual media (anthracite & sand) EBCT = 5.0 & 10 & 15 min HLR = 5.0 m/h media depth 5.0 min : 20 cm anthracite over 20 cm sand 10 min: 20 cm anthracite over 63 cm sand 15 min: 40 cm sand	**UF**	1- Biofilter removed 15 % of DOC and lower biopolymers concentrations were observed in higher EBCT biofilter 2- Biofiltration was improved UF performance by reducing IRF 3- Longer EBCTs led to higher reduction in IRF 4- Biofiltration was able to operate well even under low temperature
Halle et al. 2009	River water (Grand River) DOC = 6.2 ± 0.8 mg/L Turbidity = 0.5 - 62 NTU pH = 7.9 ± 0.24 BP = 0.1 - 0.53 mg/L HS = 3.5 - 4.9 mg/L TOC = 6.7 ± 0.9 mg/L	Biofiltration dual media (anthracite & sand) EBCT = 5.0 & 14 min HLR = 5.0 m/h media depth 5.0 min : 20 cm anthracite over 20 cm sand 14 min: 20 cm anthracite over 97 cm sand	**UF**	1- Higher EBCT improved the removal of organics and particles through biofilter 2- Biopolymers were the most rejected fraction via biofiltration (40 - 60%) and lower removal of humics (less than 30%) 3- Biofiltration improved the UF performance and reducing both RF and IRF 4- The composition of biopolymers (eg. proteins) was more important in controlling fouling rather than their concentration

2.4 Coagulation

Pre-treatment using coagulation is an attractive process (Liu and Kim 2008). As a pre-treatment, it can be employed as in-line coagulation; where a small dosage is applied immediately before membrane filtration (Wang and Wang 2006), or as enhanced coagulation; where the process is operated under low pH conditions to improve NOM removal efficiency (Bagga *et al*. 2008), and finally as a conventional coagulation-flocculation process; where coagulant is applied at higher dosages to produce larger flocs in the flocculation step which are later rejected in a sedimentation step or at the membrane surface (Liu and Kim 2008).

2.4.1 Coagulation Mechanisms

The primary coagulation mechanisms are charge neutralization, sweep flocculation, and adsorption and bridging (Dong *et al.* 2012). The first two mechanisms are obtained using metal coagulants such as alum and ferric salts, while bridging involves only polymeric coagulants. In charge neutralization, adsorption of cationic hydrolysis products on negatively charged particles occur, which in turn promotes the aggregation of neutral particles (Xia *et al*. 2007). It is important to determine an optimum coagulant dose, as overdosing will increase positively charged particles in the suspension, and subsequently a reverse charge will develop leading to restabilization (Dong *et al.* 2012).

Sweep flocculation can only obtained with a high concentration of coagulant under elevated pH conditions, where metal hydroxides (solids) are formed, so colloids and organics can co-precipitate with the formed solids (Haberkamp *et al.* 2007). The important point to be mentioned here is that this mechanism does not depend on particulate type or concentration, where a higher dosage of coagulant should be applied to form bigger amorphous hydroxide precipitates (Dong *et al.* 2012).

Adsorption and bridging can be described as the linking of fine particles by polymeric coagulants which adsorb on colloidal surfaces (Lee and Westerhoff 2006). Overdosing will adversely affect removal efficiency where the polymer will coat colloid surfaces without connecting other particles (Lee and Westerhoff 2006).

2.4.2 Role of Organics in Coagulation

Using coagulation for the removal of organic compounds found in water or wastewater has been investigated and practiced for quite some time. Organics are typically negatively charged which affects and controls the coagulation process, especially when metal coagulants are used (Edzwald 1993). It has been demonstrated that coagulation not only reduces turbidity but that this process can also reduce organic concentration measured as NOM (Edzwald 1993; Dong *et al*. 2007; Humbert *et al*. 2007). The removal of NOM by coagulation depends on pH and has a tendency to increase as pH is reduced regardless of coagulant type (MWH 2005). The main mechanism of NOM removal is charge neutralization (Pikkarainen *et al*. 2004; Oh and Lee 2005; and Hatt *et al.* 2011) which can be obtained using metal coagulants. NOM removal by charge neutralization occurs by direct precipitation or by adsorption onto flocculated suspended solids (Edzwald and van Benschoten 1990).

The presence of NOM in water requires higher coagulant doses than those required for turbidity reduction only. Edzwald and Van Benschoten (1990) conducted a study to investigate the effect of NOM on coagulant dose. They compared two different water sources, one had high turbidity and low dissolved organic carbon (DOC) and the second was of low turbidity with moderate DOC. The results showed that the coagulant dosage required for the second water was around 10 times that required for the first, demonstrating that the main parameter that controls coagulant dosage is organic matter concentration, not suspended solids. This could be because organics are highly negatively charged compounds (10 µeq/mg DOC) when compared with suspended colloids (0.5 µeq/mg) (Edzwald and Van Benschoten 1990).

Specific ultraviolet absorbance (SUVA) is used as an indicator of NOM composition as organics that have aromatic structures absorb light in UV wavelength region. SUVA is defined as the normalized UV absorbance where the value of UV measured at 254 nm is divided by DOC concentration. The organics removal efficiency of coagulation can be related to its SUVA value (Edzwald 1993). Waters with high SUVA values (from 4 – 5) contain highly hydrophobic aromatic organics of high molecular weight (humic substances). For water with high SUVA values it is expected that about 70% DOC removal efficiency can be achieved by coagulation (Edzwald 1993; Hatt *et al*. 2011). On the other hand, low SUVA values (less than 3) are indicative of the presence of low molecular weight non humic compounds, and coagulation is not nearly as effective for DOC removal in such cases (Edzwald 1993; Hatt *et al*. 2011).

2.4.3 The Role of Coagulation in Membrane Filtration

Several studies have been conducted to evaluate pre-coagulation prior to the membrane filtration (Table 2.2). Some have demonstrated that pre-coagulation is an effective method for improving polymeric membrane (Zularisam et al. 2008; Humbert et al. 2007; Dong et al. 2007) and ceramic membrane (Zhu et al. 2011; Li et al. 2011; Abbasi et al. 2012) performance and reducing fouling by reducing both turbidity and organics concentrations, while others have reported little to no effect in membrane performance (Lee et al. 2007, and Howe et al. 2006). Many studies have reported that coagulation improved both filterability and permeability, but others have shown that more cake formation was produced. This is due to the fact that coagulation is a complex chemical process that involves many reactions, and there are many factors affecting its performance especially when conducted with membrane filtration. The following section discusses coagulation and factors affecting its performance when combined with membrane filtration as a pre-treatment.

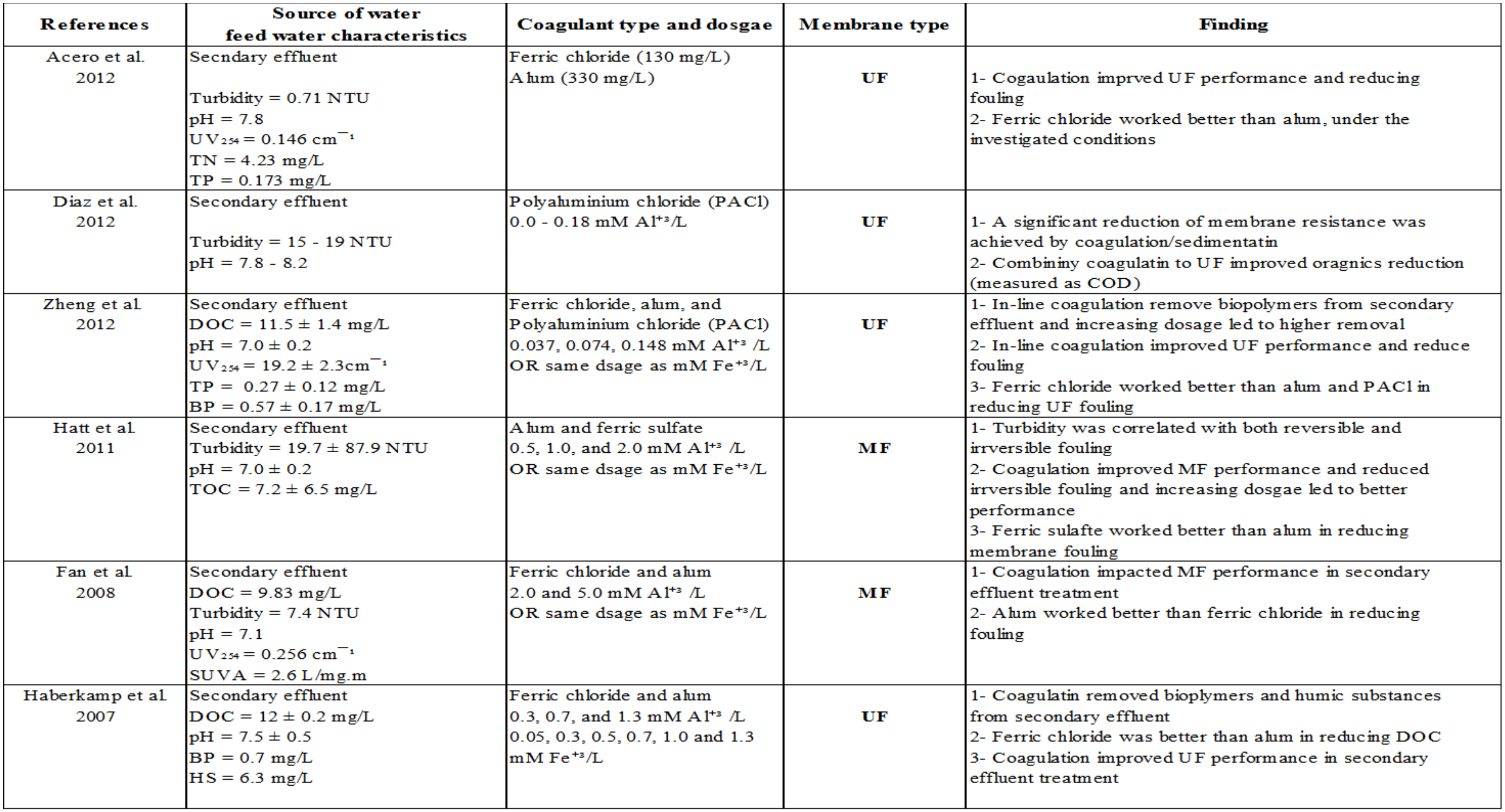
Coagulant type

Some studies have been conducted to investigate the effect of coagulant type on membrane performance. Liu and Kim (2008) compared three coagulants (alum, polyaluminum chloride, and ferric chloride) and found that when used to treat lake water, coagulation performance was substantially impacted by coagulant type with ferric chloride being better for turbidity and SUVA reduction. A similar finding was obtained by Haberkamp *et al*. (2007) comparing ferric chloride and alum in the coagulation of secondary wastewater effluent with higher DOC removal being obtained with ferric chloride than with alum. Pikkarainen *et al.* (2004) looking at the effect of four different coagulants: aluminum sulfate, polyaluminum chloride, ferric chloride, and ferric sulfate in membrane filtration of surface water with a high SUVA value (i.e. elevated humics), found that ferric-based coagulants performed better for NOM removal than those which were aluminum-based. Xiangli *et al.* (2008) studied ferric chloride as a pre-coagulant for UF in the treatment of high turbidity river water. They concluded that high quality effluent water was produced, high fluxes were maintained, and the period between chemical cleaning was extended by using ferric chloride.

Howe *et al.* (2006) studied the efficiency of three different coagulants: aluminum sulfate, ferric chloride, and ferric sulfate in the pre-treatment of five different water sources. Similar to the findings above, their results showed improvement in membrane performance using ferric salts regardless of feed water composition. They also observed that fouling reduction was dependent on floc size and coagulation substantially affected only particles ranging in size from 100 KDa to 1 µm. Moreover, alum worked well in this size range but alum flocs contributed to membrane fouling especially in the case of MF. Similar results were obtained by Acero *et al*. (2012) and Hatt *et al*. (2011) studying the effect of both ferric chloride and alum as pre-coagulants for UF in the treatment of secondary effluent. They concluded that alum increases membrane fouling rates and shortened the intervals between chemical cleaning events. Ferric chloride prior to UF produced higher quality permeate than alum. On the other hand, some studies have demonstrated that aluminum salts were effective in improving membrane performance in terms of high permeate quality and fouling reduction (Zheng *et al*. 2012, Judd and Hillis 2001, and Kim *et al.* 2005); which suggests that there are other factors that could affect the pre-coagulation process, not only the coagulant type.

Whereas coagulation is mainly dependent on pH, it was shown that ferric salts gave better results in membrane performance in the case of low pH water (Uyak and Toroz 2007), and aluminum salts improved membrane performance when applied in a range of 7.5 – 8 (Judd and Hillis 2001). Also, alkalinity affects coagulation performance where high alkalinity waters require higher coagulant dosages (Hatt *et al*. 2011).

Table 2-2 Observations from recent studies using coagulation pre-treatment for membrane filtration



References	**Source of water feed water characteristics**	**Coagulant type and dosgae**	**Membrane type**	**Finding**
Acero et al. 2012	Secndary effluent Turbidity = 0.71 NTU pH = 7.8 UV_{254} = 0.146 cm^{-1} TN = 4.23 mg/L TP = 0.173 mg/L	Ferric chloride (130 mg/L) Alum (330 mg/L)	**UF**	1- Cogaulation imprved UF performance and reducing fouling 2- Ferric chloride worked better than alum, under the investigated conditions
Diaz et al. 2012	Secondary effluent Turbidity = 15 - 19 NTU pH = 7.8 - 8.2	Polyaluminium chloride (PACl) 0.0 - 0.18 mM Al^{+3}/L	**UF**	1- A significant reduction of membrane resistance was achieved by coagulation/sedimentatin 2- Combininy coagulatin to UF improved oragnics reduction (measured as COD)
Zheng et al. 2012	Secondary effluent DOC = 11.5 ± 1.4 mg/L pH = 7.0 ± 0.2 UV_{254} = 19.2 ± 2.3cm^{-1} TP = 0.27 ± 0.12 mg/L BP = 0.57 ± 0.17 mg/L	Ferric chloride, alum, and Polyaluminium chloride (PACl) 0.037, 0.074, 0.148 mM Al^{+3} /L OR same dsage as mM Fe^{+3}/L	**UF**	1- In-line coagulation remove biopolymers from secondary effluent and increasing dosage led to higher removal 2- In-line coagulation improved UF performance and reduce fouling 3- Ferric chloride worked better than alum and PACl in reducing UF fouling
Hatt et al. 2011	Secondary effluent Turbidity = 19.7 ± 87.9 NTU pH = 7.0 ± 0.2 TOC = 7.2 ± 6.5 mg/L	Alum and ferric sulfate 0.5, 1.0, and 2.0 mM Al^{+3} /L OR same dsage as mM Fe^{+3}/L	**MF**	1- Turbidity was correlated with both reversible and irrversible fouling 2- Coagulation improved MF performance and reduced irrversible fouling and increasing dosgae led to better performance 3- Ferric sulafte worked better than alum in reducing membrane fouling
Fan et al. 2008	Secondary effluent DOC = 9.83 mg/L Turbidity = 7.4 NTU pH = 7.1 UV_{254} = 0.256 cm^{-1} SUVA = 2.6 L/mg.m	Ferric chloride and alum 2.0 and 5.0 mM Al^{+3} /L OR same dsage as mM Fe^{+3}/L	**MF**	1- Coagulation impacted MF performance in secondary effluent treatment 2- Alum worked better than ferric chloride in reducing fouling
Haberkamp et al. 2007	Secondary effluent DOC = 12 ± 0.2 mg/L pH = 7.5 ± 0.5 BP = 0.7 mg/L HS = 6.3 mg/L	Ferric chloride and alum 0.3, 0.7, and 1.3 mM Al^{+3} /L 0.05, 0.3, 0.5, 0.7, 1.0 and 1.3 mM Fe^{+3}/L	**UF**	1- Coagulatin removed bioplymers and humic substances from secondary effluent 2- Ferric chloride was better than alum in reducing DOC 3- Coagulation improved UF performance in secondary effluent treatment

Galvañ et al. 2014	Surface water Turbidity = 57 NTU TOC = 4.0 mg/L	Ferric chloride 0.5 mg/L	**UF**	1- Coagulatin with low dosage (eg. 0.5 mg/L) was sutible to maintain UF working under steady TMP even with feed water with high turbidity (>70 NTU)
Wang et al. 2014	Synthetic surface water Turbidity = 0.15 - 0.27 NTU pH =7.09 - 7.68 TOC = 1.0 - 3.8 mg/L	Alum 0.0 - 8.0 mg Al^{+3}/L	**MF**	1- Precoagulation was an effective Low pressure membrane pre-treatment 2- Increase alum dosage led to lower membrane fouling 3- Alum reduced both reversible and irreversible fouling
Wray et al. 2014	Surface water two different lake water and one River water DOC = 2.03 - 5.83mg/L Turbidity = 0.34 - 0.72 NTU pH = 8.05 - 8.18 BP = 0.22 - 0.45 mg/L HS = 0.99 - 3.24 mg/L SUVA = 1.6 - 3.05 L/mg.m	Alum 0.0, 0.5, 5.0, 10.0, and 15.0 mg/L	**UF**	1- Coagualtion improved UF performance 2- Considering water with cncentrations of DOC> 4.0 mg/L, low dosage of alum (0.5 mg/L) was suitable in reducing both reversible and irreversible fouling 3- In some cases (DOC = 2.0 mg/L), increasing alum dosage led to higher fouling 4- Reversible and irreversible fouling were correlated with bioplymers and humic substances
Ratajczak et al. 2012	Surface water Grand River Turbidity =2.0 - 16 NTU pH = 7.4 - 8.4 TOC = 5.0 - 6.9 mg/L Lake Ontario Turbidity =0.5 - 1.5 NTU pH = 7.7 - 8.3 TOC = 1.5 - 2.9 mg/L	Grand River Alum 30.0 mg/L Ferric chloride 45.0 mg/L and (40.0 and 50.0 mg/L) for Lake Ontario Alum 15.0 mg/L Ferric chloride 20.0 mg/L PACl (15.0 and 20.0 mg/L) for	**UF**	1- Alum is the most effective coagulant in reducing UF fouling when UF fed with Grand River. While PACl is more effective when UF fed with Lake Ontario water. 2- Data obtained from Jar test not necessarily a good indicator of fuling reduction

TN: total nitrogen

TP: total phosphorus

Coagulant dose and in-line coagulation

Coagulant dose affects membrane behavior. Liu and Kim (2008) investigated three different ferric chloride dosages: 0, 5, and 20 mg $FeCl_3$/L. Their results showed that coagulant addition improved feed water (lake water) quality and enhanced membrane performance even at low dosages. Another study conducted by Zheng et al. (2012) compared three different coagulants: ferric chloride, aluminum chloride and polyaluminum chloride (PACl) at different dosages to ultrafiltration fouling reduction in in-line coagulation for secondary effluent treatment. The authors concluded that at low coagulant dosage (0.037 mmol Fe^{3+}/L), higher biopolymer removals could be achieved using ferric chloride, while the removal efficiency was almost the same for the three coagulants when high dosages (0.148 mmol Fe^{3+}/L) were applied. They also noticed that DOC was better removed and UV absorbance was better reduced with PACl. The performance of the UF membrane improved regardless of coagulant type and membrane filterability was enhanced as a result of biopolymer and hydraulic resistance reduction by coagulation. On the other hand, ferric chloride performed better than the other coagulants in terms of reduced transmembrane pressure (TMP).

Lee et al. (2007) investigated the efficiency of alum at a dosage of 50 mg/L (as alum) as a pre-coagulant for UF in secondary effluent treatment. They observed that alum can improve permeate flux quality and quantity to a point but at higher dosages (70 mg/L) more resistance was created.

In-line coagulation is be defined as the addition of coagulants with low dosage continuously prior to membrane without removing particles (Wang and Wang 2006) for the purposes of changing particle and NOM characteristics (Liu and Kim 2008).

In-line coagulation is an important technology that has many advantages. For example, its footprint is very small in comparison to conventional coagulation-flocculation (Zheng *et al.* 2012). Also, lower coagulant dosages decrease both cost and sludge production. On the other hand, in conventional coagulation, jar testing is beneficial in order to be able to predict coagulant performance and appropriate dosage, but this procedure may be not helpful with in-line coagulation (Zheng *et al.* 2012). In-line coagulation appears to be an interesting alternative but it is still being investigated.

Wang and Wang (2006) studied in-line coagulation for UF in the removal of natural humic acid using aluminum sulfate. The results showed that using in-line coagulation prior UF, in comparison with direct UF, improved the removal efficiency of both DOC and UV_{254} at around pH 7. The removal efficiency of different MW sizes from 1 – 6 KDa substantially increased following in-line coagulation prior to UF. Furthermore, fouling resistance was enhanced using this procedure by preventing pore blockage and decreasing cake formation. That said, it is unlikely that the removal of humic acids contributed to this improvement. As has relatively recently been reported, it is the biopolymer fraction that is responsible for membrane fouling but it was not measured in this study.

Delgado-Diaz et al. (2012) investigated in-line coagulation with UF in secondary effluent treatment and high removal efficiencies equaling 99% and 95% were obtained for both turbidity and DOC, respectively, when combining in-line coagulation with UF. Turbidity and DOC removal by conventional coagulation were up to 93% and 70%, respectively. In-line coagulation improved the removal of the foulants responsible for reversible fouling, but the irreversible fouling rate was unaffected.

These early studies on pre-coagulation as a pre-treatment for the ultrafiltration of secondary effluent are still somewhat inconclusive due to complex chemical reactions, and differences in feed water composition and operating conditions. Some findings were inconsistent and sometimes conflicting. As such, further studies are required.

2.5 Summary and Research Needs

To produce water of appropriate quality for reuse, advanced treatment methods following conventional wastewater treatment are required. Most previous studies have used high pressure membranes combined with low pressure membranes such as MF, UF or MBR as a pre-treatment to reduce high pressure membrane fouling. Investigating low pressure membranes combined with adequate pre-treatment of secondary effluent treatment is essential. Therefore, the primary goal of this study was to extend the previous research which investigated the use of UF membranes in secondary effluent treatment for water reuse.

There are several physical and chemical processes that can be used as pre-treatment for membrane filtration. However, the study of biofiltration as a pre-treatment for low pressure membrane filtration in drinking water treatment has recently been shown to be efficient for improving membrane performance by fouling reduction as well as its benefits in protecting the environment and reducing cost. Examination of this technology for secondary effluent treatment is still under investigation. Studies directly comparing biofiltration with other physical and chemical processes used in this field such as coagulation are very limited. In the present study, the application of biofiltration as a pre-treatment for UF membranes treating secondary effluent was investigated. At the same time, in-line coagulation as a UF pre-treatment was investigated in terms of the effect of coagulant type and dosage on fouling reduction. A comparison between both processes (biofiltration and in-line coagulation) was conducted to evaluate their performance in fouling studies as well as their impact on permeate quality.

It is essential to produce high quality water, especially for direct or indirect potable water applications. Consequently, combinations of two or more processes as pre-treatment for membrane filtration are important to consider in water reuse studies. Most of the previous studies have focused on combining conventional water treatment processes with low pressure membranes as a pre-treatment for high pressure membranes with the objective of producing potable water. However, combining chemical processes, such as coagulation, with biofiltration is not yet well described and further investigations are required. The overall focus of this research, therefore, was to explore the performance of this combination and its impact on membrane behavior, fouling reduction, and permeate water quality.

Chapter 3

Materials and Methods

This thesis was written in paper format, specific information on materials and methods for a given results chapter is included at the beginning of that chapter.

3.1 Source Water

The secondary effluent investigated in this study was collected from the Waterloo Wastewater Treatment Plant (WWTP), which treats domestic wastewater from the City of Waterloo, Ontario, Canada. The average daily capacity for the WWTP was 72,730 m^3/d during the period when this study was being conducted. The Waterloo WWTP was undergoing construction during this study to upgrade both primary and secondary treatment including biological treatment. The raw sewage was treated by primary clarification with ferrous chloride addition for phosphorus removal. This was followed by conventional activated sludge as a biological treatment followed by secondary settling tanks. The secondary effluent was disinfected by UV before discharge into the environment.

Secondary effluent following UV exposure was collected twice per week in three 200 L polyethylene drums and immediately transferred to the University of Waterloo (approximately 3.5 km from the WWTP). Following collection, the secondary effluent was stored in the Douglas Wright Engineering (DWE) wastewater pilot plant area in a single mixed tank at room temperature (23°C) and flow to the biofilters and UF membranes was initiated immediately.

3.2 Biofiltration Experimental Set-up

3.2.1 Preliminary Experimental Set-up

Prior to the construction of a larger pilot scale biofiltration set-up, a preliminary experimental set-up was used to optimize biofiltration media and operational parameters. This set-up was initially constructed and operated by Dr. T. Liu (NSERC Chair post-doctoral fellow from 2011-2012). It consisted of three parallel 2.5 cm internal diameter by 1.0 m high polyethylene columns. Each biofilter contained a different media with an effective bed depth of 50 cm supported by 10 cm of gravel (Table 3.1). See appendix A for more information.

The biofilters were operated in down flow mode under identical operating conditions in order to compare the three media. Two EBCTs were investigated, 15 and 30 min, corresponding to hydraulic loading rates of 2.0 and 1.0 m/h, respectively.

Table 3-1 Characteristics of media used in preliminary biofiltration set-up

Biofilter	Media type	Material	Effective size (ES)	Uniformity coefficient (UC)	Surface area m^2
A	Kaldnes®	polyethylene	N/A	N/A	2.32
B	anthracite	coal	1.07 mm	1.5	N/A
C	Macrolite®	ceramic	1.3 mm	1.4	N/A

3.2.2 Main Experimental Set-up

The biofiltration set-up was constructed and operated in the Douglas Wright Engineering (DWE) wastewater pilot plant facility on the campus of the University of Waterloo. Figure 3.1 represents a schematic diagram of the biofiltration set-up. The set-up consisted of two parallel glass columns 5.1 cm in internal diameter and 2.1 m high with an effective bed depth of 75 cm supported by 10 cm of (3 mm ID) gravel. There was 125 cm water above the media in each column and the overflow was 200 cm from the base of the column. There were 8 sample ports in each column. The distance between the first four ports was 5 cm while it was 10 cm for the lower ports (see Appendix A). Media samples were collected weekly from the first, fifth, and eighth ports which corresponding to media at top, mid and bottom from each biofilter.

Secondary effluent was pumped to the biofiltration set-up with a feed pump (model No. 7550-50, 1.6-100 PRM, Cole-Parmer instrument Company, Barrington, USA) and backwash flow was provided with a second pump (model No. 7553-70, 6-600 RPM, Cole-Parmer instrument Company, Barrington, USA). To monitor water flow rate through biofilter, flowmeters (Model 2L09, 5-50CCM water, VRW international, USA) were connected in the effluent tubing. An air flowmeter was connected in the air backwashing tubing to adjust the air flow rate during backwashing. Polyethylene tanks were used for feed water storage and effluent water collection.

Sand and anthracite were compared as biofilter media. The uniformity coefficients of both media were 1.5 and the effective size was 0.5 and 1.0 mm for sand and anthracite, respectively. The biofilters were operated in down flow mode (at constant head, constant rate) under the same operating conditions in order to compare the two media. The EBCT of each biofilter was 60 min corresponding to a hydraulic loading rate of 0.75 m/h. To reduce media clogging, each biofilter was backwashed using its effluent. During the first six months of the biofilters operation, they were backwashed once per week. Following that, the biofilters were backwashed twice per week until the end of the experimental period.

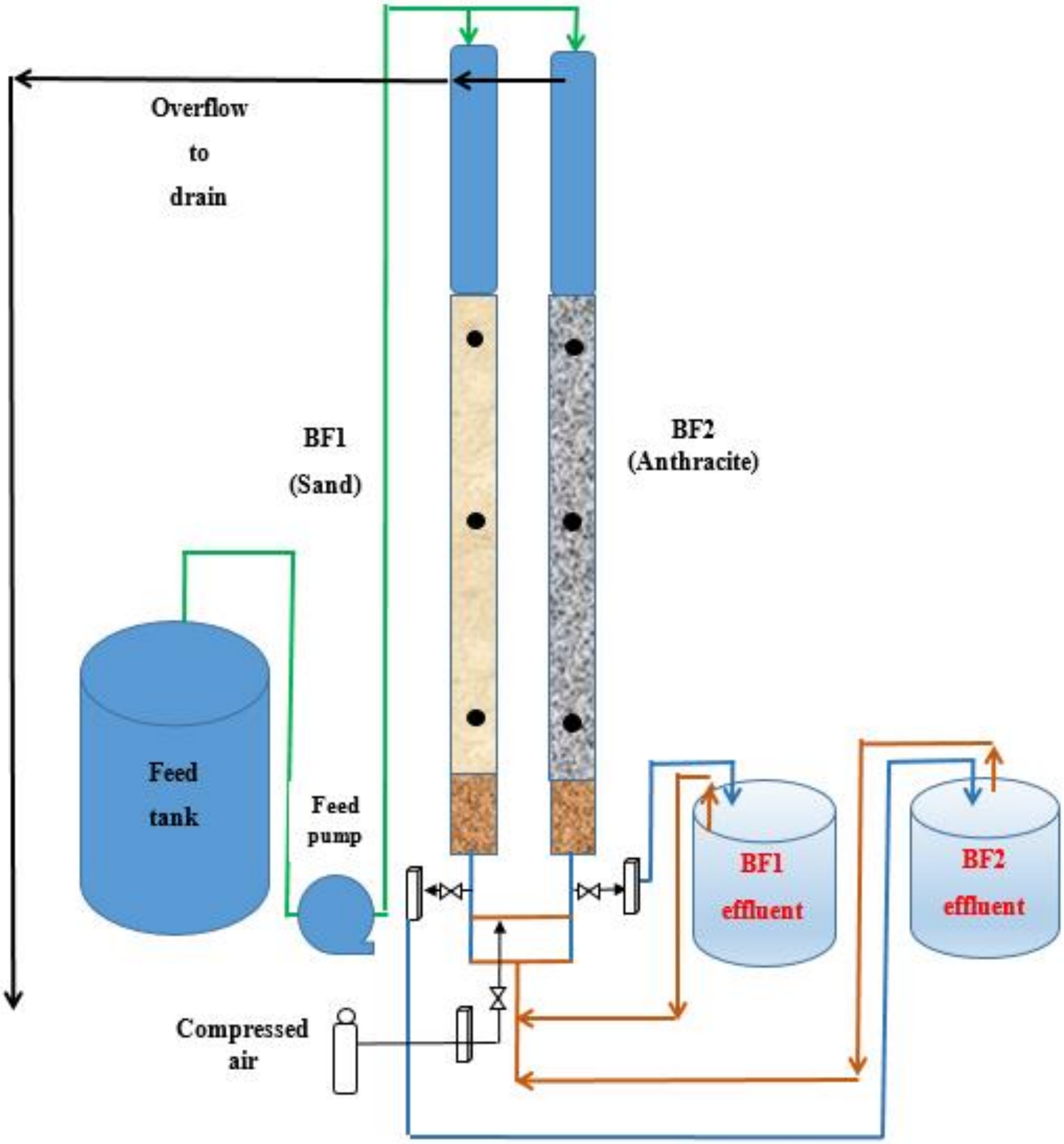


Figure 3.1 Schematic of biofiltration set-up (not to scale)

The first stage of biofilter backwashing involved air only for 1 min to break up any plugs, followed by air and water collapse pulsing for 4 min. Air flow was the stopped and water flow was gradually increased to reach 25% bed expansion and held for 1 min. Then, bed expansion was increased to 50%

for 4 min. Finally, the water flow was gradually reduced until the media returned back to its normal operating depth.

3.3 Ultrafiltration Set-up

UF membrane selection was based on previous work performed at the NSERC Chair in Water Treatment labs. The polymeric membrane used in this study was the commercially available polyvinylidene fluoride (PVDF) ultrafiltration membrane made by GE Process Technologies (Oakville, Canada). The membrane module (the Zeeweed - 1®) was constructed of 15 cm long hollow fibers (500 series), and the operation mode was outside-in. The membrane had a nominal surface area of 0.047 m^2 with a MWCO of 400 KDa (approximately 40 nm pore size) as delivered from the manufacturer. The properties and normal operating range for the membrane are shown in Table 3.2. Values shown are as provided by the manufacturer.

Table 3-2 Polymeric UF Membrane Characteristics

Parameter	Value/Range
Flux	30 - 70 LMH
Permeate flow rate	1.4 - 3.3 L/h
Pressure	0 - 10 psi
Temperature tolerance	0 – 40°C
Chlorine tolerance	1000 mg/L
pH tolerance	2 - 9

Figure 3.2 shows a schematic drawing of the UF set-up. The UF module was located vertically in a clear polyvinyl chloride 2.0 L cylindrical tank. The set-up was designed to cycle automatically where each cycle began with 30 min of permeation followed by backwashing with air sparging for 20 sec. After that, the module tank was drained (30 sec) and refilled again with the investigated water (36 sec). For continuous measurement during the experiments, a temperature sensor and flowmeter monitor (model LC alpha controller, 200-500 CCM, Alicat Scientific, Tucson, USA) were connected to a data logger (HOBO Energy Logger, model H22-001, Onset, Cape Cod, Massachusetts, USA). The digital flowmeter was used to maintain a constant pre-determined permeate flow rate through the whole UF

experiment. It was connected to a digital permeation pump (Masterflex L/S drive model number 07550-50; Cole-Parmer Canada) that was programmed to operate at a constant flow rate (25 mL/min). The flowmeter measured the actual permeate flow rate every 10 sec and the data were recorded by data logger. The actual flux could be determined at any time during the filtration run using equation 3.1 (Rahman 2013). Transmembrane pressure was measured using a pressure transducer (model 68075-02, Cole-Parmer, Montreal, Canada) which was also connected to the data logger. Fouling rates were determined using TMP data after correcting the temperature to 20°C using equation 3.2 (El-Hadidy 2011). Additional details regarding the bench-scale configuration and operation are available in El-Hadidy *et al*. 2013 and Rahman 2013.

$$\text{Flux corrected to } 20^{\circ}\text{C, } J_{20} = J \times \mu / \mu_{20} \qquad \text{Equation 3.1}$$

Where, J = flux at ambient temperature

μ = viscosity at ambient temperature

μ20 = viscosity of water at 20°C

$$\text{Corrected TMP @ } 20^{\circ}\text{C} = \text{TMP X } 1.025^{(T-20)} \qquad \text{Equation 3.2}$$

Where, T = water temperature in °C

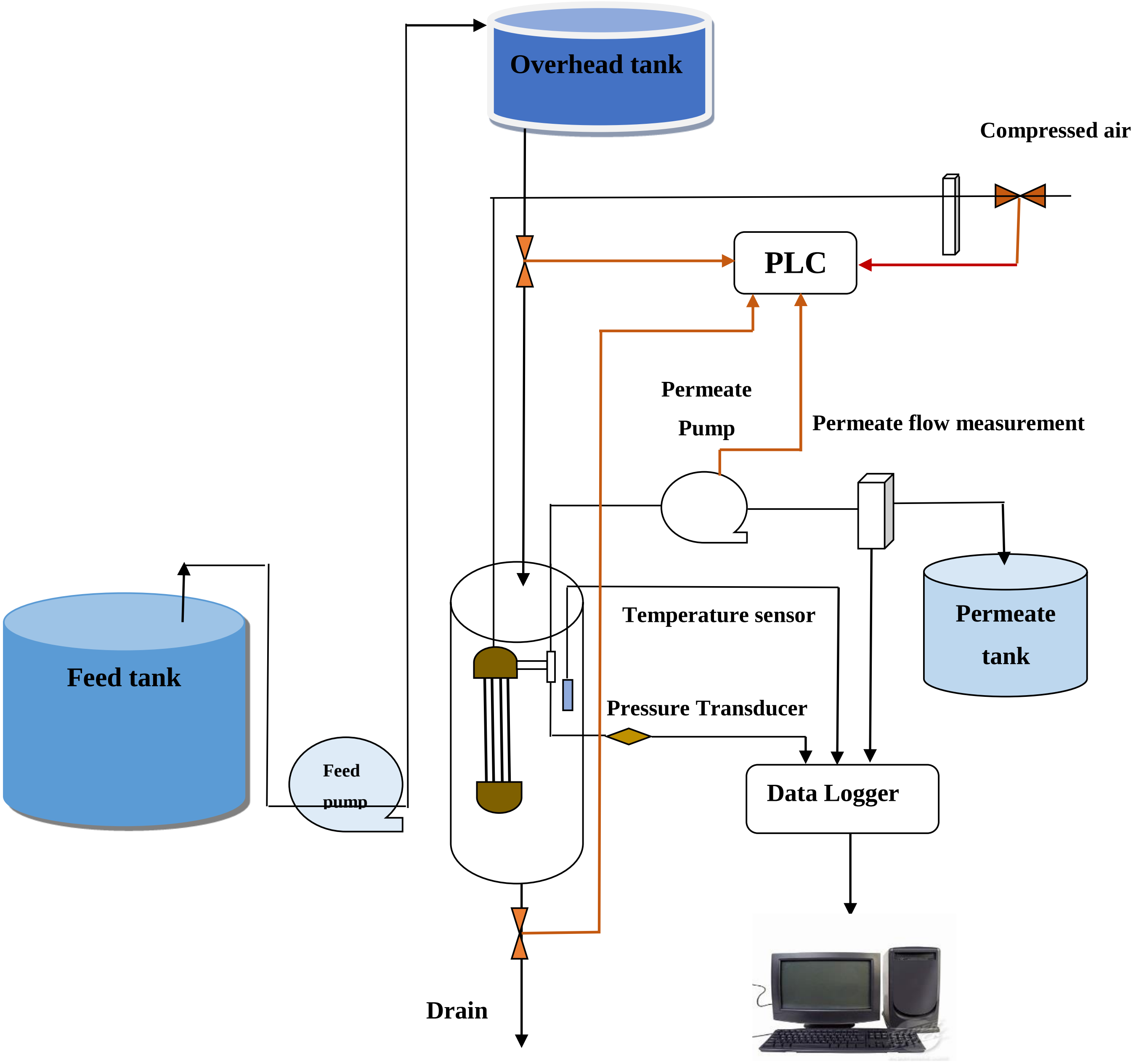


Figure 3.2 UF set-up schematic

All polymeric UF experiments were conducted in dead-end mode at a constant permeate flux of 33 L/m^2 h (LMH). To measure the UF fouling rate before and after pre-treatment using the same batch of secondary effluent the run length was set to end at 24 h or until the maximum TMP (8 psi) of the membrane was reached. Chemical cleaning was performed after each experiment by soaking the membrane in sodium hypochlorite (200 mg/L) for a minimum of 5 h followed by citric acid solution soak (5 g/L) for another 5 h. After chemical cleaning, the membrane was soaked in a glass jar containing deionized water at 4°C until usage. The UF module was integrity tested using a pressure calibrator (Meri-cal DP2001I, Meriam Instruments, Ohio, USA) prior to every experiment. The maximum allowable pressure drop through the membrane was 0.3 psi per 2 min. Additional details concerning integrity testing and chemical cleaning of the membrane are available in Appendix K). To check cleaning effectiveness, clean water permeability tests were conducted using deionized water before each experiment (Appendix L).

3.4 Coagulants

Four different coagulants were used in this study. They included aluminum sulfate (alum), polyaluminum chloride (PACl), ferric chloride, and ferric sulfate (Table 3.3). All coagulants were supplied by Kemira Water Solutions (Quebec, Canada).

Table 3-3 Coagulant Information (from supplier)

Product name	**Aluminum sulfate**	**Polyaluminum chloride**	**Ferric chloride**	**Ferric sulfate**
Commercial name (product name)	Alum (Kemira ALS)	PACl (Stern PAC)	(PIX-111)	(PIX-312)
Chemical formula	$Al_2(SO_4)_3$	$Al_{13}(OH)_{20}(SO_4)_2Cl_{15}$	$FeCl_3$	$Fe_2(SO_4)_3$
Concentration (as supplied)	29-50% as $Al_2(SO_4)_3.14H_2O$	15-40% as $Al_{13}(OH)_{20}(SO_4)_2Cl_{15}$	37-42% as $FeCl_3$	66-73% as $Fe_2(SO_4)_3$
Specific gravity	1.2-1.36	1.16-1.3	1.26-1.48	1.38-1.59
pH	< 2.5	1.8-3.4	< 2	< 2

3.5 Jar Tests

Jar tests were conducted at the wastewater pilot plant in the Douglas Wright Engineering (DWE) Building, at the University of Waterloo using a procedure based on Standard Practice for Coagulation – Flocculation Jar Test of Water (ASTM International). Raw water (secondary effluent) was thoroughly mixed for one minute prior to coagulant addition. Then, the appropriate dose of coagulant was added and mixing was continued at 100 rpm for one minute. Mixing was then slowed to 30 rpm for 20 minutes. Finally, the flocs were allowed to settle for 30 minutes. Samples were taken after settling and routine analyses were conducted.

3.6 Physical and Chemical Parameters Analyses

3.6.1 Liquid Chromatography Organic Carbon Detection (LC-OCD)

NOM constituents were identified based on their molecular weight using an LC-OCD Model 8 (DOC-LABOR, Karlsruhe, Germany). The LC-OCD incorporated a size exclusion column followed by a continuous carbon detector to separate the organic compounds in a water sample into four main fractions (Huber *et al*. 2011). These fractions were biopolymers, humic substances, building blocks (humic substance-like material of lower molecular weight), and low molecular weight acids and neutrals. These fractions are represented by peaks A, B, C, and D, respectively in Figure 3.3. The LC-OCD was also equipped with organic nitrogen (OND) and UV (UVD) detectors. Before analysis, samples were pre-filtered through 0.45 µm PVDF membrane filters (Pall Supor® Membrane Disc Filters, 0.45 µm, 47 mm plain, VWR international, USA). Samples were diluted with ultrapure water if the DOC in the sample exceeded 5 mg/L.

This instrument measures the DOC concentration in a small amount of injected sample (6 to 8%) which flows directly to the organic carbon detector without separation. Details relating to the calculation of area under the target peaks are described in Huber *et al*. (2011). Areas were calculated automatically by the software provided.

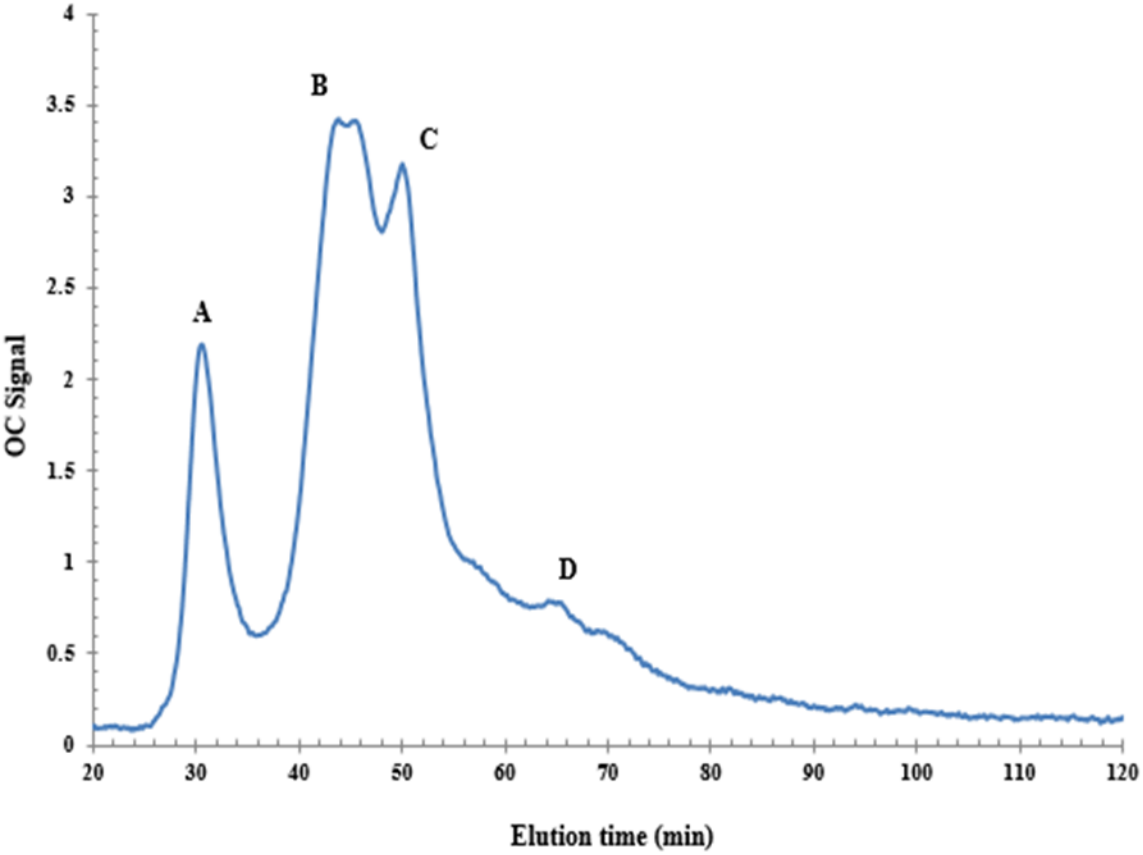


Figure 3.3 Main secondary effluent organic carbon fractions classified using the LC-OCD technique

3.6.2 Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC)

TOC and DOC were analyzed using an OI-Analytical TOC Analyzer (Model 1030, College Station, TX, USA) by combustion method as per Standard Method 5310B (Standard Methods, 2012). DOC samples were first filtered through a pre-rinsed (with 50 mL of Milli-Q water) 0.45 µm PVDF membrane filter (Pall Supor® Membrane Disc Filters, 0.45 µm, 47 mm plain, VWR international, USA) prior to analysis. The pH value of the filtered samples was adjusted to 2 using phosphoric acid (1N) immediately following filtration and stored at 4°C until analysis.

3.6.3 UV_{254} Absorption and SUVA

UV_{254} was measured as per Standard Method 5910 (Standard Methods 2012) using a Cary 100 UV-VIS spectrophotometer (Agilent Technologies, Musgrave, USA). Specific UV absorbance (SUVA) was calculated based on UV_{254} absorbance and DOC values.

3.6.4 Adenosine 5'-triphosphate (ATP)

ATP measures total microbiological concentration found in the biofilter media. A LuminUltra^{TM} DSA adenosine triphosphate (ATP) test kit was used (LuminUltra, Fredericton, New Brunswick, Canada).

3.6.5 Turbidity, dissolved oxygen, and pH

Turbidity was analyzed using a HACH 2100P turbidity meter as per Standard Method 2130 (HACH, Loveland, US). The pH was measured using an Orion 720A pH meter with an Orion 91-02 glass electrode. Dissolved oxygen in the biofilter inlet and outlet was measured with a Dissolved Oxygen pen (model NO. 97011-782, VWR international, USA). The data were acquired for use in the biomass respiration potential (BRP analysis) discussed in section 4.4.3.1.

3.6.6 Nitrogen and phosphorus compounds

Ammonia, nitrate, nitrite, total nitrogen and total phosphorus data were acquired from the City of Waterloo WWTP records. All were measured as per Standard Methods (2012).

The secondary effluent temperature was measured daily by operators at the WWTP using a general purpose thermometer.

Chapter 4

Improving Secondary Effluent Quality by Biological Filtration

Summary

Wastewater reuse is one of a number of promising ways to conserve available water resources, but to be of sufficient quality for such opportunities additional treatment is required. In this study, biological filtration was investigated as an advanced method for secondary wastewater effluent. This investigation was carried out in a pilot-scale set-up that consisted of two parallel biofilters containing different media (sand vs. anthracite) and operated continuously over 14 months under identical conditions at an HLR of 0.75 m/h (corresponding to an EBCT of 60 min). Biomass quantification revealed that higher quantities of biomass were associated with the sand biofilter than the anthracite biofilter. Biofilter inhabitants were most active near the surface of the two biofilters and their concentrations decreased with biofilter depth. Liquid chromatography–organic carbon detection analysis demonstrated that biofiltration improved the organic composition of secondary effluent. DOC and NOM fractions were removed within the biofilters and the biofilter containing sand was significantly better than that containing anthracite for DOC and biopolymer reductions, while there was no impact of media type on the reduction of particles (measured as turbidity).

4.1 Introduction

Wastewater reuse is an important contribution to the recovery of usable water that is attracting the attention of water researchers (Fan *et al.* 2008; Park *et al.* 2010; Delgado-Diaz *et al.* 2012; Filloux *et al.* 2012). The characterization of parameters found in secondary effluent, especially those of concern for human health and the environment, is essential to identify appropriate applications for wastewater reuse. One of the most important parameters that should be clearly characterized is effluent organic matter (EfOM). Previous studies (Shon *et al*. 2006a; Filloux *et al.* 2012) classify EfOM as a combination of NOM already present in surface water, soluble microbial products (SMPs) which are carried over from biological treatment, and trace chemicals or micro contaminants such as DBPs, pesticides, herbicides, and pharmaceuticals. Recently, organic matter characterization into its main fractions has been facilitated by techniques such as Liquid Chromatography Organic Carbon Detection (LC-OCD) (Hallé *et al.* 2009; Zheng *et al.* 2010; Peldszus *et al.* 2011; Rahman *et al.* 2014; Kimura et al. 2015) and Fluorescence Excitation-Emission Matrix (FEEM) (Peiris *et al.* 2010). These techniques can assist in providing valuable information about EfOM composition.

While biological treatment processes are capable of substantial removal of organics found in wastewater, reusing secondary effluent without advanced treatment is typically not recommended (Zhu *et al*. 2011). The main role of advanced treatment is to improve secondary effluent quality to conform to regulations and meet public approval. The most common processes used for advanced wastewater treatment are conventional water treatment and adsorption followed by disinfection. Biological filtration processes have been used for drinking water treatment in various forms for decades to reduce the production of disinfection by-products and limit microbial regrowth in distribution systems. This technology is also used in wastewater treatment for microorganism reduction to improve disinfection (Metcalf and Eddy 2007). Biofiltration has many benefits over other processes including less chemical addition and less sludge production which makes it safer and more environmentally-friendly. There are some important parameters such as EBCT, hydraulic loading rate, media type, and organics removal rate which should be considered when designing biofiltration processes (Graham 1999).

Biofiltration has only recently been investigated as a low pressure membrane pre-treatment for drinking water production (e.g. Peldszus *et al.* 2011; Filloux *et al.* 2012; and Rahman *et al.* 2014). In those studies, biofiltration was examined in the form of dual-media (sand/anthracite) filters at shorter EBCTs (5 – 10 min) corresponding to hydraulic loading rates around 5.0 m/h. Biofiltration was also investigated in (2011) by Reungoat *et al*. for the removal of pharmaceuticals and personal care products from secondary effluent at a higher EBCT (120 min) corresponding to an HLR of 0.2 m/h. Zheng *et al.* 2009 investigated biofiltration (with sand) as a pre-treatment to ultrafiltration (UF) for secondary effluent treatment at low hydraulic loading rates (0.25 and 0.5 m/h) typical of slow sand filtration. Biofiltration (with biological activated carbon-BAC) has also been investigated as a microfiltration (MF) pre-treatment for treating secondary effluent at an HLR of 0.2 m/h corresponding to an EBCT of around 40 min (Pramanik *et al.* 2014). In some cases, BAC has been utilized to provide higher effective surface area and better adsorptive capacity for EfOM removal. Investigating the performance of biofiltration in treating secondary effluent with different organic composition using lower EBCTs and higher HLRs than those investigated by Zheng *et al.* 2009 is essential. Studies on non-adsorbing media (e.g. sand, anthracite, etc.), and comparisons between them for the purposes of membrane pre-treatment for treating secondary effluent do not exist in the literature.

4.2 Objectives

This phase of study focused on biofilter media, operating considerations, and the quality of effluent being produced by biofiltration. It was intended to narrow down the options for further investigations with membranes discussed later in this thesis.

The specific objectives of this chapter were to:

1. Characterize the organic composition of the secondary effluent being studied using a novel technology (LC-OCD)

2. Investigate biofiltration as a pre-treatment for low-pressure (UF) membrane filtration that would be used as the first stage of an advanced wastewater treatment process. In this regard, the effect of biofiltration on improving secondary effluent properties was investigated

3. Assess biofiltration as a UF pre-treatment using three different media and two hydraulic loading conditions including:
   - Kaldnes®, Macrolite®, and anthracite media at hydraulic loading rates of 1.0 and 2.0 m/h [Phase 1]
   - Two media (sand & anthracite) at a hydraulic loading rate of 0.75 m/h [Phase 2]

4. Investigate potential seasonal effects on biofilter performance

4.3 Materials and Methods

4.3.1 Source water

The secondary effluent investigated in this study was collected from the Waterloo Wastewater Treatment Plant (WWTP), which treats municipal wastewater from the City of Waterloo, Ontario, Canada. The average daily capacity for the WWTP was 72,730 m^3/d in the period when this study was being conducted. The WWTP was undergoing construction during the investigated period of this study to upgrade both primary and secondary treatment including biological treatment. The raw sewage was first treated by primary clarification where ferrous chloride was added for phosphorus removal. This was followed by conventional activated sludge as a biological treatment followed by secondary settling tanks. The secondary effluent was UV-disinfected prior to discharge into the environment.

Secondary effluent following UV exposure was collected twice per week (every Monday and Thursday) in three 200 L polyethylene drums and immediately transferred to the University of Waterloo (approximately 3.5 km from the WWTP). The secondary effluent was transferred to a single holding tank in the Douglas Wright Engineering (DWE) wastewater pilot plant area on the campus of the University of Waterloo and pumping to the biofilters was immediately initiated. Water in the tank was allowed to increase to room temperature (23°C) and the tank was continuously mixed. The water collected on Monday was used to feed biofilters for the first three days of the week (Monday, Tuesday, and Wednesday) and that collected on Thursday was fed for the rest of the week (Thursday, Friday, Saturday, and Sunday).

4.3.2 Biofiltration Experimental Set-up

4.3.2.1 Preliminary Biofiltration Set-up

Prior to the construction of a larger pilot scale biofiltration set-up, a preliminary experimental set-up was used to select and optimize biofilter media and operational parameters. The set-up was initially constructed and operated by Dr. T. Liu (NSERC Chair post-doctoral fellow from 2011-2012). It consisted of three parallel 2.5 cm internal diameter polyethylene columns which were 1.0 m in total height. Each biofilter contained a different media with an effective bed depth of 50 cm supported by 10 cm of gravel. See Appendix A for more information.

The biofilters were operated in down flow mode under identical operating conditions in order to compare the three media. Two hydraulic loading rates, 1.0 and 2.0 m/h, corresponding to 15 and 30 min, respectively were investigated.

4.3.2.2 Primary Biofiltration Set-up

The biofiltration set-up was constructed and operated in the Douglas Wright Engineering (DWE) wastewater pilot plant area on the campus of the University of Waterloo. The set-up consisted of two parallel glass columns 5.1 cm in internal diameter and 2.1 m high with an effective bed depth of 75 cm supported by 10 cm of (3 mm) gravel. There was 125 cm water above the media in each column and the overflow was 200 cm from the base of the column. There were 8 sample ports in each column. The distance between the first four ports was 5 cm while it was 10 cm for the lower ports (see Chapter 3 and Appendix A). Media samples were collected weekly from the first, fifth, and eighth ports which corresponding to media at top, mid, and bottom points within each biofilter.

Secondary effluent was pumped to the biofiltration set-up with a peristaltic digital drive pump (model No. 7550-50, 1.6-100 PRM, Cole-Parmer Instrument Company, Barrington, USA) and a backwash pump (model No. 7553-70, 6-600 RPM, Cole-Parmer instrument Company, Barrington, USA). To monitor water flow rate through the biofilters, flowmeters (Model 2L09, 5-50 CCM water, VWR International, USA) were installed in the effluent tubing. An air flow meter was used to adjust the air flow rate during backwashing (Model 2L09, 10 - 400 CCM air, VWR International, USA). Polyethylene tanks were used for feed water storage and effluent water collection.

Sand and anthracite were compared as biofilter media. The uniformity coefficients of both media were 1.5 and the effective size was 0.5 and 1.0 mm for the sand and anthracite, respectively. The biofilters were operated in down flow mode (constant head, constant rate) under identical operating conditions in order to compare the two media. The EBCT of each biofilter was 60 min corresponding to a hydraulic loading rate of 0.75 m/h. Each biofilter was backwashed using its effluent to maintain the composition of the microorganisms homogeneous. During the first six months of biofilter operation, they were backwashed once per week. The frequency of backwash was then increased to twice per week until the end of the experimental period (12 months). The change was necessitated by the appearance of small ‘mudballs’ which can affect filter performance and flow through the media (channeling).

4.3.3 Liquid Chromatography Organic Carbon Detection (LC-OCD)

NOM compounds were identified based on their molecular weight using an LC-OCD Model 8 (DOC-LABOR, Karlsruhe, Germany). The LC-OCD incorporates a size exclusion column followed by a continuous carbon detector to separate the organic compounds in a water sample into four main fractions (Huber *et al.* 2011). These fractions are biopolymers, humic substances, building blocks (humic substance-like material of lower molecular weight), and low molecular weight acids and neutrals. These fractions are represented by peaks A, B, C, and D, respectively, in Figure 4.1. The LC-OCD is also equipped with organic nitrogen (OND) and UV (UVD) detectors. Before analysis, samples were pre-filtered using a 0.45 µm PVDF membrane filter (Pall Supor® Membrane Disc Filters, 0.45 µm, 47 mm plain, VWR international, USA) which was pre-rinsed with 30 mL of ultrapure water. Samples were diluted with ultrapure water if the DOC in the sample exceeded 5 mg/L.

This instrument has the capacity to measure the DOC concentration in a small amount of injected sample (6 to 8%) which flows directly to the organic carbon detector without separation. To calculate the concentrations of the different fractions (biopolymers, humics, etc.), the integration of fraction areas can be calculated automatically or manually. In this case the areas were calculated by the software provided.

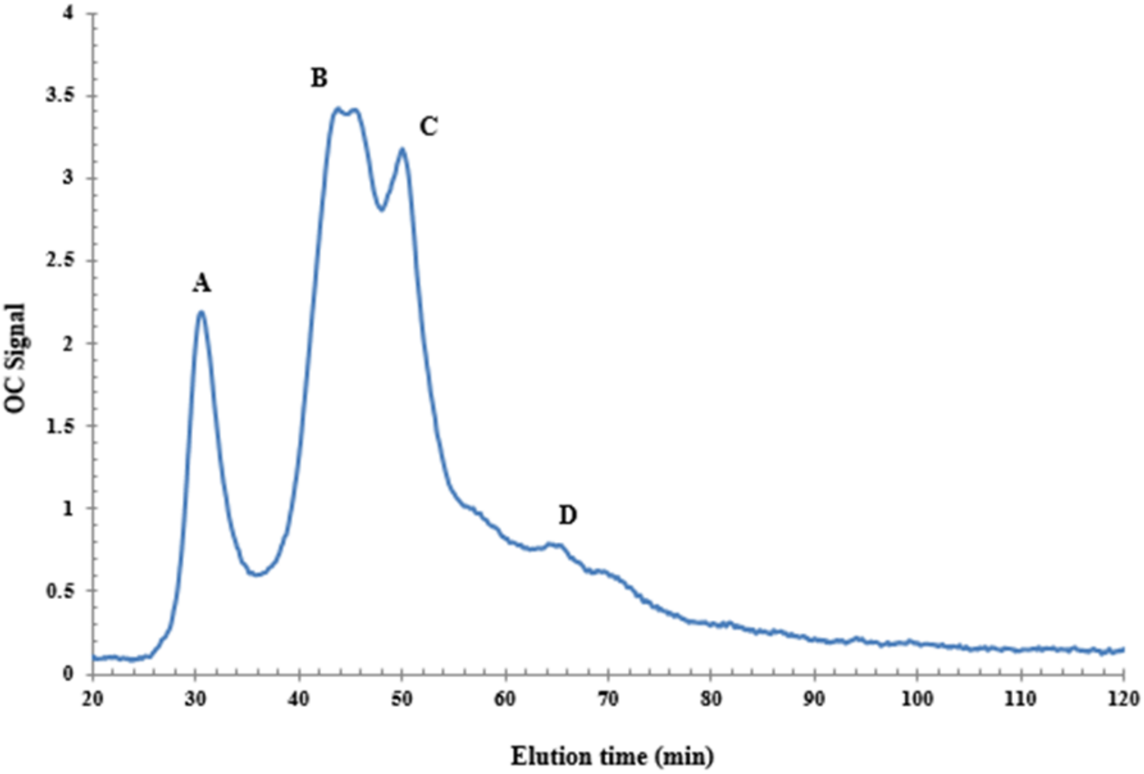


Figure 4.1 Main secondary effluent organic carbon fractions classified using the LC-OCD technique

4.3.4 Microbiological Analyses for Media Samples

Media samples were collected at depths of 10 cm, 30 cm, and 60 cm as measured from the top of the biofilter media for microbiological analysis. In the first six months of the biofilter operation, samples were collected weekly and twice per month for the rest of the investigated period. Media samples were collected before biofilter backwashing at which point the biofilters had been operating for a period of 7 days before sampling. One centrifuge tube 45 mL with screw cap was used for media collection per sampling point. The column was first drained, the screw cap on the port was removed, approximately 10 g of media were extracted using a clean glass spatula, and the cap was screwed back. Fresh media was added to the column to replace the volume removed after each sampling.

Two tests were performed on the media samples, Adenosine 5’-triphosphate (ATP) and Biomass Respiration Potential factor (BRP). Measurements were performed on the same day that media sampling occurred.

ATP measures total microbiological concentration found in the biofilter media. The LuminUltra^{TM} DSA adenosine triphosphate (ATP) test kit was used (LuminUltra, Fredericton, New Brunswick, Canada). ATP concentrations are expressed as ng ATP/cm^3 and the bulk densities used to convert the measured value (ng ATP/g) to volume were 1.5 and 0.8 g/cm^3 for sand and anthracite, respectively. BRP was determined as the difference in dissolved oxygen consumption before and after 5 h at 20 °C. More details about the BRP procedure can be found in Appendix B.

4.3.5 Analytical Methods for Water Samples

Water samples were collected from the inlet and the outlet of each biofilter. In the first six months of the biofilter operation, samples were collected weekly and then twice per month for the rest of the investigated period. Water samples were collected in clean glass 1 liter bottles before backwashing the biofilter. They were stored at 4°C until analysis which occurred within 24 h of sampling. The parameters monitored were TOC, DOC, UV_{254}, specific UV absorbance (SUVA = UV_{254}/DOC), pH, and turbidity. In addition some parameters were monitored only in the secondary effluent at the Waterloo WWTP labs. The methods used for all measured parameters are described in more detail in Chapter 3, Section 3.6.

4.4 Results

4.4.1 Source Water Selection and Composition

The initial step of this study involved the selection of an appropriate secondary effluent. Three secondary effluents from three different WWTPs in the Region of Waterloo (Elmira, Waterloo, and St Jacobs) were sampled and analyzed using LC-OCD. Figure 4.2 illustrate the LC-OCD chromatographs for the three secondary effluents. St. Jacobs’s secondary effluent had the lowest concentrations in all DOC fractions and biopolymers (BP) were virtually absent. This was notable in that the next phase of this research involved UF membrane fouling and biopolymers are known to be important membrane foulants. For that reason St. Jacobs’s secondary effluent was rejected as a source of secondary effluent. On the other hand, secondary effluents obtained from Elmira and Waterloo WWTPs had similar concentrations of all fractions. As there was little difference, Waterloo WWTP effluent was selected for investigation in this study because of its proximity to University of Waterloo labs where the biofiltration pilot plant was located.

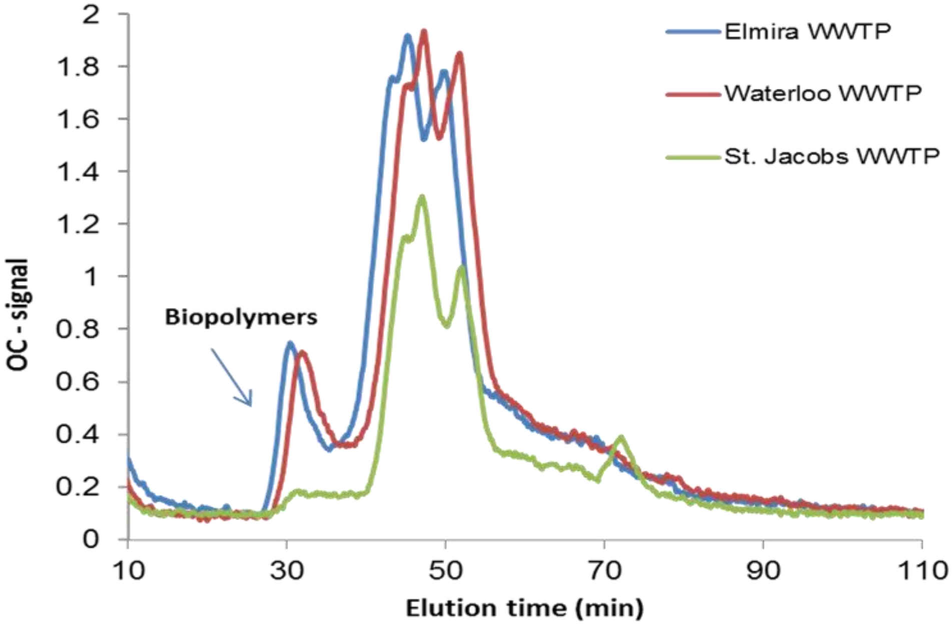


Figure 4.2 LC-OCD chromatograph for three different secondary effluents collected from three different WWTPs (Elmira, Waterloo, and St. Jacobs)

Table 4-1 Source water (Waterloo WWTP secondary effluent) quality parameters for the investigated period (Jan. 2014 to Apr. 2015)

Parameter	Unit	Average	Min	Max	Number of samples
Temperature[3]	°C	16.0 (±3.5)	10.3	25.0	41
pH[1]	---	7.5 (±0.3)	7.1	8.4	32
Turbidity[1]	NTU	4.5 (±5.6)	1.1	10.3	32
TOC[1]	mg/L	14.6 (±5.6)	5.6	24.0	16
DOC[1]	mg/L	8.9 (±1.1)	6.2	11.0	41
Biopolymer[1]	mg/L	1.3 (±0.4)	0.6	2.8	41
Humics[1]	mg/L	3.1 (±0.3)	2.2	3.6	41
UV[1]	cm^{-1}	0.138 (±0.02)	0.108	0.167	40
SUVA[1]	L/(mg/m)	1.5 (±0.2)	1.2	2.0	38
TSS[2]	mg/L	4.2 (±2.5)	1.6	12.2	44
Ammonia[2]	mg/L	20.6 (±5.8)	8.6	33.0	44
Nitrate[2]	mg/L	9.5 (±4.5)	2.0	20.8	44
Nitrite[2]	mg/L	0.7 (±0.4)	0.2	1.8	44
TKN[2]	mg/L	25.0 (±6.7)	11.9	38.0	44
Total P[2]	mg/L	0.3 (±0.1)	0.12	0.5	44

[1] Measured at University of Waterloo labs

[2] Measured at Waterloo WWTP labs

[3] Measured in field while collecting secondary effluent

This study was conducted over wide range of water temperatures (10 – 25°C) which was nonetheless relatively consistent with an average of 16.0°C ± 3.5°C. Experiments were conducted at room temperature (~23°C). The quality parameters of the selected secondary effluent monitored during the investigated period from Jan. 2014 to Apr. 2015 are presented in Table 4.1 (detailed raw data is available in Appendix C). The data show that there was no substantial variability of DOC and the major NOM fractions (biopolymers and humics) measured by LC-OCD throughout this long-term study.

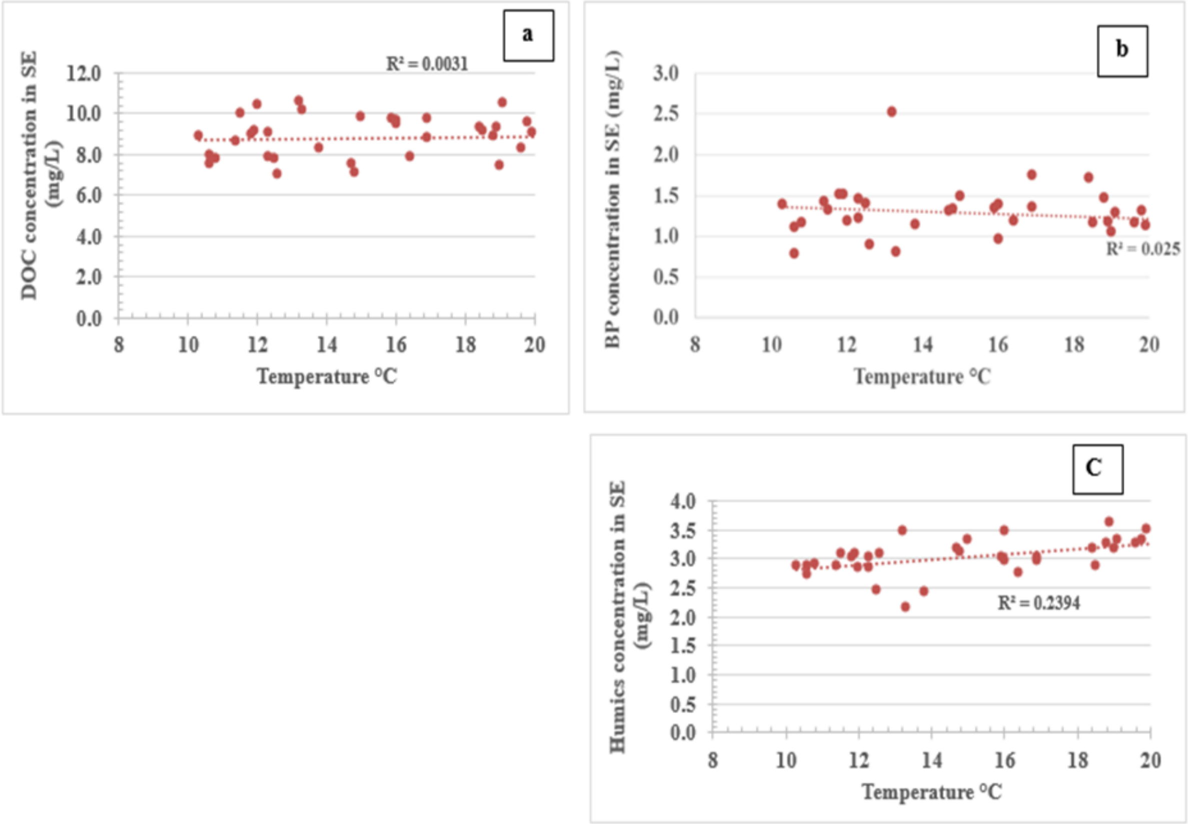


Figure 4.3 Water temperature verses a) DOC, b) biopolymer and c) humics in secondary effluent

Figure 4.3 compares DOC, BP, and humic concentrations to water temperature. There was no correlation found between water temperature and any of these parameters ($p > 0.05$, t-test). However, some studies have reported that BP concentration in secondary effluent or surface water decreased during the winter (Hallé *et al*. 2009, and Siembida-Lösch *et al*. 2015). On the other hand, some studies reported an increase in BP in secondary effluent (Zheng *et al*. 2010) or DOC in river water (Rahman *et al*. 2014) during the winter.

The LC-OCD data from the secondary effluent presented in Figure 4.4 shows that the humic substances, hydrophobic compounds with high molecular weight (1000 – 20,000 Da), made up the main fraction in all samples accounting for an average of 34% of the DOC while biopolymers, proteins and polysaccharides materials (over 20,000 Da), accounted for 18% of the DOC. The building blocks, which are the breakdown products of humic substances with molecular weight 350 – 500 Da, made up around 18% of DOC. The remaining 30% of the DOC consisted of LMW acids (16%) and LMW neutrals (14%).

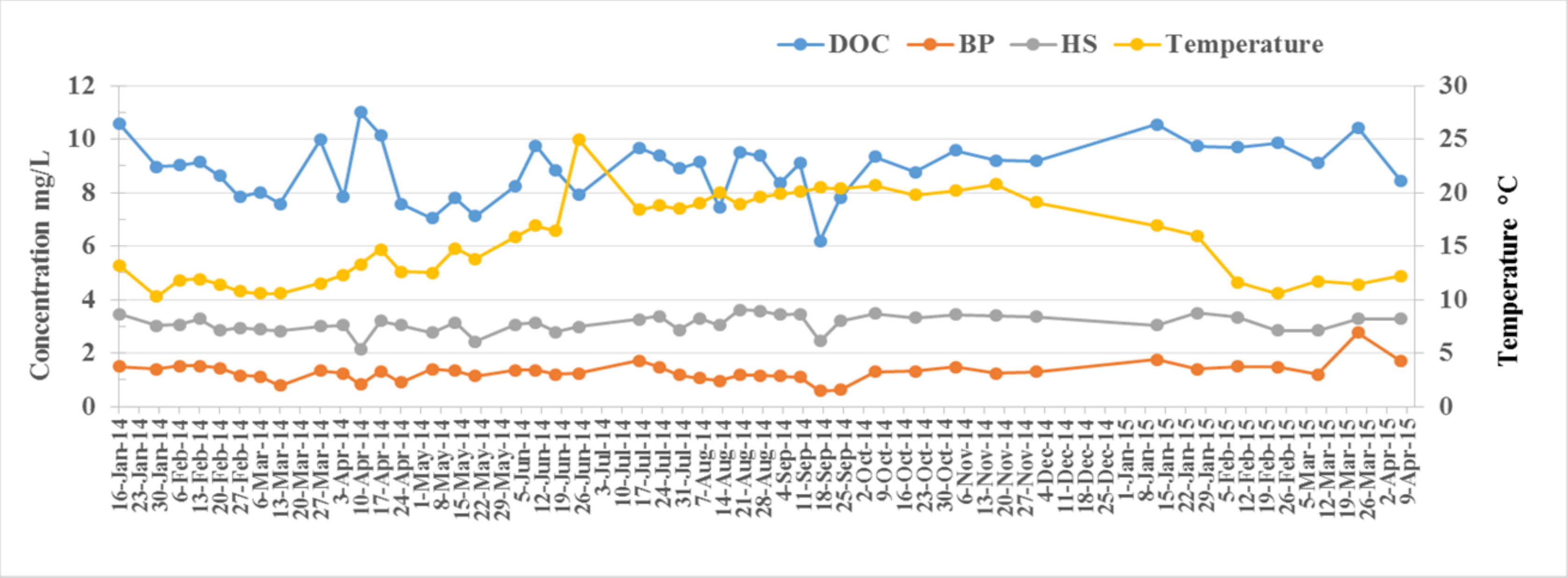


Figure 4.4 DOC, biopolymers, and humic substance concentrations in secondary effluent (Waterloo WWTP) from Jan. 2014 to Apr. 2015

The biopolymer maximum concentration is a single relatively high value (2.8 mg/L) observed on Mar. 26, 2015. The next highest concentration was 1.8 mg/L. The average BP concentration was 1.3 mg/L which is relativity high when compared with BP concentrations of secondary effluents investigated previously in the literature (Zheng *et al*. 2010, Pramanik *et al*. 2014). UV254 ranged from 0.108 to 0.167 cm^{-1} and specific ultraviolet absorbance (SUVA) values were less than 2.0 L/(m/mg). SUVA reflects the aromatic content of organic matter and the low value (< 3.0) indicates that the secondary effluent DOC was relatively hydrophilic and less aromatic (Edzwald 1993).

There was substantial variability in TOC, turbidity, nitrate, and TKN during the investigated period. Figure 4.5 plots turbidity vs. temperature during the investigated period. Higher turbidities were encountered in colder water at least in the early stage of this study.

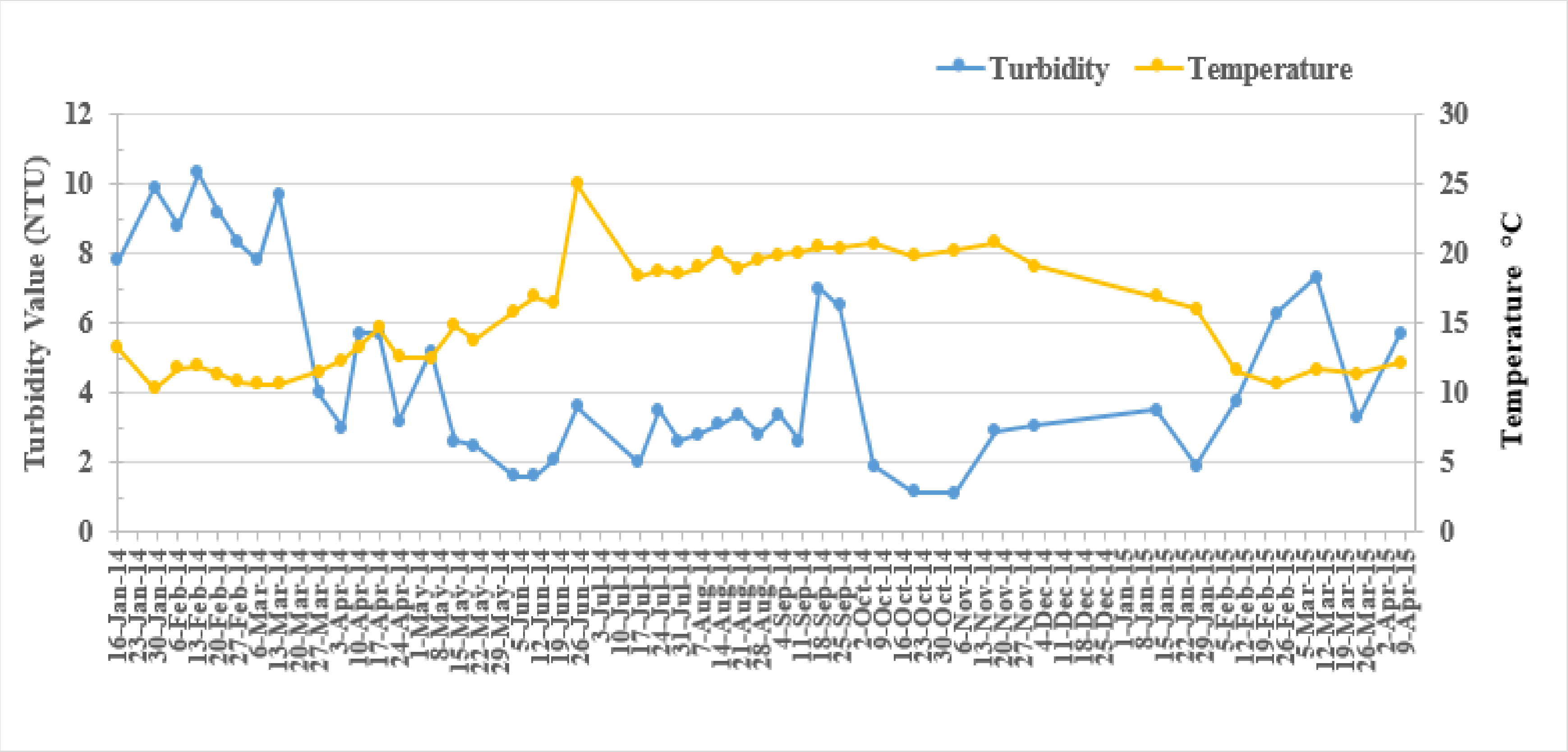


Figure 4.5 Change in secondary effluent turbidity (Waterloo WWTP) from Jan. 2014 to Apr. 2015

4.4.2 Preliminary Results-Media Type and EBCT Impact on Secondary Effluent DOC

A preliminary biofiltration set-up was constructed to investigate the impact of media type and EBCT on the secondary effluent DOC removal. Three different media were compared at two EBCTs. Figure 4.6 illustrates the impact of media type on DOC, BP, and humics removal (shown data are after 5 months of biofilters operation) at the two EBCT investigated (15 & 30 min). An improvement in DOC and BP removal was observed with increasing EBCT except in the case of the Biofilter A (BFA) (Kaldnes®). The highest BP removal was obtained by BFC (Macrolite®) which was 1.5% higher than that attained in BFB (anthracite). Statistically (paired t-test, α= 0.05) there was no difference in the performance of BFB and BFC in BP removal. For humics removal, increasing EBCT improved humics reduction except in the case of BFA. The three biofilters were not significantly different (using paired t-test, α= 0.05). The maximum DOC and BP removal achieved (15%) was slightly lower than the values reported in the literature despite the fact that EBCTs were chosen based on literature values. Due to the high BP concentration in the selected secondary effluent, these findings suggested that an EBCT longer than 30 min would be desirable. A decision was made to increase the EBCT to 60 min for the next phase of biofiltration experiments, recognizing that this time was relatively long but should allow effects of treatment to be seen.

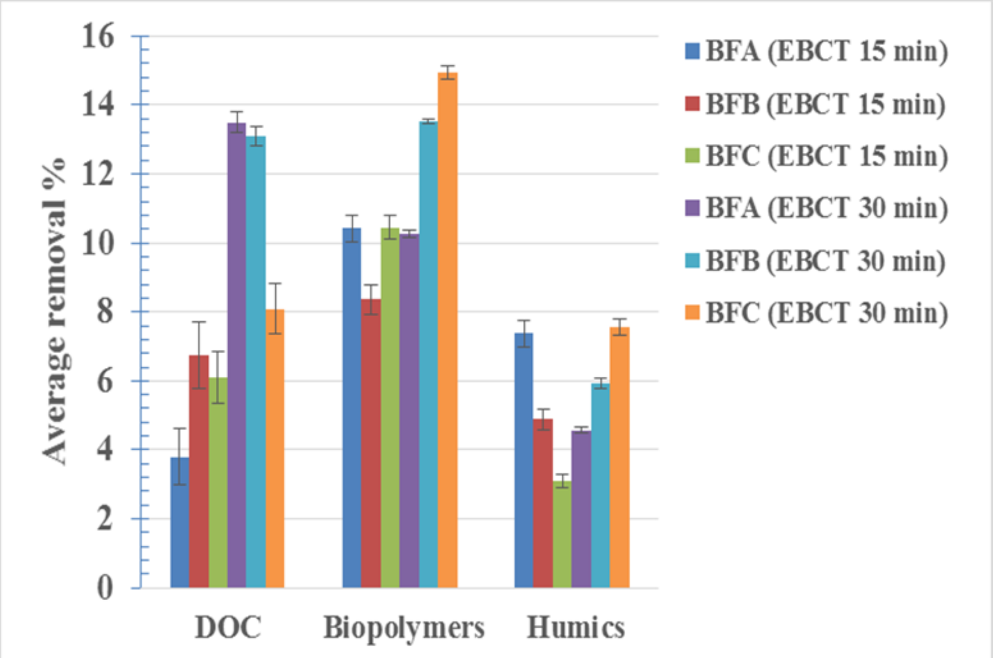


Figure 4.6 Effect of media type and biofilter EBCT on DOC, biopolymers, and humic substance removal, n=5 for 15 min EBCT and n=3 for 30 min EBCT. The error bars represent one standard deviation

4.4.3 Biofiltration performance

Based on the data obtained from the preliminary biofiltration set-up, a new biofiltration pilot plant was constructed to compare two different media (sand, anthracite) at an EBCT of 60 min (HLR = 0.75 m/h). Although the biopolymer removal by the ceramic media (Macrolite®), was comparable to that of anthracite, it was decided to go forward with anthracite as Macrolite® could not be commercially acquired following the preliminary experiments. This pilot was used for the remainder of this study. The operation and analyses were the responsibility of the author alone, with some assistance provided by visiting students or undergraduates.

4.4.3.1 Biological Analyses

In general, the removal of organics through biofilters may be attributable to adsorption or biodegradation. The two media compared in this study were sand and anthracite where adsorption is for the most part irrelevant as can be the case when using GAC. An acclimation period is required for the biological filters to allow the microorganisms present in feed water to attach and colonize the media to produce a biofilm. To monitor the growth of microorganisms, ATP measurements were used to quantify the total biomass at three different depths in the two biofilters. ATP was measured from the beginning until the end of the investigated period (Jan. 2014 to Apr. 2015). Typical acclimation periods (for drinking water biofilters) vary from 2 to 4 months based on feed water characteristics and operating conditions (Hallé *et al*. 2009; Rahman *et al*. 2014). In this study, the period of acclimation was found to be about 4 months (see figures in Appendix D).

Figure 4.7 illustrates the average ATP values per cm^3 of dry media at three different media depths in the two biofilters (sand and anthracite) (see Appendix C for raw data and ATP calculations). The average ATP concentrations observed in this study at the top of the two biofilter were 525 ± 184 and 416 ± 191 ng ATP/cm^3 for sand and anthracite, respectively. As would be expected, higher ATP concentrations were observed at the top of the two biofilters and the concentrations decreased with depth (confirmed statistically by paired t-test, $\alpha = 0.05$). The average ATP concentrations in the sand biofilter were 525 ± 184, 347 ± 190, and 306 ± 170 ng ATP/cm^3 at the top, middle, and bottom, respectively. For the anthracite biofilter the concentrations were 416 ± 191, 262 ± 172, and 195 ± 123 at the top, middle, and bottom, respectively. These data showed that sand biofilter was biologically more active than the anthracite biofilter (in terms of ATP measurement) and this result was confirmed statistically (paired t-test, $\alpha = 0.05$). Potential reasons for this difference are discussed later.

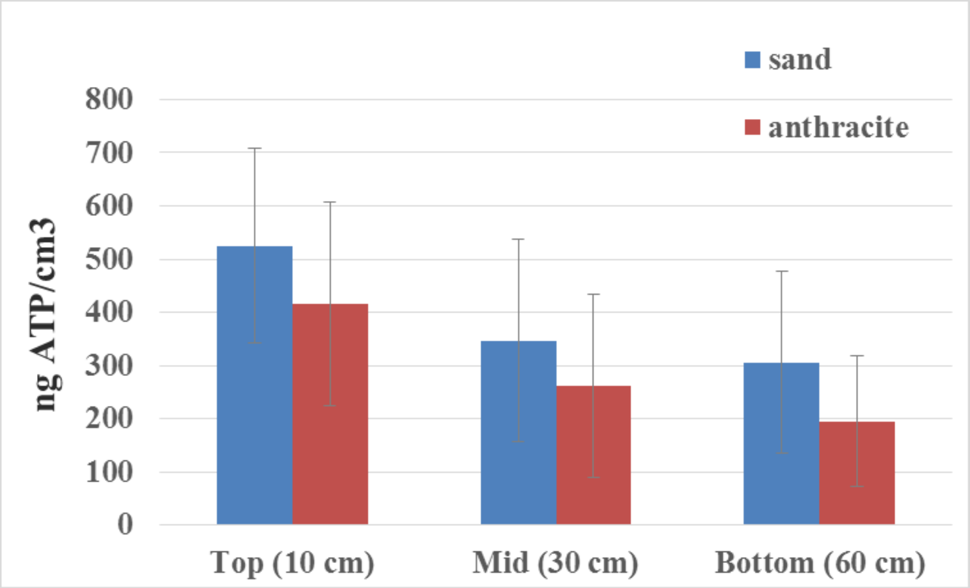


Figure 4.7 ATP average values for sand (BF1) and anthracite (BF2) through the media depth (depths in brackets as measured from the media surface). Investigation period from Jan. 2014 to Apr. 2015, n = 35. The error bars represent one standard deviation

The decrease in ATP concentrations through the biofilter were likely attributable to a reduction in the available organic substrate through the biofilter (Velten *et al*. 2011). The same observation was obtained by Zhang *et al*. (2010) in a drinking water GAC biofilter. The ATP concentrations they observed were 512, 497, and 468 ng ATP/cm^3 in top, middle, and bottom of a GAC biofilter, respectively. Rahman (2013) also observed a decrease in ATP concentration in a pilot-scale anthracite/sand dual biofilter treating surface water through biofilter. However, ATP concentrations observed by Rahman 2013 (at 163 and 148 ng ATP/cm^3 at the top of two anthracite/sand biofilters) were substantially lower than those observed in the current study. This may be related to the amount of nutrients available and/or feed water composition (surface water vs. secondary effluent in the current study). On the other hand, some previous studies have reported no change in ATP concentrations through the biofilter depth (Evans *et al.* 2013) while still others have reported an increase (Hallé *et al.* 2009; Velten *et al.* 2011).

Pharand *et al.* (2014) preformed a survey and comparison of available data on ATP in drinking water biofilters and factors affecting ATP concentrations. The authors mentioned that media type may impact the ATP concentrations but commented that there was still not enough data available in the literature to make any definitive conclusions. In the current study, a comparison between sand and anthracite as biofilter media was conducted. Higher concentrations of ATP were observed in the sand biofilter vs. the anthracite biofilter at the three sampling depths. This result was confirmed statistically with a paired t-test ($\alpha = 0.05$). The difference in the attached biomass in the sand and anthracite biofilters is attributable to differences in effective size (and as such in available surface in comparable volumes). In this case the sand grains were about half the diameter of the anthracite (0.5 mm verses 1.0 mm). Biomass results (measured as ATP) was normalized to relative surface area by assuming spherical shape of sand and anthracite particles and same porosity values (0.3) (calculations were available at Appendix J). Normalized data showed that ATP concentrations in each cm^2 of the anthracite surface were higher than those in the sand at the same comparable depth. Average normalized ATP concentrations in the top, middle, and bottom of the anthracite biofilter were 9.8, 6.0, and 4.6 ng ATP/cm^2, respectively, while the concentrations at the comparable depths of the sand biofilter were 6.2, 4.2, and 3.6 ng ATP/cm^2. Surface properties of the media such as roughness and charge may also play a role in biomass attachment. A similar observation was obtained by Wang and Summers (1996) where higher attached biomass (as measured by phospholipid concentration) was found at the top of a biofilter containing sand vs. a parallel biofilter containing anthracite. However, Magic-Knezev and Van der Kooij (2004) reported that ATP concentrations at the top of a sand biofilter were lower than at the top of a similar anthracite biofilter which operated in the range of slow sand filtration.

Biomass activity as measured by BRP was also a tool used in this research. It is a relatively easy method developed by Urfer and Huck (2001) which is based on dissolved oxygen consumption by aerobic respiration associated with the biodegradation of organic compounds. Average BRP and ATP concentrations are compared in Figure 4.8. These data were collected in the period from June 2014 to February 2015 after the two biofilters had reached steady-state conditions. The results of the biomass activity measured as BRP shown in Figure 4.8 (b) were in agreement with the data obtained from ATP measurements shown in Figures 4.7 and 4.8 (a). The data indicate that attached biomass at the top of the biofilter was not only higher in quantity than that in deeper locations but also more active which was reflected by more DO consumption at the top of the biofilter. The reduction of DO concentration was a result of the biodegradation of organic content by active biomass attached on biofilter media. Therefore, the biodegradation of organic material was mostly occurring at the top of the biofilter. That data also confirm that sand, under the investigated conditions, was biologically more active than the anthracite. Based on these results, it is generally expected that sand (due to higher surface area in comparable volumes) would be a better than anthracite for biologically improving secondary effluent quality.

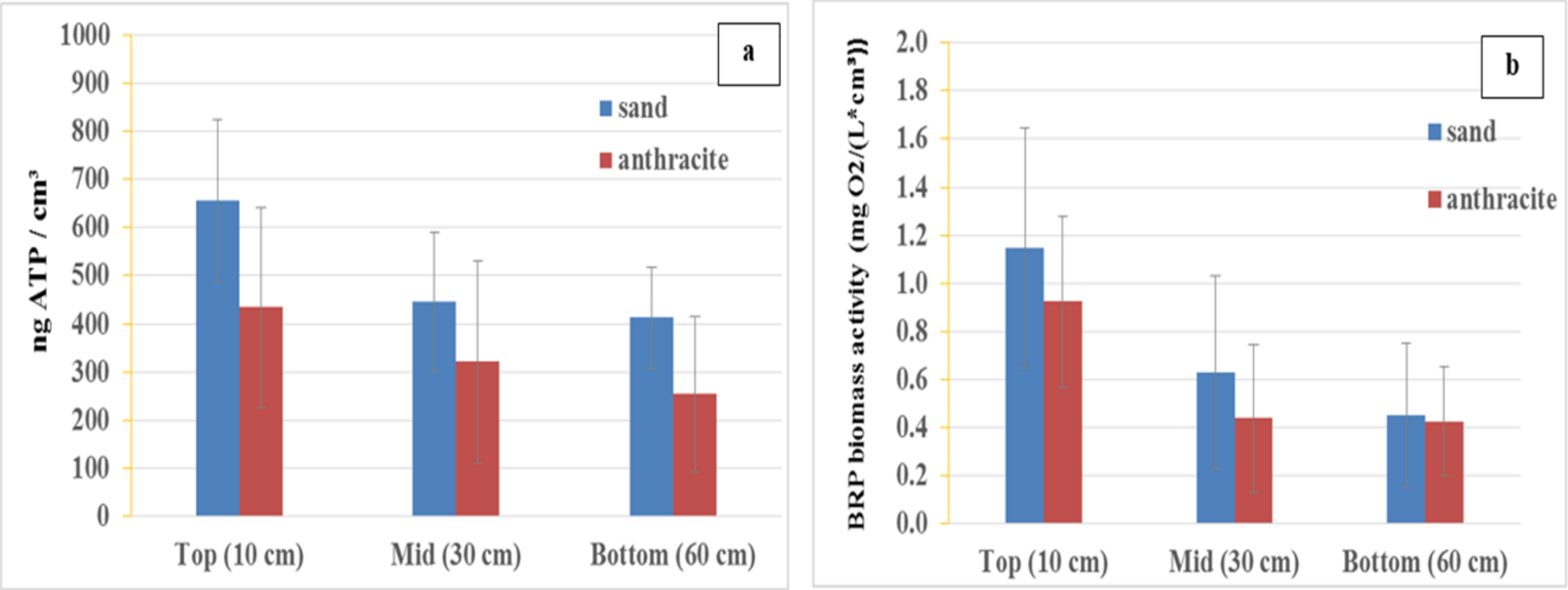


Figure 4.8 Average ATP (a) vs. biomass respiration potential (BRP) dissolved O2 concentrations (b) for sand vs. anthracite biofilter media determined at 20°C for 5 h and measured on the same days, n = 6

4.4.3.2 Biofilter Impact on Secondary Effluent Quality

The investigation of biofiltration as an advanced treatment method for secondary effluent was carried out from Jan. 2014 to Apr. 2015. In this period the two biofilters (sand vs. anthracite) were operated under identical conditions with a 60 min EBCT corresponding to an HLR of 0.75 m/h. The biofilters were backwashed once per week from Jan. 2014 until Jun. 2014. The backwashing was then switched to a twice weekly frequency until the end of the investigated period. The two biofilters were brought on line early in Jan. 2014 and steady state conditions were reached after about 4 months of operation (based on ATP measurements). Table 4.2 summarizes the average water quality parameters for secondary effluent, BF1 (sand) effluent, and BF2 (anthracite) effluent. Biofiltration improved the secondary effluent quality by reducing organics concentration and particles. The average TOC removals in BF1 and BF2 were 14% and 11%, respectively. Also, 18% and 26% reduction in DOC and BP, respectively, were observed through BF1 while lower reductions (16% and 19%) of DOC and BP, respectively, were observed through BF2. The differences between BF1 and BF2 in reducing DOC and BP were statistically significant (paired t-test, $\alpha = 0.05$). Figures 4.9 and 4.10 illustrate the DOC and BP concentrations in secondary effluent, and BF1 and BF2 effluents during the investigated period. While humics make up the main DOC fraction in secondary effluent they were not well removed through biofiltration. This has been observed previously for drinking water applications (e.g. Hallé *et al.* 2009; Rahman *et al.* 2014). The average humics removals through BF1 and BF2 were 14% and 11%, respectively. Small decreases in UV_{254} absorption through the biofilters confirm the low removal of humic material.

Table 4-2 Biofiltration impact on secondary effluent characteristics1

Parameter	Unit	Secondary effluent (BF feed)	BF1 (sand) effluent	BF2 (anthracite) effluent	Number of samples
pH	---	7.6 ± 0.3	7.6 ± 0.2	7.5 ± 0.2	32
Turbidity	NTU	4.5 ± 5.6	0.7 ± 0.3	1.0 ± 0.4	32
TOC	mg/L	14.6 ± 5.6	9.9 ± 2.9	10.0 ± 3.5	18
DOC	mg/L	8.9 ± 1.1	7.3 ± 0.9	7.6 ± 0.8	41
Biopolymers	mg/L	1.3 ± 0.4	0.8 ± 0.2	1.0 ± 0.2	41
Humics	mg/L	3.1 ± 0.3	2.7 ± 0.3	2.8 ± 0.3	41
Building blocks	mg/L	1.2 ± 0.2	1.1 ± 0.1	1.0 ± 0.1	41
LMWn	mg/L	1.7 ± 0.3	1.3 ± 0.2	1.3 ± 0.3	41
LMWa	mg/L	0.30 ± 0.1	0.25 ± 0.1	0.24 ± 0.1	41
UV	cm^{-1}	0.143 ± 0.02	0.122 ± 0.010	0.124 ± 0.013	40
SUVA	L/(mg/m)	1.60 ± 0.30	1.68 ± 0.20	1.60 ± 0.30	38

[1] Concentrations reported as mean ± standard deviation

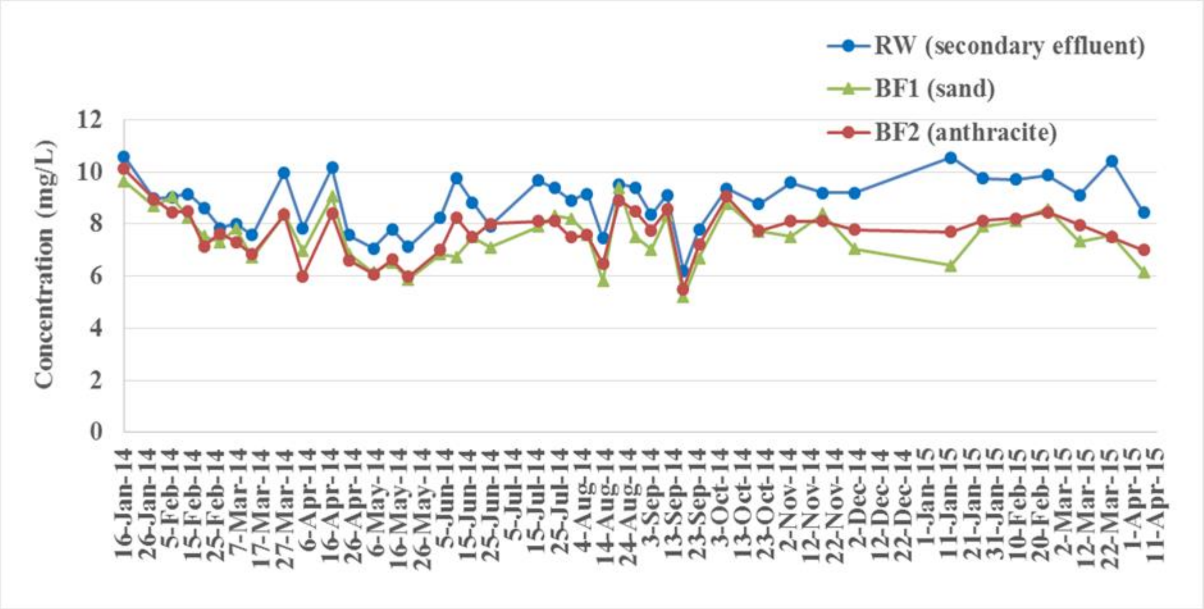


Figure 4.9 DOC concentration in secondary effluent and biofilter effluents over the period investigated

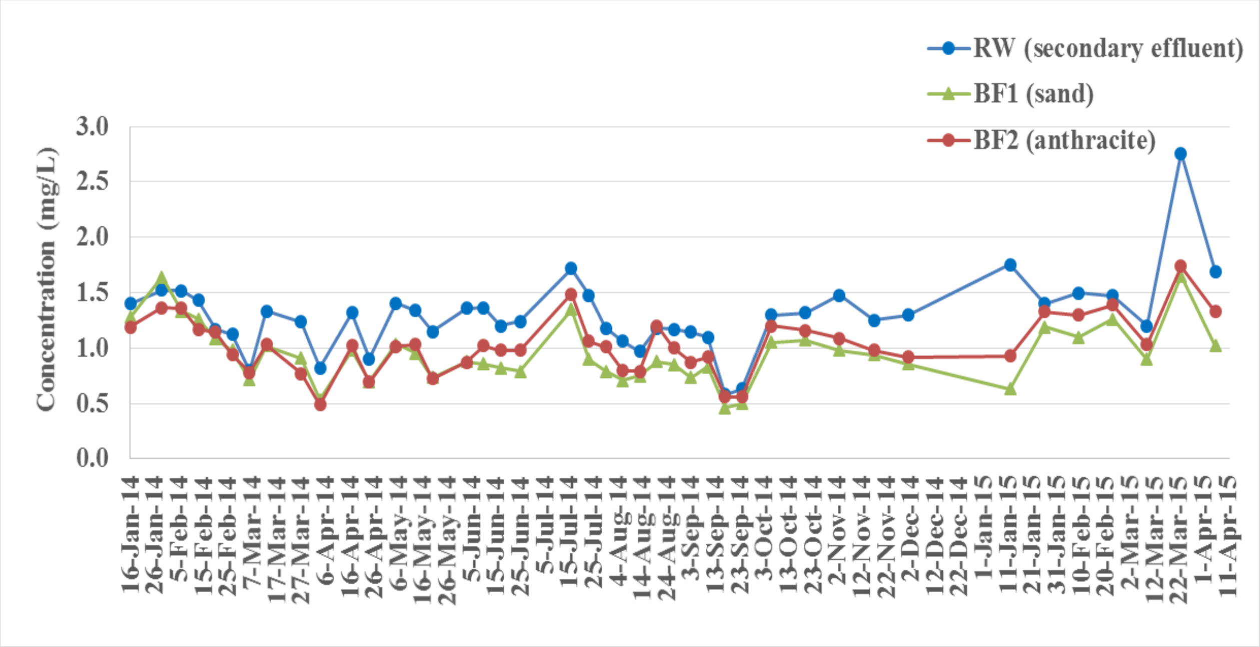


Figure 4.10 BP concentration in secondary effluent and biofilter effluents through the period investigated

There was a very small increase in SUVA through BF1 from 1.60 to 1.68 L/(mg/m) which is statistically (paired t-test,α = 0.05) not significant. Since the removal of dissolved substances through filters cannot occur by straining, their removal was attributed to biodegradation by attached biomass.

Figure 4.11 shows the turbidity values in secondary effluent and after the biofilters. The average removal of turbidity achieved by BF1 and BF2 was 76% and 70%, respectively. Statistically (paired t-test, α = 0.05) there was no difference between BF1 and BF2 in the reduction of turbidity or other parameters monitored in this study except for DOC and BP (i.e. those in Table 4.2).

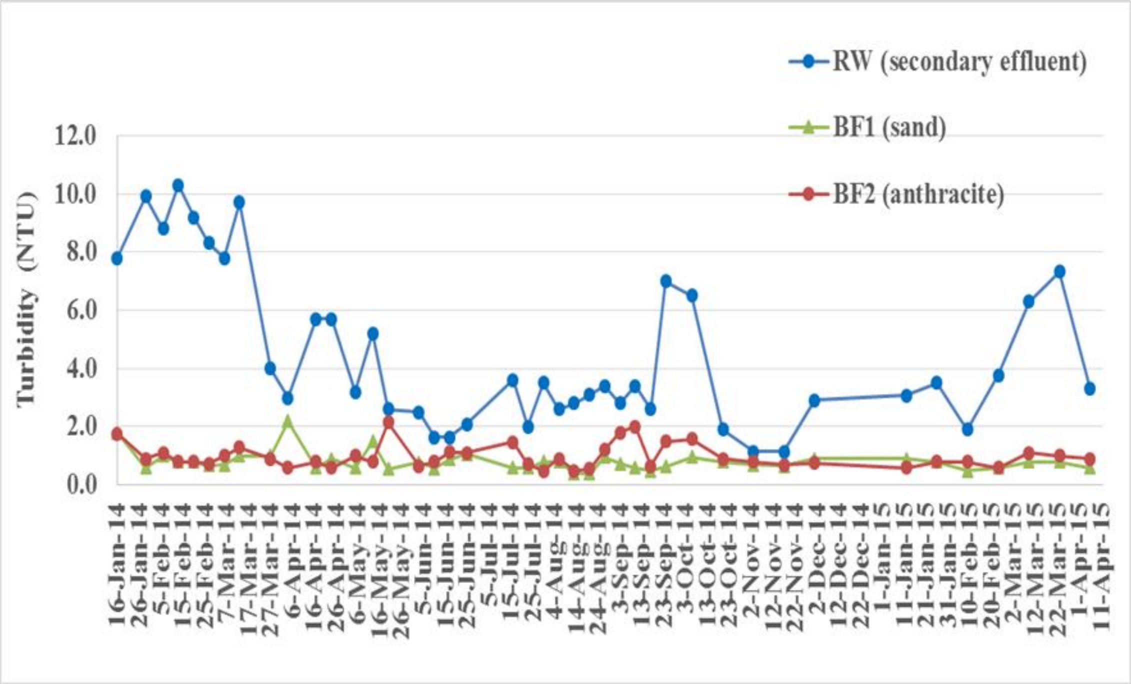


Figure 4.11 Turbidity in secondary effluent and biofilter effluents throughout the period investigated

Figure 4.12 illustrates the concentrations of DOC fractions based on molecular weight distribution as determined by LC-OCD for secondary effluent and effluents from BF1 and BF2. There was a reduction in DOC and NOM fractions through the biofiltration process and in general the lowest concentrations were measured in BF1 effluent. Biopolymers were the most substantially removed fraction through the biofilters. The average concentration of biopolymers in the effluents of BF1 and BF2 were 0.8 and 1.0 mg/L, respectively, whereas the average concentration in secondary effluent was 1.3 mg/L that is relatively higher than those values reported in literature (maximum reported biopolymer value in secondary effluent was 0.7 mg/L by Zheng *et al.* 2010). In the current study, the Waterloo WWTP raw sewage was analyzed by LC-OCD and the biopolymer concentrations was around 2.2 mg/L (Table 4.3). Although humic substances made up the largest fraction of the DOC of secondary effluent, this fraction was not readily biodegradable and not effectively removed through biofilter (in agreement with Zheng *et al*. 2010). In some instances, there was an increase in building block compounds (Appendix C), which is attributed to the breakdown of high molecular weight fractions (BP and HS) during the biodegradation process. Good removal of LMWn and LMWa was achieved through the biofilters due to the high biodegradability of those compounds (Huber *et al*. 2011).

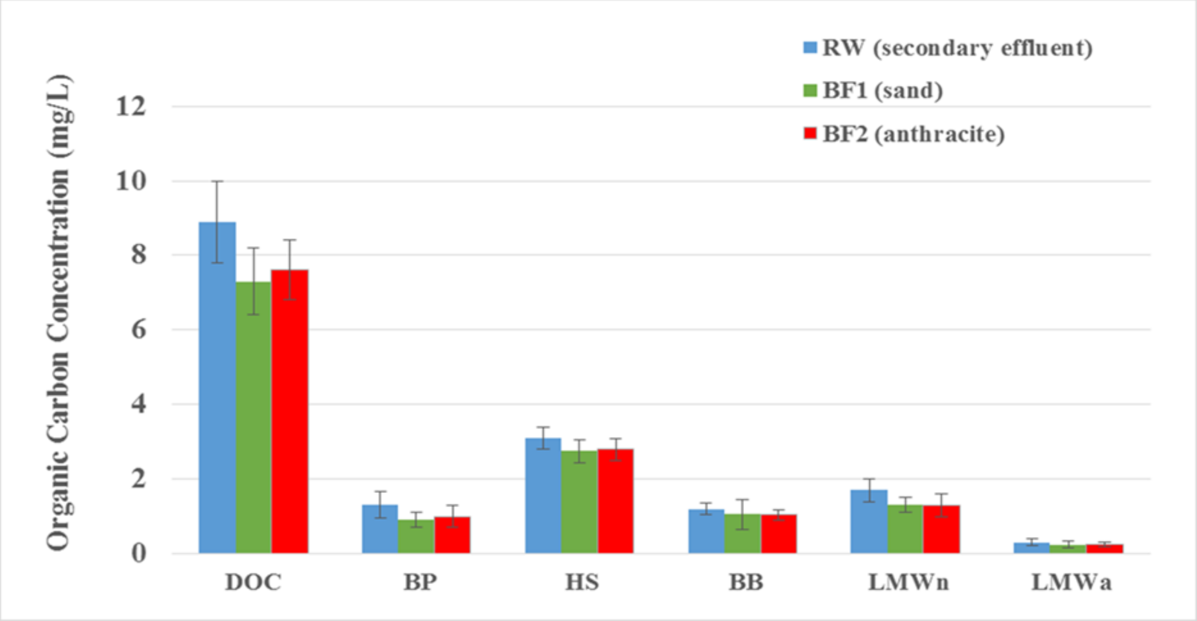


Figure 4.12 Average DOC and NOM fraction concentrations in RW (secondary effluent), BF1, and BF2 effluents (n = 41)

Table 4-3 LC-OCD data for the raw sewage of the Waterloo WWTP

Date	**DOC**	**BP**	**HS**	**BB**	**LMWa**	**LMWn**
	Concentration mg/L					
June 24, 2015	36.8	2.25	6.5	5.9	21.4	0.8
June 26, 2015	34.2	2.22	6.4	5.7	18.7	0.9

Figure 4.13 compares BP concentrations before and after biofiltration. There was a positive correlation between BP concentration removed through BF1 and BF2 and BP concentration in the feed water. Al ($p < 0.001$, t-test) though there is a reasonable correlation, it is improved by the two higher influent values in the upper right of the figure. A similar finding was reported by Rahman et al. (2014) in an investigation of river water with a relatively low BP concentration (0.08 – 0.17 mg/L). Zheng et al. (2010) found that lower BP concentrations in secondary effluent led to higher percentage removal of BP through slow sand filtration. This difference in reported results may be attributable to differences in operating conditions (e.g. EBCT and temperature) or feed water composition (river water vs. secondary effluent).

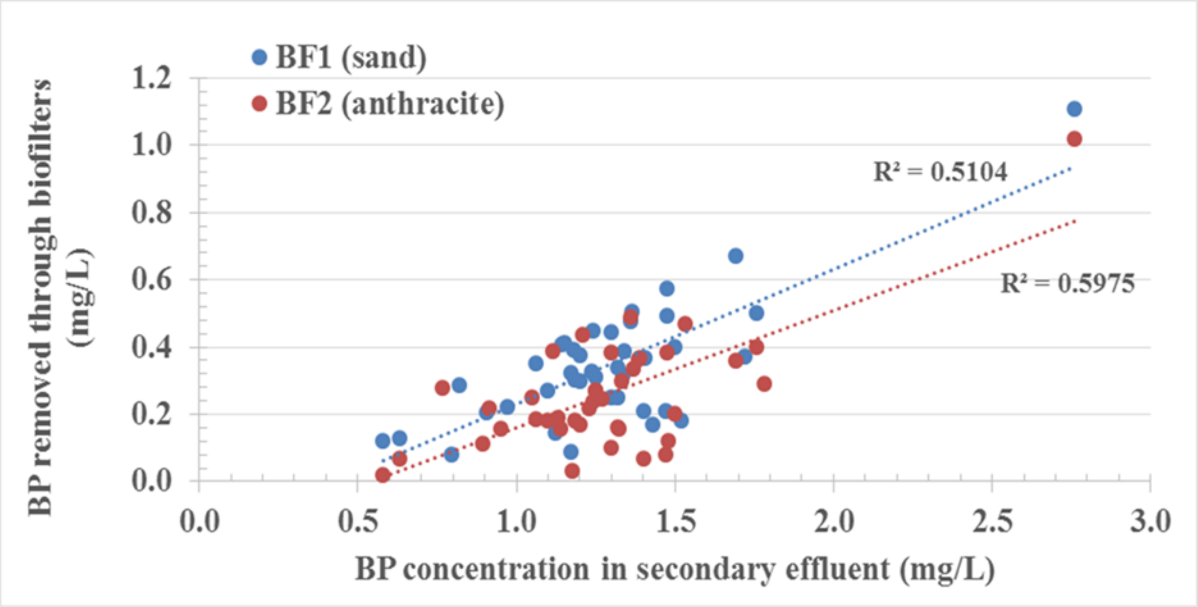


Figure 4.13 Biopolymers removed through biofilters vs. biopolymer concentrations in secondary effluent

4.4.3.3 Relationship between ATP and Biofilter Performance

In this study, higher ATP concentrations were observed in BF1 (sand) than in BF2 (anthracite) throughout the media depth and a higher organic removal was obtained by BF1. However, as shown in Figure 4.14 a and b, the removal of DOC and BP through BF1 and BF2 was not correlated with viable attached biomass measured (at least as measured as ATP). Most of the recently published studies reported that there was no relationship between biomass quantifications measured as ATP and biofilter performance (Hallé *et al*. 2009; Evans *et al*. 2013; Pharand *et al*. 2014; Siembida-Lösch *et al*. 2015; Wang 2014). Other studies have also reported that there was no relationship between biomass quantity measured by the phospholipid method and biofilter performance as measured by the removal of biodegradable organic matter (BOM) (Boon *et al*. 2011, and a review article by Huck and Sozański (2008)). Limited studies (Seger and Rothman 1996, Lauderdale *et al.* 2012) have reported an improvement in drinking water biofilter performance when ATP concentrations increased but that these improvements were not always sustained. The difference between operating conditions, especially temperature, feed water characteristics, and methods used to quantify biomass or organic matter may lead to conflicting observations. As such, additional studies are required to compare biomass quantity estimates with biofilter performance.

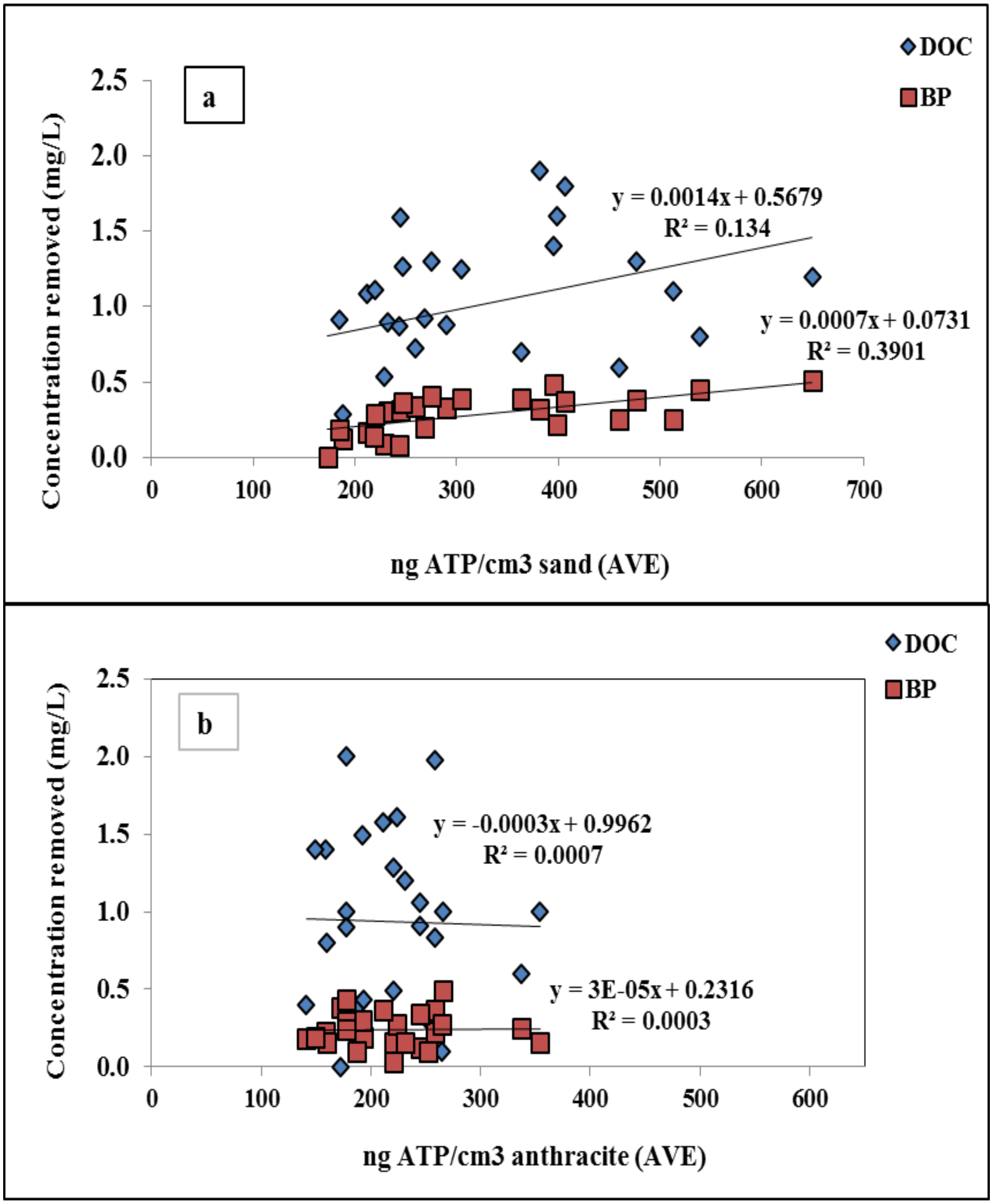


Figure 4.14 Relationship between DOC and BP concentrations removed and average ATP concentration measured in a) BF1 (sand) and b) BF2 (anthracite)

The nutrient content of biofilter feed water may impact performance and biomass growth. In this study there was no correlation between ATP concentrations measured in BF1 (sand) or BF2 (anthracite) with TKN and total phosphorus in secondary effluent (Figures 4.15 and 4.16). This confirms that those parameters were not growth-limiting nutrients for the biofilters in this study under the investigated conditions.

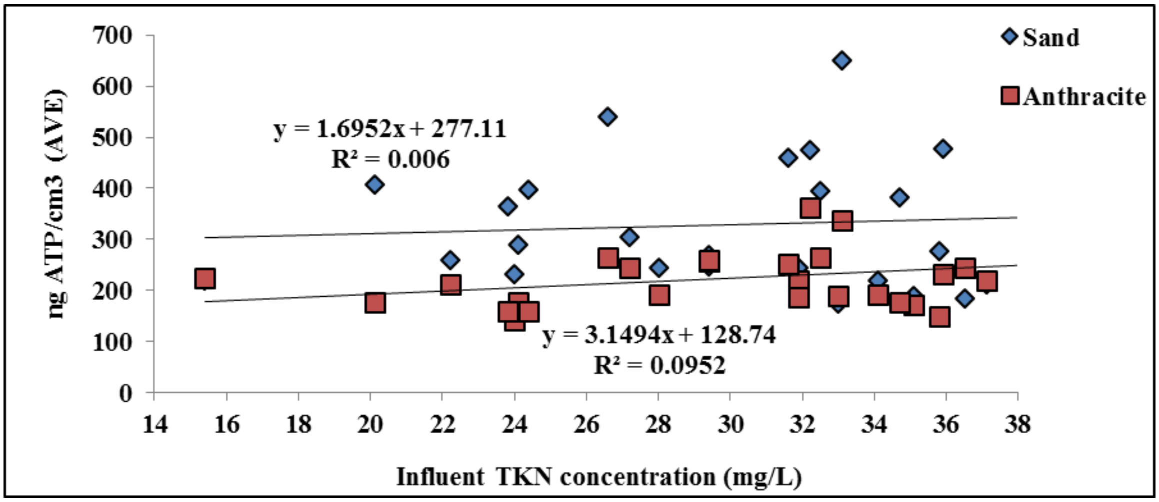


Figure 4.15 Correlation between ATP concentration in BF1 (sand) and BF2 (anthracite) and TKN concentration in secondary effluent

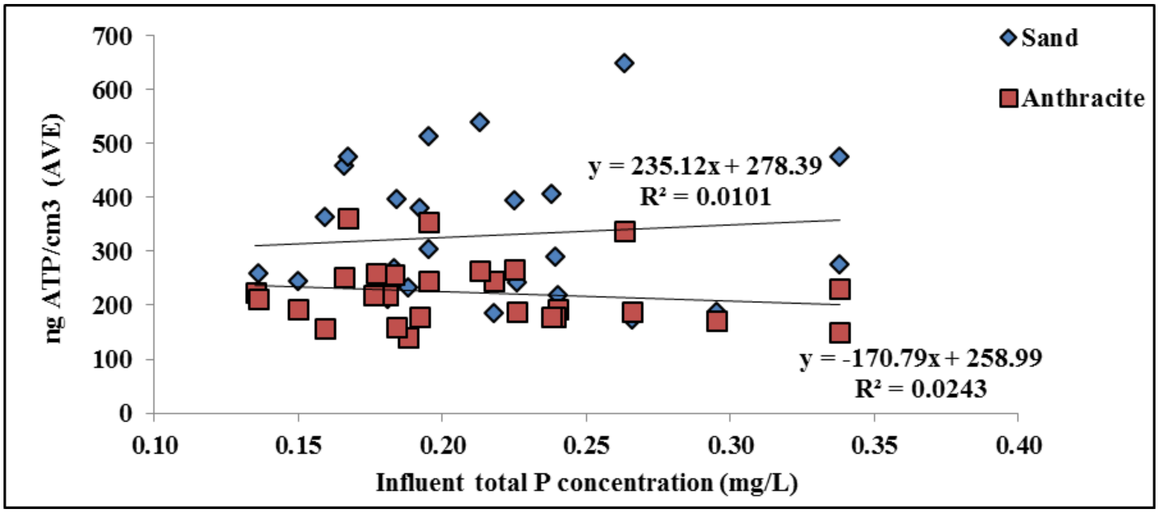


Figure 4.16 Correlation between ATP concentration in BF1 (sand) and BF2 (anthracite) total P concentration in secondary effluent

It is well known that the growth rate of biomass and attachment kinetics decrease at cold temperatures (Huck et al. 2000). Hence, it is expected that biomass quantity would be higher during the summer. However, previous studies have reported that there was no change in ATP concentrations in biofilters over a high range of investigated temperature (Evans *et al.* 2013, Pharand *et al.* 2013, and Rahman 2013). Others (Huck *et al.* 2000 and Hallé 2009) reported a reduction in DOC removal through biofilter when temperature decreased due to decrease in biomass activity. In the current study, there was no correlation between ATP concentrations and temperature can be addressed be since biofilters were operated at constant temperature. Also, there was no significant correlation between the percentage removal of biopolymer and water temperature at the treatment plant (Appendix D). Because the biofilters were operated at a constant temperature (23°C) during the investigated period, this would suggest that there were not substantial changes in the character of the biopolymers throughout the year.

4.5 Conclusions

Biofiltration was investigated as an advanced method for secondary effluent treatment. Two biofilters, each containing 0.75 m of different media (sand and anthracite) were operated at an HLR of 0.75 m/h for 16 months from January 2014 to April 2015. Under the conditions investigated the following can be concluded:

- There was no substantial change in the organic composition of the investigated secondary effluent over the length of study. There was some variability in turbidity with higher values being observed at colder temperatures. The temperature at the time of secondary effluent collection ranged from 10 to 25°C.

- Based on LC-OCD analysis of secondary effluent obtained from the Waterloo WWTP, humic substances made up the main fraction in all samples, accounting for an average of 34% of the DOC while biopolymers accounted for 18% of the DOC. The average concentrations of humic substances and biopolymers were 3.1 and 1.3 mg/L, respectively. This secondary effluent had a high biopolymer content compared to values reported in other studies. The reason for this is unknown but it is important to take this into account when analysing the findings of this study.

- A preliminary investigation revealed that media type and EBCT impacted the performance of biofiltration on DOC and biopolymer removal. Due to higher BP concentrations in this secondary effluent, higher EBCTs were required.

- As expected, the highest concentrations of ATP were observed near the surface of the media in both biofilters. The biomass concentration decreased through bed depth and the lowest biomass concentrations were measured at the bottom of the two biofilters. The concentration of biomass attached to sand was higher than that attached to anthracite at comparable media depths. This was due to the higher external surface area available for biomass attachment (lower effective size of sand) and also due to surface properties such as charge.

- The BRP and ATP methods yielded similar information, and maybe used as relatively simple ways to estimate biomass activity. Higher DO consumption was observed at the top of the both biofilters indicating that biodegradation occurred mostly in the top layer of the biofilters. This would be expected due to more availability of biodegradable organics in the top of the biofilter.

- Biofiltration improved secondary effluent characteristics by reducing organic compound concentrations and turbidity. The average removals of TOC and DOC through BF1 (sand) were 14% and 18%, respectively. Lower removals of TOC (11%) and DOC (16%) were observed in BF2 (anthracite). The average turbidity reductions achieved by BF1 and BF2 were 76% and 70%, respectively, and the biofilters were able to reduce turbidity to less than 1.0 NTU independently of influent values.

- Under the investigated conditions in this study, biopolymers were the largest DOC fraction removed through the biofilter. The average removals of biopolymers through BF1 and BF2 were 26% and 19%, respectively. Although humic substances were the predominant fraction in the investigated secondary effluent, they were not efficiently removed through biofiltration. The percentage removal of biopolymers through the biofilters was correlated with influent concentration to biofilter.

- As a biofilter media, sand was statistically significantly better than anthracite in terms of DOC and biopolymer removal. The reason for this is considered to be the higher available surface area for biomass attachment in sand as biofilter than anthracite. There was no difference between the media types for the removal of the other parameters monitored in this study.

- Finally, no seasonal impact on biofilter performance was observed during the period investigated.

Chapter 5

Reducing Polymeric Ultrafiltration Membrane Fouling By Biological Filtration for Secondary Effluent Treatment

Summary

Recent drinking water treatment studies have reproducibly demonstrated that biofiltration can reduce UF membrane fouling. However, too few studies have been published on the biofiltration/UF membrane combination for the treatment of secondary effluent to draw definitive conclusions about its value for such waters. The aim of this study was to investigate the viability of biofiltration as a UF membrane pre-treatment for secondary effluent treatment. Two parallel pilot-scale biofilters, each with different media (sand vs. anthracite), were operated under identical conditions at an HLR of 0.75 m/h. The ultrafiltration fouling experiments were conducted at bench-scale at a constant flux of 33 L/m^2 h (LMH). Liquid chromatography–organic carbon detection was used to characterize EfOM. Biofiltration removed the biopolymer fraction (polysaccharides and proteins) of the EfOM and associated particles from the secondary effluent, while there was very little removal of humic substances. Feeding the UF membrane with biofilter effluent substantially reduced both hydraulically reversible and irreversible fouling up to 60% and 80%, respectively. Effluent from the biofilters containing sand as a media was somewhat better than the effluent from the anthracite media for limiting the development of both types of fouling.

5.1 Introduction

While biological treatment processes are capable of substantial removal of organics found in wastewater, reusing secondary effluent without some form of advanced treatment is not recommended (Zhu *et al*. 2011). Low pressure membrane filtration is an efficient process for producing high quality water that may be suitable for directly reusing in some applications, or be fed to downstream processes for even further treatment for other higher quality reuse applications. Interest in the application of low pressure membranes as an advanced wastewater treatment has increased the number of research initiatives being conducted and reported upon (Haberkamp *et al*. 2008; Zheng *et al*. 2010; Filloux *et al*. 2012; Pramanik *et al*. 2014). Despite the expansion in the use of membrane technology in water and wastewater production, fouling is still an important shortcoming that could impede the development of this technology and make it less competitive with alternatives.

Fouling takes place due to the accumulation of compounds found in water on membrane surfaces and within pores (Al-Amoudi and Lovitt 2007). Reversible fouling is caused by particle deposition on membrane surfaces, and water production can be recovered by hydraulic backwashing, while irreversible fouling is primarily caused by the adsorption of organic material in membrane pores and water production can only be recovered through chemically cleaning the membrane. It has been previously suggested that humic substances substantially contribute to membrane fouling (Jucker and Clark 1994; Shon *et al*. 2006b). However, most recent studies have reported that the biopolymer fraction is responsible for polymeric ultrafiltration membrane fouling (Fan *et al*. 2008; Zheng *et al*. 2010; Peldszus *et al*. 2011; Filloux *et al*. 2012; Rahman *et al*. 2014). Due to the complex composition of effluent organic matter (EfOM), which varies from location to location, complicated fouling mechanisms, and conflicting observations related to the identification of foulants of low pressure membranes, further investigation is required.

Fouling affects membrane filtration adversely by reducing permeate flux, increasing energy requirements, decreasing intervals between cleaning, and reducing membrane life (Hatt *et al*. 2011). Therefore, mitigation and control of membrane fouling is an important consideration in the effective operation and economic feasibility of the technology. To reduce the concentration of organic foulants in treated wastewater, several pre-treatment processes have been investigated. Biological filtration processes have been used in wastewater treatment for microorganism reduction to improve disinfection (Metcalf and Eddy 2007) and the past couple of decades, biofilters are being incorporated into drinking water treatment with the aim of reducing disinfection by-product formation, oxidant demand, and microbial regrowth in distribution systems. Biofiltration has some benefits which make it safer and more environmentally-friendly than existing treatment technologies including no chemical addition and less sludge production (if upstream coagulation not practiced). Biofiltration has only relatively recently been investigated as a low pressure membrane pre-treatment for drinking water production (Peldszus *et al*. 2011, Filloux *et al*. 2012, and Rahman *et al*. 2014). In those studies, biofiltration was investigated in dual media form (anthracite over sand) at short EBCTs (5 – 10 min), corresponding to hydraulic loading rates on the order of 5 m/h. Zheng *et al*. (2009) investigated biofiltration as a pre-treatment to ultrafiltration (UF) for secondary effluent treatment with sand as media. In their study biofiltration was operated at slow sand filtration hydraulic loading rates (0.25 and 0.5 m/h). Biofiltration has also been investigated as a microfiltration (MF) pre-treatment for treating secondary effluent at an empty bed contact time of 40 min corresponding to a hydraulic loading rate of 0.2 m/h (Pramanik *et al*. 2014), where biological active carbon (BAC) was employed to provide a higher effective surface area for biofilm development and some adsorption capacity for EfOM removal. Investigating the performance of biofiltration as a pre-treatment for ultrafiltration for the treatment of secondary effluent with different organic composition at higher HLRs than those investigated by Zheng *et al*. (2009) is necessary to demonstrate the viability of the technology. Also, study to determine if differences between non-adsorbing media (e.g. sand, anthracite) exist as it relates to the rate of removal and type of specific organic fractions that contribute most to ultrafiltration fouling when treating secondary effluent.

5.2 Objectives

The objectives of this chapter are to:

1. identify the organic fractions found in secondary effluent which are responsible for polymeric UF membrane fouling
2. investigate biofiltration as a pre-treatment for ultrafiltration and study the impact of media type on reversible and irreversible fouling reduction in ultrafiltration membranes
3. determine if there is a seasonal impact on biofilter and UF performance.

5.3 Materials and Methods

5.3.1 Source Water

The secondary effluent investigated in this study was collected from the Waterloo Wastewater Treatment Plant (WWTP), which treats domestic wastewater from the City of Waterloo, Ontario, Canada. The average daily capacity for the WWTP was 72,730 m^3/d in the period when this study was being conducted. The Waterloo WWTP was undergoing primary and secondary treatment including biological treatment upgrades during this study. The raw sewage was treated by primary clarification where ferrous chloride was added for phosphorus removal. This was followed by conventional activated sludge as a biological treatment and then secondary settling tanks. The secondary effluent was UV-disinfected before being discharged into the Grand River.

Secondary effluent following UV exposure was collected twice per week in three 200 L polyethylene drums and immediately transferred to the University of Waterloo (approximately 3.5 km from the

WWTP). The secondary effluent was transferred to a holding tank in the Douglas Wright Engineering (DWE) wastewater pilot plant area on the campus of the University of Waterloo and pumping to the biofilters was immediately initiated. Water in the tank was continually mixed and allowed to increase to room temperature (23°C).

5.3.2 Biofiltration Experimental Set-up

The biofiltration set-up was constructed and operated in the Douglas Wright Engineering (DWE) wastewater pilot plant area on the campus of the University of Waterloo. It consisted of two parallel glass columns 5.1 cm in internal diameter and 2.1 m high with an effective bed depth of 75 cm supported by 10 cm of (3 mm) gravel. There was 125 cm of water above the media in each column and the overflow was 200 cm from the base of the column. There were eight sample ports in each column. The distance between the first four ports was 5 cm, while it was 10 cm for the lower ports (see chapter 3 and appendix A). Media samples were collected weekly at depths of 10 cm, 30 cm, and 60 cm as measured from the top of the biofilter media.

The biofilters were fed with a peristaltic digital drive pump (model No. 7550-50, 1.6-100 RPM, Cole-Parmer instrument Company, Barrington, USA) and backwashed with a model No. 7553-70, 6-600 rpm pump (Cole-Parmer instrument Company, Barrington, USA). To monitor water flow rate through biofilter, flowmeters (Model 2L09, 5-50 cm^3/min water, VRW international, USA) were connected in the effluent tubing. An air flow meter was used to adjust the air flowrate during backwashing (Model 2L09, 10 - 400 CCM air, VWR International, USA). Polyethylene tanks were used for feed water storage and effluent water collection.

Sand and anthracite were compared as biofilter media. The uniformity coefficients of both media were 1.5 and the effective size was 0.5 and 1.0 mm for sand and anthracite, respectively. The biofilters were operated in down flow mode (at constant head, constant rate) under the same operating conditions in order to compare the two media. The EBCT of each biofilter was 60 min corresponding to a hydraulic loading rate of 0.75 m/h. To reduce media clogging, each biofilter was backwashed using its effluent. During the first six months of the biofilter operation, they were backwashed once per week. After that, they were backwashed twice per week until the end of the experimental period.

5.3.3 Ultrafiltration Set-up

The polymeric membrane used in this study was the commercially available polyvinylidene fluoride (PVDF) ultrafiltration membrane made by GE/Zenon (Oakville, Canada). The membrane module (the

Zeeweed - 1®) contained a bundle of 15 cm long hollow fibers (500 series), and the operation mode was outside-in. The membrane had a nominal surface area of 0.047 m^2 and the MWCO was 400 KDa (approximately 40 nm pore size) as delivered from the manufacturer.

The UF module was positioned vertically in a clear polyvinyl chloride 2.0 L cylindrical tank. The set-up was designed to cycle automatically where each cycle began with 30 min permeation followed by backwashing with air sparging for 20 sec. The module tank was then drained (30 sec) and refilled again with the investigated water (36 sec). For continuous measurement during the experiments, a temperature sensor and flow meter monitor (model LC alpha controller, 200-500 CCM, Alicat Scientific, Tucson, USA) were connected to a data logger (HOBO Energy Logger, model H22-001, Onset, Cape Cod, Massachusetts, USA). The digital flowmeter was used to maintain a constant pre-determined permeate flow rate through the whole UF experiment. It was connected to a digital permeation pump (Masterflex L/S drive model number 07550-50; Cole-Parmer Canada) that was programmed to operate at a constant flow rate (25 mL/min). The flowmeter measured the actual permeate flow rate every 10 sec and the data were recorded by data logger. The actual flux could be determined at any time during the filtration run using equation 3.1 (Rahman 2013). Transmembrane pressure was measured using a pressure transducer (model 68075-02, Cole-Parmer, Montreal, Canada) which was connected to the data logger as well. Fouling rates were determined using TMP data after correction for temperature to 20°C. Additional details regarding the bench-scale configuration and operation are available in El-Hadidy (2011) and Rahman (2013).

All polymeric UF experiments were conducted in dead-end mode at a constant permeate flux of 33 L/m^2 h (LMH). To measure the UF fouling rate before and after pre-treatment using the same batch of collected secondary effluent, the run length was set to end at 24 h or when the maximum TMP of the membrane was reached (8 psi). Chemical cleaning was performed after each experiment using sodium hypochlorite (200 mg/L), for a minimum of 5 h followed by a citric acid solution (5 g/L) for another 5 h. If the membrane was not immediately placed back into use following chemical cleaning, it was stored in a glass jar containing deionized water at 4°C. The UF module was integrity tested using a pressure calibrator (Meri-cal DP2001I, Meriam Instruments, Ohio, USA) prior to every experiment. The maximum allowable pressure drop through the membrane was 0.3 psi over a period of 2 min. Additional details describing integrity testing and chemical cleaning of the membrane are available in Appendix K). To check cleaning effectiveness, clean water permeability tests were conducted using deionized water before each experiment (Appendix L).

Although the biofilters were run continuously, eight experiments with the membranes fed by the biofilter effluents were conducted over the period from January 2015 to May 2015. For comparison, the UF membrane was also fed with the non-pretreated secondary effluent (four experiments) during the same period. Three experiments were conducted per week on Monday, Wednesday, and Friday from the same batch of secondary effluent. On Monday, the membrane was fed with secondary effluent without pre-treatment. On Wednesday and Friday, the membrane was alternately fed with effluents from BF1 (sand) and BF2 (anthracite). Biofilters were backwashed on Monday and Thursday. As such, UF experiments were conducted one day after backwashing the biofilter for experiments conducted on a Friday or two days after backwashing for those conducted on a Wednesday. It has been reported in the drinking water literature, that biofilter backwashing is not important with respect to UF performance (Hallé 2009) and in the event that it somehow was, experiments in the current study were alternated between BF1 and BF2 effluent (i.e. if in a given week BF1 was used for the Wednesday experiment, the next week BF2 was used for the Wednesday experiment).

5.3.4 Liquid Chromatography Organic Carbon Detection (LC-OCD)

NOM compounds were identified based on their molecular weight using an LC-OCD Model 8 (DOC-LABOR, Karlsruhe, Germany). The LC-OCD incorporated a size exclusion column followed by a continuous carbon detector to separate the organic compounds in a water sample into four main fractions (Huber *et al.* 2011). These fractions are biopolymers, humic substances, building blocks (humic substance-like material of lower molecular weight), and low molecular weight acids and neutrals. These fractions are represented by peaks A, B, C, and D, respectively in Figure 5.1. The LC-OCD is also equipped with organic nitrogen (OND) and UV (UVD) detectors. Before analysis, samples were pre-filtered using a 0.45 µm PVDF membrane filter (Pall Supor® Membrane Disc Filters, 0.45 µm, 47 mm plain, VWR international, USA). Samples were diluted with ultrapure water if the DOC in the sample exceeded 5 mg/L.

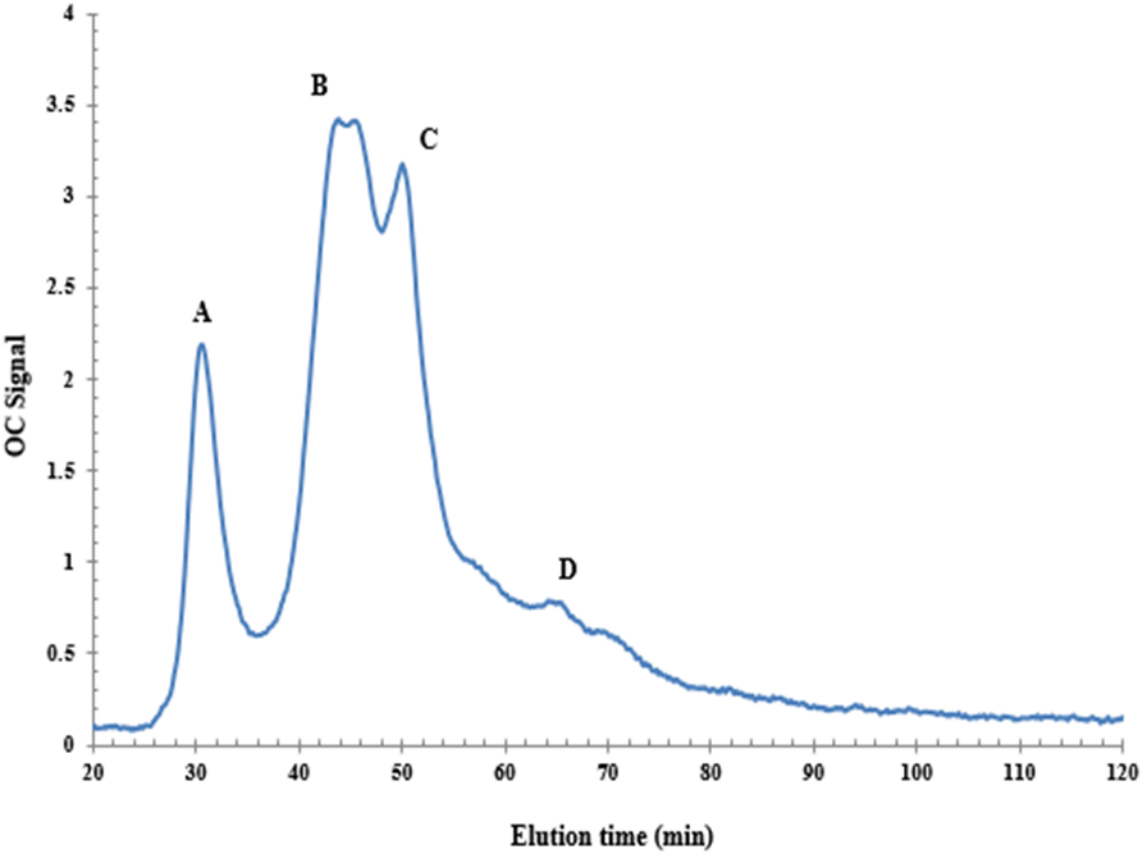


Figure 5.1 Main secondary effluent organic carbon fractions classified using the LC-OCD technique

5.3.5 Analytical Methods for Water Samples

To measure the UF fouling rate before and after pre-treatment using the same batch of collected secondary effluent, the run length was set to end at 24 h or until the maximum TMP (8 psi) of the membrane was reached, where three different experiments were conducted each week. Water samples were collected from the secondary effluent tank, the outlet of each biofilter, and from ultrafiltration permeate during each experiment as shown in Figure 5.2. Water samples were collected in clean glass 1 liter bottles before backwashing of the biofilter. Ultrafiltration permeate samples were collected after three cycles (approximately 1.5 h) of membrane run. The parameters monitored, in addition to LC-OCD analysis, were TOC, DOC, UV_{254}, specific UVA (SUVA = UV_{254}/DOC), pH, and turbidity. Some additional parameters were monitored only for secondary effluent and measured at the WWTP labs. The methods used for all measured parameters are described in more detail in Section 3.6.

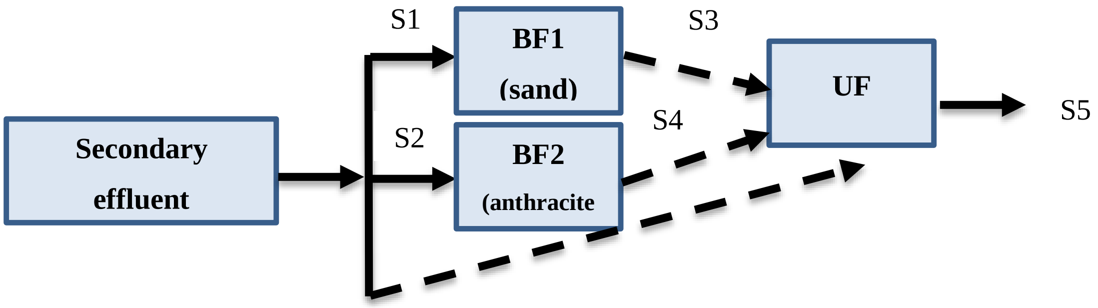


Figure 5.2 Treatment process schematic and sample locations (dashed lines indicated the alternating 24 h experiments, three experiments per week; S + number = sample location)

5.4 Results and Discussion

5.4.1 DOC Constituents and Turbidity Rejection by UF

When treating secondary effluent by low pressure membranes, colloids and dissolved organic substances are major foulants. In this section, the secondary effluent substances rejected by ultrafiltration and contributing to fouling are identified.

To better determine which dissolved substances are removed through UF and causing fouling, LC-OCD analysis was used. Figure 5.3 shows a comparison of typical LC-OCD chromatograms of secondary effluent and its UF permeate. The LC-OCD data of the secondary effluent revealed that the humic substances - which are hydrophobic compounds with high molecular weight (1000 – 20,000 Da), and appearing as the second peak at an elution time of about 40 min - made up the main fraction, accounting for an average of 34% of the DOC. Biopolymers - which consist of proteins and polysaccharide-like materials (over 20,000 Da) appearing as the first peak at elution times from 20 – 40 min - accounted for 18% of the DOC. The building blocks, which are the breakdown products of humic substances with molecular weights in the 350 – 500 Da range, made up an average 18% of the DOC. The remainder of the DOC consisted of LMWa and LMWn. Among all DOC fractions, biopolymers were the most rejected by UF, as shown in Figure 5.3, while the retention of humic substances and other DOC fractions through UF was significantly lower. Hence, biopolymers appear to play a more important role in organic fouling of UF than other DOC fractions.

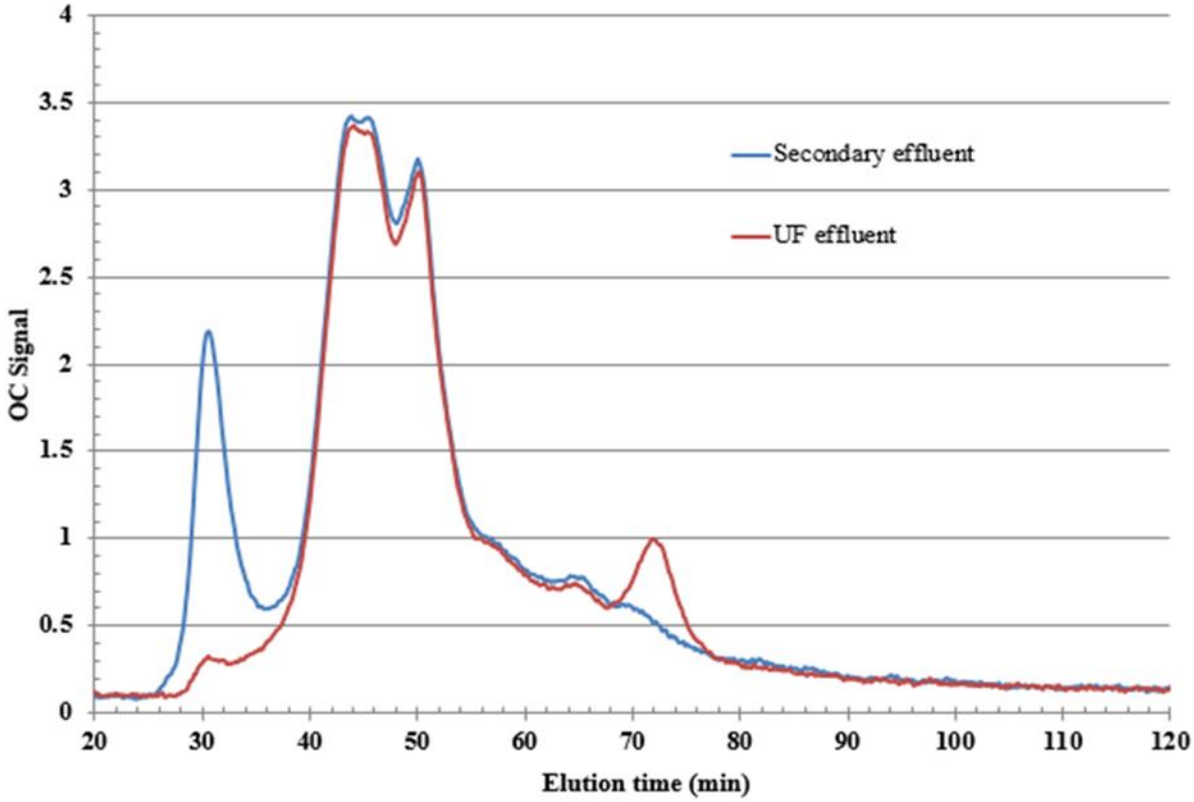


Figure 5.3 LC-OCD chromatogram for raw water (secondary effluent) and UF permeate (sampled on April 15, 2015)

Confirmation that biopolymers might be the largest contributors to low pressure membrane fouling was provided by the 12 experimental runs when the UF membrane was fed with secondary effluent. Figure 5.4 illustrates the average percentage removal of NOM constituents and turbidity rejection by UF. It can be seen that the average rejections of TOC and DOC through UF were relatively low (around 17% for each) while there was almost no rejection of humic substances through UF (less than 5%). By contrast, the average rejections of biopolymers and turbidity through the UF were 70% and 95%, respectively.

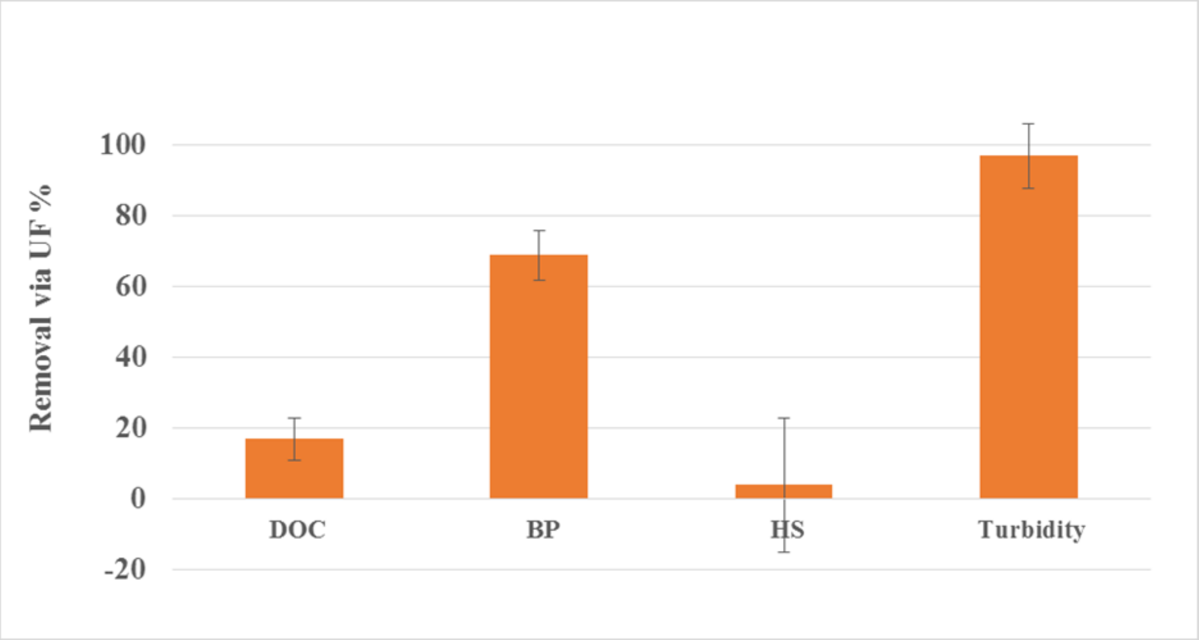


Figure 5.4 NOM constituents and turbidity rejection by UF. The error bars represent one standard deviation, n= 12

Some previous studies (e.g. Shon *et al*. 2006b) demonstrated hydrophobic organics (e.g., humic substances) were the largest contributors to membrane fouling. Other recent studies reported BP as being the most important low pressure membrane foulants treating drinking water (Amy 2008; Hallé *et al*. 2009; Peldszus *et al*. 2012; Rahman *et al*. 2014). The same observations were obtained by other authors (Haberkamp *et al*. 2008; Fan *et al*. 2008; Zheng *et al*. 2010; Pramanik *et al*. 2014) when treating domestic wastewater by low pressure membranes. Based on the data presented in Figure 5.4, it can be seen that biopolymers are largely responsible for UF fouling when treating secondary effluent (at least of the type of UF membranes studied here). In addition, particulate substances (measured as turbidity) in secondary effluent may play an important role in UF fouling. It is worth mentioning that the presence of particulates, when combined with organic components, can lead to excessive fouling as reported by Hallé *et al*. (2009) and Peldszus *et al*. (2011).

Since biopolymers and particulates are those most rejected by UF, their concentration in secondary effluent is important and the relationship between their concentration and UF fouling requires study. Figure 5.5 compares biopolymers, humics substances, and turbidity in UF feed water (secondary effluent) vs. hydraulically reversible fouling rates. Figure 5.6 illustrates the same three parameters vs.

hydraulically irreversible fouling values. Hydraulically reversible fouling values were calculated as the average ΔTMP from all filtration cycles in each experiment, whereas ΔTMP in any cycle (30 min) was calculated by subtracting the TMP measured at the start of the cycle from the TMP measured at the end of the previous cycle before backwashing. The values of TMP were taken 2 minutes after the start and 2 minutes before the end of the filtration cycle (i.e. the TMP value at t = 0.0 min was not used). Hydraulically irreversible fouling is defined as difference in the TMP at the start and the end of each experiment (e.g., 24 h or until TMP reaches 8.0 psi) and can be calculated by subtracting the initial TMP of the last cycle from the initial TMP of the first cycle of the experiment divided by the filtration time (h).

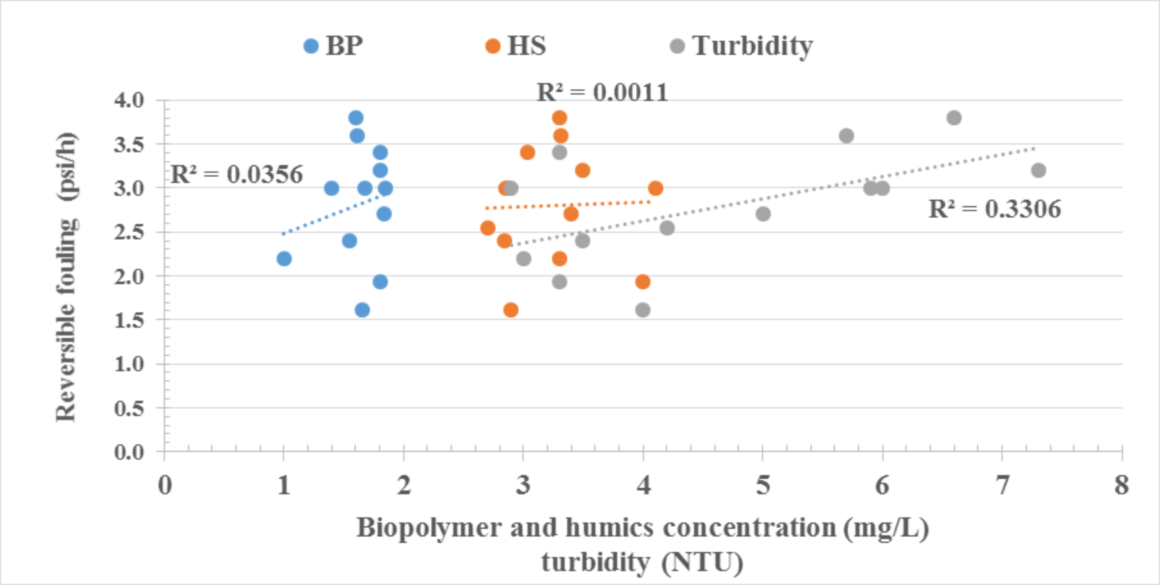


Figure 5.5 Relationship between biopolymers, humics, and turbidity in UF membrane feed (secondary effluent) and reversible fouling. n= 13 for turbidity, n= 12 for humics and biopolymers

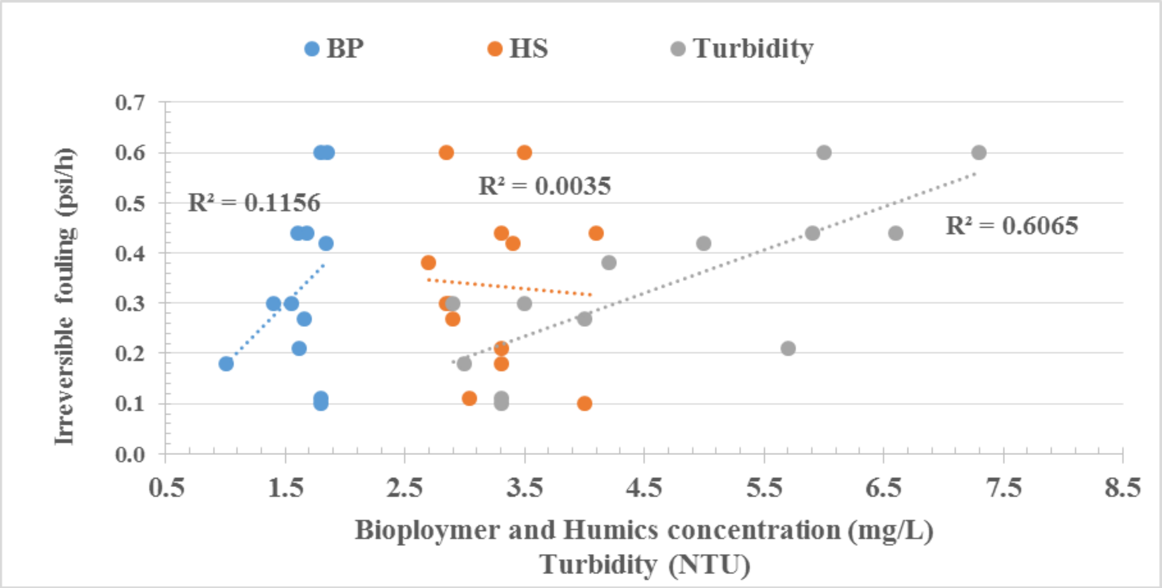


Figure 5.6 Relationship between biopolymers, humics, and turbidity in UF membrane feed (secondary effluents) and irreversible fouling. n= 13 for turbidity, n= 12 for humics and biopolymers

It can be seen that there was no correlation between humic substances concentration and reversible or irreversible fouling ($p > 0.05$, t-test). This was somewhat expected, as previous studies (Peldszus *et al*. 2011; Rahman *et al*. 2014) reported that there was no correlation between humic substances and UF fouling. Those two studies investigated the same UF membrane in two different surface waters (Grand River and Saugeen River). However, some studies (e.g. Peiris *et al*. 2010) have reported that humic substances have significantly contributed to irreversible UF fouling; this is likely attributable to the lower MWCO of membranes used (e.g. 20 and 60 KDa compared with 400 KDa in the current study) which can reject smaller humic molecules. Unexpectedly, there was no correlation between biopolymers and reversible or irreversible fouling when UF was fed with secondary effluent without any pre-treatment ($p > 0.05$, t-test). This observation conflicts with those reported from previous studies in treating drinking water (Hallé *et al*. 2009; Peldszus *et al*. 2011; Rahman *et al*. 2014) and with secondary effluent (Haberkamp *et al*. 2008; Zheng *et al*. 2010; Pramanik *et al*. 2014). This may be attributable to the high biopolymer concentrations in the investigated secondary effluent (average 1.8 mg/L) compared with those studies (maximum 0.8 mg/L by Zheng *et al*. 2010) or their composition (e.g., proteins or carbohydrates), since most of those studies reported that biopolymer composition is more important than their concentration in fouling development. In addition, most of the biopolymer concentrations shown in Figure 5.6 are in a narrow range, the range of fouling rates is quite large. This study did not aim to investigate a wide range of feed water composition. Rather, the goal was to basically repeat experiments several times with the same feed water composition~~s~~ this led to a narrow range of independent variable (e.g. biopolymers). The large relative scattering in fouling rates may be attributable to changes in biopolymer composition. Given this (scattering of data coupled with narrow range of independent variable), it was not possible to further investigate the significant of the relationship. It is also worth mentioning that the correlation between biopolymers and UF reversible and irreversible fouling was different when the UF was fed with pre-treated secondary effluent (e.g., after biofiltration) as discussed in the following section.

In terms of the impact of particulate matter on reversible and irreversible fouling, Figures 5.5 and 5.6 suggest that turbidity may have had some relationship to reversible fouling and even more with irreversible fouling. Further analysis of data shown in Figures 5.5 and 5.6 confirms that there was a significant correlation between irreversible fouling of the UF membrane and secondary effluent turbidity, where r (df = 12) = 0.78 and $p < 0.05$ (t-test). On the other hand, there was insufficient evidence to suggest that turbidity was significantly correlated with reversible fouling of the UF membrane in this study ($p > 0.05$, t-test). It is well known that particulates in membrane feed water can deposit on membrane surfaces, producing a cake layer that can typically be easily removed during backwashing (e.g. Hallé 2009). The weak correlation between particulates and reversible fouling may suggest that the characteristics of reversible fouling, which is removable by backwashing, are changing during filtration cycles. The somewhat better correlation between particulates and irreversible fouling, which has not been previously reported, implies that other foulants (e.g., biopolymers) participate in producing a particulate-associated foulant layer. This hypothesis has been considered (Howe and Clark 2002; Hallé *et al*. 2009; Peiris *et al*. 2011; Peldszus *et al*. 2011) and it is discussed in section (5.4.3) based on the data obtained from the current study.

5.4.2 Impact of Biofiltration on Feed Water (Secondary Effluent) Quality

The investigation of foulant removal (e.g., biopolymers and particulates) through biofiltration was conducted for sixteen months from January 2014 to April 2015. In this period, the two biofilters (sand vs. anthracite) were operated under identical conditions with a 60 min EBCT corresponding to a HLR of 0.75 m/h. The biofilters were backwashed once per week from January 2014 until June 2014. The backwashing was then switched to a twice weekly frequency until the end of the investigated period.

The two biofilters were brought on line early in January 2014, and steady state conditions were reached after about four months of operation based on ATP measurements (data presented in Chapter 4). The LC-OCD chromatogram for secondary effluent and biofilter effluents (Figure 5.7) illustrates the removal of different DOC fractions through the biofilter. The figure shows that the principal change during biofiltration of secondary effluent is occurring in the biopolymer fraction (first peak). On the other hand, the proportional removals of humic substances and LMW compounds were much lower. The removal of biopolymers through aerobic biodegradation is well documented in surface water treatment (Hallé *et al*. 2009; Rahman *et al*. 2014; Siembida-Lösch *et al*. 2015) as a biofiltration process and in secondary effluent treatment (Zheng *et al*. 2010; Pramanik *et al*. 2014) using slow sand filtration. The average biopolymer concentrations in the effluents of BF1 and BF2 were 0.8 ± 0.2 and 1.0 ± 0.2 mg/L, respectively, compared with the average concentration in secondary effluent of 1.3 ± 0.4 mg/L. In general, the lowest concentrations of organic compounds were measured in the effluent of BF1 (sand). A total of 44 samples were collected from secondary effluent and biofilter effluents between January 2014 and April 2015 (Appendix C). A summary of organic compound and turbidity removal through the biofilters is shown in Figure 5.8.

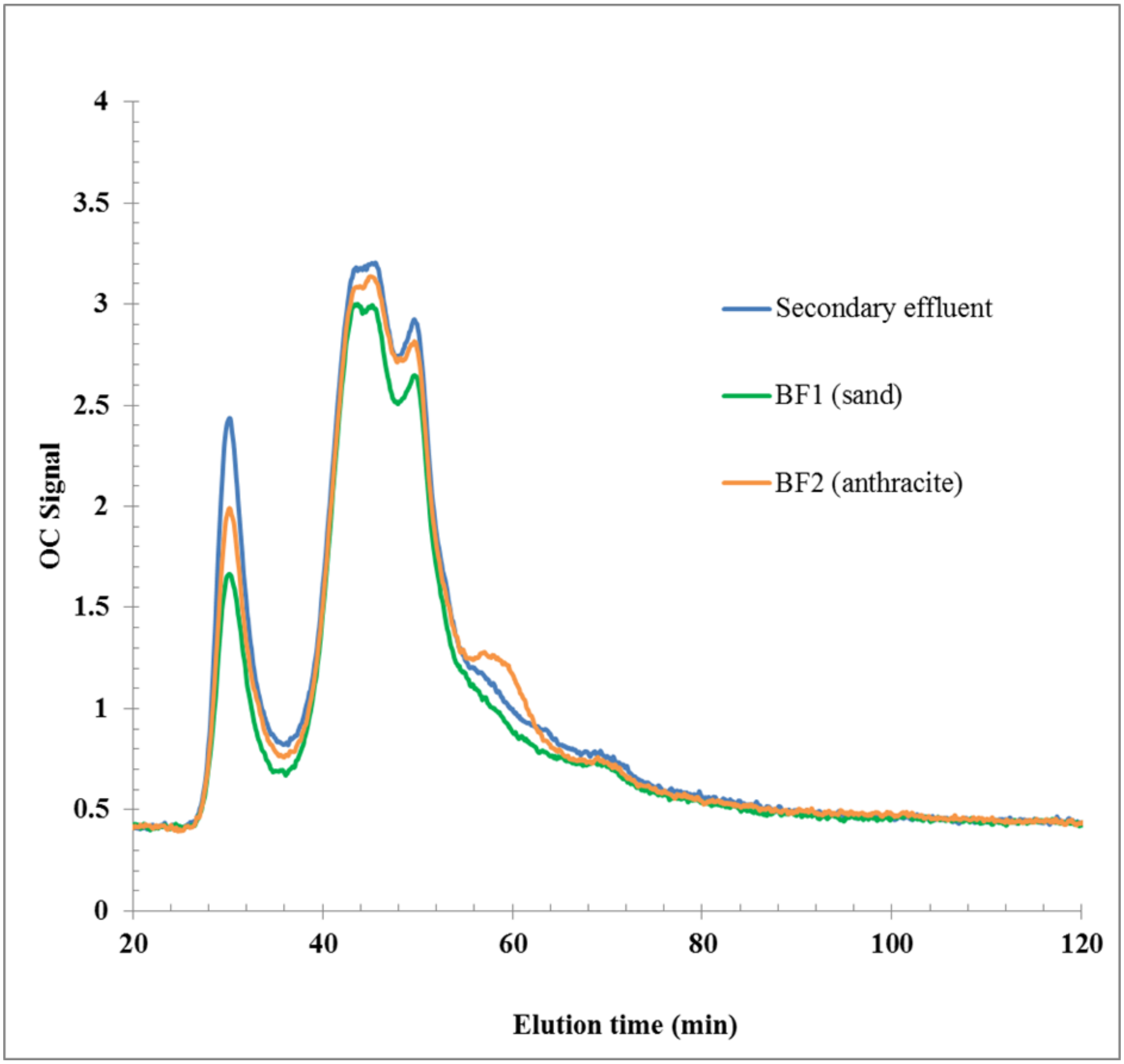


Figure 5.7 Typical LC-OCD chromatogram for secondary effluent and biofilter effluents (sampled on June 25, 2014)

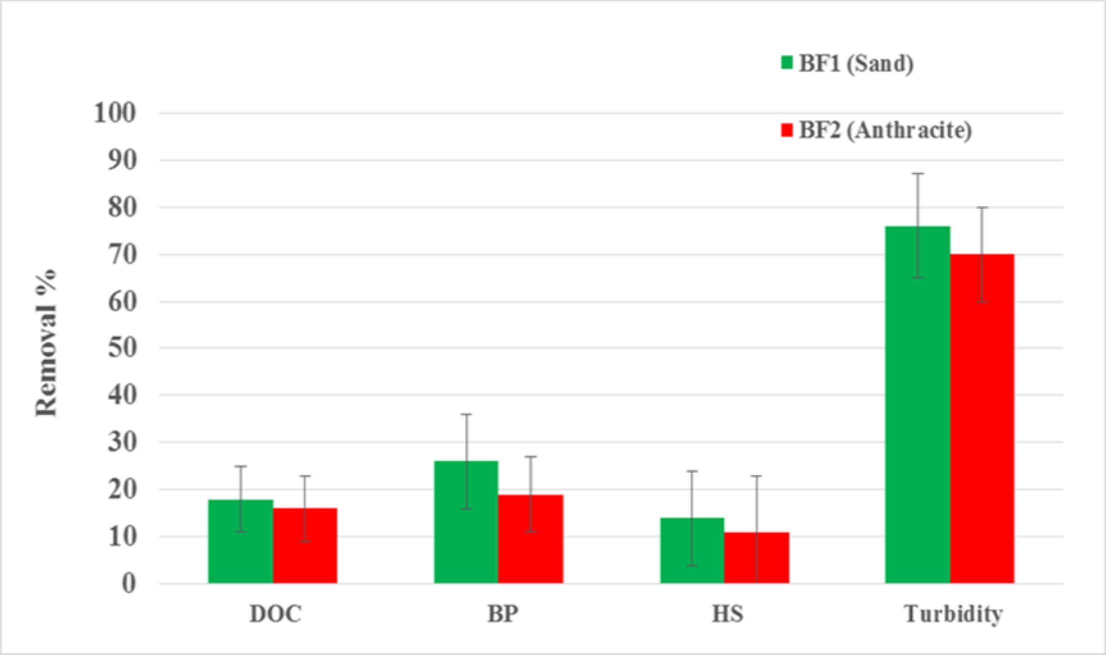


Figure 5.8 Reduction of DOC, BP, HS, and turbidity through biofilters (from Jan. 2014 to Apr. 2015). The error bars represent standard deviation, n= 44

BF1 generally achieved higher removal of organic compounds and turbidity than BF2. Reductions of 18% ± 10% and 26% ± 10% in DOC and BP, respectively, were observed through BF1 while slightly lower reductions (16% ± 8% and 19% ± 12%) of DOC and BP, respectively, were observed through BF2. The differences between BF1 and BF2 were statistically significant (paired t-test, α= 0.05). While humics make up the dominant DOC fraction in secondary effluent, they were not well removed through biofiltration. This has been observed previously in drinking water pre-treatment (e.g. Hallé *et al*. 2009; Rahman *et al*. 2014). The average humic substance removals through BF1 and BF2 were 14% ± 11% and 11% ± 10%, respectively. The average turbidity reduction achieved by BF1 and BF2 was 76% ± 15% and 70% ± 19%, respectively. Statistically there was no difference between BF1 and BF2 in the reduction of turbidity or humic substances (paired t-test, α = 0.05).

5.4.3 Impact of Biofiltration on Ultrafiltration Fouling

To investigate the impact of biofiltration on the reduction of UF fouling, a UF bench-scale setup was operated utilizing either secondary effluent or biofilter effluent as a feed from January 2015 to May 2015. During this period the UF was operated at a constant temperature-corrected permeate flux of 33

L/m^2 h (LMH). To measure the UF fouling rate before and after pre-treatment using the same batch of collected secondary effluent, the run length was set to end at 24 h or when the maximum TMP (8 psi) of the membrane was reached. Hydraulic backwashing time was for 20 seconds after each permeation cycle (30 minutes). The performance of UF for the filtration of secondary effluent and biofilter effluents was evaluated by plotting the change in TMP vs. filtration time. Figure 5.9 provides an example of a UF membrane fouling experiment comparing secondary effluent and biofilter effluents (conducted from February 27 to March 5, 2015). During filtration of secondary effluent, a rapid increase in TMP was observed, with the TMP reaching 6.0 psi after only 12 h of filtration. On the other hand, operating the UF membrane with effluent from BF1 or BF2 substantially improved performance and there was a clearly-observable lower rate of fouling development. After a filtration time of 23 h, the maximum TMPs reached by BF1 and BF2 effluents were 3.0 and 4.0 psi, respectively. Similar results were obtained for the remainder of the experiments (four in total) that were conducted from January 2015 to May 2015 (Appendix E).

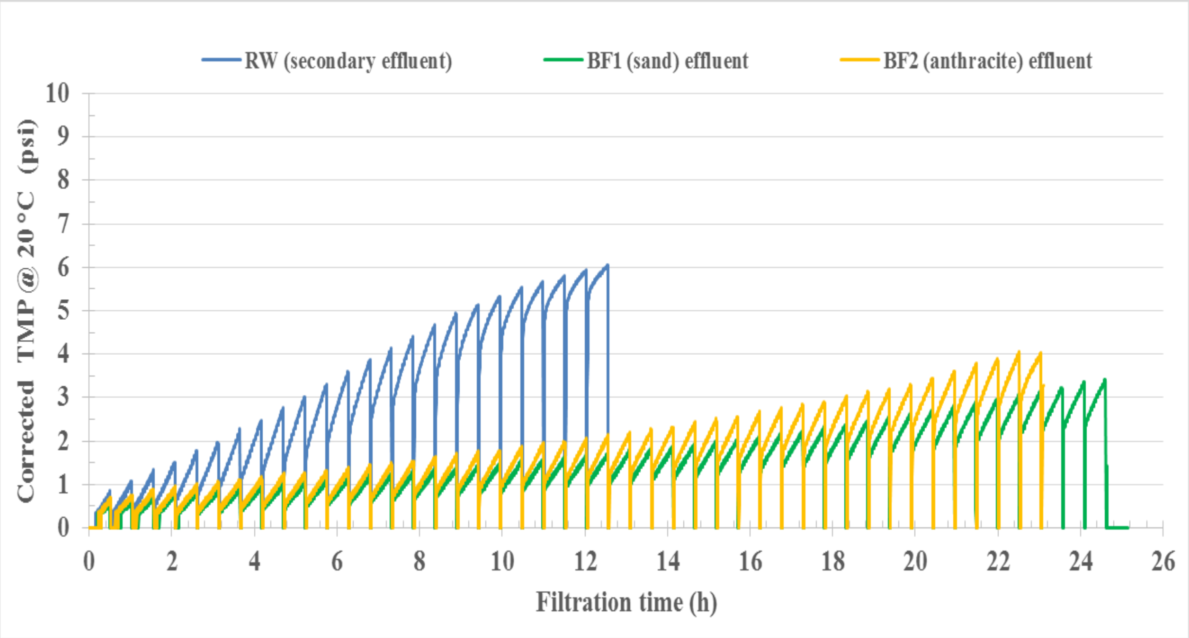


Figure 5.9 UF transmembrane pressure when fed with raw water (secondary effluent) vs. when fed with biofilter effluent (experiment conducted from Feb. 27 to Mar. 5, 2015)

Comparing the change in TMP for the secondary effluent and biofilter effluents demonstrated the impact of the dissolved organic compounds and the particulate matter on the development of UF membrane fouling. The biopolymers and turbidity in secondary effluent, in the experiment illustrated in Figure 5.9, were 1.5 mg/L and 3.5 NTU. The removal of biopolymers through BF1 and BF2 was 32% and 30%, respectively, which led to a less rapid TMP increase compared with direct filtering of secondary effluent (no pre-treatment before UF).

It is worth noting that for the experiment in Figure 5.9, the concentrations of biopolymers in the effluents of BF1 and BF2 were virtually identical at 1.05 and 1.03 mg/L, respectively, while the turbidity values were 0.5 NTU in BF1 effluent compared with 1.2 NTU in the effluent of BF2. Based on these data, it can be seen that the deposition of particles (not only biopolymers) appear to have had an effect on UF fouling. Hence, the TMP improvement obtained by using BF1 effluent (when compared with BF2 effluent) appears to be the result of lower particulate amounts, not differences in biopolymer concentrations at least for this example. A similar observation was obtained by Pramanik *et al.* (2014). In their study, microfiltration performance was monitored during treatment of biologically treated secondary effluent, diluted secondary effluent (with Milli-Q water), and a pre-filtered secondary effluent sample (1.6 µm) to investigate the impact of particulates on membrane fouling. They observed that, despite the fact that the three samples contained the same amounts of dissolved organic matter, the lowest flux decline was obtained by pre-filtered secondary effluent, reflecting the significance of particulate matter in fouling development. However, in the present study the difference in fouling rate between the two biofilter effluents was much smaller than the difference related to the presence or absence of biopolymers.

However, the difference related to particulate matter alone was not the case with the rest of the experiments. For example, another experiment was conducted in the period from May 11 to May 15, 2015 (Appendix E) and in that experiment the biopolymer concentrations in the BF1 and BF2 effluents were 1.5 and 1.1 mg/L, respectively, while the turbidities were 1.2 and 1.6 NTU in the effluents of BF1 and BF2, respectively. In that experiment, the TMP reached 4.0 psi after 23 h of filtration time running the UF with BF2 effluent, while the TMP remained constant (2.0 psi) for the entire duration of the experiment (24 h) when UF was operated using effluent of BF1. In this case, the lower development in TMP obtained by BF1 effluent was attributed to the reduction in both biopolymers and turbidity.

It is well known that increasing TMP during filtration cycles is attributable to the development of hydraulically reversible and/or irreversible fouling. In the experiment described in Figure 5.9, the use of BF1 effluent yielded 62% and 83% reductions in the reversible and irreversible fouling, respectively, during the first 12 h of filtration time. The use of BF2 effluent also improved the UF performance, where 48% and 80%, respectively, reductions in reversible and irreversible fouling were observed. The reductions in reversible and irreversible fouling rates were calculated based on average values of reversible and irreversible fouling determined for each run (e.g. secondary effluent vs. BF1 and BF2 effluents) as explained previously on pg. 81. Reversible fouling and irreversible fouling rates determined during each cycle are presented in Figures 5.10 and 5.11 and illustrate the change in reversible and irreversible fouling rates, respectively, for a UF experiment conducted from February 27 to March 5, 2015 comparing secondary effluent and biofilter effluents. The value of the reversible fouling during a given cycle was calculated by subtracting the TMP measured at the start of the cycle from the TMP measured at the end of the previous cycle before backwashing. When using the secondary effluent as UF feed, there was a dramatic increase in the hydraulically reversible fouling rate reaching 1.5 psi/h within the first 12 filtration cycles (one cycle = 30 min permeation). Using the effluents from BF1 and BF2 as feed for UF reduced the rate at which hydraulically reversible fouling occurred. The hydraulically reversible fouling values never reached 1.5 psi/h, peaking only at 1.0 psi/h at the end of the experiment (24 h) for both BF1 and BF2, however, lower fouling rates were observed using BF1 effluent during different cycles. Hydraulically irreversible fouling was also reduced when the UF membrane was fed with biofilter effluents and to determine irreversible fouling rate, the value of TMP at the beginning of each cycle was monitored (Figure 5.6). When the UF membrane was fed with secondary effluent without pre-treatment the initial TMP rapidly increased to reach almost 4.0 psi within 12 h of filtration time. On the other hand, the value of the initial TMP at the end of the 24h experiment were 2.0 and 3.0 psi for BF1 and BF2 effluents, respectively.

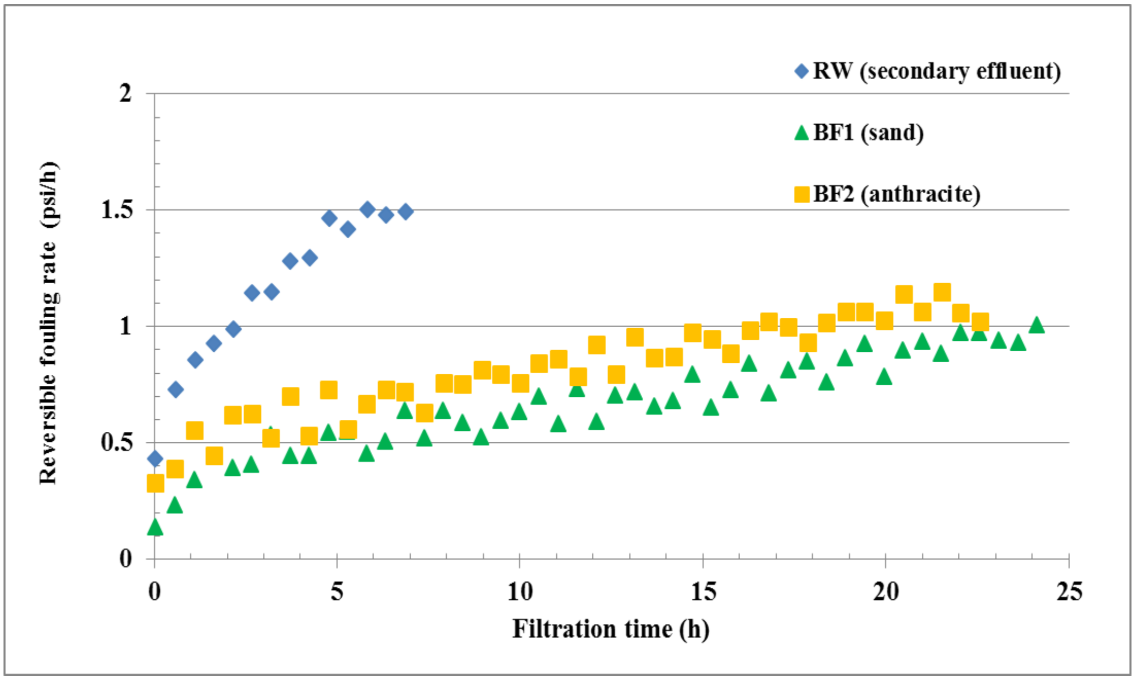


Figure 5.10 Increase in reversible UF fouling over a 24 h experiment with raw water (secondary effluent) and biofilter effluents as UF feeds (experiment conducted from Feb. 27 to Mar. 5, 2015)

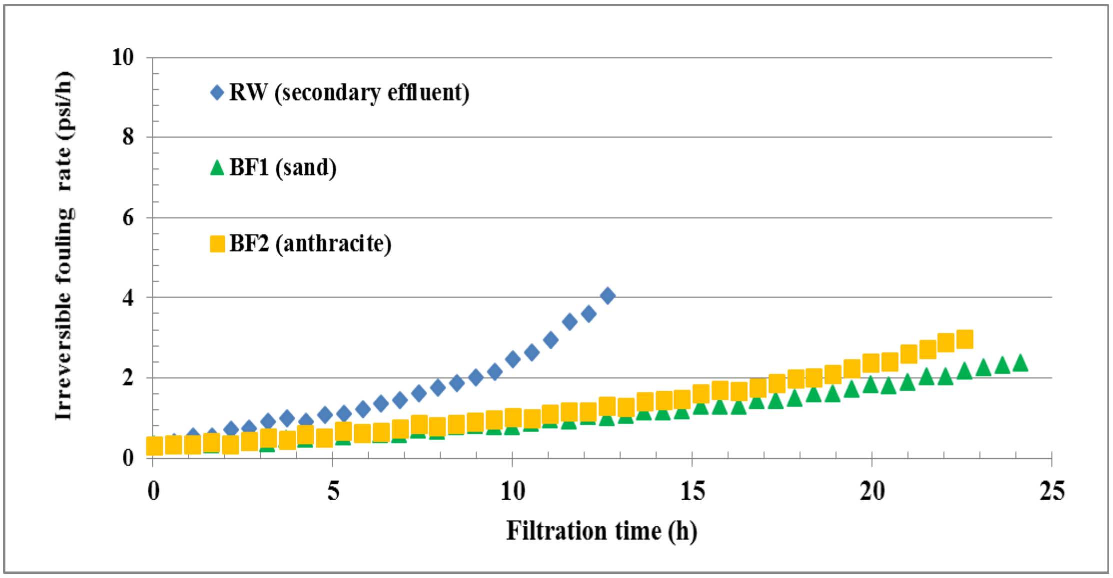


Figure 5.11 Increase in irreversible UF fouling over a 24 h experiment with raw water (secondary effluent) and biofilter effluents as UF feeds (experiment conducted from Feb. 27 to Mar. 5, 2015)

The difference in the reduction of both reversible and irreversible fouling obtained by BF1 and BF2 is largely attributable to a higher removal of biopolymers and particulates achieved with BF1. It has previously been reported that biopolymers were most correlated to UF fouling when treating secondary effluent (Haberkamp *et al*. 2008; Zheng *et al*. 2009; Pramanik *et al*. 2014). The same observations were found in surface water treatment with UF (Hallé *et al*. 2009; Peldszus *et al*. 2011; Rahman *et al*. 2014). Also, Siembida-Lösch *et al*. (2015) observed that the higher the biopolymer concentration delivered to the membrane, the higher the biopolymer deposition and the more severe the fouling.

Biopolymers contain a mixture of polysaccharides and protein-like materials (Huber *et al*. 2011). Based on the N/C ratio obtained from the organic carbon detector (OCD) and organic nitrogen detector (ONC) obtained from the LC-OCD, approximate values of the protein content of the biopolymers can be estimated (Filloux *et al*. 2012; Siembida-Lösch *et al*. 2015). In addition to the quantitative removal of particulates and biopolymers through biofilters, there was a dramatic reduction of proteins as well (Appendix F). The concentration of proteins in secondary effluent ranged from 0.05 to 0.31 mg/L, constituting about 13% of the biopolymers (as an average percentage). The concentration of proteins in BF1 effluent varied between 0.02 and 0.20 mg/L and in BF2 effluent varied between 0.04 and 0.20 mg/L. In general, BF1 (sand) achieved a higher removal of proteins than BF2 (anthracite) at 62 ± 17% and 49 ± 18%, respectively, which was significantly different (paired t-test, α= 0.05). In this study, there was an average reduction of 83 ± 9.0% of proteins through UF, regardless the type of the feed water (e.g., secondary effluent or biofilter effluent), which reflected the importance of those compounds on UF fouling. The significance of protein-like materials present in secondary effluent in UF fouling has been reported (Haberkamp *et al*. 2008; Henderson *et al*. 2011; Filloux *et al*. 2012). Despite the fact that biologically treated wastewater (e.g., secondary effluent) generally contains a higher protein content than that in surface water, the same phenomena was observed when UF membranes were used in surface water treatment (Hallé *et al*. 2009; Peldszus *et al*. 2011). On the other hand, Parmanik *et al*. (2014) reported that polysaccharides (carbon-like materials) were retained more than proteins, causing severe membrane fouling when treating biologically treated wastewater. This conflict in observations may be attributed to the use of MF in their study, which has a larger pore size than UF.

Since UF fouling reduction with biofiltration is attributable to the removal/transformation of biopolymers and particulates, the relationship between their concentrations and UF fouling merits investigation. Figures 5.12 and 5.13 plot biopolymer concentrations, humic substance concentrations, and turbidity in UF feed water (from both biofilter effluents) vs. hydraulically reversible and irreversible fouling values, respectively. It can be seen that the rates of reversible fouling and irreversible fouling were not constant over the filtration period (Figures 5.10 and 5.11). The values of reversible and irreversible fouling were determined as an average value of the entire run and used to generate Figures 5.12 and 5.13). As expected, no relationship between humic substances concentration and reversible or irreversible UF fouling was observed ($p > 0.05$, t-test). The R^2 of 0.44 suggests a potential weak correlation between turbidity in biofilter effluent and reversible fouling, while turbidity was not correlated with irreversible fouling. Further analysis of data illustrated in Figures 5.12 and 5.13 revealed that a statistically significant correlation between turbidity in the biofilter effluent and reversible fouling did exist (r (df = 8) = 0.67, $p < 0.001$, t-test). This observation is consistent with previous studies (Hallé *et al*. 2009; Peldszus *et al*. 2011; Rahman *et al*. 2014) where most particulate compounds deposit on the membrane surface producing a cake layer which can be removed through backpulsing/flushing with water (Howe and Clark 2002; Gao *et al*. 2011). The fact that the correlation observed between turbidity and reversible fouling was not higher implies that particulate compounds alone may not be directly responsible for the reversible fouling production. The results shown in the two figures indicate that biopolymer concentrations in the UF feed water (biofilter effluent) were positively correlated with both reversible (r (df = 7) = 0.78, $p < 0.001$, t-test) and irreversible fouling (r (df = 7) = 0.81, $p < 0.001$, t-test). In a recent study conducted by Wang (2014) to investigate the impact of ozonation-biofiltration pre-treatment in controlling UF fouling in a full scale drinking water treatment plant, no correlation was found between biopolymers and hydraulically irreversible fouling, while biopolymers in feed water were linearly correlated with hydraulically reversible fouling. Hallé *et al*. (2009) reported similar findings in a bench-scale UF experiment treating surface water. Similarly, Haberkamp *et al*. (2011) reported a high correlation between hydraulically reversible fouling of UF membranes and biopolymer content in secondary effluent. On the other hand, Rahman *et al*. (2014) reported that biopolymer concentration in UF feed water (surface water or biofilter effluents) was highly correlated ($R^2 = 0.95$) with hydraulically irreversible fouling. Also, Peiris *et al*. (2010) and Peldszus *et al*. (2011) observed a high correlation between protein content in biopolymer fraction and irreversible fouling in UF membranes. In these two studies, a weak correlation between biopolymers and hydraulically reversible fouling was observed.

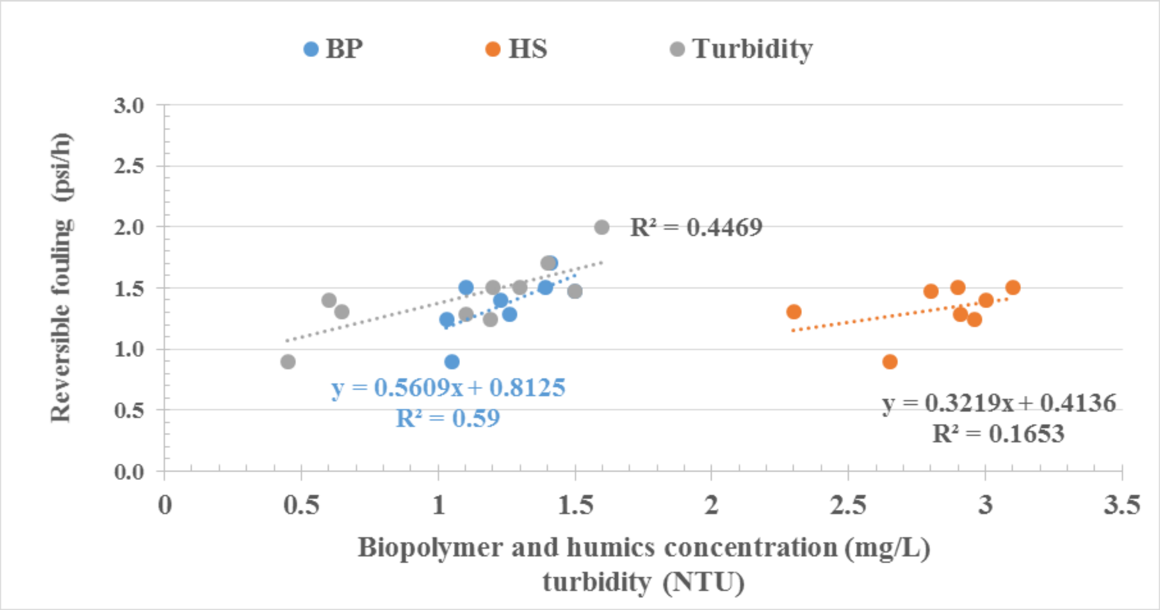


Figure 5.12 Relationship between biopolymers, humics, and turbidity in membrane feed (biofilter effluent) vs. reversible UF fouling. n= 9 for turbidity and 8 for humics and biopolymers

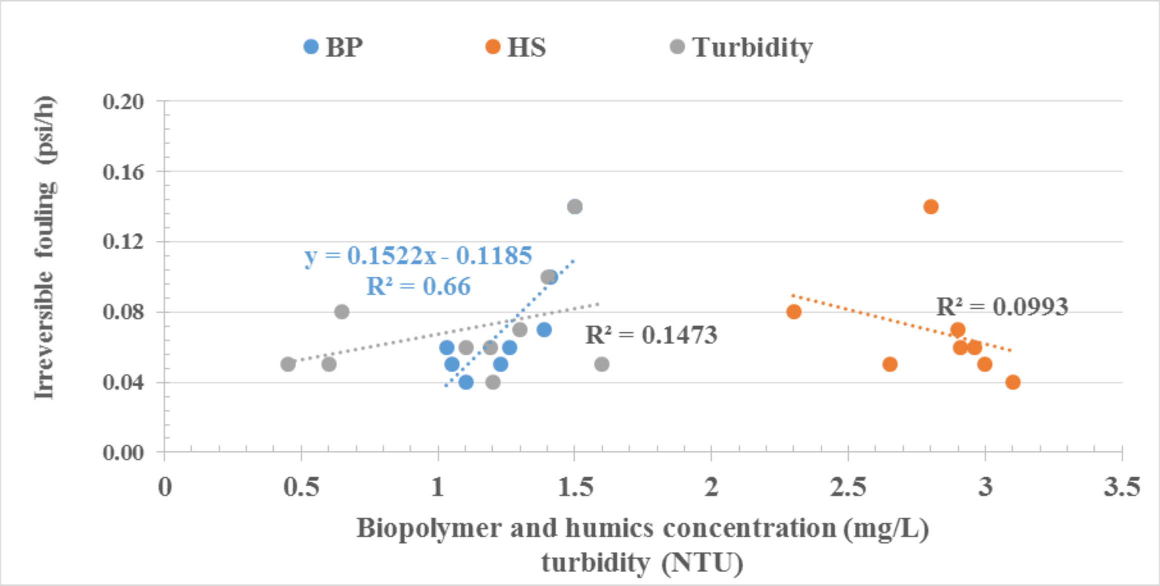


Figure 5.13 Relationship between biopolymers, humics, and turbidity in membrane feed (biofilter effluent) vs. irreversible UF fouling. n= 9 for turbidity and 8 for humics and biopolymers

It has been reported that the fouling mechanism of biopolymers is mainly attributable to pore blocking (Zheng *et al.* 2009). In the early stages of filtration, open pores are first blocked by molecules equivalent in diameter to the membrane pores. As more molecules accumulate on the membrane surface, a cake layer then forms (Haberkamp *et al*. 2008). It has been suggested that a combined fouling layer of biopolymers and particulate matter can alter the reversible fouling to irreversible fouling (Hallé *et al*. 2009; Peldszus *et al*. 2011) or change the membrane separation characteristics (Haberkamp *et al*. 2011) which in turn can provide unexpected/unusual correlations between compounds present in UF feed water and UF fouling. Figures 5.14 and 5.15 plot turbidity and biopolymer concentrations vs. reversible and irreversible fouling of the UF membrane, respectively. Since investigating the combined impact of biopolymers and turbidity on UF fouling was not within the scope of the current study and there was no way to perform an independent experiment, Figures 5.14 and 5.15 were drawn based on the data obtained from UF experiments that were conducted to investigate the impact of biofiltration as an UF pre-treatment. It can be seen that both biopolymers and turbidity impacted membrane fouling and any increase at these compounds greatly increase reversible ad irreversible fouling. Also, the combined impact of biopolymers and particles on UF fouling appeared to have more impact when the membrane was fed with secondary effluent. These observations help to explain why biopolymers in this study were correlated with both reversible and irreversible fouling when membrane was fed with biofilter effluents. Due to high biopolymer concentrations in the investigated secondary effluent (and even after biofiltration), most of the UF membrane pores can be rapidly blocked. With more biopolymers delivered to the UF surface a cake layer forms which is likely accompanied by the particulate matter present in the feed water (secondary effluent or biofilter effluents). These fundamentals can also explain why only turbidity correlated with reversible and irreversible UF fouling when fed with secondary effluent without any pre-treatment (section 5.4.1).

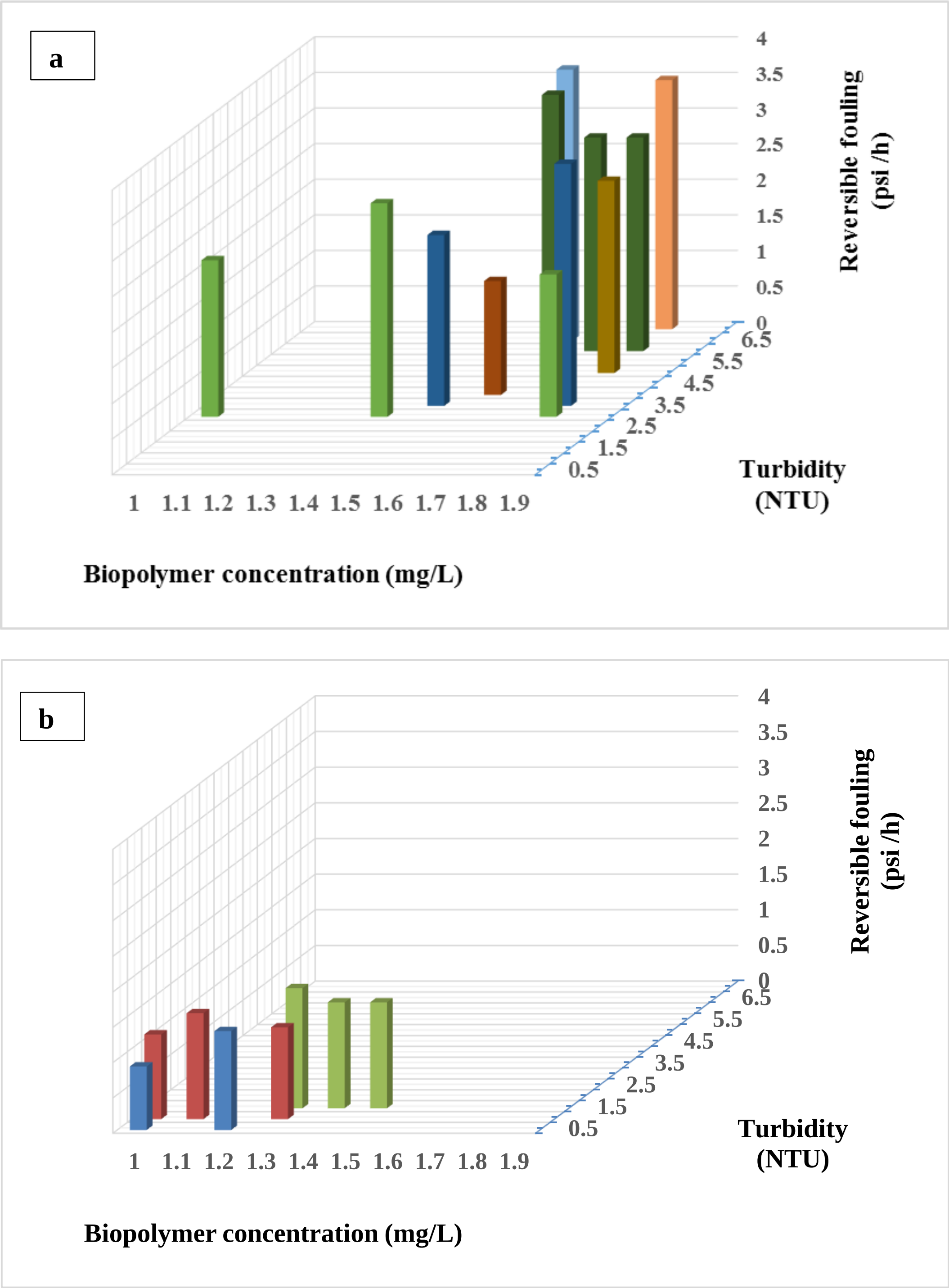


Figure 5.14 The combined impact of turbidity and biopolymer concentrations in a) secondary effluent and b) biofilter effluents on reversible fouling of the UF membrane

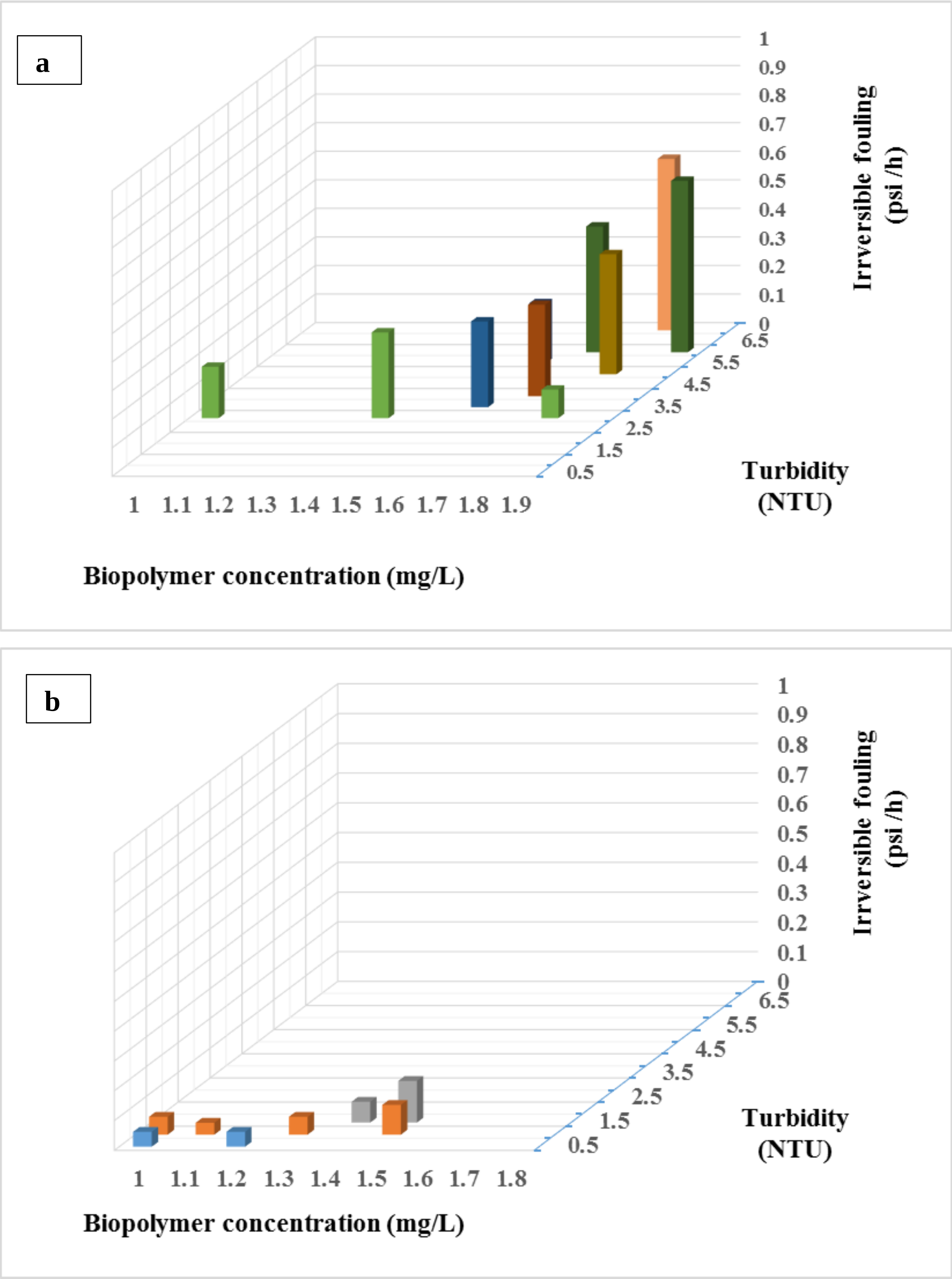


Figure 5.15 The combined impact of turbidity and biopolymer concentrations in a) secondary effluent and b) biofilter effluents on irreversible fouling of the UF membrane

5.4.4 Seasonal Performance of Biofilters and Impacts on Ultrafiltration

While the biofiltration/ultrafiltration experiments were conducted at room temperature, the raw secondary effluent was collected over a period which experienced a range of water temperature (10 – 25°C). The secondary effluent temperature at time of collection was nonetheless relatively consistent with an average of 16.0°C ± 3.5°C. The data show that there was no substantial variability in the DOC and NOM fractions measured by LC-OCD throughout this long-term study. There was some variability in turbidity during the investigated period, which ranged from 1.1 NTU to 10.3 NTU. Higher turbidities were encountered in colder water, at least in the early stage of this study. All experiments were conducted at room temperature (~23°C) and there was no substantial change in biofilter performance during the investigated period. Figure 5.16 presents the increase of TMP due to UF fouling development. The ΔTMP shown in the figure was calculated by subtracting the TMP measured at the end of the cycle from the TMP measured at the beginning of the cycle (reflecting the value of total fouling observed during an individual cycle). This figure compares two different experiments conducted in two different seasons. The first one was conducted during winter (from Feb. 19 to 23, 2015) where average temperature of ‘as-collected’ secondary effluent was 10°C. The second experiment was conducted during spring (from May 11 to 15, 2015) when temperature was a little bit higher (14°C). The concentrations of biopolymers in secondary effluent were 1.6 and 1.8 mg/L in the first and second experiments, respectively, while turbidity values were 5.7 and 3.3 NTU in the first and second experiments, respectively. Biofiltration improved the secondary effluent characteristics during both experiments and in general higher removal of biopolymers (e.g., proteins) and turbidity were achieved by BF1. The TMP per cycle reached 2.2 psi after almost 10 h (20 cycles) of filtration in the first experiment (lower biopolymer and higher turbidity than second experiment). In the second experiment, the TMP per cycle reached 2.0 psi after 15 h (30 cycles). The data obtained from these two experiments was significantly different based on regression analysis ($p < 0.05$, t-test), which confirms that secondary effluent characteristics impacted the performance of UF membrane. During the filtration of BF2 effluent, the average TMP per cycle reached 1.2 psi at the end of the two experiments (24h), whereas the average TMP per cycle stayed almost constant (0.75 psi) during the filtration of BF1 effluent. Based on these results, it can be concluded that the characteristics of secondary effluent impacted the UF performance, while the performance of biofilters (and in turn UF performance when fed with biofilter effluents) stayed consistent ($p > 0.05$, t-test) regardless of the composition of secondary effluent and/or season change.

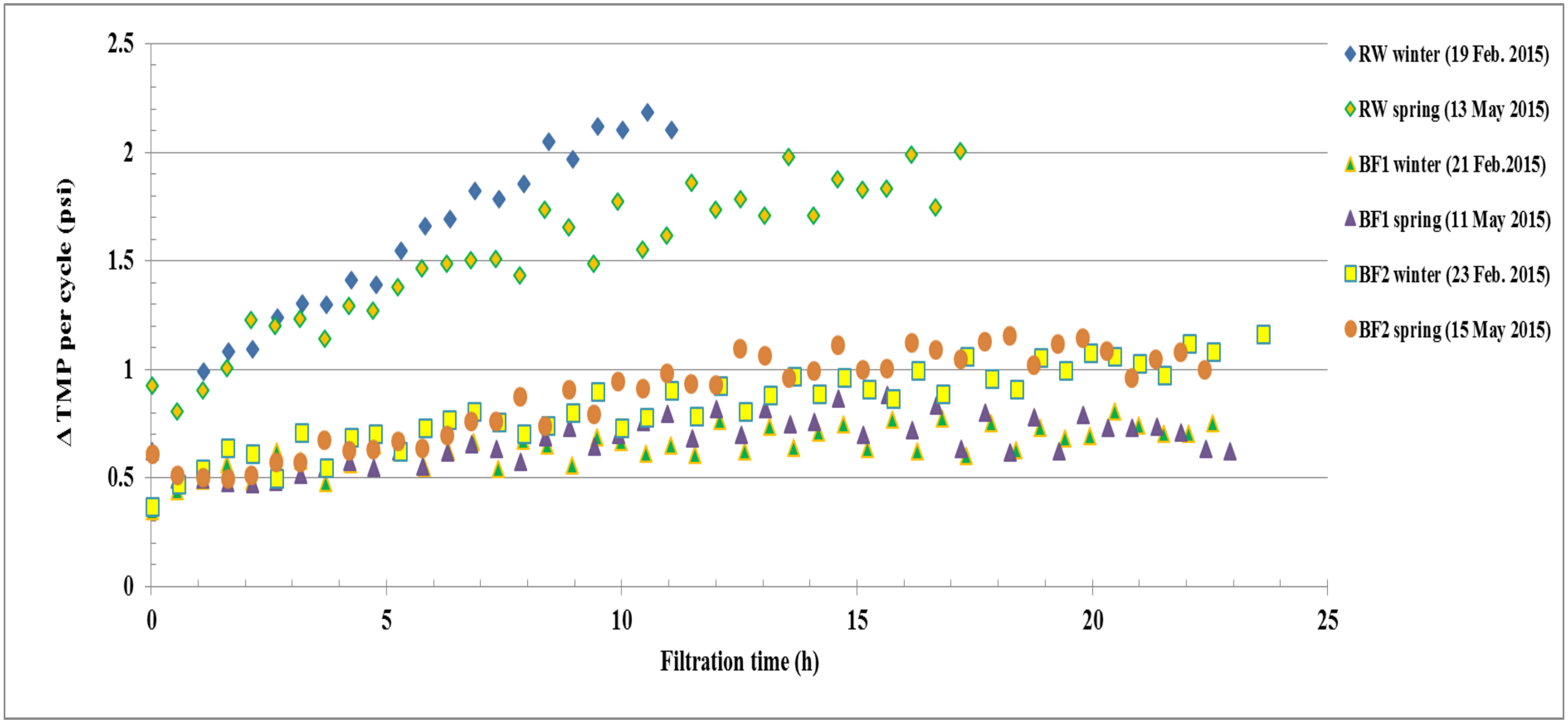


Figure 5.16 Increase in TMP with raw water (secondary effluent) and biofilter effluents in two different seasons

5.5 Conclusions

Biofiltration was investigated as a pre-treatment method for UF of secondary effluent treatment. Two biofilters, each containing 0.75 m of different media (sand vs. anthracite) were operated at an HLR of 0.75 m/h, corresponding to an EBCT of 60 min. The fouling experiments were conducted from January to May 2015. To measure the UF fouling rate before and after pre-treatment using the same batch of collected secondary effluent, the run length was set to end at 24 h or until the maximum TMP (8 psi) of the membrane was reached, which ever occurred first. Under the conditions investigated the following can be concluded:

- LC-OCD chromatograms of the secondary effluent and permeate following ultrafiltration (without biofiltration) demonstrated that biopolymers were the largest fraction of DOC rejected by UF (70 ± 19%). Lower removals of humic substances (4 ± 9%) and other DOC constituents through UF were observed. Turbidity was reasonably well removed through UF (97 ± 2%). Based on these observations, it is evident that biopolymers and particulate matter (measured as turbidity) were the main UF foulants in secondary effluent obtained from Waterloo WWTP.

- Biofiltration improved secondary effluent characteristics by reducing organic compound concentrations and turbidity. While removals could be to some extent physical it is likely that organics are transformed and utilized by biofilm organisms for energy, growth, and synthesis of biofilm structures. Biopolymers were the largest DOC fraction removed through the biofilter. The average removals of biopolymers through BF1 and BF2 were 26% and 19%, respectively. This is despite the fact that secondary treatment at the WWTP involves biological treatment as well. In term of protein compounds, there was a significant reduction through the two biofilters with an average removal of 64% and 49% through BF1 and BF2, respectively. There was an average reduction of turbidity of 76% and 70% through BF1 and BF2, respectively. As a biofilter media, sand was statistically significantly better than anthracite in terms of DOC and biopolymer removal.

- Using secondary effluent (without any pre-treatment) as feed water to a UF membrane is not a viable treatment approach. Severe reversible and irreversible fouling were experienced with normalized TMP reaching 6.0 psi after just 12 h of ultrafiltration. Both reversible and irreversible fouling were correlated with particulate matter (measured as turbidity in this study) when the UF membrane was fed with secondary effluent which had not been pretreated.

- Biofiltration dramatically improved the performance of ultrafiltration by reducing fouling development. The normalized TMP reached 4.0 psi and 3.0 psi at the end of a 24 h experiment when effluent of BF2 (anthracite) and BF1 (sand), respectively, were used as feed water for UF. The observed reduction in TMP is attributable to the removal/transformation of biopolymers (especially proteins) and turbidity through biofiltration.

- Humic substances were not correlated with reversible or irreversible fouling regardless of whether or not the UF was fed with secondary effluent or biofilter effluent. When the UF was fed with biofilter effluent, both reversible and irreversible fouling were correlated with biopolymer concentrations in feed water. Particulate matter was weakly correlated with UF reversible fouling. This study demonstrated that a combined layer of organic compounds (e.g., biopolymers) and particulate matter can develop and lead to increased irreversible fouling and/or alter the separation mechanisms of UF.

- While seasonal changes in secondary effluent character were not particularly evident, turbidity varied a somewhat, as did the ratios of some NOM constituents. However, no seasonal impact was observed in the performance of the biofilters or UF membrane.

5.6 Disclaimer

The mention of trade names or commercial products does not constitute endorsement of or recommendation for their use.

Chapter 6

In-line Coagulation Optimization for Polymeric Ultrafiltration Fouling Reduction to Treat Secondary Effluent for Water Reuse

Summary

Low pressure membranes are attracting attention for their potential to improve secondary effluent quality, but membrane fouling can limit their widespread applicability. In this study, in-line coagulation as pre-treatment to ultrafiltration was investigated using a bench-scale hollow fiber membrane at a constant flux of 33 L/m^2 h (LMH). Membrane fouling was monitored by observing change in trans-membrane pressure (TMP) for secondary effluent and in-line coagulated secondary effluent over a 24h period. The impact of four coagulants at different dosage on reversible and irreversible membrane fouling and permeate quality was studied. It was found that in-line coagulation improved UF performance to varying degrees depending on coagulant type and dosage. Generally, higher reduction of fouling was achieved by increasing coagulant dosage within 0.5 – 5.0 mg/L range investigated. Ferric-based coagulants were better than aluminum-based coagulants with respect to improving membrane performance, for the secondary effluent investigated, even at low dosages (0.5 mg/L). Further investigations are required to figure out how in-line coagulation affect organic compounds removal through ultrafiltration membranes.

6.1 Introduction

Improving membrane feed water quality by pre-treatment processes is a promising strategy for fouling mitigation. Coagulation is a widely used technology in surface water and wastewater treatment which not only reduces turbidity but under certain conditions can also remove natural organic matter (Edzwald 1993; Dong *et al*. 2007; Humbert *et al*. 2007). Coagulation promotes cake layer formation which protects membrane pores from smaller foulants (Haberkamp *et al*. 2007) and leads to an improvement at the membranes performance (Howe *et al*. 2006). The cake layer can be easily removed by hydraulic backwashing (Zularisam *et al*. 2006).

Several studies have been conducted to evaluate pre-coagulation prior to the membrane filtration. When it is applied for this purpose it is often in the form of conventional coagulation with rapid mix and a tank to allow time for floc development followed by settling basin before membrane filtration (Fan *et al.* 2008; Chon *et al.* 2012; Delgado-Diaz *et al.* 2012) or just floc formation tank (Hillis 2006; Guo and

Hu 2012; Ratajczak *et al.* 2012). As such, substantial space and energy are required. On the other hand, some studies have demonstrated the effectiveness of coagulants in reducing low pressure membranes when applied as in-line coagulation (Wang and Wang 2006; Delgado-Diaz *et al.* 2012; Zheng *et al*. 2012). In-line coagulation is defined as the continuous addition of coagulants at low doses prior to the membrane without removing particles (Wang and Wang 2006), for the purposes of changing particle and NOM characteristics (Liu and Kim 2008). This technology has many advantages, such as the small size of its footprint relative to conventional coagulation/flocculation and/or sedimentation (Zheng *et al*. 2012), and lower coagulant dosages decreasing both cost and sludge production.

Some studies have demonstrated that pre-coagulation is an effective method for improving polymeric membrane (Dong *et al*. 2007; Humbert *et al.* 2007; Zularisam *et al.* 2008) and ceramic membrane (Li *et al*. 2011; Zhu *et al.* 2011; Abbasi *et al*. 2012) performance. While others have reported little to no effect on membrane performance (Howe *et al*. 2006; Lee *et al*. 2007). Studies have been conducted to investigate the effect of coagulant type on membrane performance. Some have demonstrated that iron-based coagulants (e.g. ferric chloride) are better at reducing membrane fouling when treating surface water (Howe *et al*. 2006; Liu and Kim 2008) or secondary effluent (Haberkamp *et al*. 2007; Hatt *et al*. 2011; Acero *et al*. 2012). On the other hand, some have demonstrated that aluminum salts were more effective in improving membrane performance, in terms of high permeate quality and fouling reduction (Judd and Hillis 2001; Kim *et al*. 2005; Fan *et al*. 2008; Zheng *et al*. 2012).

The impact of coagulant dosage on membranes treating surface water (Ratajczak *et al*. 2012; Wray *et al*. 2014) or secondary effluent (Liu and Kim 2008; Haberkamp *et al*. 2007; Fan *et al.* 2008; Zheng *et al*. 2012) has also been investigated, but conflicting observations have been reported. This is due to the fact that coagulation is a complex chemical process that involves multiple reactions, and there are many factors affecting its performance especially when conducted with membrane filtration.

6.2 Objectives

The objectives of this chapter were to:

1. Investigate the potential of using in-line coagulation as a UF pre-treatment treating secondary effluent
2. Study the effect of coagulant type and dosage for the reduction of reversible and irreversible UF fouling
    - A control and two dosages (0.0, 0.5, and 5.0 mg/L) were investigated for each coagulant (alum, PACl, ferric chloride, and ferric sulfate)

6.3 Materials and Methods

6.3.1 Source Water

The secondary effluent investigated in this study was collected from Waterloo Wastewater Treatment Plant (WWTP), which treats domestic wastewater from the City of Waterloo, Ontario, Canada. The average daily capacity for the WWTP was 72,730 m^3/d in the period when this study was being conducted. The WWTP was undergoing construction during the investigated period of this study to upgrade both primary and secondary treatment, including biological treatment. The raw sewage was first treated by primary clarification where ferrous chloride was added for phosphorus removal. This was followed by conventional activated sludge as a biological treatment, followed by secondary settling tanks. The secondary effluent was UV-disinfected prior to discharge into the environment.

Secondary effluent following UV exposure was collected twice per week in three 200 L polyethylene drums and immediately transferred to the University of Waterloo (approximately 3.5 km from the WWTP). Secondary effluent was transferred into a storage tank immediately upon arrival in the Douglas Wright Engineering (DWE) wastewater pilot plant area on the campus of the University of Waterloo. The temperature of the tank was not controlled and the water increased to room temperature (23°C). Mixing to keep material from settling was accomplished by aeration and pumping to the UF membranes was initiated immediately after the tanks were filled.

6.3.2 Experimental Set-up

The ultrafiltration membrane used in this investigation was the commercially available polyvinylidene fluoride (PVDF) version made by GE Process Technologies (Oakville, Canada). The membrane module (the Zeeweed - 1®) was constructed of 15 cm long hollow fibers (500 series), and the operation mode was outside-in. The membrane had a nominal surface area of 0.047 m^2 with a MWCO of 400 KDa (approximately 40 nm pore size) as delivered from the manufacturer.

Figure 6.1 shows a schematic drawing of the UF set-up. Secondary effluent was pumped to the overhead tank with a peristaltic digital drive pump (model No. 7550-50, 1.6-100 PRM, Cole-Parmer Instrument Company, Barrington, USA). Coagulant was pumped in-line by a peristaltic digital drive pump (model No. 7553-70, 6-600 RPM, Cole-Parmer instrument Company, Barrington, USA) immediately before membrane influent. Two streams (secondary effluent and coagulant) were mixed together where an in-line static mixer (Koflo Corporation, Cary, IL) was connected (1.0 meter tubing before UF module entrance). The UF module was located vertically in a clear polyvinyl chloride cylindrical tank. The set-up was designed to cycle automatically, where each cycle began with 30 min of permeation followed by backwashing with air sparging for 20 sec. After that, the module tank was drained (30 sec) and refilled again with the investigated water (36 sec). For continuous measurement during the experiments, a temperature sensor and flowmeter monitor (model LC alpha controller, 200-500 CCM, Alicat Scientific, Tucson, USA) were connected to a data logger (HOBO Energy Logger, model H22-001, Onset, Cape Cod, Massachusetts, USA). The flow meter was used to maintain a consistent permeate flow rate throughout the whole UF experiment. It is connected with a digital permeation pump (Masterflex L/S drive model number 07550-50; Cole-Parmer Canada) that adjusted to operate at a constant flow rate (25 mL/min). The flowmeter measured the actual permeate flow rate each 10 sec and data was recorded by a data logger. The actual flux can be determined at any time during the filtration run using equation 3.1 (Rahman 2013). Transmembrane pressure was measured using a pressure transducer (model 68075-02, Cole-Parmer, Montreal, Canada) which was connected to the data logger as well. Fouling rates were determined using TMP data after correction for temperature at 20°C. Additional details regarding the bench-scale configuration and operation are available in El-Hadidy (2011) and Rahman (2013).

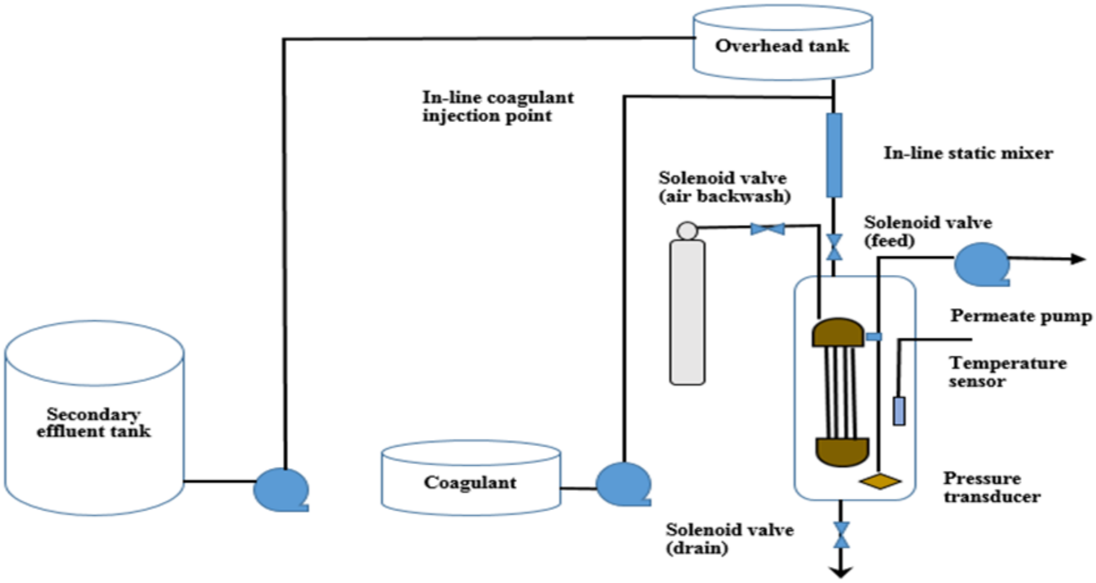


Figure 6.1 Membrane and in-line coagulation bench-scale schematic

All polymeric UF experiments were conducted in dead-end mode at a constant permeate flux of 33 L/m^2 h (LMH). To measure the UF fouling rate before and after pre-treatment using the same batch of collected secondary effluent, the run length was set to end at 24 h or when the maximum TMP (8 psi) of the membrane was reached. Chemical cleaning was performed after each experiment using sodium hypochlorite (200 mg/L) for a minimum of 5 h followed by a citric acid solution (5 g/L) for another 5 h. After chemical cleaning, the membrane was soaked in a glass jar containing deionized water at 4°C until usage. The UF module was integrity tested using a pressure calibrator (Meri-cal DP2001I, Meriam Instruments, Ohio, USA) prior to every experiment. The maximum allowable pressure drop through the membrane was 0.3 psi per 2 min. More details about the procedure of integrity test and membrane chemical cleaning are available in Appendix K). To check cleaning effectiveness, clean water permeability tests were conducted using deionized water before each experiment (Appendix L).

6.3.3 Coagulants

Four different coagulants were used in this study. They included aluminum sulfate (alum), polyaluminum chloride (PACl), ferric chloride, and ferric sulfate (Table 6.1). All coagulants were supplied by Kemira Water Solutions (Quebec, Canada).

Table 6-1 Coagulant information (from supplier)

Product name	**Aluminum sulfate**	**Polyaluminum chloride**	**Ferric chloride**	**Ferric sulfate**
Commercial name (product name)	Alum (Kemira ALS)	PACl (Stern PAC)	(PIX-111)	(PIX-312)
Concentration (as supplied)	29-50% as $Al_2(SO_4)_3.14H_2O$	15-40% as $Al_{13}(OH)_{20}(SO_4)_2Cl_{15}$	37-42% as $FeCl_3$	66-73% as $Fe_2(SO_4)_3$
Specific gravity	1.2 - 1.36	1.16 - 1.3	1.26 - 1.48	1.38 - 1.59
pH	< 2.5	1.8-3.4	< 2	< 2

Coagulants were first optimized for the removal of DOC, biopolymers, and humic substances by preliminary jar tests that were performed at dosages of 0.0, 0.5, 1.0, 2.5, 5.0, and 10.0 mg/L. All jar tests were carried out at the wastewater pilot plant in the Douglas Wright Engineering (DWE) Building, University of Waterloo using a procedure based on Standard Practice for Coagulation – Flocculation Jar Test of Water (ASTM Int'l2). Initially raw water (secondary effluent) was mixed for one minute before the addition of coagulant dosage. Then, the appropriate dose of coagulant was added and mixing was continued at approximately 100 rpm for one minute after which it was turned down to 30 rpm for

20 minutes. Finally, the flocs were allowed to settle for 30 minutes. Samples were taken after settling and routine analyses were conducted.

Based on the data obtained from jar tests, two dosages (0.5 and 5.0 mg/L as coagulant) were selected to be investigated as in-line coagulants in reducing UF fouling. Table 6.2 summarizes the dosages of coagulants and the corresponding added amount as the active metal ion. Dosage calculations for preliminary jar tests and in-line coagulation experiments are available in Appendix G.

Table 6-2 Dosages of the coagulants applied for in-line coagulation experiments and the corresponding amount added

Coagulant	**Chemical formula**	**Dosage mg/L as coagulant**	**Amount added mg Al^{3+} or Fe^{3+}/L**	**Amount added mmole Al^{3+} or Fe^{3+}/L**
Alum	$Al_2(SO_4)_3.14H_2O$	0.5	0.045	$1.7x10^{-3}$
		5.0	0.450	$1.7x10^{-2}$
PACl	$Al_{13}(OH)_{20}(SO_4)_2Cl_{15}$	0.5	0.125	$5x10^{-3}$
		5.0	1.250	$5x10^{-2}$
Ferric chloride	$FeCl_3$	0.5	0.174	$3x10^{-3}$
		5.0	1.740	$3x10^{-2}$
Ferric sulfate	$Fe_2(SO_4)_3$	0.5	0.140	$2.5x10^{-3}$
		5.0	1.400	$2.5x10^{-2}$

6.3.4 Liquid Chromatography Organic Carbon Detection (LC-OCD)

NOM compounds were identified based on their molecular weight using an LC-OCD Model 8 (DOC-LABOR, Karlsruhe, Germany) as per Huber *et al.* (2011). Before analysis, samples were pre-filtered using a 0.45 µm PVDF membrane filter (Pall Supor® Membrane Disc Filters, 0.45 µm, 47 mm plain, VWR international, USA) which was pre-rinsed with 30 mL of ultrapure. Samples were diluted with ultrapure water if the DOC in the sample exceeded 5 mg/L.

6.3.5 Analytical Methods for Water Samples

Water samples were collected from the inlet and the outlet of each biofilter in clean glass 1-liter bottles. Water samples were preserved at 4°C until sample analysis which occurred within 24 h of sampling. The parameters monitored were TOC, DOC, UV_{254}, specific UV absorbance (SUVA = UV_{254}/DOC), pH, and turbidity. In addition some parameters were monitored only in the secondary effluent at the Waterloo WWTP labs. The methods used for all measured parameters are described in detail in Section 3.6.

6.4 Results

6.4.1 Impact of Coagulant Type and Dosage on Secondary Effluent Characteristics

Jar test experiments were conducted to examine the impact of four coagulants (alum, PACl, ferric chloride, and ferric sulfate) on the characteristics of selected secondary effluent. It is recognized that jar tests do not necessarily model what might be encountered in an in-line coagulation application. They could, however, provide some performance information which might assist with the selection of conditions for the in-line tests. A no coagulant control and 5 dosages of each coagulant were investigated for the removal of DOC, humic substances, and biopolymers (0.0, 0.5, 1.0, 2.5, 5.0, and 10 mg/L). Figure 6.2 (a, b, and c) illustrates the removal of DOC, humic substances, and biopolymers, respectively, obtained for the different concentrations of alum, PACl, ferric chloride, and ferric sulfate. In general, increasing coagulant dosage increased the removal of all three groups of compounds. The highest DOC removal, 11.5%, was achieved using PACl at 10 mg/L, while alum was the least effective coagulant for the reduction of DOC (a maximum reduction of 2.0% at 5.0 mg/L). By comparison, similar higher DOC reductions were achieved by ferric chloride and ferric sulfate, where almost 7.5% reduction of DOC was observed at the highest dosage applied (10 mg/L). As expected, there was almost no impact of coagulants on humic substances removal as shown in Figure 6.2b. This was attributed to the low amounts of hydrophobic compounds in the selected secondary effluent as indicated by SUVA values (Table 6.3), where low SUVA values (less than 3) are indicative of the presence of low molecular weight non humic compounds, and coagulation is not nearly as effective for DOC removal in such cases (Edzwald 1993; Hatt *et al*. 2011). The pH of coagulation at the dosages employed was not sufficiently low to induce substantial enhanced coagulation DOC removal. Similar observations were reported by Paar *et al*. (2011) when studying the impact of in-line coagulation on reducing UF fouling in surface water treatment. Wray and Andrews (2014) also reported that coagulation was not efficient for removing organic compounds from lake water (Lake Ontario) that had low SUVA (< 2.0 L/mg.m). There was no change observed in the low molecular weight fraction concentrations regardless of coagulant type and dosage, which is in agreement with previous studies (Haberkamp *et al*. 2007; Wray and Andrews 2014)

In terms of biopolymer removal, for all coagulants, increasing coagulant dosage increased biopolymer removal. At the highest dosage applied (10 mg/L), the highest removals of 29% and 28% were achieved by PACl and ferric chloride, respectively. The lowest biopolymer removal was 10% observed with alum at the highest dosage (10.0 mg/L) followed by ferric sulfate with an 18% biopolymer removal at the same dosage. The preferential removal of biopolymers by chemical coagulation was also observed in some previous studies (Haberkamp *et al*. 2007; Paar *et al*. 2011; Zheng *et al*. 2012; Wray *et al*. 2014).

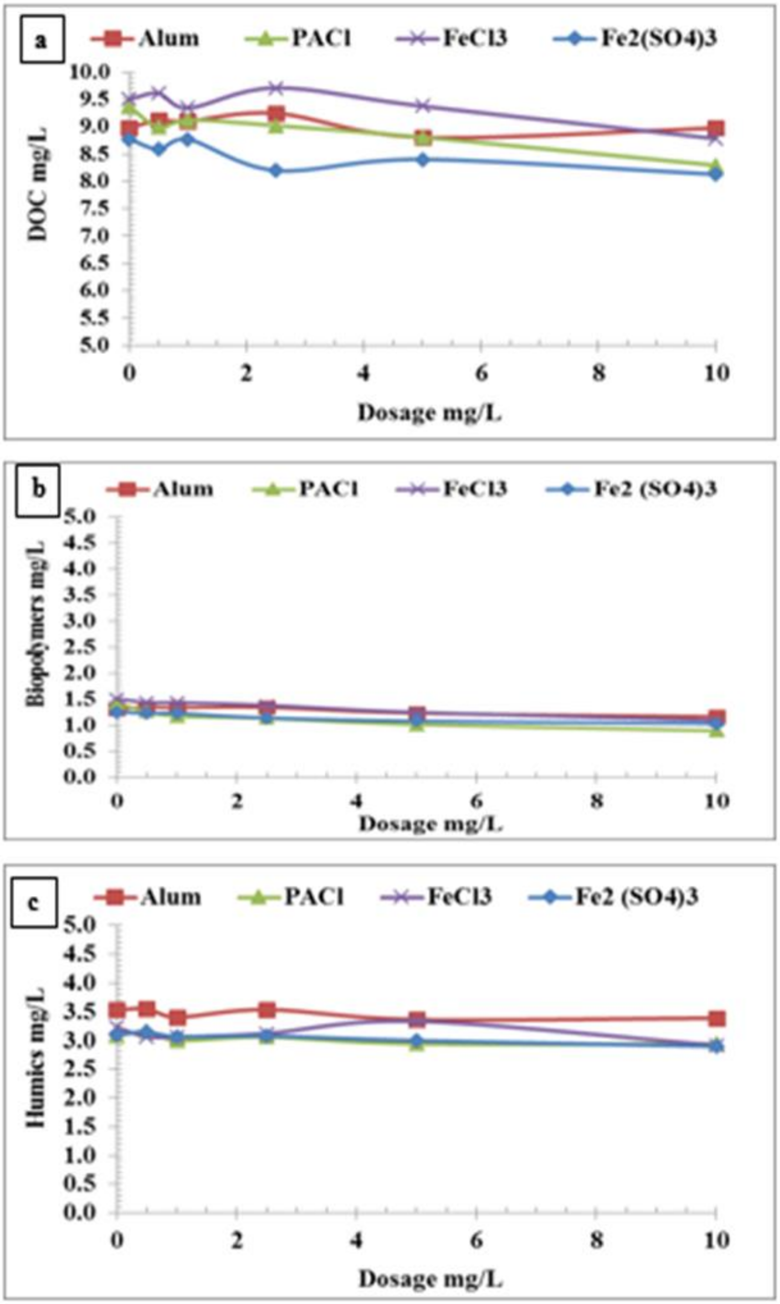


Figure 6.2 Impact of coagulant type and dosage on secondary effluent a) DOC, b) biopolymers, and c) humic substance concentrations using jar tests

Table 6-3 Impact of coagulant type and dosage on secondary effluent pH, UV254, and SUVA

Dosage (mg/L)	Alum			PACl			Ferric chloride			Ferric sulfate		
	pH	UV254 1/cm	SUVA L/mg.m	pH	UV_{254} 1/cm	SUVA L/mg.m	pH	UV_{254} 1/cm	SUVA L/mg.m	pH	UV_{254} 1/cm	SUVA L/mg.m
0.0	8.50	0.1491	1.66	8.04	0.1276	1.36	7.60	0.1483	1.56	8.23	0.1296	1.47
0.5	8.51	0.1457	1.60	8.08	0.1212	1.35	7.58	0.1439	1.50	8.21	0.1278	1.49
1.0	8.48	0.1451	1.59	8.04	0.1185	1.30	7.51	0.1405	1.50	8.18	0.1261	1.44
2.0	8.45	0.1455	1.57	8.06	0.1179	1.31	7.46	0.1389	1.43	8.15	0.1220	1.49
5.0	8.36	0.1407	1.60	8.05	0.1131	1.28	7.39	0.1243	1.33	8.09	0.1208	1.44
10.0	8.32	0.1376	1.53	7.97	0.1105	1.33	7.21	0.1089	1.24	8.01	0.1186	1.46

It is worth mentioning that under the conditions investigated in the current study, coagulation also removed organic nitrogen compounds (e.g. proteins) based on LC-OCD analysis (Figure 6.3). As shown, coagulants were efficient in reducing organic nitrogen even at the lowest applied dosage (0.5 mg/L) - except in the case of ferric chloride. The highest organic nitrogen reductions, 70% and 50%, were achieved at the highest applied dosages (10 mg/L) of PACl and ferric sulfate, respectively. This finding is in agreement with Zheng *et al*. (2012), who reported that the highest organic nitrogen reduction of secondary effluent was achieved by PACl at 0.148 mmole AL^{3+}/L in jar tests. It can be seen that there was no impact of ferric chloride on organic nitrogen when applied at dosages lower than 10 mg/L. This observation is inconsistent with that obtained by Zheng *et al*. (2012). In their study, ferric chloride was superior to $AlCl_3$ and PACl for the reduction of organic nitrogen from secondary effluent even at low doses (0.037 mmole Fe^{3+}/L, which is equivalent to 2.0 mg Fe^{3+}/L), while increasing the dosage to 0.148 mmole Fe^{3+}/L (8.3 mg Fe^{3+}/L) provided no additional improvement in organic nitrogen reduction.

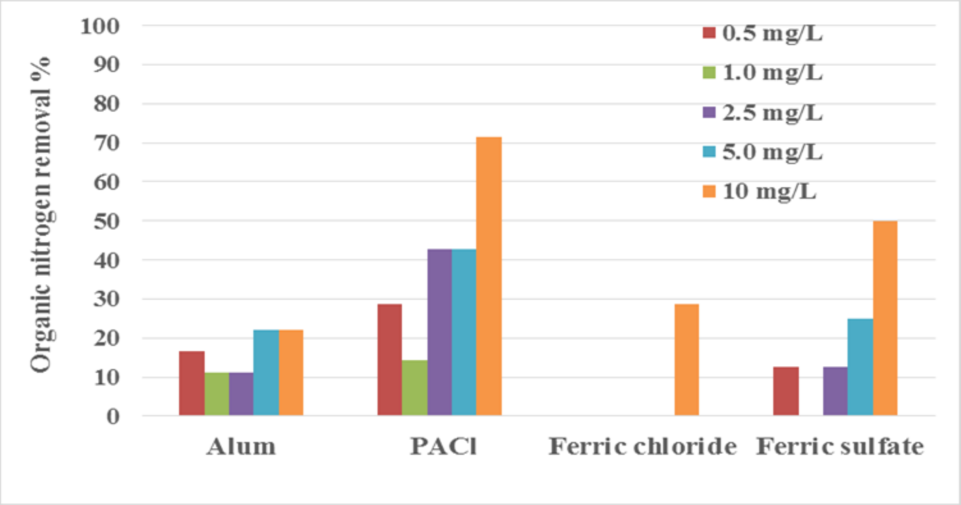


Figure 6.3 Impact of coagulant type and dosage on organic nitrogen from secondary effluent

6.4.2 In-line Coagulation to Control Ultrafiltration Fouling

To examine the impact of different coagulant types and dosage on ultrafiltration performance, three membrane experiments were conducted using secondary effluent alone and after in-line coagulant at two different dosages (0.5 and 5.0 mg/L). While 10 mg/L was preferable from the jar test results, it was decided that, for practical purposes, lower dosages made more sense in real world applications. The in-line coagulation experiments were conducted from January 15 to April 11, 2015. During this period, one no-coagulant control, and one coagulant type at two different dosages (0.0, 0.5, and 5.0 mg/L) were investigated each week. Raw data for these experiments are available in Appendix H.

Table 6.4 summarizes DOC, biopolymers, humic substances, and turbidity reduction for each of the different coagulants and dosages. Based on LC-OCD analysis, UF alone (when fed with secondary effluent without in-line coagulants) retained 73 ± 13% of biopolymers, while there was almost no removal of the remaining NOM fractions (primarily humic substances). There was a 96 ± 2.0% reduction of secondary effluent turbidity through UF. These results indicate that both biopolymers and turbidity played an important role in UF fouling.

Table 6.5 summarizes the impact of in-line coagulants and dose in altering the organic composition of UF feed water (secondary effluent). For water analysis, in-line coagulated samples were taken immediately before entering the UF module (following 20 seconds of coagulant contact) at the same flow rate as is fed to the membrane (1.5 L/h). Turbidity was measured soon after sample was collected.

For DOC and LC-OCD analyses, samples were pre-filtered using a 0.45 μm PVDF membrane filter. At the highest applied dosage (5.0 mg/L), it can be seen that ferric sulfate was the most effective coagulant for changing organic compounds (biopolymers and humic substances) followed by PACl. The highest reduction of organic compounds at the low dose (0.5 mg/L) was achieved by ferric chloride (35 and 15% reductions of biopolymers and humics, respectively). Increasing alum dosage from 0.5 to 5.0 mg/L had an adverse impact on biopolymers, but it provided the highest reduction in turbidity (at 5.0 mg/L alum). In general, the most effective impact of in-line coagulation was observed in turbidity reduction, even at the low dosages tested. The biopolymer reduction obtained by in-line coagulants is likely attributable to phase transformation from dissolved to particulate compounds which are retained during sample filtration. The low reduction of humic substances was expected as in-line coagulation was applied at pH conditions which are not favorable for enhanced coagulation (pH > 7.0).

Table 6-4 Impact of different treatment conditions on the reduction of DOC, biopolymers, humic substances, and turbidity

Coagulant	Treatment	DOC %	BP%	HS%	Turbidity %
Alum	UF alone (fed with secondary effluent)	11	75	0	96
	Impact of 0.5 mg/L on UF feed*	12	19	5	34
	Impact of 5.0 mg/L on UF feed*	-10	-12	3	79
	UF after 0.5 mg/L (pre-post UF)	17	79	0	94
	UF after 5.0 mg/L (pre-post UF)	28	67	10	74
	Overall 0.5 mg/L (feed water-UF permeate)	27	83	5	96
	Overall 5.0 mg/L (feed water-UF permeate)	26	65	11	95
PACl	UF alone (fed with secondary effluent)	9	61	0	96
	Impact of 0.5 mg/L on UF feed*	17	28	21	45
	Impact of 5.0 mg/L on UF feed*	11	22	15	60
	UF after 0.5 mg/L (pre-post UF)	12	79	0	95
	UF after 5.0 mg/L (pre-post UF)	2	53	0	96
	Overall 0.5 mg/L (feed water-UF permeate)	27	85	17	97
	Overall 5.0 mg/L (feed water-UF permeate)	11	63	5	98
Ferric chloride	UF alone (fed with secondary effluent)	26	80	4	95
	Impact of 0.5 mg/L on UF feed*	26	37	14	32
	Impact of 5.0 mg/L on UF feed*	17	11	7	54
	UF after 0.5 mg/L (pre-post UF)	15	82	3	94
	UF after 5.0 mg/L (pre-post UF)	22	91	6	95
	Overall 0.5 mg/L (feed water-UF permeate)	37	89	17	96
	Overall 5.0 mg/L (feed water-UF permeate)	35	92	13	98
Ferric sulfate	UF alone (fed with secondary effluent)	7	67	0	98
	Impact of 0.5 mg/L on UF feed*	20	13	16	77
	Impact of 5.0 mg/L on UF feed*	17	58	58	43
	UF after 0.5 mg/L (pre-post UF)	7	87	-15	91
	UF after 5.0 mg/L (pre-post UF)	23	57	-54	96
	Overall 0.5 mg/L (feed water-UF permeate)	26	88	3	98
	Overall 5.0 mg/L (feed water-UF permeate)	36	82	18	98

*Collected immediately prior to entering membrane module tank following a static mixer and 20 seconds contact time in influent pipe.

Table 6-5 Impact of in-line coagulant type and dosage on biopolymers, humic substances, and turbidity reduction (samples were collected after coagulant addition and before entering UF)

Coagulant	Dosage (mg/L)	Reduction %		
		Biopolymers	Humic substances	Turbidity
Alum	0.5	19	5	34
	5	-9	3	79
PACl	0.5	28	21	45
	5	22	15	60
Ferric chloride	0.5	37	14	32
	5	11	7	54
Ferric sulfate	0.5	13	16	77
	5	58	58	43

Figure 6.4 shows the impact of coagulant type and dose on reversible UF fouling. The reversible fouling rate during a cycle was calculated by subtracting the TMP measured at the start of the cycle from the TMP measured at the end of the previous cycle before backwashing. To determine the irreversible fouling rate, the TMP at the beginning of each cycle was averaged over the time period being investigated (Figure 6.5). There was a rapid increase in TMP during the first hours of the filtration of secondary effluent without coagulant addition (TMP figures are available in Appendix H), after which the rise in fouling rate slowed. The accelerated fouling rate at the beginning stage of the operation was attributed to membrane pore blocking (Kim *et al*. 2005) by organics or particles which were close to the diameter of membrane pores (Ma *et al*. 2013). Pore blocking leads to the development of irreversible fouling (Juang *et al*. 2007) which is hard to recover by backwashing compared with cake layer formation (Paar *et al*. 2011) which causes stabilization in the fouling rate (Mosqueda-Jimenez *et al*. 2008). The same observation was obtained by Kim *et al*. (2005) during treatment of secondary effluent and Ratajczak *et al*. (2012) treating river water (Grand River, ON) using UF.

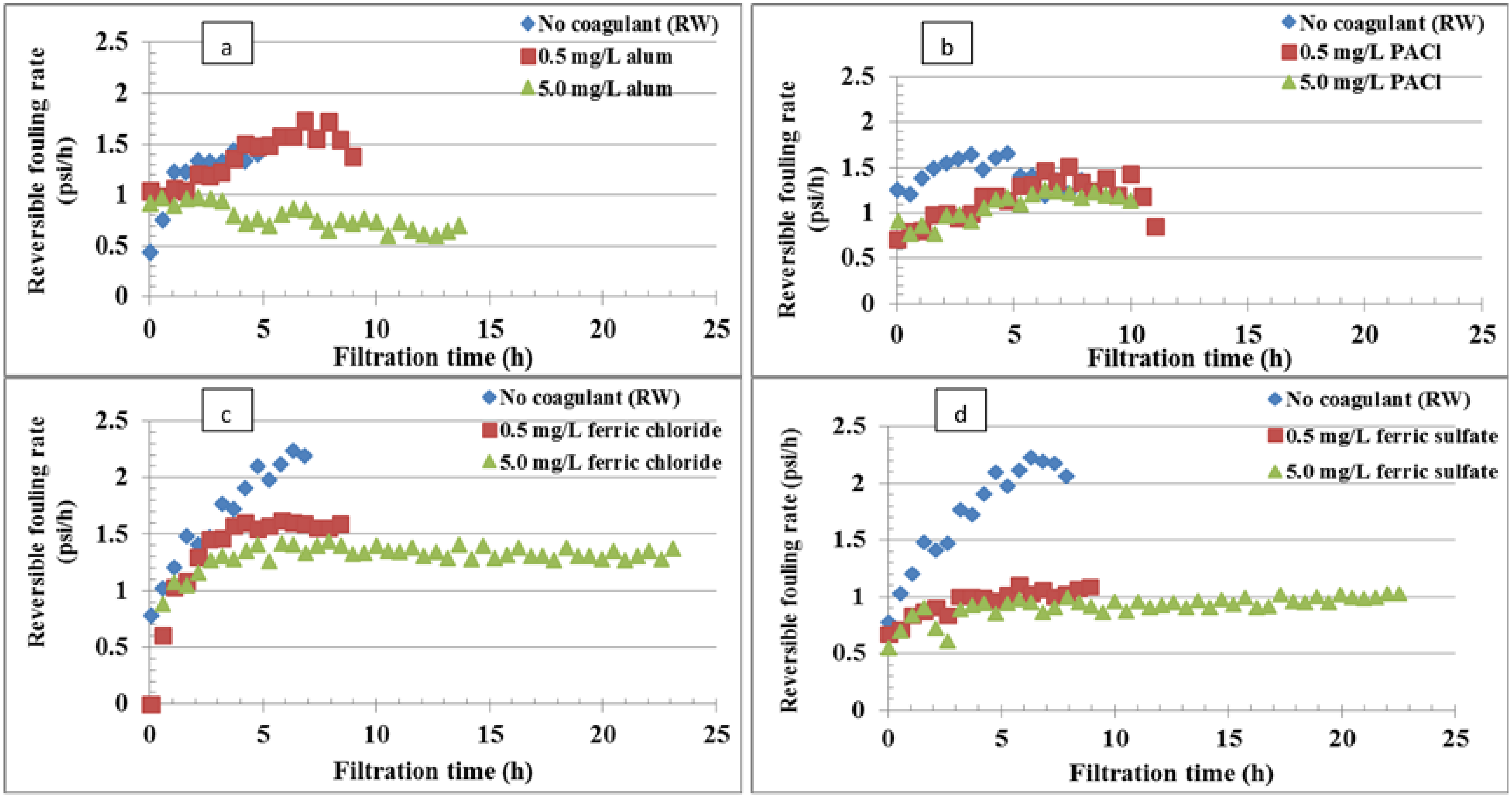


Figure 6.4 Hydraulically reversible fouling rates for different coagulant types and dosages, a) alum ($Al_2(SO_4)_3.14H_2O$), b) PACl ($Al_{13}(OH)_{20}(SO_4)_2Cl_{15}$), c) ferric chloride ($FeCl_3$), and d) ferric sulfate ($Fe_2(SO_4)_3$)

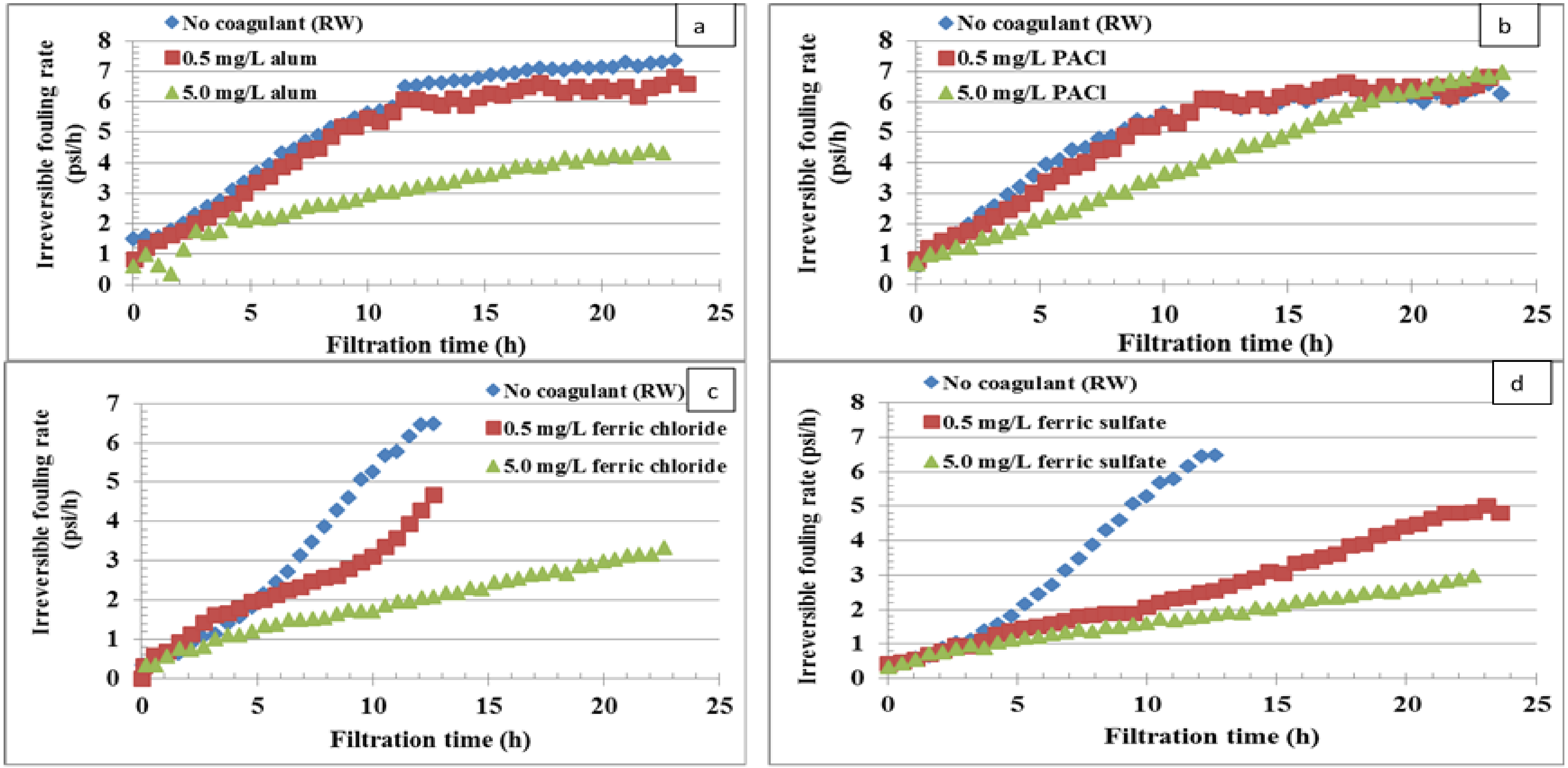


Figure 6.5 Hydraulically irreversible fouling rates for different coagulant types and dosages, a) alum ($Al_2(SO_4)_3.14H_2O$), b) PACl ($Al_{13}(OH)_{20}(SO_4)_2Cl_{15}$), c) ferric chloride ($FeCl_3$), and d) ferric sulfate ($Fe_2(SO_4)_3$)

In this study, the irreversible fouling rate was characterized by an initial rapid increase in the early stages of the UF run (10 h or less) and is described as the ‘first period’. This was followed by a ‘second period’, where the rate stabilized or decreased (usually when a TMP of 8 psi approached or was reached) (see Figure 6.5 a, b and c for example, no coagulant and 0.5 mg/L dose). For data interpretation, only the first period was taken into account for performance analysis which is summarized in Table 6.6. The percentage reductions in reversible and irreversible fouling were calculated based on the average rates of reversible and irreversible fouling determined for each run (e.g. using the zero coagulant dose (raw secondary effluent) as the basis for reductions attributable to BF1 and BF2 pre-treatment).

Table 6-6 Reduction in UF reversible fouling (RF) and irreversible fouling (IRF) rates in association with coagulant addition for the whole run, and first and second periods

			Whole run			First Period			Second period		
Coagulant	Date	Dosage	Run time	RF	IRF	Time	RF	IRF	Time	RF	IRF
		mg/L	h	% Reduction		h	% Reduction		h	% Reduction	
Alum	19-Jan-15	0.0	23			6			17		
	22-Jan-15	0.5	23.5	-6	15	6	4	5	17.5	-40	11
	15-Jan-15	5.0	23	17	66	6	11	29	17	9	44
PACl	30-Jan-15	0.0	22.5			5			17.5		
	26-Jan-15	0.5	23.5	7	-6	5	8	7	18.5	-18	-45
	28-Jan-15	5.0	23.5	11	-24	5	19	33	18.5	15	-82
Ferric chloride	6-Feb-15	0.0	22			8.5			13.5		
	2-Feb-15	0.5	24	12	40	8.5	8	34	15.5	6	-59
	4-Feb-15	5.0	23.5	22	75	8.5	14	66	15	-71	29
Ferric sulfate	13-Feb-15	0.0	18			8			10		
	11-Feb-15	0.5	23.6	32	55	8	44	57	15.6	-10	8
	9-Feb-15	5.0	22.5	36	76	8	50	77	14.5	-1	58

It has been demonstrated that coagulation leads to the rapid formation of a cake layer (Bagga *et al.* 2008) that is easily backwashed (Galvañ *et al.* 2014), and which serves as a protective layer from membrane pore blocking. It can be seen from Figures 6.4 and 6.5 that there was a significant improvement of the UF membrane performance when in-line coagulation was applied. However, the impact on reversible and irreversible fouling reduction differed based on coagulant type and dosage. It is acknowledged that there was some difference in the observed fouling rate in each experiment (based on coagulant type) and each experiment was conducted from a different secondary effluent batch. However, the intent in each experiment was to compare the pre-treatments to a base case which was the no-coagulant condition. With all coagulant types, there was a slight improvement in UF performance (especially in the case of irreversible fouling) when the dose of coagulant was increased from 0.5 to 5 mg/L. The UF membrane fouling reduction by in-line coagulation appears to be attributable to the size modification of particles that contribute to pore blocking (Zheng *et al*. 2012). The reduction in irreversible fouling observed in this study for all coagulant tested reflected the elimination of pore blocking at the initial stages of the filtration run (Paar *et al.* 2011) caused by the aggregation of colloids and organics (Howe *et al.* 2006). Furthermore, increasing coagulant dose led to the formation of larger particles which further improved UF performance; where the larger the size flocs produced, the lower development of membrane fouling (Dong *et al.* 2012) (at least in the ranges of doses investigated here).

As can be seen in Table 6.6, the largest reduction in reversible and irreversible fouling was achieved by ferric sulfate at the higher of the two dosages tested (5.0 mg/L). Although PACl was the second most effective coagulant in reducing organic compounds at the high dosage, ferric chloride outperformed PACl in fouling control at the same dosage (5.0 mg/L).

Under the conditions investigated, iron-based coagulants (e.g. ferric chloride and ferric sulfate) were more effective than aluminum-based coagulants for controlling membrane fouling. A similar finding has been reported by Haberkamp *et al*. (2007) and Acero *et al*. (2012) when comparing ferric chloride and alum for secondary effluent treatment by UF. A study conducted by Zheng *et al*. (2012) to compare between ferric chloride, alum, and PACl as in-line coagulant pre-treatment for UF in secondary effluent found that ferric chloride generally outperformed both alum and PACl for TMP control. This may be attributed to larger size of flocs produced by iron-based coagulants than those formed by aluminum-based coagulants (Ratajczak *et al*. 2012). It is also possible that the interactions between the membrane surface and flocs formed by iron-based coagulants are weaker than those of the aluminum-based coagulants (Zheng *et al*. 2012). On the other hand, some studies (Fan *et al*. 2008; Ratajczak *et al*. 2012) reported that alum and PACl were more effective than ferric chloride for reducing membrane fouling. The conflicting observations may be attributable to differences in feed water characteristics (e.g. turbidity and NOM concentrations), coagulant dosages (and their calculation), membrane properties, and the flocs produced during coagulation.

It should be noted that based on data obtained from jar tests (section 6.4.1), PACl was the most effective coagulant for reducing biopolymers (organic carbon and organic nitrogen) but it was not the most effective for reducing UF fouling (as measured by change in TMP). As such, jar tests may be not be a practical predictor or indictor of membrane fouling reduction especially when coagulant is applied in the form of in-line pre-treatment.

Besides the impact of in-line coagulation on the reduction of UF fouling, the effect of pre-treatment on permeate quality was also monitored. Based on data summarized on Table 6.4, the removal of biopolymers and turbidity through UF was increased (in most cases) by the application of in-line coagulation and, simultaneously, fouling was reduced. At neutral pH and low coagulant doses, the main mechanism of coagulation is charge neutralization where small particles and organic compounds aggregate to create larger compounds that easily settled on membrane surface preventing pore blocking. Under such conditions, in-line coagulation can assist in reducing membrane fouling while at the same time higher removal of organics and particles can be achieved. No clear conclusions with the respect to the impact of combining in-line coagulation with UF for reducing DOC could be drawn (Figure 6.6, these experiments had only single points (no replicates)). At the low coagulant dosage (0.5 mg/L) for each of the 4 coagulants, there was an improvement in DOC reduction by UF. Increasing applied dosage of ferric sulfate to 5.0 mg/L yielded to an additional 10% of DOC removal by UF. For alum and ferric chloride, increasing the coagulant dosage to 5.0 mg/L did not yield any additional removal of DOC. On the other hand, the removal of DOC by UF was decreased after increasing the dose from 0.5 to 5 mg/L for the PACl. These observations suggest that further investigation with replicates points will be required. If it is borne out that only very small dosages are required and that higher dosages are detrimental, then coagulation optimization for in-line coagulant addition becomes critically important.

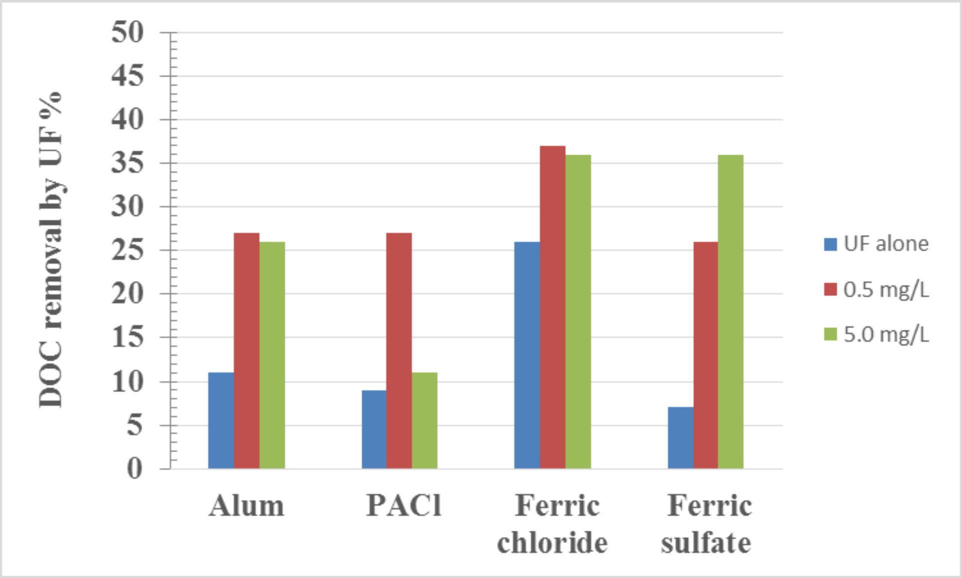


Figure 6.6 The impact of combining in-line coagulation with UF for DOC reduction

6.4.3 Extended Investigation

It is evident (based on observations above) that in-line coagulation can improve UF performance for secondary effluent treatment. Coagulant type and dosage impacted the reduction of reversible and irreversible fouling. To further investigate the impact of coagulant type and dosage on reducing both reversible and irreversible fouling, two coagulants (alum and ferric sulfate) were selected for further investigation. In this section, alum at dosages of 0.5, 2.5 and 5.0 mg/L and ferric sulfate at dosages of 0.5, 1.0 and 5.0 mg/L were investigated as in-line coagulation pretreatment for UF. Raw data for water samples and change in normalized TMP during experiments are available in Appendix H. Figures 6.7 and 6.8 illustrate the impact of different applied dosages of alum and ferric sulfate, respectively, on the reduction of UF reversible and irreversible fouling. At low doses of alum (0.5 mg/L), as can be seen from Figure 6.7, the reduction of UF reversible and irreversible fouling did not exceed 10%. Increasing the alum dose from 0.5 to 2.5 mg/L increased the reduction of reversible and irreversible fouling to 32% and 78%, respectively. On the other hand, increasing alum dosage to 5.0 mg/L did not further significantly improve the effect. The reversible and irreversible reduction achieved at 5.0 mg/L of alum were 34% (about the same as the 2.5 mg/L dose) and 40% (half of that obtained by 2.5 mg/L), respectively. In the case of ferric sulfate, except at a dosage 1.0 mg/L, increasing dosage had generally a positive impact in controlling fouling (Figure 6.8). The highest reduction of reversible and irreversible fouling was 45 ± 7.0% and 84 ± 10%, respectively, achieved at 5.0 mg/L. In general, the more considerable impact of in-line coagulation was observed for irreversible fouling reduction which is ultimately more important for sustainable membrane operation, as it reduces the frequency of chemical cleaning while increasing membrane life.

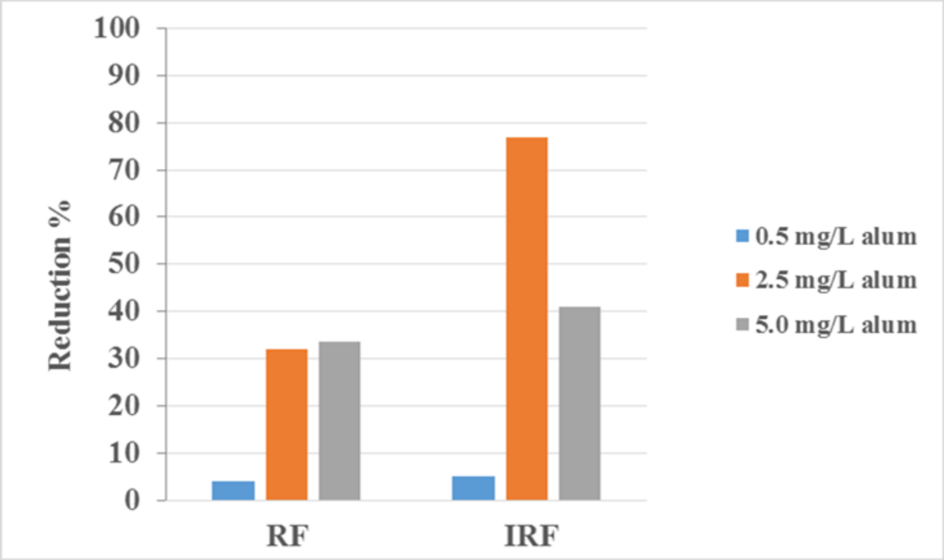


Figure 6.7 Reduction in reversible and irreversible UF membrane fouling using alum at three different dosages (0.5, 2.5, 5.0 mg/L), n = 2 for 0.5 and 5.0 mg/L and only one point for 2.5 mg/L

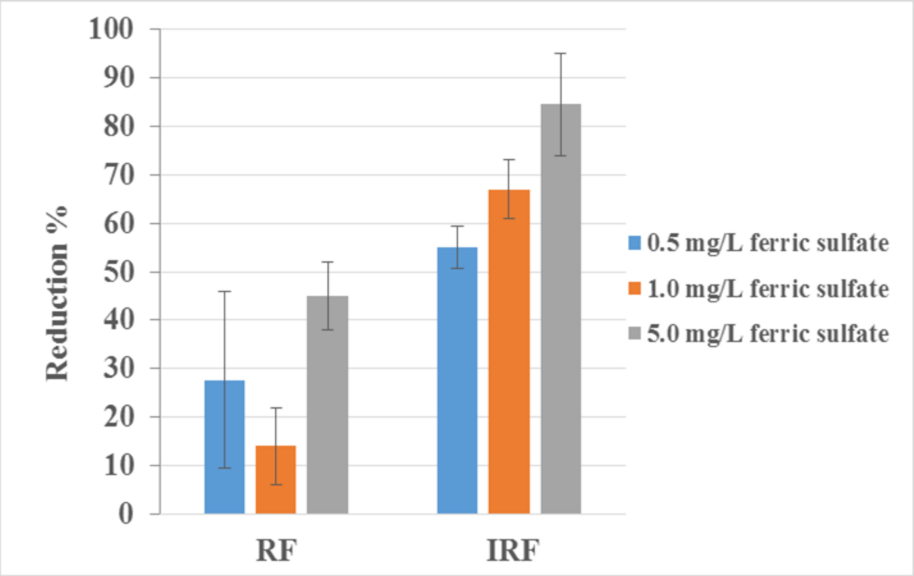


Figure 6.8 Average reduction in reversible and irreversible UF membrane fouling using ferric sulfate at three different dosages (0.5, 1.0, and 5.0 mg/L), n= 4 for 0.5 mg/L, and n = 3 for 1.0 and 5.0 mg/L

With respect to alum, adding more coagulant (5.0 mg/L) resulted in less improvement in membrane fouling. This may be attributed to feed water variation. The biopolymer concentration was 2.0 mg/L in coagulated secondary effluent when the 5.0 mg/L dose test was done, while it was 1.7 mg/L when 2.5 mg/L of alum was applied. Also, the turbidity was lower in coagulated secondary effluent for the 2.5 mg/L dose test (Table H.1). The same observation was reported by Zheng *et al.* (2012) where a lower operation time of the UF was observed with increasing alum dosage from 0.074 to 0.148 mmole Al^{3+}/L. Higher deposition of aluminum hydroxide on the membrane surface (Wray *et al*. 2014), which may increase membrane fouling (Galvañ *et al.* 2014), could have contributed to the observed phenomena.

Based on data presented in Figure 6.8, it is unclear why the least reduction in the reversible fouling rate occurred at 1.0 mg/L of ferric sulfate. This suggested that a difference in the flocs formed or in the interaction between formed flocs and foulants (e.g. organic compounds) was responsible for the lower reduction in reversible fouling at that dosage. In a pilot plant study conducted by Paar *et al.* (2011) to investigate the impact of in-line coagulation by ferric chloride to reduce fouling of a UF membrane treating secondary effluent, dosing at 1.0 mg Fe^{3+}/L did not have any impact on the membrane performance but this was not observed at the other investigated dosages (2.0 and 5.0 mg Fe^{3+}/L).

Although in-line coagulation improved UF performance for the treatment of the selected secondary effluent, coagulant dose should be cautiously adjusted (Galvañ *et al.* 2014). Lower dosages may be not sufficient for the transformation of particles and organics into more rejectable compounds (Ratajczak *et al*. 2012), while higher dosages can increase depositions of coagulant on membrane surface producing additional resistance (Wray and Andrews 2014; Galvañ *et al.* 2014). Ma *et al.* (2013) found that there was a critical coagulant dosage, which was impacted by feed water pH which dramatically influenced membrane performance leading to severe fouling. Also, the interaction between organic compounds and particles in feed water has not been well reported (Galvañ *et al.* 2014). In addition, the data obtained from this study reflected that jar tests may be not a useful indictor of optimum coagulant type and dosage for controlling fouling. Therefore, the goals of the pretreatment (e.g. fouling reduction and/or higher permeate quality) should be carefully considered before conducting tests.

Figures 6.9a and b plot turbidity, and biopolymers and humic substances concentrations in UF feed water vs. reversible and irreversible fouling, respectively, at different alum dosages. The same parameters are plotted in Figures 6.10 a and b for ferric sulfate.

With respect to alum, correlation between parameters and membrane fouling can be assessed with the 4 recorded values, however, it is recognized that additional data would strengthen this finding. There was sufficient evidence to confirm that both reversible and irreversible membrane fouling (Figures 6.9a and 6.9b) were positively correlated with turbidity ($p < 0.05$, t-test). The positive correlation between turbidity and membrane fouling was expected. The highest rate of irreversible fouling (0.4 psi/h) at high turbidity value (3.3 NTU) occurred at the low alum dosage (0.5 mg/L) applied. Previous studies reported that the higher the alum dosage, the bigger sized formed floc (Ma *et al.* 2013). Wray and Andrews 2014 reported that the size of the flocs formed at 0.5 mg/L alum were similar to size of particles in raw water, which confirmed the observed correlation.

No correlations were observed between reversible membrane fouling and biopolymers, humic substances, or turbidity (Figure 6.10a) when secondary effluent coagulated by different dosages of ferric sulfate, while irreversible fouling was negatively correlated with turbidity (Figure 6.10 b, $p < 0.05$, t-test). The negative correlation between irreversible fouling and turbidity can be interpreted based on the following finding from previous studies. During a low turbidity event, low dosages may not be sufficient to aggregate particles (Farahbakhsh *et al.* 2004; Ratajczak *et al.* 2012) and high dosages may cause additional resistance by coagulant deposition on membrane surface (Wray and Andrews 2014;

Galvañ *et al.* 2014). These findings demonstrated that coagulant dosage should be carefully controlled during low turbidity events.

Although the size of particles in raw water was not measured in this study, it was important to mention that particle size and the size of formed flocs have a direct impact on membrane fouling. Howe *et al.* (2006) conducted a study to investigate the impact of particles and flocs size on MF and UF fouling when surface water was coagulated using alum or ferric chloride. They observed that the fraction of particles larger than 1.0 µm in size did not contribute to MF or UF fouling when raw water was coagulated with ferric chloride, while this fraction was significantly correlated with membranes fouling when alum was applied. The difference was attributed to differences in cake layer composition in each instance.

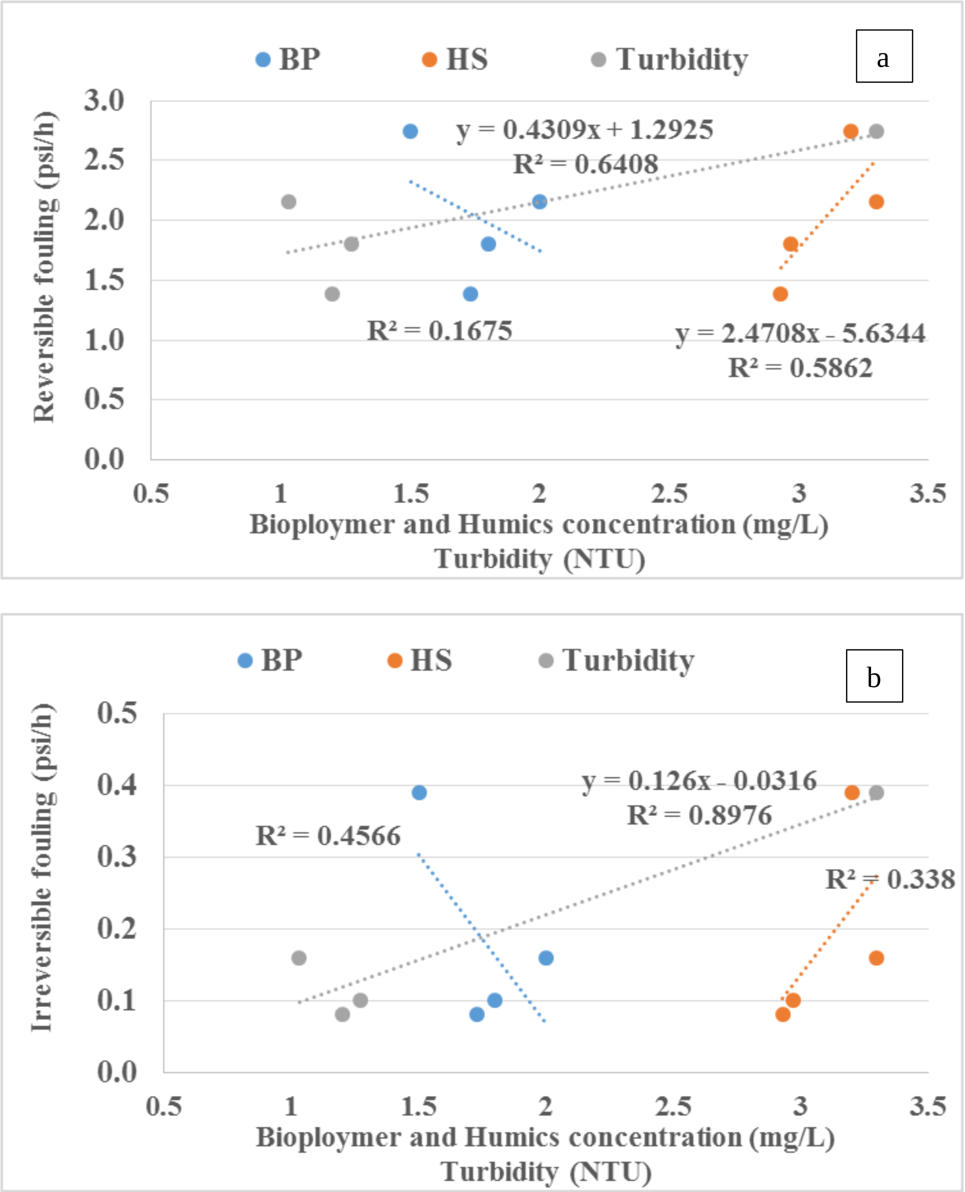


Figure 6.9 Relationship between a) reversible membrane fouling and b) irreversible membrane fouling and turbidity and biopolymer and humics concentrations in membrane feed water (at different dosages of alum ($Al_2(SO_4)_3.14H_2O$)) n= 4

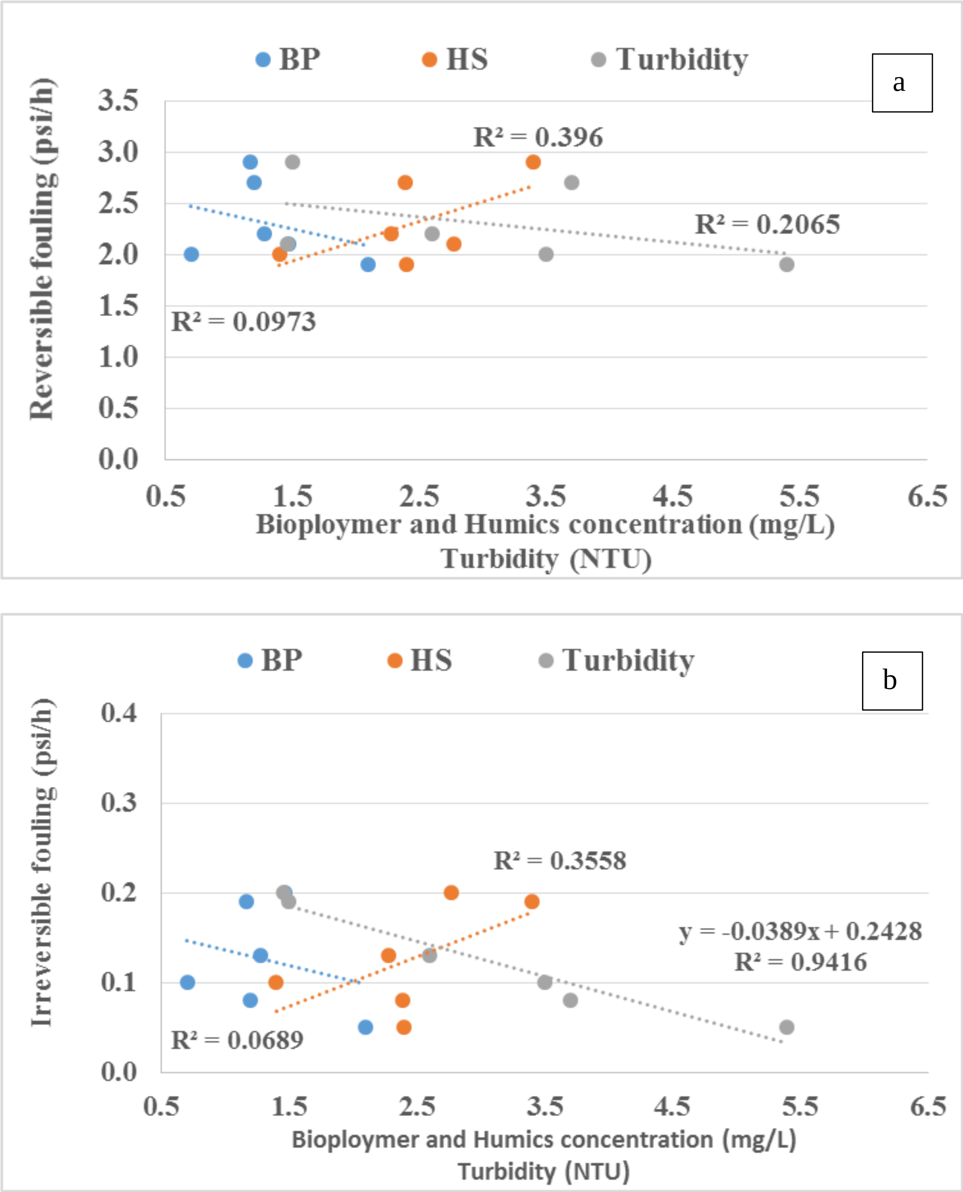


Figure 6.10 Relationship between a) reversible membrane fouling and b) irreversible membrane fouling and turbidity and biopolymer and humics concentrations in membrane feed water (at different dosages of ferric sulfate [$Fe_2(SO_4)_3$]) n= 6

6.5 Conclusions

The following findings can be drawn from this investigation on the viability of in-line coagulation as a UF pre-treatment, using various coagulant types and dosages.

Major conclusions:

- This study demonstrated the viability of in-line coagulation as a pre-treatment for UF for the selected secondary effluent under the conditions investigated. Generally, the beneficial impact of in-line coagulation was more clearly evident with respect to irreversible fouling reduction which is more important for sustainable membrane operation. These improvements can lead to decreases in the frequency of chemical cleaning ultimately extending the life of a membrane.

- Coagulant type and dosage substantially impacted the performance of UF. In general, an increase in coagulant dosage led to higher foulant removal and greater reduction of membrane reversible and irreversible fouling. Under the conditions investigated, the ferric-based coagulants were better for UF fouling control than the aluminum-based coagulants.

- The reduction in UF fouling by in-line coagulation was primarily attributed to the removal of foulants (biopolymers and turbidity) and/or the size modification of particles that contributed to membrane pore blocking.

- Based on jar tests, PACl was the best coagulant for the reduction of biopolymers and organic nitrogen even at low dosages. However, both ferric chloride and ferric sulfate outperformed PACl when it came to reducing membrane fouling. As such, the data obtained from this study suggest that jar testing may be not a useful indictor of optimum coagulant type and dosage for controlling fouling. Therefore, the goals of the pre-treatment (e.g. fouling reduction and/or higher permeate quality) should be carefully considered before accepting or rejecting various coagulants.

Additional conclusions:

- Based on jar testing and LC-OCD analysis, coagulation altered the organic composition of the selected secondary effluent. The largest removals were observed in biopolymer fraction (both organic carbon and organic nitrogen). There was almost no impact of coagulation on humic substances removal due to low level of hydrophobicity (SUVA < 3.0) and pH (>7) of the investigated secondary effluent.

- At the higher in-line coagulation dosage (5.0 mg/L), ferric sulfate outperformed the three other coagulants in terms of biopolymer reduction (58% reduction) and humic substances (58% reduction). At the lower applied dosage (0.5 mg/L) ferric chloride was the most effective coagulant reducing biopolymers by 35% of their concentration in secondary effluent. Overall, the primary impact of coagulants was observed for turbidity reduction (32 – 80%) depending on coagulant type and dosage.

- Based on LC-OCD analysis, UF alone (without in-line coagulants) removed 73 ± 13% of biopolymers while there was almost no removal observed of other NOM fractions (e.g. humic substances). There was a 96 ± 2.0 % reduction of secondary effluent turbidity through UF and the permeate turbidity never exceeded 0.27 NTU in any samples (with or without pre-treatment). There were no clear observations with respect to the impact of combining in-line coagulation with UF for the reduction of DOC. This will require additional investigation with replicated data points and different source waters.

- In extended investigations with alum and ferric sulfate at different dosages, turbidity positively correlated with UF reversible and irreversible fouling when secondary effluent was coagulated with alum and negatively with irreversible fouling when ferric sulfate was employed.

6.6 Disclaimer

The mention of trade names or commercial products does not constitute endorsement of or recommendation for their use.

Chapter 7

In-line Coagulation prior to Biofiltration for Ultrafiltration Fouling Reduction for Secondary Effluent Treatment

Summary

Combining pre-treatment processes may provide further improvement on fouling reduction and permeate water quality. The purpose of this study was to investigate the impact of combining in-line coagulation prior to biofiltration on the reduction of UF fouling treating secondary effluent. The investigation involved the in-line application of a 1.0 mg/L dose of ferric sulfate prior to a pilot-scale anthracite biofilter operated at an HLR of 0.75 m/h. Effluent from the biofilter was then used to conduct bench-scale ultrafiltration fouling experiments at a constant flux of 33 L/m^2 h (LMH). The removal of organics and particles through biofiltration was improved by the application of low dosage coagulant. Hydraulically reversible and irreversible fouling was reduced by the integration of the two pre-treatment processes, more than by either process alone. The most dramatic impact of in-line coagulation prior to biofiltration was observed on the reduction of the irreversible fouling, especially over time. In addition, improved UF permeate quality resulted from the integrated in-line coagulation and biofiltration processes.

7.1 Introduction

Although low pressure membranes have been used widely for water production, fouling is their primary limitation. Combining membrane processes with an adequate pre-treatment can assist in reducing fouling. A variety of studies have been conducted to investigate the appropriate methods for fouling reduction. Some of the previous studies have indicated the potential of direct biofiltration (no coagulant) as a low pressure membrane treatment for drinking water treatment (Peldszus *et al*. 2011, Filloux *et al*. 2012, and Rahman *et al*. 2014). Biofiltration has also been investigated, in the form of slow sand filtration, for secondary effluent treatment (Zheng *et al*. 2009; Pramanik *et al*. 2014) and it was demonstrated to be an effective method for reducing low pressure membrane fouling. Recently, some studies are investigating the enhancement of the performance of biological filtration by adjusting nutrient ratios (C:N:P) (Lauderdale *et al.* 2012; Rahman 2013) or by the addition of hydrogen peroxide (Urfer and Huck 2000; Lauderdale *et al.* 2012; Azzeh *et al.* 2015). Enhancing biological filtration performance by low dosage coagulant has only recently been investigated for drinking water production (Azzeh *et al.* 2015).

Coagulation has been used in surface water and wastewater treatment for the removal of particulate matter. This process can also be used for organic reduction measured as NOM (Edzwald 1993; Dong *et al*. 2007; Humbert *et al*. 2007). It has also been demonstrated that coagulation can assist in reducing membrane fouling (Howe *et al*. 2006). This process promotes cake layer formation that works as a barrier between smaller foulants and membrane pores (Haberkamp *et al*. 2007). Zularisam *et al*. (2006) reported that the cake layer can be easily removed by hydraulic backwashing. As pre-treatment for membranes, coagulation can be applied in different ways. It is often applied in the form of conventional coagulation, with rapid mix and a tank to allow time for floc development followed by settling tank (Howe *et al*.; 2006, Haberkamp *et al*.; 2007). Recently, some studies have demonstrated the effectiveness of low coagulant dosages for reducing low pressure membrane fouling (Wang and Wang 2006; Delgado-Diaz *et al.* 2012; Zheng *et al*. 2012; Wray et al. 2014). In these applications, coagulants were added in-line continuously prior to the membrane without removing particles (Wang and Wang 2006), altering feed water composition (Liu and Kim 2008). A small footprint is required for in-line coagulation in comparison to conventional coagulation-flocculation (Zheng *et al*. 2012), and lower coagulant dosages decrease both cost and sludge production making in-line coagulation an attractive and competitive alternative.

Fouling mitigation is an important objective when treating secondary effluent with membranes of any type. In addition, the production of high quality treated wastewater is key to environmental protection. Therefore, a combination of pre-treatment methods has the potential to achieve the two targets (fouling mitigation and high permeate quality). Azzeh *et al.* (2015) reported the effectiveness of combining in-line coagulation (< 0.5 mg/L alum) prior to biofiltration in reducing UF fouling treating river water (Otonabee River, ON). The investigation of such combinations for secondary effluent treatment by membrane filtration is needed.

7.2 Objectives

The objectives of this component of research were to:

1. Study the impact of low dosage in-line coagulation prior to biofiltration on biofilter effluent characteristics

2. Investigate the effect of in-line coagulation prior to biofiltration on UF permeate water quality and the reduction of fouling

7.3 Materials and Methods

7.3.1 Source Water

The secondary effluent investigated in this study was collected from Waterloo Wastewater Treatment Plant (WWTP), which treats domestic wastewater from the City of Waterloo, Ontario, Canada. The average daily capacity for the WWTP was 72,730 m^3/d in the period when this study was being conducted. The WWTP was undergoing construction during the investigated period of this study, to upgrade both primary and secondary treatment including biological treatment. The raw sewage was first treated by primary clarification where ferrous chloride was added for phosphorus removal. This was followed by conventional activated sludge as a biological treatment followed by secondary settling tanks. The secondary effluent was UV-disinfected prior to discharge into the environment.

Secondary effluent following UV exposure was collected twice per week in three 200 L polyethylene drums and immediately transferred to the University of Waterloo (approximately 3.5 km from the WWTP).

7.3.2 Experimental Set-up

Figure 7.1 illustrates a schematic diagram of the experimental set-up. The set-up was constructed and operated in the Douglas Wright Engineering (DWE) wastewater pilot plant area on the campus of the University of Waterloo. Both secondary effluent and the in-line coagulant stream were pumped to the biofilter with two peristaltic digital drive pumps (model No. 7550-50, 1.6-100 PRM, Cole-Parmer Instrument Company, Barrington, USA) immediately before the inlet of the biofilter. Two streams (secondary effluent and coagulant) were mixed together where an in-line static mixer (Koflo Corpratin, Cary, IL) was connected (1.0 meter tubing before the inlet of the biofilter). Ferric sulfate was added in-line to the filter influent at a dose of 1.0 mg/L. The contact time between the addition of the coagulant and entry into the biofilter tank was 20 seconds. The biofilter was constructed of a glass column 5.1 cm in internal diameter and 2.1 m high with an effective bed depth of 75 cm of anthracite (uniformity coefficient was 1.5, and the effective size was 0.5) supported by 10 cm of (3 mm) gravel. There was 125 cm water above the media and the overflow was 200 cm from the base of the column. The biofilter was operated in down flow mode (constant head, constant rate) at an EBCT of 60 min corresponding to a hydraulic loading rate of 0.75 m/h. To monitor water flow rate through the biofilter, a flowmeter (Model 2L09, 5-50 CCM water, VWR International, USA) were installed in the effluent tubing. The biofilter was backwashed twice per week using its effluent to maintain the composition of the microorganisms with a backwash pump (model No. 7553-70, 6-600 RPM, Cole-Parmer instrument Company, Barrington, USA). An air flow meter was used to adjust the air flow rate during backwashing (Model 2L09, 10 - 400 CCM air, VWR International, USA). Polyethylene tanks were used for feed water storage and effluent water collection.

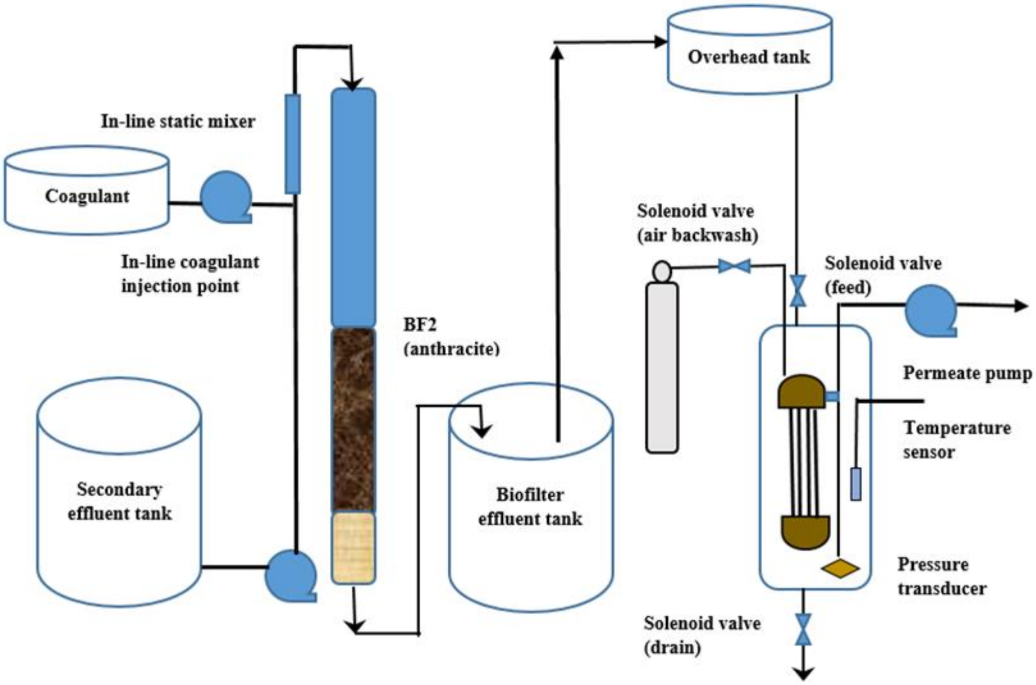


Figure 7.1 Schematic of experimental set-up

The polymeric membrane used in this study was the commercially available polyvinylidene fluoride (PVDF) ultrafiltration membrane fabricated by GE Process Technologies (Oakville, Canada). The membrane module (Zeeweed - 1®) was constructed of 15 cm long hollow fibers (500 series), and the operation mode was outside-in. The membrane had a nominal surface area of 0.047 m^2 with a MWCO of 400 KDa (approximately 40 nm pore size) as delivered from the manufacturer.

The UF module was located vertically in a clear polyvinyl chloride 2.0 L cylindrical tank. The set-up was designed to cycle automatically where each cycle began with 30 min of permeation, followed by backwashing with air sparging for 20 sec. After that, the module tank was drained (30 sec) and refilled again with the investigated water (36 sec). For continuous measurement during the experiments, a temperature sensor and flowmeter monitor (model LC alpha controller, 200-500 CCM, Alicat Scientific, Tucson, USA) were connected to a data logger (HOBO Energy Logger, model H22-001, Onset, Cape Cod, Massachusetts, USA). The flow meter was used to maintain the same permeate flow rate through the whole UF experiment. It was connected to a digital permeation pump (Masterflex L/S drive model number 07550-50; Cole-Parmer Canada) that was set to operate at a constant flow rate (25 mL/min). The flowmeter measured the actual permeate flow rate every 10 sec and data was recorded using a data logger. The actual flux could be determined at any time during the filtration run using equation 3.1 (Rahman 2013). Transmembrane pressure was measured using a pressure transducer (model 68075-02, Cole-Parmer, Montreal, Canada) which was connected to the data logger as well. Fouling rates were determined using TMP data after correction for temperature at 20°C using equation 3.2. Additional details regarding the UF bench-scale configuration and operation are available in El-Hadidy (2011) and Rahman (2013).

All polymeric UF experiments were conducted in dead-end mode at a constant permeate flux of 33 L/m^2 h (LMH). Four experiments were conducted in batch mode during the investigated period; each experiment included three UF runs. The membrane first was fed with secondary effluent with a run length set to end at 24 h or when the maximum TMP (8 psi) of the membrane was reached. In the second run, the membrane was fed with biofilter effluent (no coagulant addition prior to the biofilter). Finally, in-line coagulation was applied prior to the biofilter and UF membrane was fed with the biofilter effluent. Between each run, chemical cleaning was performed using sodium hypochlorite (200 mg/L) for a minimum of 5 h followed by a citric acid solution (5 g/L) for another 5 h. After chemical cleaning, the membrane was soaked in a glass jar containing deionized water at 4°C until use. The UF module was integrity tested using a pressure calibrator (Meri-cal DP2001I, Meriam Instruments, Ohio, USA) prior to every experiment. The maximum allowable pressure drop through the membrane was 0.3 psi per 2 min. Additional details about the integrity test procedure and chemical cleaning of the membrane are available in Appendix K). To check cleaning effectiveness, clean water permeability tests were conducted using deionized water before each experiment (Appendix L).

7.3.3 Liquid Chromatography Organic Carbon Detection (LC-OCD)

NOM compounds were identified based on their molecular weight using an LC-OCD Model 8 (DOC-LABOR, Karlsruhe, Germany) as per the method of Huber et al. (2011). Prior to analysis, samples were pre-filtered using a 0.45 µm PVDF membrane filter (Pall Supor® Membrane Disc Filters, 0.45 µm, 47 mm plain, VWR international, USA) which was pre-rinsed with 30 mL of ultrapure. Samples were diluted with ultrapure water if the DOC in the sample exceeded 5 mg/L.

7.3.4 Analytical Methods for Water Samples

Water samples were collected from the inlet and the outlet of the biofilter. Water samples were collected in clean glass 1 liter bottles before backwashing the biofilter. Water samples were preserved at 4°C until to analysis which occurred within 24 h of sampling The parameters monitored were TOC, DOC, UV_{254}, specific UV absorbance (SUVA = UV_{254}/DOC), pH, and turbidity. In addition some parameters were monitored only in the secondary effluent at the Waterloo WWTP labs. The methods used for all measured parameters are described in more detail in Chapter 3, Section 3.6.

7.4 Results and Discussion

7.4.1 Impact of In-line Coagulation on Biofilter Performance

The investigation of the impact of in-line coagulation on biofiltration was carried out from April 13 to May 30, 2015. The biofilter (anthracite media) was operated at a 60 min EBCT corresponding to an HLR of 0.75 m/h and it was backwashed twice per week. This experiment was conducted 15 months after this biofilter was brought on-line (January 2014). Steady state conditions in the filter were reached after about 4 months of operation. Figure 7.2 summarizes the average removal of DOC, biopolymers, humic substances, and turbidity through the biofilter alone and following the combination of in-line coagulation addition (1.0 mg/L ferric sulfate) and subsequent biofiltration.

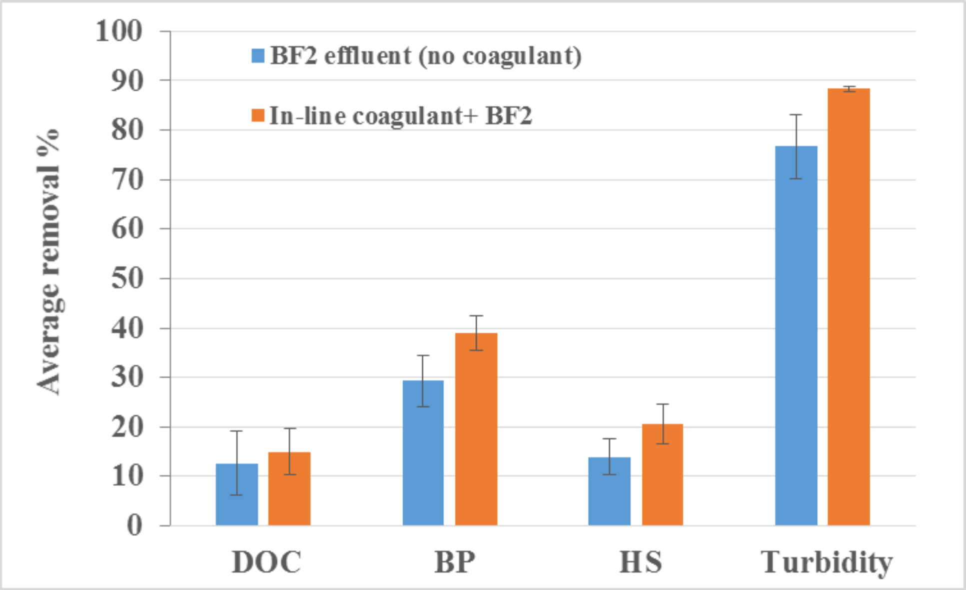


Figure 7.2 Impact of in-line coagulant on BF2 (anthracite) performance for the reduction of DOC, BP, HS, and turbidity, n= 4

Biofiltration alone improved the secondary effluent quality by reducing the concentration of organics and particles. The average DOC removal through the biofilter was 13 ± 6%, which is comparable with previous studies investigating biofiltration for river water treatment (Hallé *et al.* 2009; Peldszus *et al.* 2012; Rahman *et al.* 2014). The average biopolymer removal was 29 ± 5%, while a slight reduction of humic substances (14 ± 3%) was observed through the biofilter. The average removal of turbidity achieved by the biofilter was 77 ± 6%.

A ferric sulfate dose of 1.0 mg/L prior to biofiltration further improved the performance of the biofilter for the reduction of organics and particles. At this low dosage of applied coagulant, an additional 3% and 6% percentage points DOC and humic substances removals were observed, respectively. A statistically significant difference in the reduction of biopolymers and turbidity was found to be attributable to in-line coagulant addition, where the average removals of biopolymers and turbidity increased to 40 ± 4% and 88 ± 0.6%, respectively. Azzeh *et al.* (2015) reported that the application of an alum dose of 0.1 and 0.25 mg/L prior to biofiltration in river water treatment removed an additional 3% and 4% of biopolymers, respectively. In the present study, an additional 10% removal of biopolymers was observed with a ferric sulfate dose of 1.0 mg/L. This observation emphasizes the impact of coagulant type and dosage on biofiltration performance. Despite the improvement in organics and particle removal, which is attributed to size modification by coagulant addition (Zheng *et al*. 2012), no adverse impact was associated with in-line coagulant addition with respect to head loss.

7.4.2 Impact of Pre-treatment Combination on Ultrafiltration Performance

The UF bench-scale setup was operated using raw secondary effluent, biofilter effluent (no coagulant), and biofilter effluent with prior ferric sulfate addition (at 1.0 mg/L) from April 13 to May 30, 2015. The UF was operated at a constant permeate flux of 33 L/m^2 h (LMH) and the run length was set to end at 24 h or when the maximum TMP (8 psi) of the membrane was reached. Hydraulic backwashing time was 20 seconds after each permeation cycle (30 minutes). Figure 7.3 shows an example of the UF membrane fouling experiment (conducted from April 21 to 25, 2015) for secondary effluent and biofilter effluents (with and without coagulant). During the first few hours of secondary effluent filtration by UF, there was a rapid increase in TMP, reaching 6.0 psi after 16 h. This is attributed to fouling development due to pore blocking. This was followed by a stabilization or decrease in TMP (usually when the maximum TMP of 8 psi was approached or was reached). On the other hand, there was a substantial reduction in fouling development when the UF membrane was operated with biofilter effluent without coagulant or after in-line coagulant addition prior to the biofilter. The maximum TMP obtained using biofilter effluent without coagulant was 4.0 psi after 23 h of filtration. The pre-treatment strategy combination performed even better with the TMP reaching only 3.0 psi after 23 h of filtration. The results obtained for the remaining four experiments that were conducted during the investigated period were similar (Appendix I).

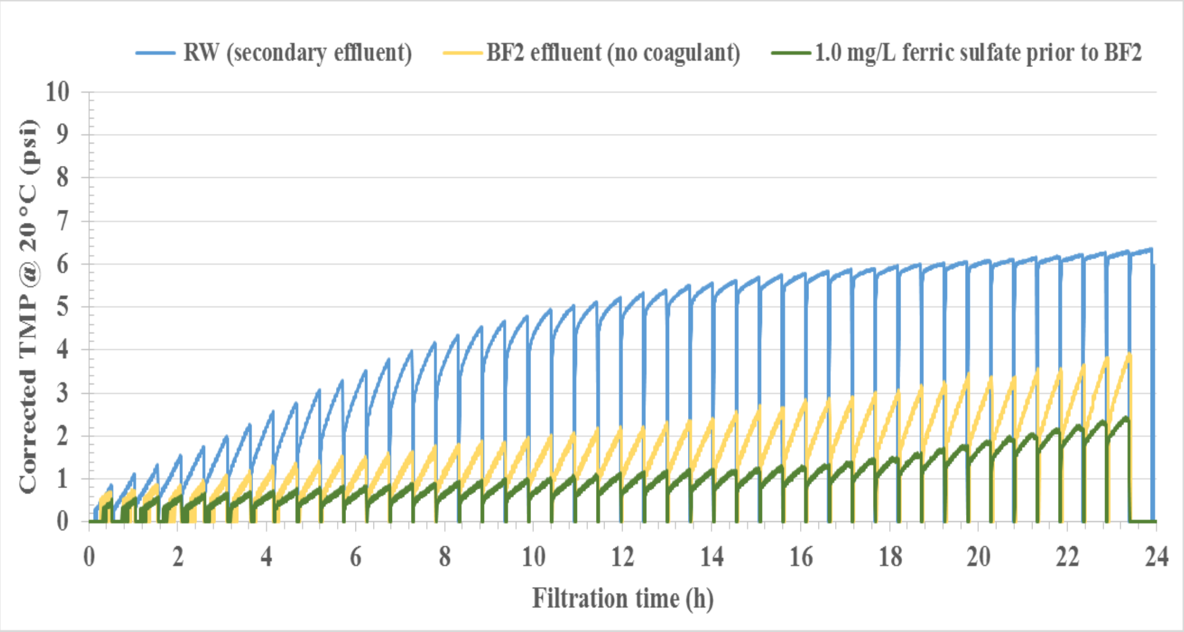


Figure 7.3 UF transmembrane pressure for raw water (secondary effluent), biofilter 2 (anthracite) effluent, and in-line coagulation prior to biofilter 2 effluent, experiment was conducted from Apr. 21 to 25, 2015

Reversible fouling is that which can be recovered by hydraulic backwashing, while irreversible fouling cannot. Figure 7.4 illustrates the change in reversible fouling for a UF experiment conducted from April 21 to 25, 2015 for secondary effluent and biofilter effluents (with and without prior in-line coagulant). The reversible fouling rate of any cycle was calculated by subtracting the TMP measured at the start of the cycle from the TMP measured at the end of the previous cycle before backwashing. When using secondary effluent as UF feed, there was a dramatic increase in hydraulically reversible fouling, reaching 1.5 psi/h within the first 12 filtration cycles (one cycle = 30 min permeation). The hydraulically reversible fouling rate reached 1.5 psi/h at the end of the experiment (24 h, 48 filtration cycles) for BF2 (no coagulant), however, even lower values were observed for BF2 effluent with prior in-line coagulant addition. Hydraulically irreversible fouling was also reduced when the UF was fed with biofilter effluent (with and without coagulant). The hydraulically irreversible fouling rate can be determined by monitoring the progressive increase of the initial TMP at the beginning of each filtration cycle (Figure 7. 5). The initial TMP rapidly increased to reach almost 6.0 psi at the end of the experiment (24 h) when the secondary effluent was used as the UF feed. On the other hand, TMPs at the end of the 24 h experiment were 2.7 and 2.0 psi for BF2 effluent and BF2 effluents with prior coagulant addition, respectively. The total reduction in reversible and irreversible fouling for any experiment can be calculated based on the average values of reversible and irreversible fouling determined for each run (as described previously in Chapter 5, pg. 81). Membrane filtration of BF2 effluent (no coagulant) resulted in 31% and 74% reductions in the rate of reversible and irreversible fouling, respectively, during the first 12 h of filtration time. At a ferric sulfate dose of 1.0 mg/L, added prior to BF2, reductions in the rates of reversible and irreversible fouling were 69% and 87%, respectively.

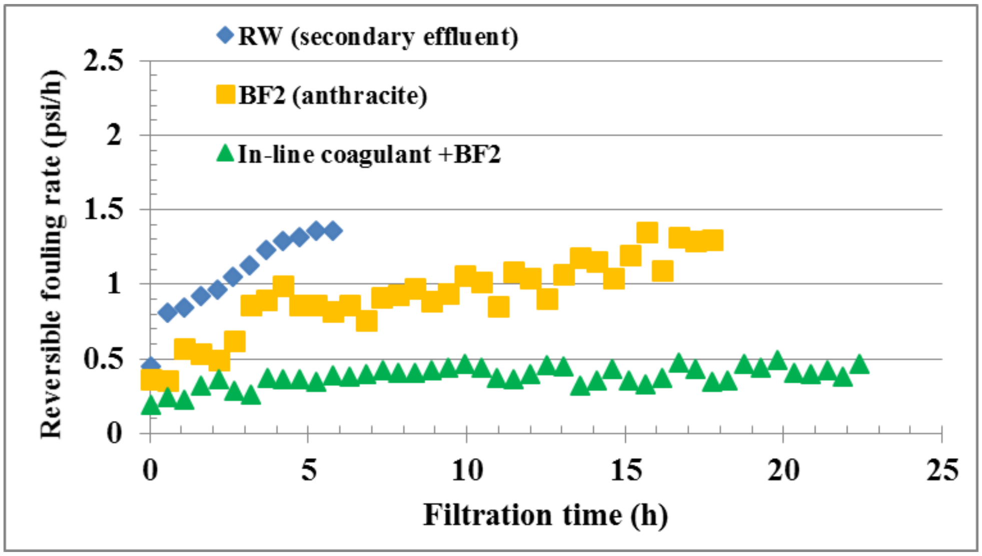


Figure 7.4 Hydraulically reversible fouling rates for raw water (secondary effluent), BF2 effluent, and in-line coagulant prior to BF2 effluent. Experiment was conducted from Apr. 21 to 25, 2015

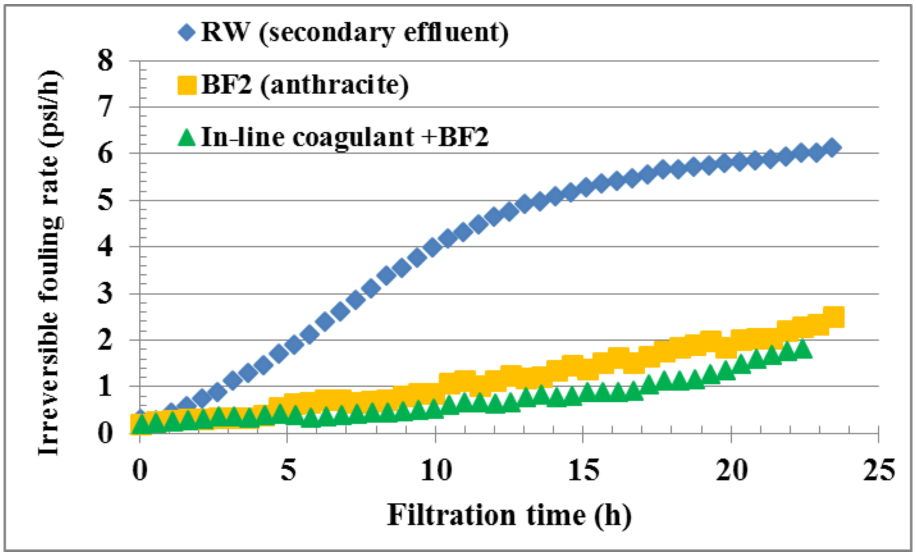


Figure 7.5 Hydraulically irreversible fouling rates for raw water (secondary effluent), BF2 effluent, and in-line coagulant prior to BF2 effluent. Experiment was conducted from Apr. 21 to 25, 2015

It has previously been reported that biopolymers were the most correlated of the NOM constituents to UF fouling when treating secondary effluent (Haberkamp *et al*. 2008; Zheng *et al*. 2009; Pramaink *et al*. 2014) and surface water treatment with UF (Hallé *et al*. 2009; Peldszus *et al*. 2011; Rahman *et al*. 2014). Therefore, the fouling reduction observed by the pretreatment methods (biofiltration alone or in-line coagulant prior to biofiltration) was due to the physical removal and/or biological transformation of contaminants.

In general, the application of 1.0 mg/L ferric sulfate prior to biofiltration improved the quality of UF permeate (Table 7.1). The TOC concentration in UF permeate was 16.0 ± 0.6 mg/L when the UF was fed with biofilter effluent combined with in-line coagulation, while it was 20.0 ± 1.9 mg/L when UF was fed with biofilter effluent alone. On the other hand, there was no impact of this combination (in-line coagulation prior to biofiltration) on the reduction of turbidity through the UF membrane. The permeate turbidity never exceeded 0.2 NTU in any samples (with or without pre-treatment).

TOC removals (from RW) through the UF with prior biofiltration and with prior in-line coagulation/biofiltration were 20% and 36%, respectively. The DOC removals (from RW) through the UF with prior biofiltration and with prior in-line coagulation/biofiltration were somewhat higher at 32% and 44%, respectively. DOC removals from the previous pre-treatment step through the UF membrane were also better than TOC removals. The reasons for the lower percentage reduction of TOC through the UF membrane compared with the removal of particulate matter and DOC are not completely understood. They might be real but may also be attributed to a technical issue associated with the TOC analyzer during this period. The TOC and DOC are analyzed using two different methods (combustion and UV/persulfate oxidation). The TOC analyzer stopped working during this period due to a failure associated with the TIC (Total Inorganic Carbon) reaction chamber. Some downtime was experienced while waiting for parts in the instrument. During this period water samples were kept refrigerated after acidification for approximately four weeks before measurement (sample storage is not recommended by the instrument supplier as the method used is combustion-see section 3.6.2). Since the focus of this investigation was the reduction of UF foulants (e.g. biopolymers and particles), the potential problem with the TOC data was, however, not considered crucial to the interpretation of the overall results.

Table 7-1 Average concentration and standard deviations for some selected parameters for raw water and following various treatment processes (n=4)

Parameter	**Unit**	**RW (secondary effluent)**	**BF2 effluent**	**In-line coagulation + BF2**	**BF2 + UF**	**In-line coagulation + BF2 + UF**
TOC	**mg/L**	**25.0 ± 5.0**	**22.0 ± 5.0**	**18.0 ± 1.0**	**20.0 ± 1.9**	**16.0 ± 1.0**
DOC (LC-OCD)	**mg/L**	**9.8 ± 0.8**	**8.5 ± 0.8**	**7.4 ± 1.6**	**6.7 ± 0.5**	**5.5 ± 1.0**
BP	**mg/L**	**1.8 ± 0.1**	**1.4 ± 0.2**	**1.1 ± 0.1**	**0.6 ± 0.3**	**0.5 ± 0.3**
HS	**mg/L**	**3.5 ± 0.6**	**3.2 ± 0.3**	**2.9 ± 0.4**	**2.8 ± 0.3**	**2.3 ± 0.2**
UV_{254}	**cm^{-1}**	**0.14 ± 0.01**	**0.13 ±0.01**	**0.11 ± 0.01**	**0.12 ±0.01**	**0.09 ± 0.01**
Turbidity	**NTU**	**5.0 ± 1.3**	**1.2 ± 0.6**	**0.6 ± 0.1**	**0.2 ± 0.1**	**0.2 ± 0.1**

The pre-treatment strategy combination of in-line coagulation prior to biofiltration removed more of the various NOM fractions (e.g., biopolymers and humic substances) and turbidity which impacted the overall process, resulting in the production of higher quality permeated water. Figure 7.6 illustrates the LC-OCD chromatograms for secondary effluent and UF permeates when the UF was fed with biofilter effluent with and without prior in-line coagulation. There was almost no improvement in the biopolymer removal by the UF for the pre-treatment combination (vs. biofiltration alone), while some impact of in-line coagulation prior to biofiltration on UF permeate was observed in the reduction of humic substances and building blocks (humic substances-like material of lower molecular weight). There was an increase in the concentration of building blocks in the UF permeate when fed with biofilter effluent alone, which may be attributed to the biodegradation of high molecular weight compounds (e.g., biopolymers).

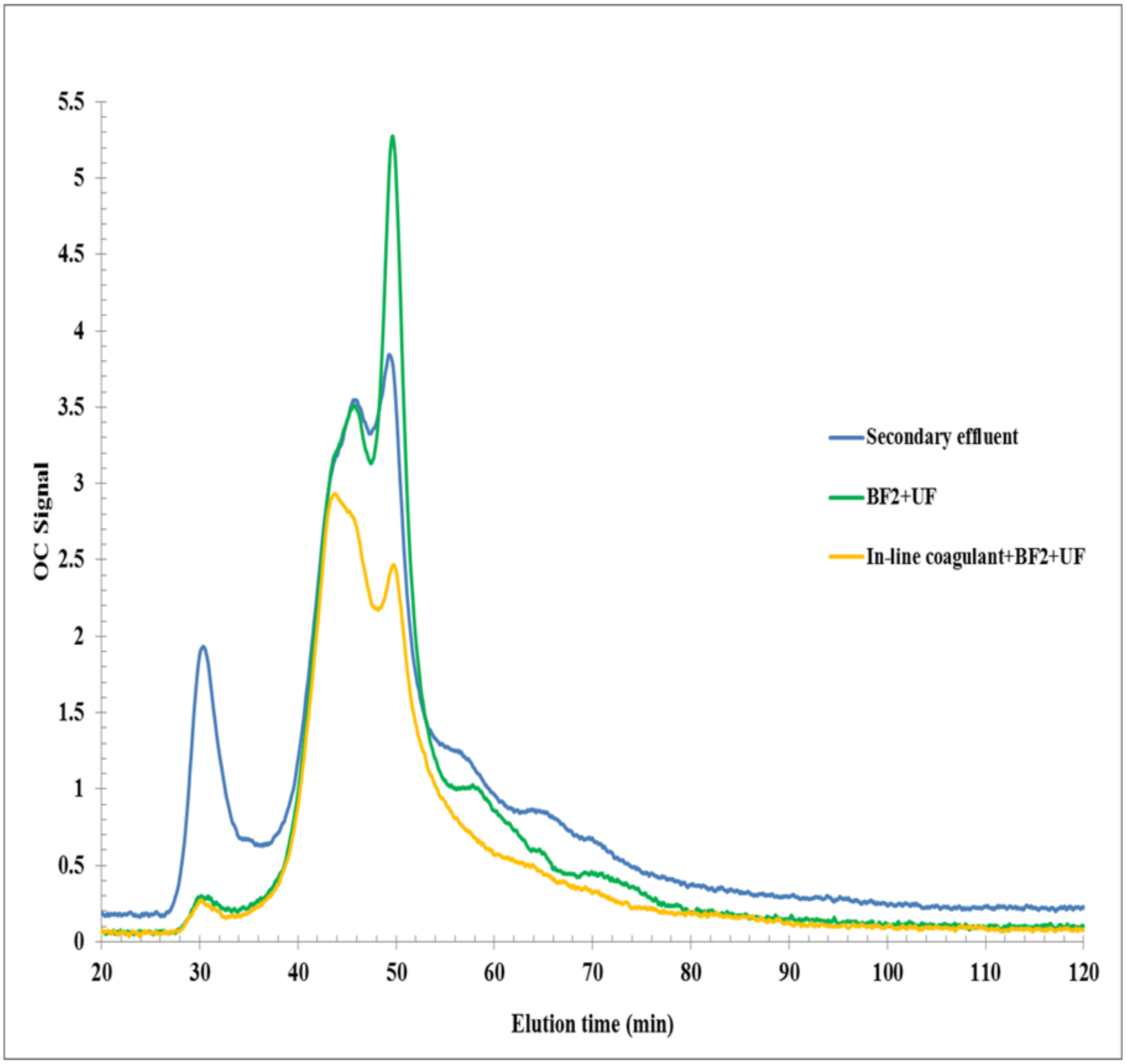


Figure 7.6 LC-OCD chromatograph for secondary effluent and membrane permeate fed with BF2 effluent alone and in-line coagulant prior to BF2, experiment was conducted from Apr. 21 to 25, 2015

7.4.3 Extended Run Experiment

This experiment was conducted in the period from May 4 to 9, 2015 during which time the run length was increased from 24 to 48 h. The UF was operated at the same operating conditions as the previous experiments. Figure 7.7 compares the change in UF TMP vs. filtration time using biofilter effluent (with and without coagulant) as feeds. The TMP reached 5.0 psi at the end of the 48 h experiment during filtration of biofilter effluent alone. There was a significant improvement in the performance of the UF membrane with the in-line coagulant/biofilter effluent, with the TMP remaining virtually constant (less than 1.0 psi) over the length of the experiment.

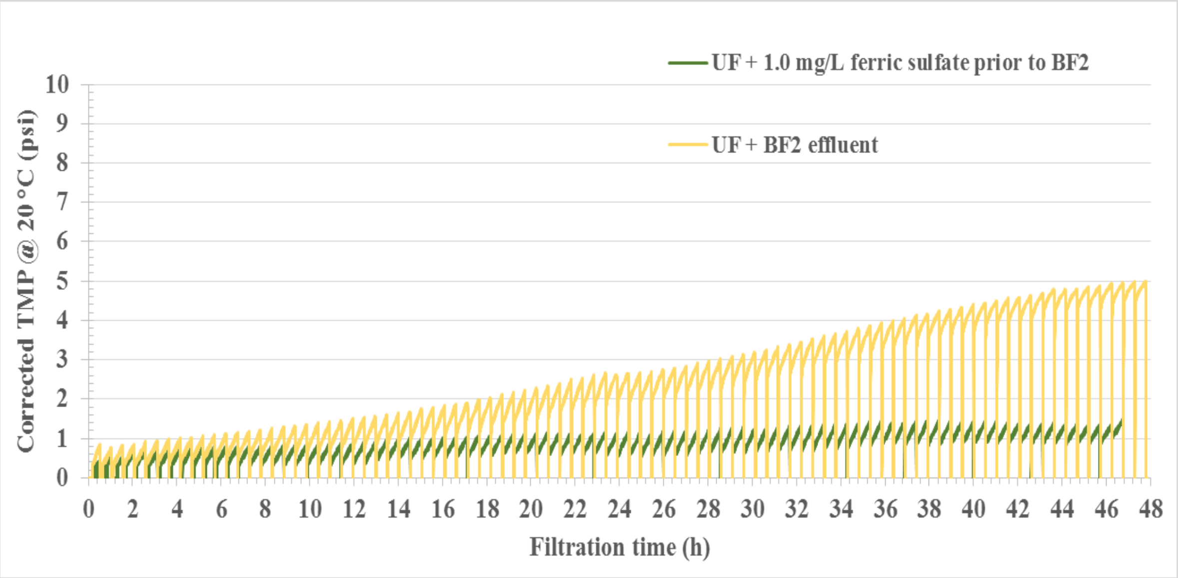


Figure 7.7 UF transmembrane pressure for biofilter 2 effluent and in-line coagulant prior to biofilter 2, experiment was conducted from May 3 to 9, 2015

Figures 7.8 and 7.9 illustrate the change in reversible and irreversible fouling rates, respectively, for two different UF experiments for biofilter effluents (with and without in-line coagulant). One was conducted for the usual filtration time (24 h) from April 21 to 25, 2015 and the other was conducted for the extended filtration time (48 h) from May 3 to 9, 2015. In both experiments, there was a reduction in reversible fouling development when the UF was fed with the biofilter effluent with prior in-line coagulant addition, however, the greater reduction was observed during the shorter (24h) experiment. Hydraulically irreversible fouling was also reduced when the UF was fed with biofilter effluent with prior in-line coagulant addition. The TMP reached 2.5 psi at the end of the two experiments (24 h and 48 h) for biofilter effluent (no coagulant). At the end of the 48 h run, the TMPs were 4.5 and 1.0 psi/h when UF fed with biofilter effluent (no coagulant) and with 1.0 mg/L ferric sulfate addition, respectively. Slowing the rate of irreversible fouling can reduce the frequency of chemical cleaning and membrane lifetime can be increased as well. Therefore, the findings of these experiments reflect the potential viability of in-line coagulation prior to biofiltration as a sustainable pretreatment for UF membranes.

In-line coagulation enhanced the conditions for subsequent removal of particles and organics through the biofilter providing additional improvement in the performance of the UF membrane. At such low dosages, coagulants alter the characteristics of colloids and organics by reducing surface charge by charge neutralization and small, but nonetheless aggregated forms of particles and organics can be produced. The aggregated compounds can then be more easily rejected through biofiltration by straining which provides additional removal of organics in addition to biodegradation by the attached biomass.

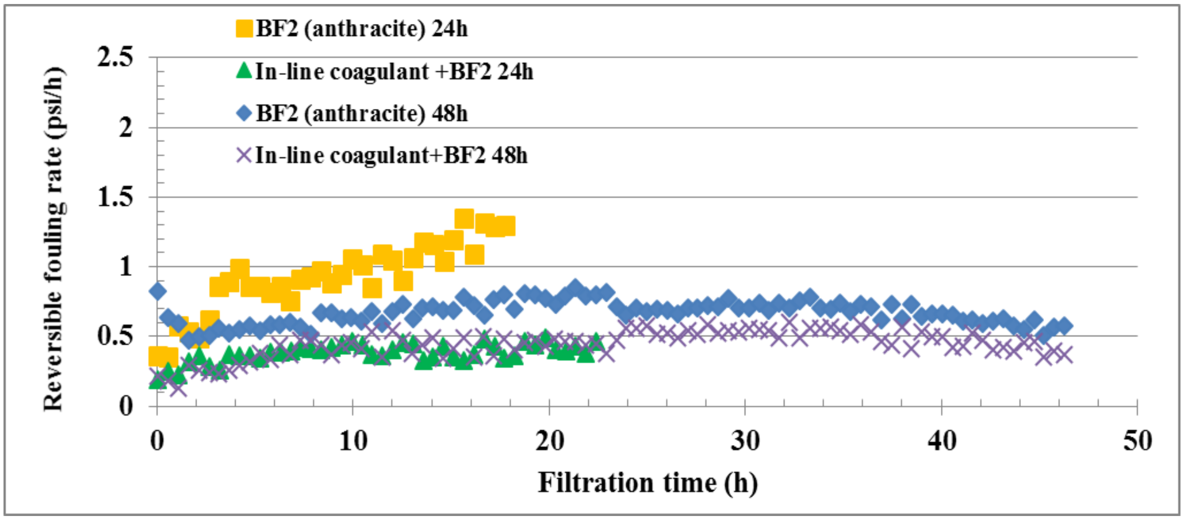


Figure 7.8 Hydraulically reversible fouling rates for the UF membrane fed with biofilter 2 effluent and in-line coagulant prior to biofilter 2 in 24 h and 48 h experiments. The 24 h experiment was conducted from April 21 to 25, 2015 and the 48 h experiment was conducted from May 3 to 9, 2015

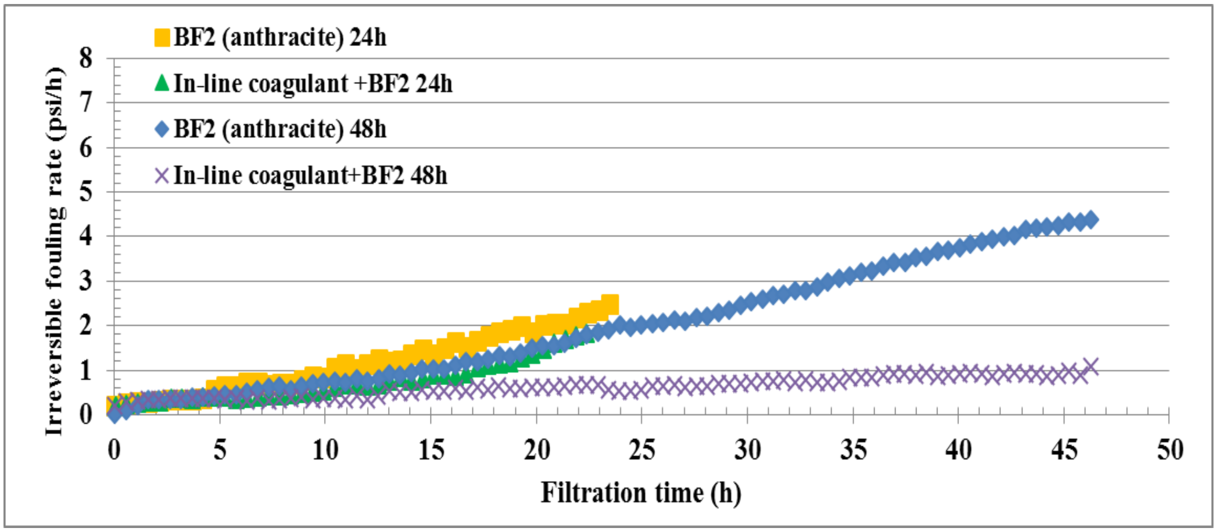


Figure 7.9 Hydraulically irreversible fouling rates for the UF membrane fed with biofilter 2 effluent and in-line coagulant prior to biofilter 2 in 24 h and 48 h experiments. The 24 h experiment was conducted from April 21 to 25, 2015 and the 48 h experiment was conducted from May 3 to 9, 2015

7.5 Conclusions

Based on the observations obtained from this study to investigate the impact of combining in-line coagulation prior to biofiltration on UF performance, the following conclusions can be drawn:

- In-line coagulation prior to biofiltration improved the performance of the anthracite media-containing biofilter by reducing organic concentrations and particulate matter without any adverse impact of in-line coagulant addition on head loss. Biofiltration alone removed 13 ± 6% and 29 ± 5% of secondary effluent DOC and biopolymer concentrations, respectively. The application of a ferric sulfate dose of 1.0 mg/L prior to biofiltration resulted in an additional removal of 3 and 10 percentage points of DOC and biopolymers, respectively. The average removal of turbidity achieved by the biofilter alone was 77 ± 6%, and an average reduction of 88 ± 0.6% was achieved when combining in-line coagulation prior to biofiltration. The improvement in organics and particle removal was attributed to size modification induced by coagulant addition.

- A rapid increase in normalized TMP was observed when filtering secondary effluent through the UF membrane without pre-treatment, with TMP reaching 6.0 psi after 16 h of filtration. On the other hand, operating the UF membrane with biofilter effluent without coagulant or after in-line coagulant addition substantially improved the performance, and there was a large reduction in fouling development. Biofilter effluent (no coagulant) resulted in 31% and 74% reductions in the reversible and irreversible fouling, respectively, during the first 12 h of filtration time. Adding ferric sulfate at dose of 1.0 mg/L prior to the biofilter yielded reductions in the reversible and irreversible fouling of 69% and 87%, respectively. The significant biopolymer and turbidity reduction by the pre-treatment strategy combination (in-line coagulation prior to biofiltration) resulted in substantial improvement in UF performance.

- The most dramatic impact of in-line coagulation prior to biofiltration was observed on the reduction of the irreversible fouling (especially over time) which is ultimately more important for sustainable membrane operation.

- In general, the application of 1.0 mg/L ferric sulfate prior to biofiltration improved the quality of UF permeate. The TOC concentration in the UF permeate averaged 16.0 ± 0.6 mg/L when the UF was fed with biofilter effluent combined with in-line coagulation, while it was 20.0 ± 1.9 mg/L when UF was fed with biofilter effluent alone. On the other hand, there was no impact of this combination (in-line coagulation prior to biofiltration vs. biofiltration alone) on the reduction of turbidity through UF and the permeate turbidity did not exceed 0.2 NTU in any sample (with or without pre-treatment).

Chapter 8

Conclusions and Recommendations

8.1 Synthesis and Conclusions

This research investigated the potential of ultrafiltration as an advanced treatment for secondary effluent. To reduce membrane fouling, three different pre-treatment methods were investigated: biofiltration, in-line coagulation, and the combination of in-line coagulation prior to biofiltration.

The first phase of this study involved an assessment of the impact of biofiltration on secondary effluent characteristics. Biofiltration experiments were performed at pilot-scale with two different biofilter media (sand and anthracite) operated at identical conditions with an EBCT of 60 min, corresponding to an HLR of 0.75 m/h.

Following this, the potential of biofiltration pre-treatment to reduce UF fouling was assessed. Membrane filtration experiments were performed with bench-scale modules and commercially available membranes. The impact of in-line coagulation for the prevention of UF fouling was subsequently investigated using the same UF membrane set-up. Four coagulants (aluminum sulfate, polyaluminum chloride, ferric chloride, and ferric sulfate) at two different dosages of each (0.5 and 5.0 mg/L) were compared to a non-coagulated control.

Enhancing the performance of the biofilter by the installation of in-line coagulation prior to the biofilter for treating secondary effluent has not been reported in the literature. Therefore, the final component of this study was to examine the effect of in-line coagulation on biofilter performance, and the impact of this combination on UF fouling and permeate quality.

Waterloo WWTP secondary effluent was selected to be investigated in this study. This secondary effluent provided a unique opportunity to investigate a secondary effluent with a high biopolymer content (compared to values reported in the literature) and substantial variability in turbidity, nitrate, and TKN. In general, the pre-treatment processes tested were essential to maintain the sustainable operation of membranes when treating such types of secondary effluent. This study demonstrates the potential of both biofiltration and in-line coagulation as UF pre-treatment for secondary effluent with respect to biofilter media type and coagulant type and dosage. Enhancing biofiltration with a low in-line coagulant dose was observed to be a good treatment option for fouling reduction and the production of high quality UF permeate.

In this investigation, BF1 (sand) effluent improved UF membrane performance by average reductions of 60% and 79% in reversible and irreversible fouling, respectively. The maximum reductions of reversible and irreversible fouling achieved by in-line coagulation of secondary effluent (with no biofiltration) were 50% and 77%, respectively, at a 5.0 mg/L of ferric sulfate. The performance of BF2 (anthracite) was enhanced by a 1.0 mg/L of ferric sulfate applied in-line prior to the biofilter. For this combination the reductions of reversible and irreversible fouling of the UF membrane reached 69% and 87%, respectively (compared with average reductions of 30% and 60% in reversible and irreversible fouling, respectively, without in-line coagulation prior to biofiltration). Membrane pre-treatment is necessary to maintain good membrane performance of membrane and the pre-treatment processes investigated in this study provided valuable information for controlling UF fouling for secondary effluent treatment.

The most significant conclusions related to the composition of the selected secondary effluent and the impact of biofiltration with different filter media on secondary effluent treatment are as follows:

- Based on LC-OCD analysis of secondary effluent obtained from the Waterloo WWTP, humic substances made up the largest fraction in all samples, accounting for on average 34% of the DOC while biopolymers (BPs) accounted for 18% of DOC. The average concentrations of humic substances and biopolymers were 3.1 and 1.3 mg/L, respectively. This secondary effluent had a high biopolymer content compared to values reported in other studies. The reason for this is unknown but it is important to take this into account when analysing the findings of this research, where a preliminary investigation of biofiltration impact on secondary effluent treatment revealed that higher EBCTs were required due to higher BP concentrations in this secondary effluent.

- Biofiltration improved secondary effluent characteristics by reducing organic compound concentrations and turbidity. Under the investigated conditions in this study, biopolymers were the largest DOC fraction removed through the biofilter. The removal of biopolymers through the biofilters was correlated with biofilter influent concentrations. Although humic substances were the predominant fraction in the investigated secondary effluent, they were not efficiently removed through biofiltration.

- As a biofilter media, sand was statistically significantly better than anthracite in terms of DOC and biopolymer removal. There was no difference between the media types for the removal of the other parameters monitored in this study.

The most significant conclusions related to the potential of biofiltration with different media as UF pre-treatment for secondary effluent are:

- Secondary effluent LC-OCD data and UF permeate monitoring demonstrated that biopolymers were the largest fraction of DOC rejected by UF (70 ± 19%), suggesting that biopolymers were the primary UF organic foulants in secondary effluent. Biofiltration improved secondary effluent characteristics by reducing organic compound concentrations, especially the biopolymer fraction (proteins, polysaccharides), and turbidity.
- Under the conditions investigated, sand was better than anthracite for the reduction of UF fouling.
- When the UF was fed with biofilter effluent, both reversible and irreversible fouling were correlated with biopolymer concentrations in feed water. Particulate matter was weakly correlated with UF reversible fouling. These observations suggest that a combination of organic compounds (e.g., biopolymers) and particulate matter was formed which can increase irreversible fouling, and/or alter the separation mechanisms of UF.

The most significant conclusions related to the impact of in-line coagulation with various coagulant types on UF performance treating secondary effluent include:

- The viability of in-line coagulation as a pre-treatment for UF for the selected secondary effluent under the investigated conditions has been demonstrated. Fouling reduction by in-line coagulation was primarily attributed to the removal of two foulants (biopolymers and turbidity) and/or the size modification of particles that contribute to membrane pore blocking. Generally, the most dramatic impact of in-line coagulation was on irreversible fouling reduction which is more important than reversible fouling for sustainable membrane operation.

- Coagulant type and dosage substantially impacted UF performance. In general, an increase in coagulant dosage led to higher foulant removal and greater reduction of reversible and irreversible fouling. Under the investigated conditions, the ferric-based coagulants were better for UF fouling control than the aluminum-based coagulants.

The most significant conclusions obtained from investigating the impact of in-line coagulation prior to biofiltration on UF performance treating secondary effluent are:

- In-line coagulation prior to biofiltration improved the performance of the investigated biofilter (anthracite) for reducing organic and particulate matter without any adverse impact on head loss. The improvement in organics and particle removal is attributed to size modification by coagulant addition.

- Operating the UF membrane with biofilter effluent without coagulant or with in-line coagulant addition (without biofiltration) also substantially improved the performance, and there was a substantial reduction in fouling development. However, superior biopolymer and turbidity reduction by the combined pre-treatment strategy (in-line coagulation prior to biofiltration) further improved UF performance.

- As was the case with in-line coagulation alone prior to ultrafiltration, the impact of in-line coagulation prior to biofiltration was observed to have even more beneficial impact on irreversible fouling which will be attractive in real-world applications.

- In general, the application of 1.0 mg/L ferric sulfate prior to biofiltration improved the quality of UF permeate especially for organics reduction. On the other hand, there was no impact of this combination (in-line coagulation prior to biofiltration) on the reduction of turbidity through UF. The UF permeate turbidity never exceeded 0.2 NTU (with or without pre-treatment).

Additional relevant conclusions obtained from this study

1- **Based on biomass quantifications**

- The highest concentrations of ATP were observed near the surface of both the sand and anthracite media biofilters. The biomass concentration decreased through bed depth and the lowest biomass concentrations were measured at the bottom of the two biofilters. The amount of biomass attached to the sand was higher than that attached to anthracite at comparable media depths. This may be due to the higher external surface area available for biomass attachment (smaller effective size of sand) or due to surface properties such as charge and/or roughness.

- Although there was a substantial variability of nitrate and TKN, no correlation was observed between biomass quantifications (measured as ATP) and those parameters. Also, no correlation was observed between biomass quantifications and phosphorus concentration at secondary effluent. This suggested that those parameters were not growth-limiting nutrients for the biofilters in this study.

- The BRP and ATP methods yielded similar information, and either could be used as a relatively simple way to roughly estimate biomass activity and organic matter biodegradation. Higher DO consumption was observed at the top of both biofilters indicating that biodegradation occurred mostly in those top layers.

2- **Based on seasonal variation investigations**

- There was no substantial change in the organic composition of the investigated secondary effluent over the length of study. There was some variability in turbidity with higher values being observed at colder temperatures. The temperature at the time of secondary effluent collection ranged from 10 to 25°C.

- No seasonal impact was observed in the performance of the biofilter or UF membrane (under the conditions investigated). Although secondary effluent, as collected, ranged in temperature as indicated above the experiments were all conducted at room temperature (and membrane flux was corrected to 20°C).

3- **Based on jar test experiments**

- PACl was the superior coagulant of the four that were tested for biopolymer and organic nitrogen removal even at low dosages. However, both ferric chloride and ferric sulfate outperformed PACl as it pertained to reducing membrane fouling when applied as in-line coagulants. Hence, the data obtained from this study suggest that jar tests may not be a useful indictor of optimum coagulant type and/or dosage for controlling fouling. Therefore, the goals of the pre-treatment (e.g. fouling reduction and/or higher permeate quality) should be carefully considered.

- Based on LC-OCD analysis, coagulation as practiced in jar testing altered the organic composition of the selected secondary effluent. The greatest removal was observed in the biopolymer fraction (both organic carbon and organic nitrogen). There was almost no impact of coagulants on humic substance removal, likely due to low hydrophobicity of the investigated secondary effluent (SUVA < 3.0) and pHs not amenable to enhanced coagulation.

8.2 Recommendation for Future Work

1- This study focused on the improvement of secondary effluent characteristics through the removal of organics and particles. Future work should include the impact of biofiltration and UF on organic trace contaminant (e.g., disinfection by-products and pharmaceutically active compounds) removal from treated secondary effluent.

2- It was observed that there was variability in turbidity, with higher values being observed at colder temperatures. In addition, a high correlation between secondary effluent turbidity and membrane fouling was observed when the UF was fed with secondary effluent alone without pre-treatment. Roughing filters to reduce turbidity could be considered in future investigations.

3- In this study, Liquid Chromatography-Organic Carbon Detection (LC-OCD) analyses were performed on all water samples to quantify the organic compound fractions found in secondary effluent and after pre-treatment. It was used to determine which NOM fraction was most correlated with membrane fouling. Future work should incorporate fluorescence excitation emission matrix (FEEM) analyses and include a comparison of data obtained with LC-OCD. FEEM may assist with a more accurate assessment of the impact of the interaction of organic compounds and particles on UF fouling.

4- This study confirmed the potential for biofiltration and in-line coagulation as pre-treatment methods for UF for secondary effluent treatment. Biofiltration will occupy a larger footprint than a plant employing in-line coagulation pre-treatment. Future investigations should consider an economic assessment to compare the feasibility of the two pre-treatment processes.

5- In this study, the biofiltration set-up was operated at a constant room temperature (23°C). Previous studies (e.g., Hallé *et al*. 2009) have reported a decrease in biofilter performance at colder temperatures (< 10°C). Follow-up studies should investigate the impact of biofiltration at lower temperature for treating secondary effluent.

6- Since membrane fouling will be affected by membrane characteristics and secondary effluent composition, the pre-treatment processes examined here should be investigated with other type of membranes, such as those which are ceramic-based, and secondary effluents of different composition.

7- In future work, standard fouling models can be used to provide additional information about the predominant UF fouling mechanism.

8- In this study, no clear findings regarding the impact of in-line coagulation on permeate water quality could be teased out due to insufficient data (and lack of replication). Thus, additional investigation will be required to address this shortcoming.

9- This study demonstrated that combining in-line coagulation with biofiltration significantly improved the performance of the biofilter for the reduction of organics and particles without adversely impacting filter headloss. In addition, this combination substantially improved UF performance by reducing the fouling development, especially over time, and producing permeate water with better quality. In this study, only one coagulant was investigated (1.0

mg/L ferric sulfate). The impact of different coagulants at wider ranges of dosage should be investigated.

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Appendix A
Project Photos

Figure A. 1 Preliminary experimental set-up

Figure A. 2 Main biofiltration experimental set-up

Figure A. 3 Biofilter media sampling

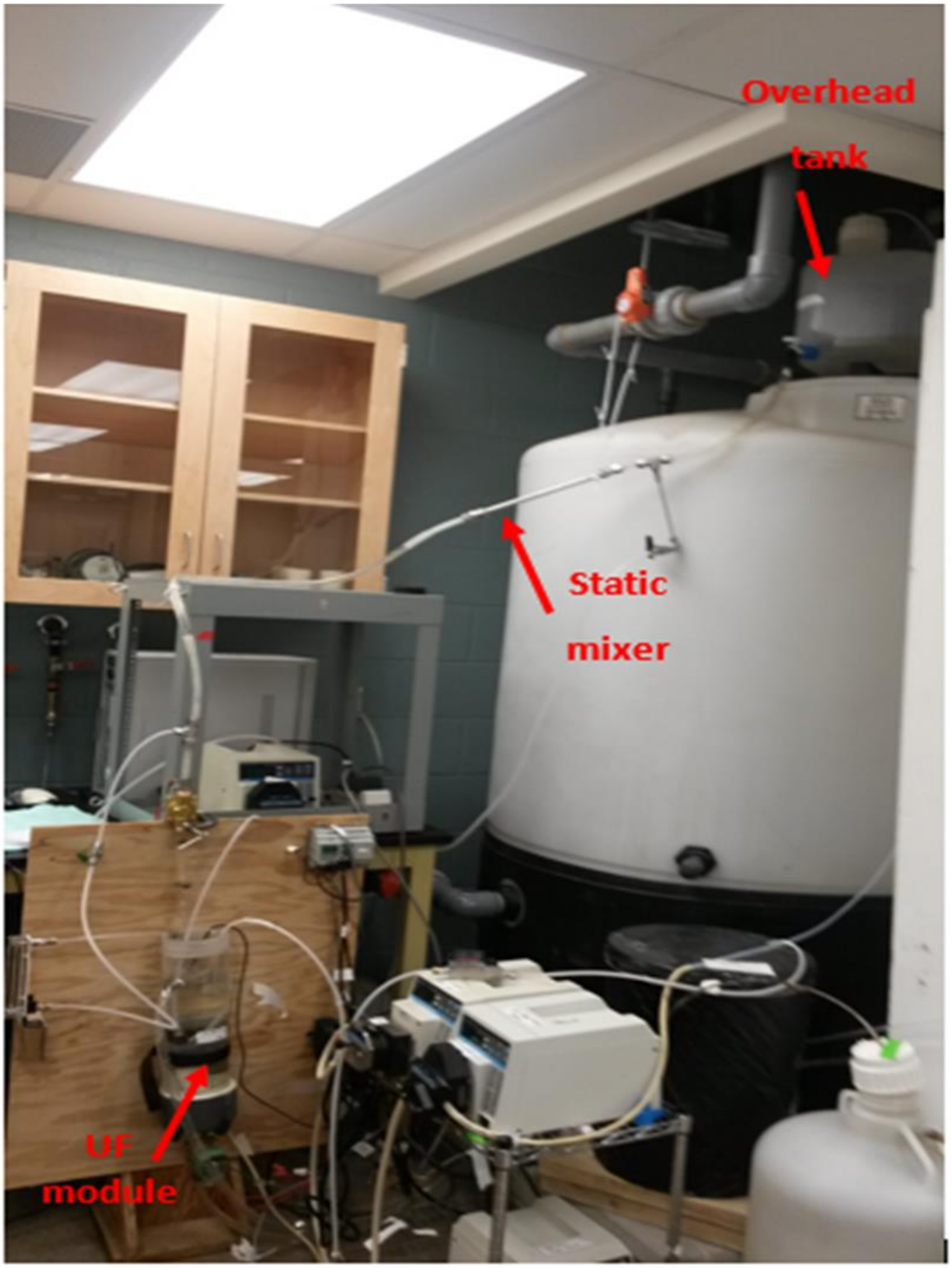


Figure A. 4 Ultrafiltration experimental set-up

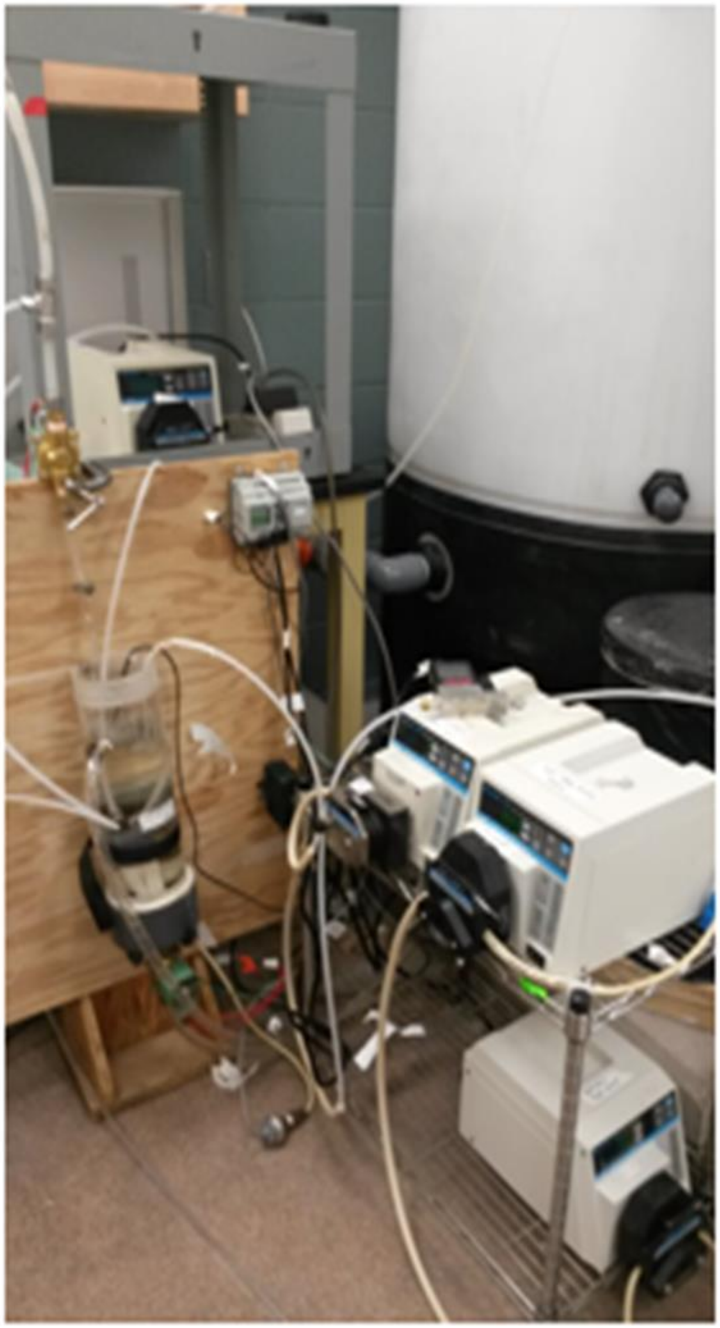


Figure A. 5 Ultrafiltration module and permeation pump

Figure A. 6 Clean and fouled membranes

Appendix B

Biomass Respiration Potential (BRP) Method

1- Media collection from the drained biofilter into a weighting dish

2- Weight wet media

3- Place media in a clean 50 mL polyethylene centrifuge tube

4- Fill the tube with biofilter influent (secondary effluent) and measure initial DO with DO-probe (Dissolved Oxygen pen, model NO. 97011-782, VWR international, USA)

5- Use biofilter influent and refill to the top the centrifuge tubes and close with the tube plug the tube carefully to avoid the production any air bubbles

6- Cover tubes with foil to prevent entrance of light

7- Place tubes on shaker table (I 24 incubator shaker, New Brunswick Scientific, Enfield CT, USA) at medium speed for 5 hours at room temperature (20 °C)

8- Measure final DO concentration with DO probe (Dissolved Oxygen pen, model NO. 97011-782, VWR international, USA)

9- Calculate biomass activity (BRP) as mg O_2/L per Cm^3 of filter using the following equation

$$BRP = \frac{media\ density}{dry\ weight}\left(DO\ final - DO\ initial\right)$$

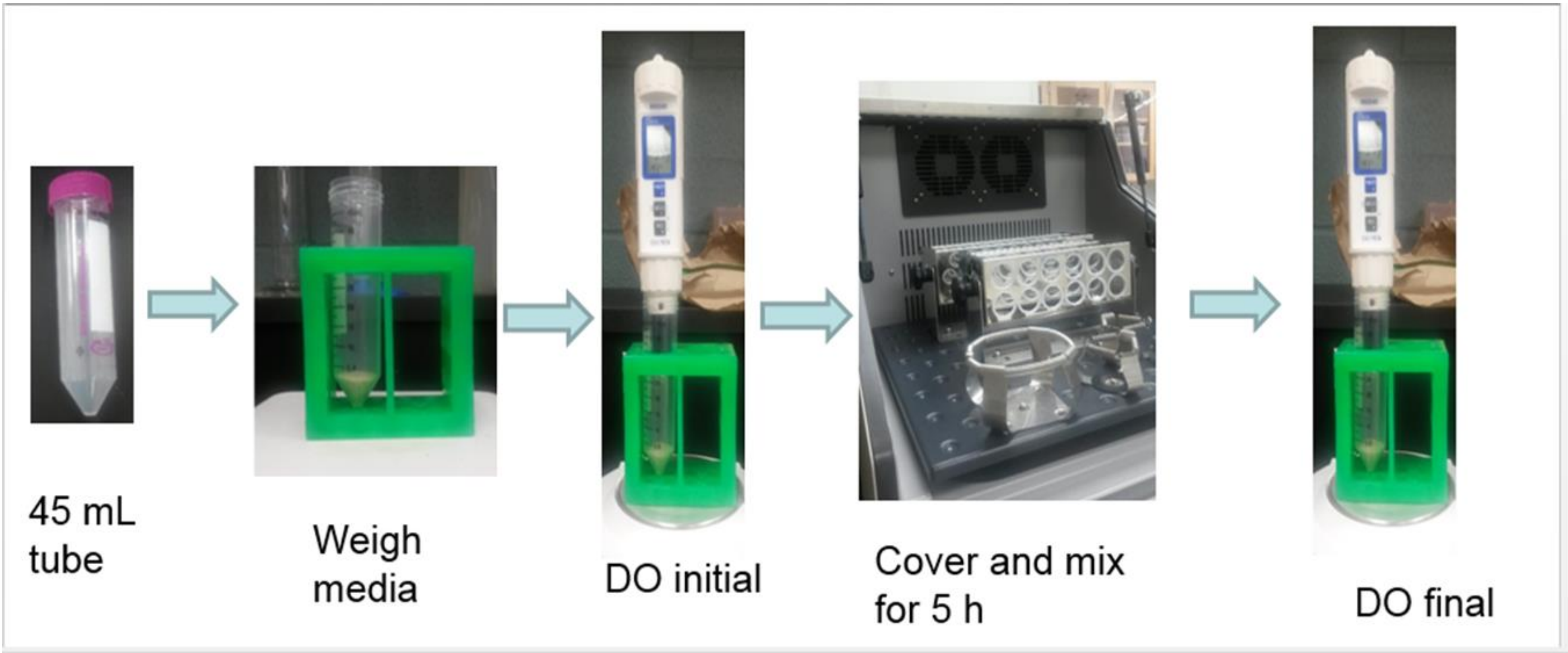


Figure B. 1 BRP method procedure

Appendix C

Raw Data for Water Samples

Table C. 1 University of Waterloo raw data for water samples

Date	Sample ID	TOC analyzer data				Analysis							LC-OCD											
		TOC		DOC		UV		SUVA		Turbidity		pH	DOC		biopolymer		humics		building blocks		LMW neturals		LMW acids	
		mg/L	Rem. %	mg/L	Rem. %	cm-1	Rem. %	L/mg. m	Rem. %	NTU	Rem. %		mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %
16-Jan-14	RW1	21		12.0		0.1468		1.39		10		7.5	10.6		2.54		3.46		1.23		1.99		0.24	
	RW2	22		14.0		0.1493		1.42		11.2		7.45	10.5		2.48		3.47		1.18		1.95		0.24	
	BF1 (sand)	14	33.33	11.8	1.7	0.1434	2.32	1.49	-7.31	1.81	81.9	7.18	9.6	9.0	2.23	12.03	3.49	-0.78	1.24	-0.41	1.91	4.11	0.20	17.72
	BF2 (anth.)	16	27.27	13.0	7.1	0.1412	5.43	1.40	1.64	1.76	84.3	7.16	10.1	3.8	2.29	7.47	3.50	-1.01	1.26	-6.59	1.84	5.89	0.24	2.89
29-Jan-14	RW1	24		18.2		0.1226		1.37		10.3		7.52	9.0		1.40		3.03		1.14		1.87		0.40	
	RW2	25		18.0		0.1220		1.37		9.8		7.51	8.9		1.57		2.88		1.07		1.63		0.35	
	BF1 (sand)	18	25	14.0	23.1	0.1170	4.57	1.35	1.43	0.6	94.2	7.49	8.7	3.2	1.28	8.86	3.04	-0.26	1.32	-15.89	1.81	3.26	0.34	15.40
	BF2 (anth.)	21	16	17.0	5.6	0.1144	6.23	1.28	6.75	0.9	90.8	7.51	8.9	-0.6	1.19	24.17	3.03	-5.28	1.14	-7.12	1.71	-4.79	0.35	-0.87
6-Feb-14	RW1					0.1392		1.54		3.8		7.52	9.0		1.52		3.06		1.32		1.90		0.30	
	RW2					0.1403		1.59		1.7		7.51	8.8		1.59		3.03		1.25		1.77		0.28	
	BF1 (sand)					0.1282	7.90	1.42	7.96	1.4	63.2	7.49	9.0	-0.1	1.64	-7.55	3.03	0.95	1.17	11.67	1.85	2.64	0.37	-24.32
	BF2 (anth.)					0.1302	7.20	1.54	2.80	1.1	35.3	7.51	8.4	4.5	1.37	14.04	2.87	5.06	1.23	1.76	1.60	9.34	0.32	-15.41
13-Feb-14	RW1	12.4		10.1		0.1391		1.52		15.7		7.6	9.1		1.52		3.28		1.21		1.84		0.43	
	RW2	12.6		11.3		0.1323		1.41		13.3		7.57	9.4		1.48		3.10		1.21		1.70		0.51	
	BF1 (sand)	10.8	12.90	9.5	5.9	0.1264	9.13	1.54	-0.94	1	93.6	7.58	8.2	10.0	1.34	12.06	2.96	9.58	1.16	3.90	1.59	13.33	0.50	-14.55
	BF2 (anth.)	10.6	15.87	9.6	15.0	0.1249	5.59	1.48	-4.54	0.8	94.0	7.59	8.5	9.7	1.36	8.12	2.97	4.10	1.12	7.11	1.58	7.24	0.27	46.55
20-Feb-14	RW1	12.3		12.0		0.1250		1.45		23.5			8.6		1.43		2.85		1.16		1.63		0.26	
	RW2	12		12.2		0.1194		1.42		19.2			8.4		1.32		2.91		1.12		1.65		0.30	
	BF1 (sand)	9.7	21.14	8.6	28.3	0.1058	15.36	1.40	3.18	0.8	96.60		7.5	12.6	1.26	11.88	2.62	7.90	1.05	9.63	1.45	10.89	0.25	4.98
	BF2 (anth.)	10.1	15.83	9.1	25.4	0.1047	12.31	1.46	-3.49	0.8	95.83		7.1	15.3	1.17	11.78	2.65	8.87	1.06	5.52	1.40	15.50	0.21	28.41
27-Feb-14	RW1					0.1275		1.63		23.5			7.8		1.17		2.95		1.18		1.78		0.29	
	RW2					0.1271		1.57		21.7			8.1		1.18		2.93		1.20		1.67		0.30	
	BF1 (sand)					0.1167	8.47	1.60	1.76	0.67	97.15		7.3	6.8	1.08	7.59	2.75	6.59	1.06	10.16	1.41	20.75	0.31	-8.42
	BF2 (anth.)					0.1176	7.47	1.54	1.52	0.74	96.59		7.6	6.0	1.14	2.81	2.80	4.57	1.08	9.59	1.46	12.56	0.29	5.28
6-Mar-14	RW1	25.4		16.0		0.1245		1.56		18.9			8.0		1.12		2.89		1.16		1.57		0.28	
	RW2	26		16.0		0.1229		1.59		16.6			7.7		1.13		2.91		1.14		1.59		0.31	
	BF1 (sand)	11	56.69	10.2	36.3	0.1140	8.43	1.46	6.16	0.7	96.30		7.8	2.4	0.98	12.81	2.78	3.84	1.02	12.40	1.40	11.18	0.28	-0.72
	BF2 (anth.)	12.3	52.69	10.5	34.4	0.1110	9.68	1.52	4.33	1	93.98		7.3	5.6	0.94	16.83	2.80	3.88	1.00	12.46	1.37	13.42	0.30	3.28

Date	Sample ID	Analysis											LC-OCD											
		TOC		DOC		UV		SUVA		Turbidity		pH	DOC		biopolymer		humics		building blocks		LMW neturals		LMW acids	
		mg/L	Rem. %	mg/L	Rem. %	cm-1	Rem. %	L/mg. m	Rem. %	NTU	Rem. %		mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %
13-Mar-14	RW1	12		10.0		0.1221		1.61		5.6		7.46	7.6		0.79		2.84		1.15		1.67		0.29	
	RW2	15		11.2		0.1205		1.71		6.7		7.58	7.0		0.89		2.74		1.13		1.63		0.34	
	BF1 (sand)	6.5	45.8	6.2	38.0	0.1146	6.14	1.71	-6.05	1	82.14	7.64	6.7	11.5	0.72	9.95	2.75	2.89	1.10	4.09	1.54	7.56	0.29	0.35
	BF2 (anth.)	7	53.333	6.6	41.1	0.1137	5.64	1.66	2.86	1.3	80.597	7.41	6.8	2.9	0.78	12.67	2.71	1.06	1.10	2.84	1.53	6.21	0.29	14.54
27-Mar-14	RW1					0.1399		1.40		4.1		7.42	10.0		1.34		3.00		1.60		2.59		0.38	
	RW2					0.1379		1.40		4		7.43	9.8		1.33		3.09		1.36		2.42		0.39	
	BF1 (sand)					0.1346	3.79	1.60	-14.41	1	75.61	7.49	8.4	15.9	1.02	23.58	2.69	10.47	1.25	21.90	2.13	17.81	0.34	10.05
	BF2 (anth.)					0.1251	9.28	1.50	-6.91	0.9	77.50	7.48	8.3	15.1	1.03	22.48	2.68	13.39	1.21	11.16	1.99	17.52	0.32	16.75
4-Apr-14	RW1	9.2		8.8		0.1135		1.45		3		7.39	7.8		1.24		3.04		1.01		1.56		0.27	
	RW2	8.5		8.3		0.1107		1.37		2.8		7.39	8.1		1.21		3.02		1.01		1.57		0.25	
	BF1 (sand)	7.1	22.83	7.2	18.2	0.1225	-7.93	1.76	-21.57	6.5	-116.67	7.41	7.0	11.2	0.91	26.54	2.18	28.06	1.40	-38.89	1.43	8.16	0.39	-43.54
	BF2 (anth.)	7.2	15.29	6.5	21.7	0.1006	9.12	1.68	-22.28	0.6	78.57	7.4	6.0	25.7	0.77	36.15	2.16	28.67	1.34	-32.80	1.07	31.99	0.20	20.32
11-Apr-14	RW1					0.1009		0.49		5.8		7.46	20.5		0.82		2.15		0.92		17.40		0.09	
	RW2					0.1009		0.47		5.6		7.47	21.5		0.77		2.14		1.06		16.75		0.04	
	BF1 (sand)					0.1052	-4.26	0.54	-9.25	2.2	62.07	7.54	19.6	4.6	0.53	35.08	1.32	38.66	1.15	-24.46	16.80	3.45	0.04	55.29
	BF2 (anth.)					0.0882	12.59	0.46	2.94	0.8	85.71	7.49	19.3	9.9	0.49	36.20	1.85	13.71	0.74	30.57	16.90	-0.90	0.04	16.67
17-Apr-14	RW1					0.0961		0.95		5.9		7.46	10.2		1.32		3.21		1.32		2.31		0.40	
	RW2					0.0964		0.96		5.5		7.47	10.0		1.38		3.19		1.42		2.30		0.37	
	BF1 (sand)					0.0847	11.86	0.94	1.01	0.6	89.83	7.54	9.0	11.0	0.98	25.66	2.90	9.48	1.21	8.37	2.02	12.56	0.32	20.75
	BF2 (anth.)					0.0852	11.62	1.02	-5.31	0.6	89.09	7.49	8.4	16.1	1.02	26.32	2.91	8.79	1.19	16.17	2.01	12.83	0.30	17.26
24-Apr-14	RW1	7.8				0.1233		1.63		3.1		7.12	7.6		0.90		3.04		1.09		1.62		0.28	
	RW2	7.9				0.1274		1.56		3.2		7.13	8.2		0.92		3.10		1.12		1.66		0.31	
	BF1 (sand)	7.7	1.28			0.1108	10.14	1.62	0.63	0.9	70.97	7.22	6.9	9.6	0.70	22.57	2.69	11.45	0.94	13.77	1.29	20.419	0.25	10.71
	BF2 (anth.)	7.2	8.86			0.1108	13.03	1.68	-7.79	1	68.75	7.17	6.6	19.3	0.70	24.04	2.74	11.80	0.95	15.18	1.30	21.87	0.22	29.03
5-May-14	RW1					0.1127		1.60		5.1		7.27	7.1		1.41		2.77		0.90		1.22		0.23	
	RW2					0.1122		1.63		5.3		7.24	6.9		1.39		2.47		1.14		1.08		0.19	
	BF1 (sand)					0.1077	4.44	1.76	-9.91	0.6	88.24	7.36	6.1	13.0	1.04	26.17	2.33	15.91	1.02	-13.59	0.98	19.84	0.18	21.40
	BF2 (anth.)					0.1077	4.01	1.78	-9.17	0.8	84.91	7.32	6.1	12.1	1.02	26.60	2.50	-1.13	0.80	29.65	0.97	10.31	0.16	12.83

Date	Sample ID	Analysis											LC-OCD											
		TOC		DOC		UV		SUVA		Turbidity		pH	DOC		biopolymer		humics		building blocks		LMW neturals		LMW acids	
		mg/L	Rem. %	mg/L	Rem. %	cm-1	Rem. %	L/mg. m	Rem. %	NTU	Rem. %		mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %
13-May-14	RW1					0.1274		1.64		2.57		7.48	7.8		1.34		3.15		1.16		1.70		0.30	
	RW2					0.1268		1.47		2.8		7.47	8.6		1.37		3.12		1.14		1.79		0.34	
	BF1 (sand)					0.1222	4.08	1.87	-14.54	1.53	40.47	7.46	6.5	16.3	0.95	28.88	2.64	16.15	1.00	13.41	1.50	11.84	0.24	20.53
	BF2 (anth.)					0.1205	4.97	1.82	-23.36	2.16	22.86	7.35	6.6	23.0	1.03	24.62	2.67	14.32	0.99	13.41	1.36	23.98	0.24	30.23
20-May-14	RW1					0.1202		1.69		1.84		7.71	7.1		1.15		2.43		1.23		1.26		0.14	
	RW2					0.1180		1.68		2.9		7.7	7.0		1.11		2.42		1.22		1.25		0.15	
	BF1 (sand)					0.1134	5.66	1.93	-14.34	0.56	69.57	7.41	5.9	17.5	0.74	36.00	2.27	6.46	1.21	1.87	1.02	18.97	0.15	-2.10
	BF2 (anth.)					0.1117	5.34	1.87	-11.47	0.65	77.59	7.19	6.0	15.1	0.73	34.83	2.26	6.52	1.21	0.66	1.15	8.29	0.21	-45.89
3-Jun-14	RW1					0.1268		1.54		1.62		7.84	8.3		1.36		3.06		1.14		1.69		0.30	
	RW2					0.1251		1.56		1.64		7.84	8.0		1.36		3.05		1.16		1.60		0.32	
	BF1 (sand)					0.1161	8.44	1.70		0.77	52.47	7.77	6.8	17.3	0.88	35.25	2.71	11.48	0.96	15.72	1.33	21.30	0.23	21.81
	BF2 (anth.)					0.1154	7.75	1.65		0.79	51.83	7.53	7.0	12.6	0.87	36.03	2.81	7.72	0.84	27.40	1.34	16.25	0.24	25.55
10-Jun-14	RW1					0.1248		1.28		2.05		7.75	9.8		1.37		3.14		1.22		1.61		0.30	
	RW2					0.1211		1.38		2.2		7.77	8.8		1.27		2.98		1.07		1.50		0.28	
	BF1 (sand)					0.1144	8.33	1.70	-32.92	0.58	71.71	7.8	6.7		0.71	48.06	2.73	13.14	0.97	20.75	1.18	26.36	0.16	45.82
	BF2 (anth.)					0.1171	3.30	1.42	-3.25	1.13	48.64	7.76	8.2		1.02	19.53	2.73	8.34	1.02	4.85	1.22	18.55	0.24	14.08
17-Jun-14	RW1					0.1323		1.50		3.65		7.38	8.8		1.20		2.79		1.30		1.73		0.33	
	RW2					0.1310		1.51		3.6		7.4	8.7		1.14		2.78		1.25		1.71		0.32	
	BF1 (sand)					0.1264	4.46	1.69	-12.53	0.89	75.62	7.59	7.5	15.1	0.82	31.50	2.78	0.29	1.06	18.27	1.33	23.07	0.23	30.28
	BF2 (anth.)					0.1258	3.97	1.68	-11.57	1.11	69.17	7.7	7.5	13.9	0.98	13.86	2.88	-3.60	1.09	12.96	1.24	27.78	0.17	48.77
25-Jun-14	RW1					0.1287		1.63		1.84		7.88	7.9		1.24		2.98		1.11		1.45		0.26	
	RW2					0.1287		1.59		2.08		7.89	8.1		1.25		2.95		1.17		1.43		0.21	
	BF1 (sand)					0.1215	5.59	1.71	-5.03	1.06	42.39	7.83	7.1	10.1	0.79	36.29	2.70	9.40	1.01	8.76	1.29	11.03	0.21	19.23
	BF2 (anth.)					0.1232	4.27	1.54	3.20	1.48	28.85	7.72	8.0	1.1	0.98	21.60	2.90	1.69	1.12	4.27	1.65	-15.38	0.19	10.38
14-Jul-14	RW1					0.1309		1.35					9.7		1.72		3.27		1.28		1.77		0.45	
	RW2					0.1304		1.44					9.1		1.78		3.20		1.15		1.59		0.36	
	BF1 (sand)					0.1333	-1.83	1.69	-24.65				7.9	18.3	1.35	21.51	3.02	7.65	0.96	25.00	1.34	24.25	0.21	53.33
	BF2 (anth.)					0.1331	-2.07	1.64	-14.39				8.1	10.8	1.49	16.29	2.84	11.25	1.02	10.99	1.29	18.87	0.23	36.11

Date	Sample ID	Analysis											LC-OCD											
		TOC		DOC		UV		SUVA		Turbidity		pH	DOC		biopolymer		humics		building blocks		LMW neturals		LMW acids	
		mg/L	Rem. %	mg/L	Rem. %	cm-1	Rem. %	L/mg. m	Rem. %	NTU	Rem. %		mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %
21-Jul-14	RW1					0.1527		1.63				7.39	9.4		1.48		3.38		1.19		1.78		0.35	
	RW2					0.1537		1.60				7.36	9.6		1.53		3.26		1.30		1.76		0.32	
	BF1 (sand)					0.1476	3.34	1.78	-9.24			7.55	8.3	11.5	0.90	38.98	3.27	3.28	1.07	10.08	1.49	16.29	0.26	26.57
	BF2 (anth.)					0.1470	4.36	1.81	-13.71			7.54	8.1	15.9	1.06	30.72	3.09	5.21	1.15	11.54	1.38	21.59	0.24	25.63
29-Jul-14	RW1					0.1429		1.61				7.37	8.9		1.18		2.87		1.22		1.48		0.33	
	RW2					0.1404		1.58				7.31	8.9		1.23		2.88		1.17		1.50		0.29	
	BF1 (sand)					0.1339	6.30	1.63	-1.70			7.34	8.2	7.9	0.79	33.22	2.60	9.31	0.94	22.70	1.28	13.51	0.23	30.30
	BF2 (anth.)					0.1331	5.20	1.78	-12.60			7.29	7.5	15.8	1.01	17.72	2.80	2.78	1.00	14.33	1.40	6.67	0.26	9.72
5-Aug-14	RW1					0.1463		1.60				7.8	9.2		1.06		3.30		1.09		1.55		0.37	
	RW2					0.1465		1.61				7.85	9.1		1.05		3.20		1.05		1.57		0.35	
	BF1 (sand)					0.1413	3.42	1.86	-16.28			7.45	7.6	16.9	0.71	33.21	2.80	15.15	0.99	9.26	1.21	21.94	0.27	27.03
	BF2 (anth.)					0.1395	4.78	1.84	-14.51			7.42	7.6	16.8	0.80	24.00	2.88	10.00	0.88	16.19	1.11	29.30	0.20	42.86
12-Aug-14	RW1					0.1268		1.70				7.88	7.4		0.97		3.05		0.95		1.30		0.24	
	RW2					0.1252		1.72				7.9	7.3		0.95		2.96		1.02		1.22		0.29	
	BF1 (sand)					0.1202	5.21	2.07	-21.37			7.9	5.8	21.9	0.75	23.07	2.65	13.09	0.79	16.84	0.95	27.31	0.25	-4.17
	BF2 (anth.)					0.1188	5.11	1.84	-6.74			7.83	6.5	11.1	0.79	16.72	2.70	8.75	0.79	22.74	0.99	18.77	0.33	-13.79
18-Aug-14	RW1					0.1446		1.52				7.3	9.5		1.18		3.63		1.24		1.66		0.22	
	RW2					0.1466		1.54				7.3	9.5		1.18		3.62		1.24		1.66		0.22	
	BF1 (sand)					0.1354	6.36	1.45	4.94			7.18	9.4	1.5	0.88	25.55	3.40	6.21	1.01	18.11	1.48	10.84	0.40	-83.49
	BF2 (anth.)					0.1397	4.71	1.57	-1.85			7.3	8.9	6.4	1.20	-1.52	3.23	10.85	1.11	10.02	1.36	18.07	0.19	12.84
25-Aug-14	RW1					0.1407		1.50		7		7.25	9.4		1.17		3.57		1.32		1.66		0.31	
	RW2					0.1418		1.52		7.3		7.35	9.3		1.24		3.26		1.35		1.62		0.21	
	BF1 (sand)					0.1314	6.61	1.75	-16.74	0.6	91.43	7.47	7.5	20.0	0.85	27.47	3.20	10.36	0.92	30.58	1.19	28.28	0.07	78.43
	BF2 (anth.)					0.1343	5.29	1.58	-4.28	0.72	90.14	7.47	8.5	9.2	1.00	19.35	3.20	1.84	1.04	23.43	1.39	13.93	0.17	17.07
2-Sep-14	RW1									6.5		7.67	8.4		1.14		3.44		1.27		1.57		0.11	
	RW2									7.1		7.73	9.2		1.06		3.53		1.27		1.69		0.40	
	BF1 (sand)									0.6	90.77	7.63	7.0	15.8	0.74	35.75	3.16	8.34	0.96	24.17	1.21	22.93	0.12	-9.09
	BF2 (anth.)									0.5	92.96	7.56	7.8	15.7	0.87	17.64	3.10	12.06	1.12	11.81	1.33	21.30	0.32	20.25

Date	Sample ID	Analysis											LC-OCD											
		TOC		DOC		UV		SUVA		Turbidity		pH	DOC		biopolymer		humics		building blocks		LMW neturals		LMW acids	
		mg/L	Rem. %	mg/L	Rem. %	cm-1	Rem. %	L/mg. m	Rem. %	NTU	Rem. %		mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %
8-Sep-14	**RW1**	13.5				0.1521		1.67		1.9		7.77	9.1		1.10		3.46		1.18		1.55		0.36	
	RW2	13.45				0.1485		1.56		2		7.76	9.5		1.10		3.54		1.22		1.69		0.38	
	BF1 (sand)	12.9	4.44			0.1430	5.98	1.72	-3.08	0.8	57.89	7.72	8.3	8.8	0.83	24.55	3.30	4.62	1.00	15.18	1.38	10.97	0.43	-19.44
	BF2 (anth.)	13.3	1.12			0.1470	1.01	1.72	-9.86	0.9	55.00	7.65	8.6	9.9	0.92	16.36	3.10	12.43	1.40	-15.23	1.37	18.93	0.45	-18.42
15-Sep-14	**RW1**	6.99				0.1220		1.97		1.15		7.91	6.2		0.58		2.45		1.20		1.08		0.21	
	RW2	6.8				0.1220		1.97		1.15		7.91	6.2		0.58		2.45		1.20		1.08		0.21	
	BF1 (sand)	6.3	9.87			0.1136	6.89	2.18	-11.02	0.49	57.39	7.59	5.2	16.1	0.46	20.69	2.28	6.94	0.99	17.50	0.85	21.30	0.17	19.05
	BF2 (anth.)	6.17	9.26			0.1154	5.41	2.10	-6.63	0.5	56.52	7.51	5.5	11.3	0.56	3.45	2.24	8.57	1.01	15.83	0.91	15.74	0.18	14.29
22-Sep-14	**RW1**	9.4				0.1345		1.72		1.14		8.07	7.8		0.63		3.20		1.06		1.40		0.34	
	RW2	9.4				0.1345		1.72		1.14		8.04	7.8		0.63		3.20		1.06		1.40		0.34	
	BF1 (sand)	8.29	11.81			0.1262	6.17	1.89	-9.56	0.39	65.79	7.95	6.7	14.4	0.50	20.63	2.50	21.88	1.16	-9.43	1.12	20.00	0.18	46.43
	BF2 (anth.)	8.45	10.11			0.1268	5.72	1.76	-2.13	0.56	50.88	7.61	7.2	7.7	0.56	11.11	2.90	9.38	0.80	24.53	1.13	19.29	0.40	-19.05
6-Oct-14	**RW1**	11.2				0.1667		1.78		2.91			9.4		1.30		3.47		1.24		1.84		0.21	
	RW2	11.2				0.1665		1.78		2.91			9.4		1.30		3.47		1.24		1.84		0.21	
	BF1 (sand)	9.6	14.29			0.1511	9.33	1.72	3.44	1.17	59.79		8.8	6.1	1.05	19.23	2.61	24.78	1.40	-12.90	1.39	24.46	0.23	-7.62
	BF2 (anth.)	9.5	15.18			0.1549	6.97	1.71	3.78	1.15	60.48		9.0	3.3	1.20	7.69	3.26	6.05	1.06	14.52	1.44	21.74	0.35	-66.67
20-Oct-14	**RW1**	12				0.1481		1.69		3.07		7.91	8.8		1.32		3.32		1.16		1.59		0.18	
	RW2	11.7				0.1481		1.69		3.07		7.9	8.8		1.32		3.32		1.16		1.59		0.18	
	BF1 (sand)	10	16.67			0.1368	7.63	1.77	-4.93	0.97	68.40	7.76	7.7	12.0	1.07	18.94	2.75	17.17	1.20	-3.45	1.44	9.43	0.18	2.78
	BF2 (anth.)	8.2	29.91			0.1363	7.97	1.76	-4.41	1.2	60.91	7.73	7.7	11.9	1.16	12.12	2.60	21.69	1.30	-12.07	1.20	24.53	0.18	0.56
3-Nov-14	**RW1**					0.1588		1.66		3.5		8.38	9.6		1.48		3.44		1.32		1.65		0.22	
	RW2					0.1588		1.66		3.5		8.38	9.6		1.48		3.44		1.32		1.65		0.22	
	BF1 (sand)					0.1399	11.90	1.87	-12.53	0.73	79.14	7.78	7.5	21.7	0.98	33.56	3.00	12.79	1.11	15.65	1.12	32.12	0.19	13.24
	BF2 (anth.)					0.1461	8.00	1.80	-8.81	1.81	48.29	8.02	8.1	15.4	1.09	26.10	3.30	4.07	0.96	27.05	1.33	19.39	0.21	4.55
17-Nov-14	**RW1**					0.1568		1.70		1.92		7.42	9.2		1.25		3.40		1.26		1.84		0.34	
	RW2					0.1568		1.70		1.92		7.42	9.2		1.25		3.40		1.26		1.84		0.34	
	BF1 (sand)					0.1500	4.34	1.79	-4.77	0.6	68.75	7.8	8.4	8.7	0.94	24.80	3.14	7.65	0.84	33.07	1.26	31.52	0.29	15.13
	BF2 (anth.)					0.1470	6.25	1.81	-6.48	2	-4.17	7.5	8.1	12.0	0.98	21.60	2.40	29.41	1.43	-13.94	1.01	45.11	0.26	22.85

Table C. 1 Waterloo WWTP raw data for secondary effluent

DATE	Temp.	Concentration as mg/L							
	C°	Ammonia-N	BOD (5days)	Nitrate-N	Nitrite-N	phousphours	TKN-HL	TSS	CBOD (5days)
15/01/2014	14.2	21.0	7.1	1.6	0.4	0.2	24.0	1.0	7.2
22/01/2014	11.4	26.0	11.3	1.5	0.2	0.3	35.1	1.6	5.6
29/01/2014	10.3	29.1	7.9	1.1	0.2	0.3	33.0	2.2	5.0
05/02/2014	11.7	29.6	10.0	1.2	0.2	0.2	36.5	3.2	7.0
12/02/2014	11	30.0	10.6	1.4	0.6	0.2	37.1	1.6	3.7
19/02/2014	11.6	26.0	17.6	1.6	0.5	0.2	31.9	3.2	2.7
26/02/2014	11.7	28.0	14.6	2.2	0.8	0.2	34.1	2.0	3.4
05/03/2014	11.3	26.5	13.9	2.7	0.6	0.2	31.9	3.6	3.5
12/03/2014	12.9	25.5	12.9	2.9	0.7	0.2	61.0	2.8	4.5
19/03/2014	11.6	23.7	28.0	2.9	0.3	0.2	26.3	3.0	4.2
26/03/2014	11.5	25.8	17.5	2.7	0.3	0.1	28.0	3.2	6.3
02/04/2014	12.3	20.3	13.3	1.1	0.5	0.2	24.1	1.0	2.5
09/04/2014	13.3	14.2	2.7	0.6	0.2	0.1	15.4	2.0	2.5
16/04/2014	14.4	20.8	7.8	1.1	0.3	0.1	22.2	1.0	3.3
23/04/2014	12.1	24.4	23.3	0.7	0.4	0.2	29.4	5.0	4.2
30/04/2014	11.8	20.5	7.9	1.3	0.3	0.1	22.6	3.0	4.3
07/05/2014	12	25.2	13.3	0.8	0.0	0.2	29.4	7.2	4.2
14/05/2014	14.9	26.3	12.1	1.6	0.4	0.2	27.2	3.2	3.8
16/05/2014	13.8	22.9						5.4	3.4
20/05/2014	13.8	20.1						1.6	2.8
21/05/2014	14	23.8	28.4	3.7	0.4	0.2	26.9	3.4	3.7
23/05/2014	14.3	24.1						4.0	4.2
26/05/2014	14.9	19.6						1.0	3.8
28/05/2014	16	19.7	36.0	4.3	0.5	0.1	23.4	4.4	3.1
30/05/2014	15.7	19.9						1.0	3.2
02/06/2014	16	17.3						3.2	3.9
04/06/2014	16.8	29.4	34.0	3.4	0.3	0.2	32.5	4.2	3.8
06/06/2014	16.2	23.3						6.0	2.4
09/06/2014	16	17.0						5.0	2.9
11/06/2014	16.1	30.9	27.0	5.2	0.9	0.3	33.1	2.8	5.3
13/06/2014	17.3	23.5						1.2	3.5
16/06/2014	25	15.8						2.6	3.7
18/06/2014	25	30.6	54.0	2.8	0.7	0.3	35.9	7.4	8.9
20/06/2014	17.7	23.3						2.6	2.0
23/06/2014	18.6	16.9						2.0	2.9
25/06/2014	18.4	25.0	29.8	6.4	1.4	0.2	26.6	3.4	3.6
27/06/2014	25	29.2						2.4	3.7
30/06/2014	25	19.7						5.1	6.4
02/07/2014	18.8	17.5	6.2	9.1	1.9	0.1	17.9	1.0	2.9
04/07/2014	18.3	18.0						2.0	3.7
07/07/2014	18.5	20.1						2.6	4.9
09/07/2014	18.5	16.9	7.8	5.4	1.1	0.2	19.9	1.0	2.9
11/07/2014	18.4	15.8						1.0	2.9

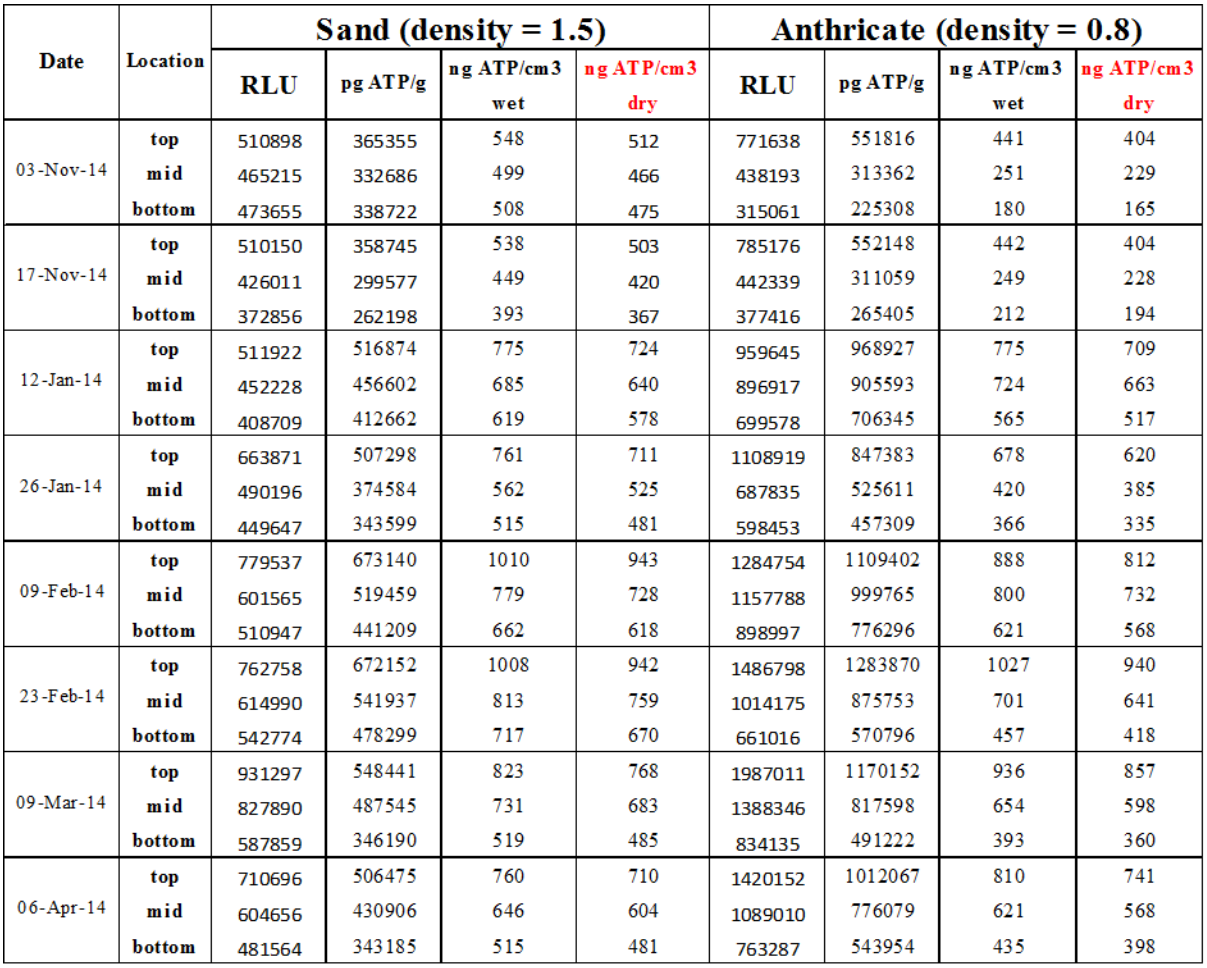
DATE	Temp.	Concentration as mg/L							
	C°	Ammonia-N	BOD (5days)	Nitrate-N	Nitrite-N	phousphours	TKN-HL	TSS	CBOD (5days)
14/07/2014	19.6	12.4						2.0	2.6
16/07/2014		19.3	13.8	7.3	1.3	0.2	20.1	3.2	5.1
18/07/2014	18.6	14.5						2.6	2.6
22/07/2014	19.7	18.4						4.0	3.1
23/07/2014	20	14.0	5.5	6.4	0.7	0.1	15.4	1.0	3.2
25/07/2014	19.3	23.5						1.0	2.9
28/07/2014	19.2	11.0						1.4	5.5
30/07/2014	18.9	22.1	8.6	7.1	0.5	0.2	23.8	2.2	3.5
01/08/2014	18.7	20.2						1.6	2.0
06/08/2014	19.6	14.4	5.3	8.2	0.6	0.2	15.1	1.6	3.5
07/08/2014	19.6	23.4						3.4	2.6
08/08/2014	19.2	22.1						4.4	5.4
11/08/2014	19.5	7.9						2.6	2.1
13/08/2014	19.9	21.0	8.6	7.1	0.3	0.2	24.4	2.8	2.5
15/08/2014	19	22.7						2.8	2.5
19/08/2014	19.5	26.2						3.4	4.8
20/08/2014	20.1	22.1	6.5	4.8	0.8	0.2	24.8	1.2	2.7
22/08/2014	20.5	22.6						2.2	2.7
25/08/2014	19.8	7.4						1.0	2.2
27/08/2014	20.5	21.3	4.9	6.5	1.1	0.2	24.8	1.8	2.4
29/08/2014	20.5	15.7						4.8	3.3
02/09/2014	20.4	14.8						10.5	5.6
03/09/2014	20.4	27.4	16.0	2.4	0.7	0.3	34.7	8.6	6.9
05/09/2014	21.2	25.7						4.6	2.7
08/09/2014	19.9	15.3						4.8	2.7
10/09/2014	20.7	27.4	11.0	4.9	0.9	0.2	35.8	4.0	3.2
12/09/2014	19.3	16.6						5.4	3.0
15/09/2014	19	11.0						1.0	2.3
17/09/2014	19.8	23.9	8.6	5.1	1.2	0.2	27.5	3.4	2.6
19/09/2014		25.5						1.8	2.6
22/09/2014	19.3	16.6						2.5	2.5
24/09/2014	20.2	25.8	9.0	4.6	1.0	0.1	31.6	2.6	2.9
26/09/2014	20.8	26.8						3.8	3.4
29/09/2014	20.3	22.4						4.8	4.0
01/10/2014	20.4	28.9	23.0	3.2	0.8	0.2	35.5	6.0	3.9
03/10/2014	21.3	30.5						4.0	4.5
06/10/2014	20.8	19.2						4.4	4.1
09/10/2014	19.4	33.1	31.0	2.0	0.8	0.3	38.5	4.8	12.0
10/10/2014	19.4	31.2						2.0	5.0
14/10/2014	20.6	18.6						2.8	6.5
15/10/2014	21.8	27.8	21.0	4.3	1.8	0.2	35.2	3.2	6.0
17/10/2014	20.7	28.4						4.4	5.7
20/10/2014	19.1	20.0						2.4	5.0

	Temp.	Concentration as mg/L							
DATE	**C°**	**Ammonia-N**	**BOD (5days)**	**Nitrate-N**	**Nitrite-N**	**phousphours**	**TKN-HL**	**TSS**	**CBOD (5days)**
22/10/2014	17.9	28.4	14.0	5.4	1.9	0.2	32.2	2.2	4.9
24/10/2014	18.0	21.8						2.8	3.8
27/10/2014	17.5	16.6						4.7	
29/10/2014	18.4		14.0						5.0
03/11/2014	16.90	10.3						4.2	6.5
05/11/2014	17.50	19.7	23.0	11.8	1.0	0.3	23.7	5.0	5.1
07/11/2014	17.3	19.0						5.4	4.2
10/11/2014	16.9	10.0						2.8	4.1
12/11/2014	17.1	12.9	10.8	16.6	1.2	0.3	16.8	4.4	3.4
14/11/2014	17.3	15.5						3.2	2.7
17/11/2014	16.4	9.4						2.4	3.4
19/11/2014	15.8	20.5	14.0	12.6	1.0	0.2	24.0	2.8	5.0
21/11/2014	16	22.2						1.6	4.0
24/11/2014	15.4	14.3						1.6	1.9
26/11/2014	15.5	14.3	11.0	9.0	0.8	0.1	17.6	2.4	2.0
01/12/2014	15.2	18.3						3.2	2.7
15/12/2014	15	16.8	10.1	11.5	0.7	0.2	20.0	3.2	3.3
03/12/2014	15.1	18.9						2.8	3.4
05/12/2014	15.1	15.0	9.7	12.8	0.5	0.4	20.4	3.4	2.5
08/12/2014	14.5	17.9	23.0	13.5	0.5	0.5	19.2	3.6	3.6
12/12/2014	15.2	16.8						6.8	7.3
17/12/2014	15	14.0						2.8	5.2
19/12/2014	15.3								
30/12/2014	14.6	8.6	9.9	20.8	0.7	0.2	11.9	3.4	5.1
07/01/2014	12.1	20.0	13.6	14.8	0.6	0.3	23.3	6.2	7.2
14/01/2014	12.2	23.7	8.2	11.8	0.4	0.3	26.4	12.2	6.6
21/01/2014	12.7	28.8	12.3	10.5	0.2	0.5	33.9	6.8	4.9
28/01/2014	12.3	23.0	11.5	10.0	0.2	0.4	26.1	3.0	8.8
04/02/2014		20.0	8.8	10.3	0.2	0.3	25.4	3.8	4.4
11/02/2014		21.1	11.2	11.1	0.2	0.2	23.0	2.4	3.6
18/02/2014		21.9	12.4	12.4	0.3	0.2	24.6	6.8	4.8
25/02/2014		19.6	15.9	15.9	0.3	0.3	23.8	9.0	6.3
04/03/2014		22.5	8.1	13.2	0.5	0.3	26.7	6.8	6.0
11/03/2014		23.3	10.2	14.2	0.5	0.3	28.7	6.0	5.9
18/03/2014		20.8	8.3	11.0	0.2	0.2	23.9	4.0	5.8
25/03/2014		22.0	5.6	7.8	0.3	0.2	23.6	3.2	3.4
01/04/2014		24.5	5.2	7.9	0.3	0.2	29.4	2.4	2.4
08/04/2014		21.8	9.5	5.9	0.3	0.2	25.9	2.6	5.7
15/04/2014		17.0	8.5	5.8	0.3	0.2	18.5	1.4	3.0
22/04/2014		22.3	10.2	7.5	0.3	0.2	24.3	2.8	4.6
29/04/2014		17.2	8.9	9.7	0.3	0.2	20.0	1.4	3.6

Table C. 2 ATP calculation for BF1 (sand) and BF2 (anthracite)

Date	Location	Sand (density = 1.5)				Anthricate (density = 0.8)			
		RLU	pg ATP/g	ng ATP/cm3 w wet	ng ATP/cm3 dry	RLU	pg ATP/g	ng ATP/cm3 w wet	ng ATP/cm3 dry
16-Jan-14	**top**	315556	381465	572	534	302857	366114	293	268
	mid	77778	94023	141	132	97143	117433	94	86
	bottom	11111	13432	20	19	76667	92680	74	68
29-Jan-14	**top**	317506	311156	467	436	572151	560708	449	410
	mid	49547	48556	73	68	346307	339381	272	248
	bottom	36580	35848	54	50	153658	150585	120	110
06-Feb-14	**top**	378278	244964	367	343	777827	503702	403	369
	mid	108979	70572	106	99	402242	260482	208	191
	bottom	74552	48278	72	68	364086	235773	189	173
13-Feb-14	**top**	422966	235030	353	329	889367	494197	395	362
	mid	146295	81292	122	114	666288	370238	296	271
	bottom	129878	72169	108	101	420252	233523	187	171
20-Feb-14	**top**	484610	244256	366	342	919870	463639	371	339
	mid	224348	113077	170	158	498583	251299	201	184
	bottom	172420	86904	130	122	361946	182431	146	134
27-Feb-14	**top**	470205	264273	396	370	919870	463639	371	339
	mid	210821	118489	178	166	498583	251299	201	184
	bottom	175640	98716	148	138	361946	182431	146	134
06-Mar-14	**top**	399978	250061	375	350	704789	440625	353	323
	mid	174994	109404	164	153	314530	196640	157	144
	bottom	159627	99797	150	140	238538	149131	119	109
13-Mar-14	**top**	425424	232559	349	326	845697	462301	370	338
	mid	322187	176124	264	247	325753	178073	142	130
	bottom	226919	124046	186	174	271628	148486	119	109
27-Mar-14	**top**	378817	243653	365	341	728658	468669	375	343
	mid	229966	147913	222	207	253635	163137	131	119
	bottom	207846	133685	201	187	213844	137543	110	101
04-Apr-14	**top**	484020	255576	383	358	618192	326423	261	239
	mid	235777	124497	187	174	302189	159564	128	117
	bottom	247179	130517	196	183	186117	98275	79	72
10-Apr-14	**top**	340877	157592	236	221	779099	360187	288	264
	mid	212323	98160	147	138	343011	158578	127	116
	bottom	180896	83630	125	117	272724	126084	101	92
17-Apr-14	**top**	356679	225381	338	316	853721	539456	432	395
	mid	285885	180647	271	253	269981	170598	136	125
	bottom	220961	139623	209	196	194572	122948	98	90
24-Apr-14	**top**	402022	188251	282	264	926118	433665	347	317
	mid	309408	144884	217	203	460746	215749	173	158
	bottom	182926	85657	128	120	256255	119994	96	88
05-May-14	**top**	411078	204853	307	287	972083	484419	388	355
	mid	218073	108672	163	152	307186	153080	122	112
	bottom	313848	156400	235	219	368261	183516	147	134

Date	Location	Sand (density = 1.5)				Anthricate (density = 0.8)			
		RLU	pg ATP/g	ng ATP/cm3 wet	ng ATP/cm3 dry	RLU	pg ATP/g	ng ATP/cm3 wet	ng ATP/cm3 dry
13-May-14	**top**	415557	208477	313	292	750851	376687	301	276
	mid	219270	110004	165	154	461377	231464	185	169
	bottom	380852	191066	287	268	344287	172722	138	126
03-Jun-14	**top**	465719	453193	680	635	553611	538721	431	394
	mid	199703	194332	291	272	329538	320675	257	235
	bottom	203307	197839	297	277	236113	229762	184	168
10-Jun-14	**top**	773205	551368	827	772	985368	702660	562	514
	mid	588876	419924	630	588	617350	440228	352	322
	bottom	588327	419532	629	588	334925	238833	191	175
17-Jun-14	**top**	942196	500604	751	701	845101	449015	359	329
	mid	563351	299317	449	419	525008	278945	223	204
	bottom	413988	219958	330	308	416115	221088	177	162
25-Jun-14	**top**	881058	516701	775	724	785971	460937	369	337
	mid	559406	328067	492	460	628328	368486	295	270
	bottom	528367	309864	465	434	434719	254943	204	187
17-Jul-14	**top**	507126	346796	520	486	454050	310500	248	227
	mid	428225	292839	439	410	317455	217090	174	159
	bottom	336721	230265	345	323	292530	200045	160	146
30-Jul-14	**top**	493286	337331	506	473	360160	246294	197	180
	mid	336829	230339	346	323	296724	202913	162	149
	bottom	309269	211492	317	296	291398	199271	159	146
13-Aug-14	**top**	501911	347050	521	486	390682	270140	216	198
	mid	376860	260583	391	365	292593	202316	162	148
	bottom	354585	245181	368	343	263282	182048	146	133
25-Aug-14	**top**	488193	329060	494	461	407714	274814	220	201
	mid	429170	289276	434	405	358830	241864	193	177
	bottom	295758	199352	299	279	312658	210743	169	154
04-Sep-14	**top**	348182	234687	352	329	411121	277110	222	203
	mid	257994	173897	261	244	257225	173379	139	127
	bottom	270117	182069	273	255	238727	160911	129	118
18-Sep-14	**top**	704918	475140	713	666	763890	514889	412	377
	mid	380499	256470	385	359	454510	306356	245	224
	bottom	375834	253326	380	355	312521	210650	169	154
06-Oct-14	**top**	551835	458152	687	642	776476	644657	516	472
	mid	406355	337370	506	473	574962	477353	382	349
	bottom	365436	303397	455	425	395602	328442	263	240
20-Oct-14	**top**	670016	511994	768	717	854401	652892	522	478
	mid	323863	247481	371	347	579458	442794	354	324
	bottom	337108	257602	386	361	508991	388947	311	285



Date	Location	Sand (density = 1.5)				Anthricate (density = 0.8)			
		RLU	pg ATP/g	ng ATP/cm3 wet	ng ATP/cm3 dry	RLU	pg ATP/g	ng ATP/cm3 wet	ng ATP/cm3 dry
03-Nov-14	**top**	510898	365355	548	512	771638	551816	441	404
	mid	465215	332686	499	466	438193	313362	251	229
	bottom	473655	338722	508	475	315061	225308	180	165
17-Nov-14	**top**	510150	358745	538	503	785176	552148	442	404
	mid	426011	299577	449	420	442339	311059	249	228
	bottom	372856	262198	393	367	377416	265405	212	194
12-Jan-14	**top**	511922	516874	775	724	959645	968927	775	709
	mid	452228	456602	685	640	896917	905593	724	663
	bottom	408709	412662	619	578	699578	706345	565	517
26-Jan-14	**top**	663871	507298	761	711	1108919	847383	678	620
	mid	490196	374584	562	525	687835	525611	420	385
	bottom	449647	343599	515	481	598453	457309	366	335
09-Feb-14	**top**	779537	673140	1010	943	1284754	1109402	888	812
	mid	601565	519459	779	728	1157788	999765	800	732
	bottom	510947	441209	662	618	898997	776296	621	568
23-Feb-14	**top**	762758	672152	1008	942	1486798	1283870	1027	940
	mid	614990	541937	813	759	1014175	875753	701	641
	bottom	542774	478299	717	670	661016	570796	457	418
09-Mar-14	**top**	931297	548441	823	768	1987011	1170152	936	857
	mid	827890	487545	731	683	1388346	817598	654	598
	bottom	587859	346190	519	485	834135	491222	393	360
06-Apr-14	**top**	710696	506475	760	710	1420152	1012067	810	741
	mid	604656	430906	646	604	1089010	776079	621	568
	bottom	481564	343185	515	481	763287	543954	435	398

Appendix D

Chapter 4 Figures

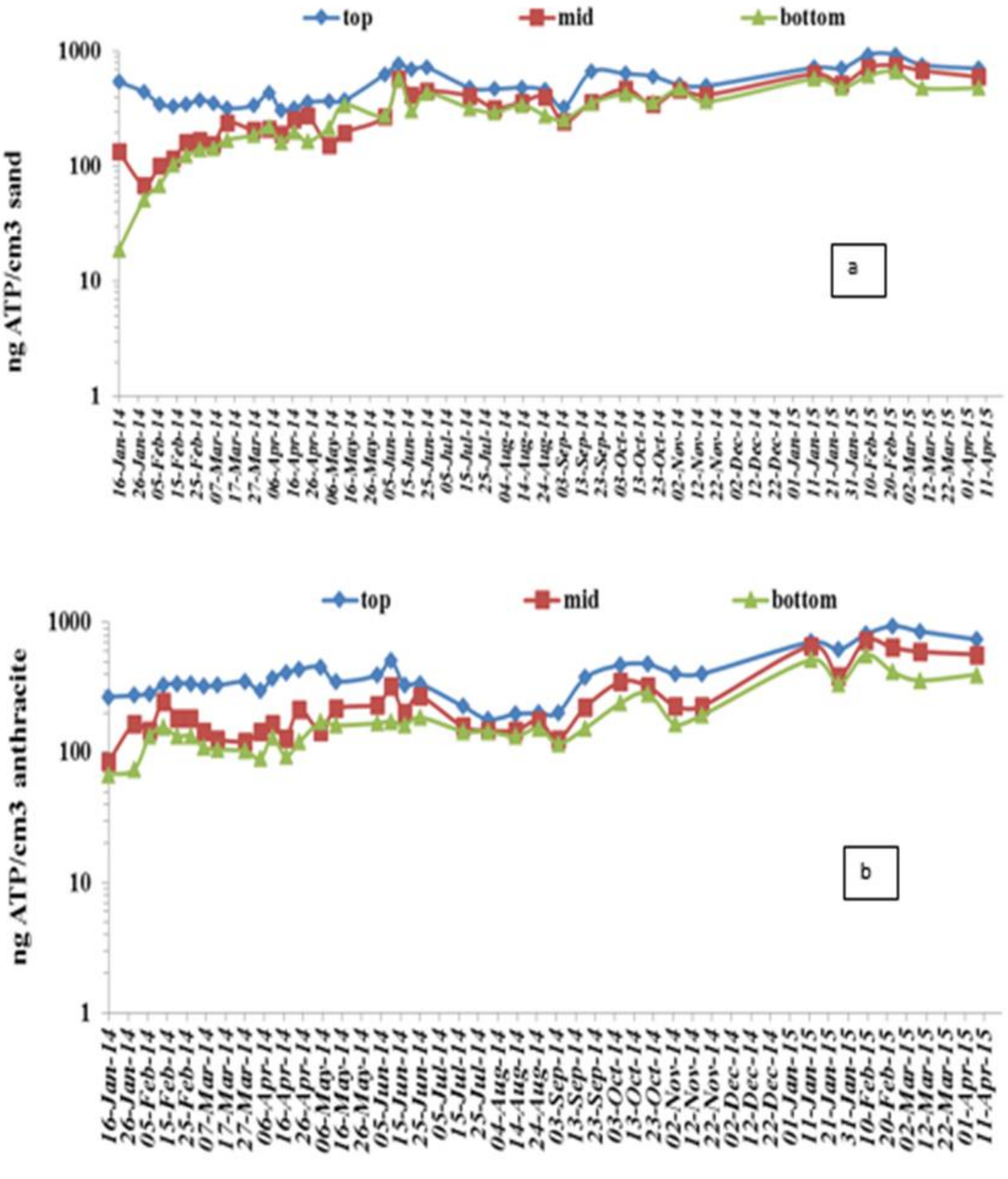


Figure D. 1 ATP data for a) BF1 (sand) and b) BF2 (anthracite) during investigated period (Jan. 2014-Apr. 2015)

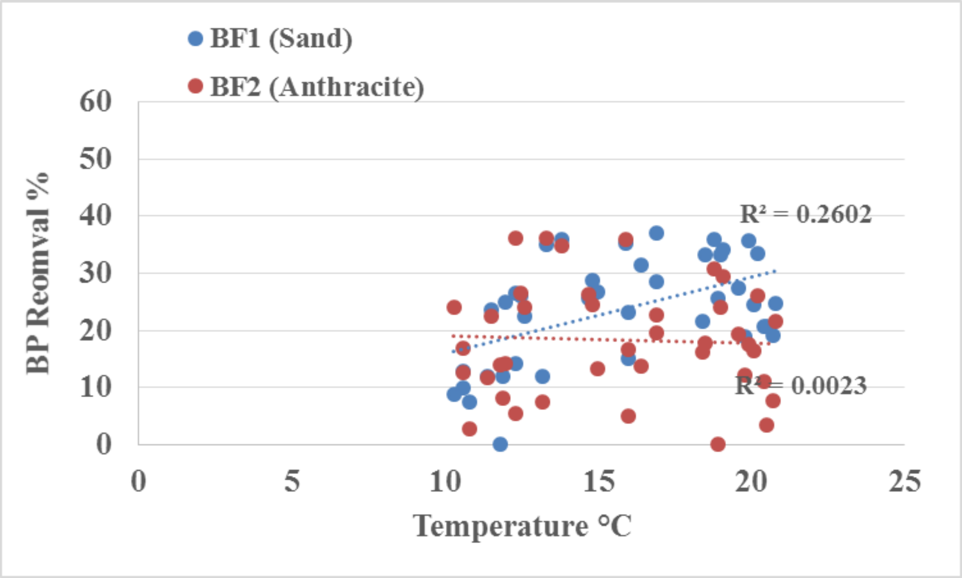


Figure D. 2 Correlation between percentage removal of biopolymer through biofilter and secondary effluent temperature (measured at field)

Appendix E

Raw Data for Biofiltration Pre-treatment Experiments

Table E. 1 Raw data for water samples analysis and LC-OCD

Date	Sample ID	Analysis									LC-OCD											
		TOC		UV		SUVA		Turbidity		pH	DOC		biopolymer		humics		building blocks		LMW neturals		LMW acids	
		mg/L	Rem. %	cm-1	Rem. %	L/mg. m	Rem. %	NTU	Rem. %		mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %
24-Nov-14	UF in (RW)			0.1227		1.62		3.37		7.63	7.6		1.01		2.80		0.95		1.57		0.26	
	UF out			0.1290	-5.13	1.90	-17.19	0.29	91.39	8.04	6.8	10.3	0.26	74.18	2.70	3.57	1.13	-18.95	1.44	8.28	0.26	0.00
28-Nov-14	UF in (BF1)			0.1216		1.78		1.24		7.76	6.8		0.79		2.40		0.93		1.08		0.26	
	Uf out			0.1154	5.10	1.78	0.27	0.23	81.5	7.85	6.5	4.8	0.15	81.27	2.20	8.33	1.16	-24.73	1.10	-1.85	0.22	16.35
2-Dec-14	Uf in (RW)			0.1486		1.62		3.77		7.45	9.2		1.30		3.36		1.30		1.87		0.35	
	UF out			0.1343	9.6	1.55	3.98	0.28	92.57	7.77	8.7	5.9	0.26	80.00	3.33	0.89	1.18	9.23	1.98	-5.88	0.33	5.71
4-Dec-14	UF in (BF2)			0.1404		1.80		0.65		8.11	7.8		0.92		3.09		0.89		1.33		0.22	
	UF out			0.1318	6.13	1.65	8.83	0.2	69.2	7.82	8.0		0.23	74.89	3.29	-6.47	1.15	-29.21	2.03	-52.26	0.27	-22.73
8-Dec-14	UF in (BF2)			0.1411		1.79		1.69		7.79	7.9		0.84		3.10		1.04		1.10		0.22	
	UF out			0.1343	4.82	1.95	-9.05	0.19	88.8	7.82	6.9	12.7	0.17	79.76	3.15	-1.61	1.06	-1.92	1.20	-9.09	0.17	22.73
11-Dec-14	UF in (BF1)			0.1259		1.88		1.48		7.53	6.7		0.74		2.80		0.97		1.12		0.26	
	Uf out			0.1210	3.89	1.61	14.40	0.16	89.2	7.6	7.5	-12.3	0.19	74.32	3.30	-17.86	1.09	-12.37	1.27	-13.39	0.26	0.00
19-Feb-15	UF in (RW)			0.1077		1.20		5.7		7.1	9.0		1.61		3.31		1.55		2.19		0.23	
	UF out			0.0769	28.6	1.07	10.6	0.15	97.4	7.39	7.2	20.1	0.45	72.0	3.40	-2.7	1.49	3.9	1.70	22.4	0.15	34.8
23-Feb-15	UF in (BF2)			0.1069		1.48		1.3		8	7.2		1.39		2.90		1.00		1.65		0.23	
	UF out			0.0910	14.9	1.44	2.7	0.14	89.2	7.75	6.3	12.5	0.33	76.5	2.88	0.7	1.05	-5.0	1.64	0.6	0.24	-4.3
25-Feb-15	UF in (BF1)			0.1106		1.29		1.1		8.3	8.6		1.26		2.91		1.02		1.60		0.21	
	UF out			0.1400	-26.6	1.43	-10.8	0.23	79.1	7.59	9.8	-14.2	0.50	60.3	3.70	-27.1	1.47	-43.9	2.60	-62.5	0.11	46.7
27-Feb-15	UF in (RW)			0.1250		1.27		3.5		7.4	9.9		1.50		2.84		1.27		2.40		0.38	
	UF out			0.1638	-31.0	1.83	-44.0	0.13	96.3	7.2	9.0	9.0	0.49	67.3	3.00	-5.6	1.53	-20.5	2.20	8.3	0.22	42.1
2-Mar-15	UF in (BF2)			0.1152		1.38		1.19		7.54	8.3		1.03		2.96		1.12		1.37		0.23	
	UF out			0.1142	0.9	1.28	7.2	0.15	87.4	7.48	8.9	-6.8	0.39	62.1	3.13	-5.7	1.50	-33.9	1.70	-24.1	0.70	-204.3
5-Mar-15	UF in (BF1)			0.1186		1.56		0.5		7.7	7.6		1.05		2.65		1.08		1.28		0.24	
	UF out			0.0981	17.3	1.36	12.7	0.14	72.0	7.49	7.2	5.3	0.50	52.4	2.77	-4.5	1.10	-1.9	1.37	-7.0	0.20	16.7
13-May-15	UF in (RW)			0.1408		1.4367		3.5		7.27	9.8		1.85		3.04		1.06		3.10		0.38	
	UF out			0.1366	3.0	1.6458	-14.6	0.15	95.7	7.34	8.3	15.3	0.40	78.4	2.80	7.9	1.40	-32.1	3.20	-3.2	0.33	13.2
15-May-15	UF in (BF2)			0.1371		1.9870		1.6		7.61	6.9		1.50		2.40		1.70		3.50		0.35	
	UF out			0.1336	2.6	2.4291	-22.3	0.13	91.9	7.56	5.5	20.3	0.48	68.0	2.30	4.2	1.07	37.1	2.00	42.9	0.50	-42.9
11-May-15	UF in (BF1)			0.1361		1.8644		1.2		7.72	7.3		1.10		3.10		1.10		1.60		0.28	
	UF out			0.1380	-1.4	1.8158	2.6	0.17	85.8	7.48	7.6	-4.1	0.80	27.3	3.60	-16.1	1.20	-9.1	1.70	-6.2	0.30	-7.1
20-May-15	UF in (RW)			0.1458		1.9973		4.2		7.21	7.3		1.70		2.70		1.20		3.10		0.50	
	UF out			0.1506	-3.3	2.5966	-30.0	0.15	96.4	7.2	5.8	20.5	0.40	76.5	2.80	-3.7	1.30	-8.3	2.30	25.8	0.40	20.0
22-May-15	UF in (BF2)			0.1529		2.7304		1.5		7.47	5.6		1.60		2.80		1.00		2.20		0.38	
	UF out			0.1462	4.4	2.5207	7.7	0.14	90.7	7.48	5.8	-3.6	0.50	68.8	3.00	-7.1	1.03	-3.0	1.80	18.2	0.37	2.6
18-May-15	UF in (BF1)			0.1343		2.7979		0.65		7.6	4.8		1.30		2.30		1.10		1.30		0.37	
	UF out			0.1500	-11.7	2.5862	7.6	0.13	80.0	7.54	5.8	-20.8	0.40	69.2	3.20	-39.1	1.02	7.3	2.20	-69.2	0.30	18.9

Table E. 2 Reversible and irreversible fouling values and their reduction when UF operated with biofilter effluent

		Whole Run					First period				
Date	UF feed water	Run time	RF	IRF	RF	IRF	Run time	RF	IRF	RF	IRF
		h	psi/h	psi/h	% Reduction		h	psi/h	psi/h	% Reduction	
19-Feb-15	RW	24	2.7	0.36			11	3.6	0.21		
25-Feb-15	BF1	25	1.4	0.07	48	81	11	1.3	0.06	64	71
23-Feb-15	BF2	23.5	1.8	0.08	32	77	11	1.5	0.07	58	67
27-Feb-15	RW	23.5	1.9	0.36			12	2.4	0.30		
4-Mar-15	BF1	24.5	1.4	0.08	26	78	12	0.9	0.05	62	83
2-Mar-15	BF2	22.5	1.8	0.11	5	69	12	1.2	0.06	48	80
13-May-15	RW	19	3.4	0.11							
11-May-15	BF1	23	1.5	0.04	56	64					
15-May-15	BF2	22	2.0	0.05	43	55					
20-May-15	RW	22	1.8	0.35			6	2.5	0.38		
18-May-15	BF1	16	1.8	0.07	0	81	6	1.2	0.07	53	82
22-May-15	BF2	22	1.9	0.21	-3	40	6	1.5	0.13	42	66

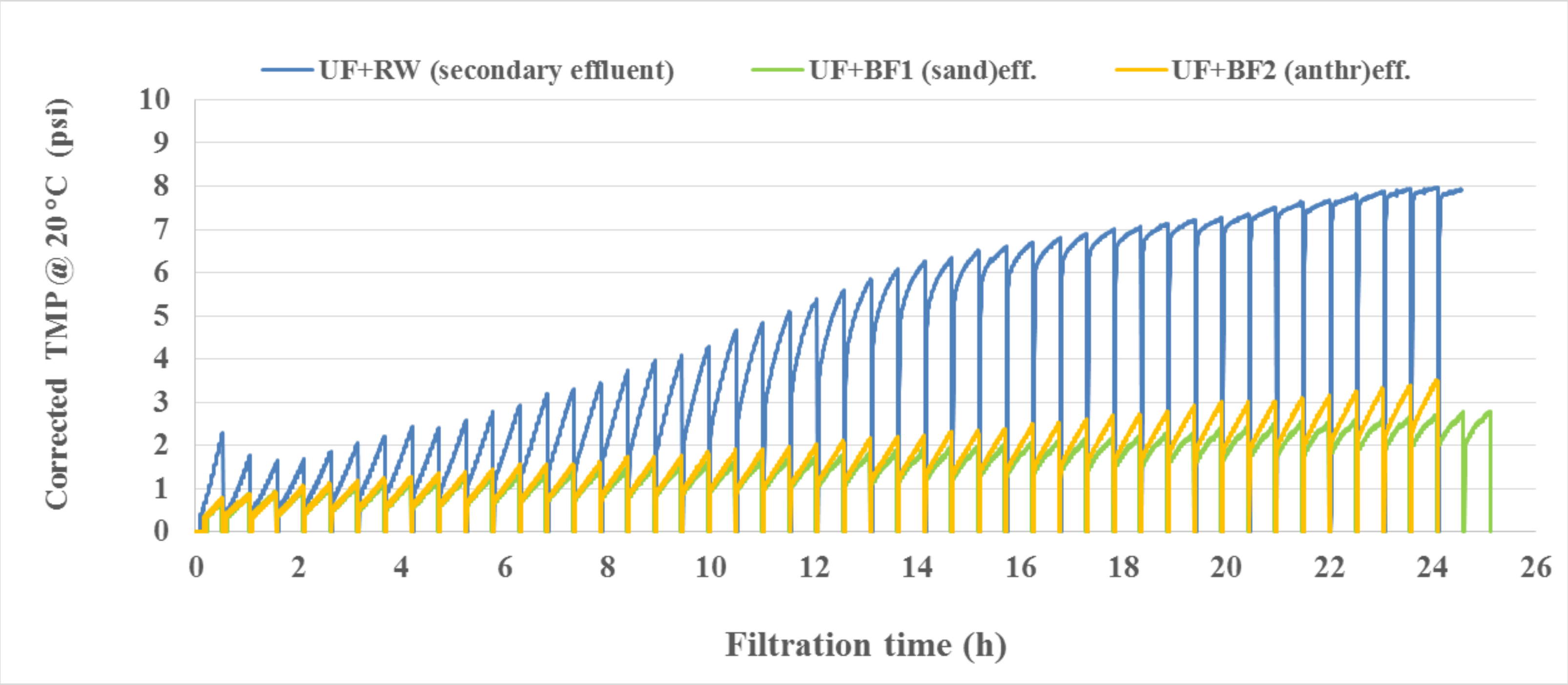


Figure E.1 UF transmembrane pressure when fed with raw water (secondary effluent) vs. transmembrane pressure when fed with effluents from BF1 (sand) and BF2 (anthracite) (experiment conducted from Feb. 19 to Feb. 23, 2015)

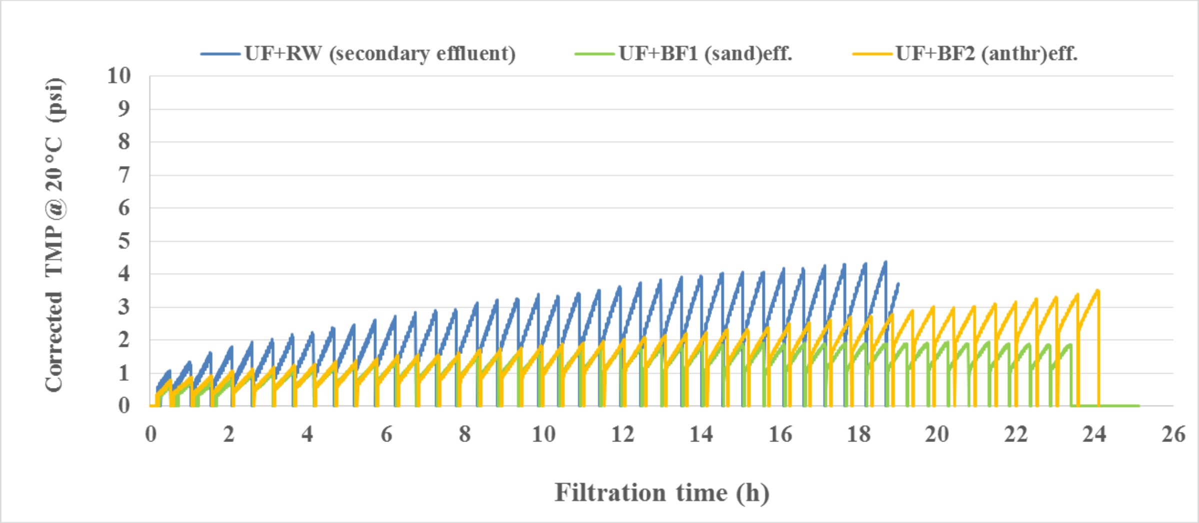


Figure E.2 UF transmembrane pressure when fed with raw water (secondary effluent) vs. transmembrane pressure when fed with effluents from BF1 (sand) and BF2 (anthracite) (experiment conducted from May 11 to May 15, 2015)

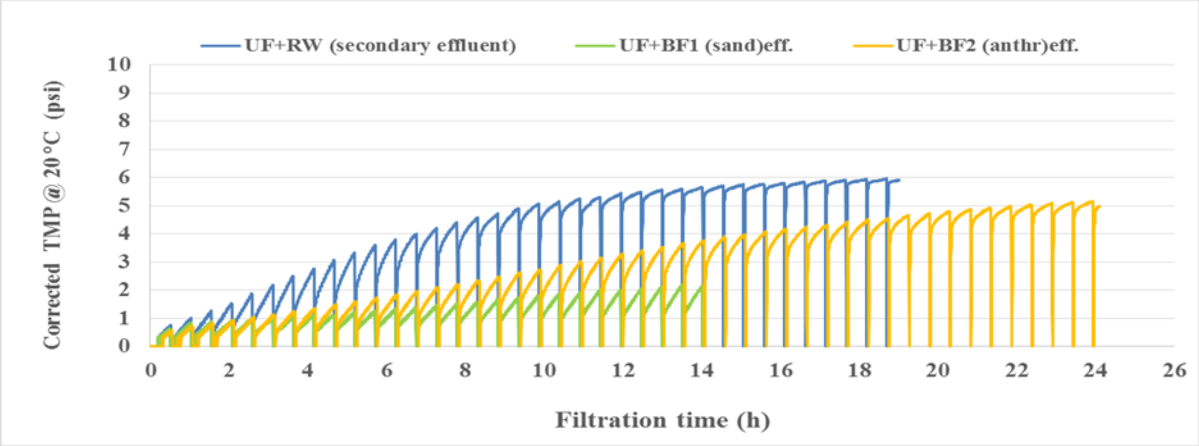


Figure E.3 UF transmembrane pressure when fed with raw water (secondary effluent) vs. transmembrane pressure when fed with effluents from BF1 (sand) and BF2 (anthracite) (experiment conducted from May 18 to May 22, 2015)

Appendix F

Organic Nitrogen Data (LC-OCD)

Table F. 1 Organic nitrogen concentrations and its percentage of biopolymer

Date	Organic nitrogen in biopolymers							
	RW		BF1		BF2		UF	
	mg/L	% of BP	mg/L	% of BP	mg/L	% of BP	mg/L	% of BP
07-Oct-14	0.13	10	0.07	6.6	0.09	7.5		
20-Oct-14	0.2	15	0.06	5.6	0.07	6.0		
03-Nov-14	0.17	11	0.05	5.0	0.07	6.0		
17-Nov-14	0.16	13	0.02	2.0	0.04	4.0		
25-Nov-14	0.14	11	0.03	3.0	0.04	4.0	0.02	8
27-Nov-14			0.04	5.0			0.01	7
01-Dec-14	0.2	15	0.06	7	0.08	8	0.02	8
04-Dec-14					0.07	8	0.03	5
08-Dec-14	0.2	13	0.1	7			0.02	6
11-Dec-14	0.2	15			0.14	12	0.02	7
13-Jan-15	0.3	18	0.1	9	0.15	10	0.04	7
14-Jan-15	0.29	18	0.1	8	0.15	9	0.05	5
16-Jan-15	0.31	20					0.04	8
20-Jan-15	0.29	16					0.04	7
30-Jan-15	0.18	10						
07-Feb-15	0.23	14						
19-Feb-15	0.1	6						
23-Feb-15			0.08	6			0.01	3
25-Feb-15					0.09	6	0.01	2
27-Feb-15	0.06	4					0.01	2
02-Mar-15					0.06	6	0.01	3
05-Mar-15			0.05	5			0.007	2
09-Mar-15	0.05	3	0.04	4	0.05	4	0.02	3
23-Mar-15			0.2	12	0.2	10	0.03	4
27-Mar-15	0.31	12					0.01	3
30-Mar-15	0.25	12					0.02	3
10-Apr-14			0.16	10	0.18	11	0.02	2
15-Apr-15	0.06	3					0.01	3
23-Apr-15	0.24	14						

Table F. 2 Organic nitrogen percentage removal through biofilter and ultrafiltration membrane

Date	% removal		
	BF1 (sand)	BF2 (anthracite)	UF
07-Oct-14	46	31	
20-Oct-14	70	65	
03-Nov-14	71	58	
17-Nov-14	87	75	
25-Nov-14	78	70	86
27-Nov-14			75
01-Dec-14	70	60	90
04-Dec-14			57
08-Dec-14	50		80
11-Dec-14		30	80
13-Jan-15	67	50	86
14-Jan-15	65	48	83
16-Jan-15			87
20-Jan-15			86
07-Feb-15			
19-Feb-15			
23-Feb-15	60		86
25-Feb-15		52	89
27-Feb-15			83
02-Mar-15			83
05-Mar-15	65		80
09-Mar-15	20	10	60
23-Mar-15	66	66	85
27-Mar-15			96
30-Mar-15			92
10-Apr-14	36	30	88
15-Apr-15			83
23-Apr-15			

Appendix G

Coagulant Dosage Calculation

Jar Test Experiments

An example of an alum dosing calculation for jar tests is shown below. A similar procedure was used for the three other coagulants. Table G.1 provides the average active concentrations and specific gravities of the coagulants that were used in calculations.

Table G. 1 Active concentration and specific gravity for coagulants

Coagulant	**Active concentration** Range as supplier (value used)	**Specific gravity** Range as supplier (value used)
Alum	29 – 50% (40%)	1.20 – 1.36 (1.28)
PACl	15 – 40% (28%)	1.16 – 1.30 (1.23)
Ferric chloride	37 – 42% (40%)	1.26 – 1.48 (1.37)
Ferric sulfate	66 – 73% (70%)	1.38 – 1.59 (1.5)

Coagulant concentration (based on values showed at Table G.1)

Coagulant concentration (alum) = 40 (gram-alum / 100 gram solution) x (1.28 gram solution / 1.0 mL solution) x (1000mL / L)

Alum concentration = 512 mg alum/mL

Stock solution preparation

The following equation was used to prepare a stock solution when add 1.0 mL of it in 1.0 L of D.I water, the final dosage is 5.0 mg/L.

$$C_1V_1 = C_2V_2$$

Where,

C_1 = Concentration of stock solution (?)

C_2 = target concentration of coagulant (5.0 mg/L)

V_1 = desired pipetting volume (1.0 mL)

V_2 = volume of jar (1.0 L)

From this equation, C_1 (stock solution concentration) = 5.0 mg/mL

To prepare 250 mL of stock solution, the same equation can be used as describe below:

$$C_1V_1 = C_2V_2$$

Where,

C_1 = Concentration of alum in original solution (512 mg alum/mL)

C_2 = Concentration of stock solution (5.0 mg/mL)

V_1 = unknown volume of original alum solution that should be used to prepare 250 mL of stock solution

V_2 = volume of stock solution (250 mL)

Then, V_1 = 2.4 mL of original alum solution

Add 2.4 mL of original alum solution to 247.6 mL of D.I water.

In-line coagulation Experiments

A sample in-line dosing calculation for 0.5 mg/L alum is described below. The same procedure was used to determine the in-line dosing of other coagulants and dosages.

Chemical formula: $Al_2(SO_4)_3.14H_2O$

Molar mass = 594 gram/mol

Alum concentration in original solution = 512 mg/mL

Volume of dosing tank = 20 L

Flow of raw water through membrane = 25 mL/ min (1.5 L/h)

Chemical pump rate = 10 mL/min (0.6 L/h)

Concentration of alum required in feed tank = (0.5 mg/L x 1.5 L/h) / 0.6 L/h = 1.25 mg alum/L

Volume of coagulant solution to be added to 20 L feed tank = (1.25 mg alum/L x 20 L)/ (512 mg alum/mL of original solution) = 0.05 mL of original alum solution (50 µL)

Appendix H

In-line Coagulation prior to Ultrafiltration Experiments (Raw Data for Water Samples and Normalized TMP Figures)

Table H. 1 Raw data for water samples of in-line coagulating experiments

Date	Sample ID	Analysis											LC-OCD									
		TOC		DOC		UV		SUVA		Turbidity		pH	biopolymer		humics		building blocks		LMW neturals		LMW acids	
		mg/L	Rem. %	mg/L	Rem. %	cm-1	Rem. %	L/mg. m	Rem. %	NTU	Rem. %		mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %
15-Jan-15	UF in (5 Alum)			9.2		0.1492		1.62		1.03		7.83	2.06		3.36		1.46		1.94		0.33	
	UF out			6.6	28.3	0.1006	32.57	1.52	6.01	0.26	74.8	7.75	0.64	68.93	3.02	10.12	1.09	25.34	1.56	19.59	0.33	0.00
19-Jan-15	UF in (RW)	21		8.9		0.1405		1.58		5		7.53	1.84		3.40		1.35		2.00		0.27	
	UF out	11.2	46.67	7.9	11.2	0.1145	18.51	1.45	8.19	0.2	96.0	7.8	0.46	75.00	3.60	-5.88	1.44	-6.67	2.03	-1.50	0.35	-29.63
22-Jan-15	UF in (0.5 Alum)			7.8		0.1213		1.56		3.31		7.6	1.48		3.20		1.23		1.63		0.18	
	UF out			6.5	16.7	0.1070	11.79	1.65	-5.85	0.2	94.0	7.28	0.31	79.05	3.24	-1.25	1.07	13.01	1.50	7.98	0.33	-83.33
26-Jan-15	UF in (0.5 PACl)			7.1		0.1017		1.43		3.97		7.45	1.29		2.76		1.03		1.67		0.33	
	UF out			6.2	12.7	0.0967	4.92	1.56	-8.89	0.18	95.5	7.59	0.27	79.07	2.90	-5.07	1.09	-6.24	1.53	8.27	0.34	-3.03
28-Jan-15	UF in (5 PACl)			7.6		0.1328		1.75		2.9		7.5	1.40		2.99		1.22		1.70		0.29	
	UF out			7.7	-0.8	0.1129	15.0	1.47		0.12	95.9	7.7	0.66	52.9	3.30	-10.4	1.50	-23.0	1.80	-5.9	0.40	-37.9
30-Jan-15	UF in (RW)			8.6		0.1268		1.47		7.33		7.48	1.80		3.50		1.34		2.03		0.34	
	UF out			7.8	9.3	0.0992	21.8	1.27	13.7	0.23	96.9		0.70	61.1	3.55	-1.4	1.24	7.2	2.01	1.0	0.30	10.7
3-Feb-15	UF in (0.5FeCl3)			7.4		0.1379		1.86		4.01		7.57	1.05		3.50		0.90		1.63		0.28	
	UF out			6.3	14.9	0.1151	16.5	1.83	2.0	0.24	94.0	7.54	0.18	82.9	3.40	2.9	1.04	-15.6	1.52	6.7	0.15	45.8
5-Feb-15	UF in (5FeCl3)			8.3		0.1400		1.69		2.7		7.4	1.50		3.80		1.01		1.83		0.19	
	UF out			6.5	21.7	0.1080	22.9	1.66	1.5	0.12	95.6	7.6	0.13	91.3	3.57	6.1	0.96	5.0	1.73	5.5	0.13	31.6
7-Feb-15	UF in (RW)			10.0		0.1588		1.59		5.92		7.51	1.68		4.10		1.77		2.30		0.16	
	UF out			7.4	26.0	0.1220	23.2	1.65	-3.8	0.26	95.6	7.55	0.34	79.8	3.94	3.9	1.04	41.2	1.90	17.4	0.14	12.5
9-Feb-15	UF in (5Fe2(SO4)3)			7.4		0.0580		0.78		3.5		7.27	0.70		1.40		1.00		0.93		3.39	
	UF out			5.7	23.0	0.0990	-70.7	1.74	-121.6	0.13	96.3	7.45	0.30	57.1	2.70	-92.9	1.10	-10.0	1.35	-45.2	0.29	91.4
11-Feb-15	UF in (0.5Fe2(SO4)3)			7.1		0.1120		1.58		1.46		7.2	1.47		2.77		1.12		1.40		0.25	
	UF out			6.6	7.0	0.0970	13.4	1.47	6.8	0.13	91.1	7.23	0.19	87.1	3.19	-15.2	1.30	-16.1	1.57	-12.1	0.26	-4.0
13-Feb-15	UF in (RW)			8.9		0.1340		1.51		6.6		7.63	1.68		3.30		1.55		2.19		0.23	
	UF out			8.3	6.7	0.1256	6.3	1.51	-0.5	0.15	97.7	7.46	0.56	66.7	3.44	-4.2	1.98	-27.7	2.09	4.6	0.22	4.3

11-Mar-15	**UF in (5Fe2(SO4)3)**	21.8		6.6		0.1075		1.63		3.75		7.12	1.20		2.39		1.00		1.67		0.32	
	UF out	10.6	51.4	7.8	-18.2	0.1095	-1.9	1.40		0.13	96.5	7.22	0.70	41.7	3.70	-54.8	1.16	-16.6	2.00	-19.8	0.28	12.5
9-Mar-15	**UF in (0.5Fe2(SO4)3)**	20.4		7.6		0.1230		1.62		1.54		7.31	1.17		3.40		1.23		1.49		0.3	
	UF out	9.8	52.0	7.4	2.6	0.0989	19.6	1.34	17.4	0.15	90.3	7.53	0.30	74.4	2.60	23.5	2.22	-80.5	2.16	-45.0	0.139	53.7
13-Mar-15	**UF in (RW)**	22.9		7.8		0.1149		1.47		6		7.48	1.85		2.85		1.34		2.07		0.35	
	UF out	12.5	45.4	9.3	-19.2	0.1342	-16.8	1.44	2.0	0.27	95.5	7.44	1.00	45.9	4.00	-40.4	1.40	-4.5	2.50	-20.8	0.37	-5.7
25-Mar-15	**UF in (0.5 Fe2(SO4)3)**	22.7		6.1		0.1000		1.64		2.65		7.55	1.28		2.28		0.96		1.31		0.22	
	UF out	11.1	51.1	7.5	-23.0	0.1442	-44.2	1.92	-17.3	0.14	94.7	7.47	0.50	60.9	2.70	-18.4	1.95	-103.1	2.09	-59.5	0.29	-27.2
23-Mar-15	**UF in (1.0 Fe2(SO4)3)**	23		7.4		0.1141		1.55		5.4		7.31	2.10		2.24		1.15		1.68		0.21	
	UF out	10.2	55.7	6.9	5.6	0.0970	15.0	1.40	10.0	0.18	96.7	7.53	0.37	82.4	2.80	-25.0	1.40	-21.7	1.97	-17.3	0.23	-9.5
27-Mar-15	**UF in (RW)**			10.4		0.1358		1.30		3		7.48	2.76		3.29		1.55		2.16		0.24	
	UF out			8.6	17.5	0.2029	-49.4	2.36	-81.2	0.16	94.7	7.45	0.38	86.2	3.20	2.7	2.16	-39.4	2.57	-18.8	0.28	-16.7
30-Mar-15	**UF in (RW)**	22.7		8.5		0.1348		1.59		2.86		7.51	2.10		2.82		1.43		1.90		0.26	
	UF out	19	16.3	6.3	25.9	0.1072	20.5	1.70	-7.3	0.17	94.1	7.66	0.18	91.4	2.73	3.2	1.35	5.6	1.65	13.2	0.22	16.0
1-Apr-15	**UF in (5.0 Alum)**	16.8		7.9		0.1321		1.67		1.27		7.6	1.80		2.97		1.22		1.68		0.20	
	UF out	14	16.7	9.1	-15.2	0.2065	-56.3	2.27	-35.7	0.12	90.6	7.61	0.50	72.2	2.99	-0.7	2.69	-120.5	2.61	-55.4	0.28	-40.0
3-Apr-15	**UF in (2.5 Alum)**	20.2		7.7		0.1331		1.73		1.15		7.6	1.73		2.93		1.26		1.60		0.19	
	UF out	9.3	54.0	9.1	-18.2	0.2327	-74.8	2.56	-47.9	0.14	87.8	7.47	0.29	83.2	3.10	-5.8	1.93	-53.2	3.46	-116.3	0.28	-46.3
7-Apr-15	**UF in (1.0 Fe2(SO4)3)**	21.7		7.1		0.1147		1.62		3.6		7.46	1.33		2.91		0.84		1.69		0.27	
	UF out	10	53.9	6.3	11.3	0.0971	15.3	1.54	4.6	0.25	93.1	7.46	0.34	74.4	3.00	-3.1	1.09	-29.8	1.60	5.3	0.24	11.1
9-Apr-15	**UF in (5.0 Fe2(SO4)3)**	20		4.3		0.0780		1.81		4.8		7.02	0.67		1.88		0.53		1.05		0.17	
	UF out	8.9	55.5	7.6	-76.7	0.1365	-75.0	1.80	1.0	0.18	96.3	7.35	0.80	-19.4	3.90	-107.4	0.81	-52.8	1.90	-81.0	0.21	-23.5
11-Apr-15	**UF in (RW)**	22.6		8.5		0.1342		1.58		3.12		7.57	1.80		3.28		1.14		2.04		0.31	
	UF out	10.4	54.0	6.9	18.8	0.1145	14.7	1.66	-5.1	0.21	93.3	7.46	0.40	77.8	3.10	5.5	1.20	-5.3	1.92	5.9	0.26	15.9

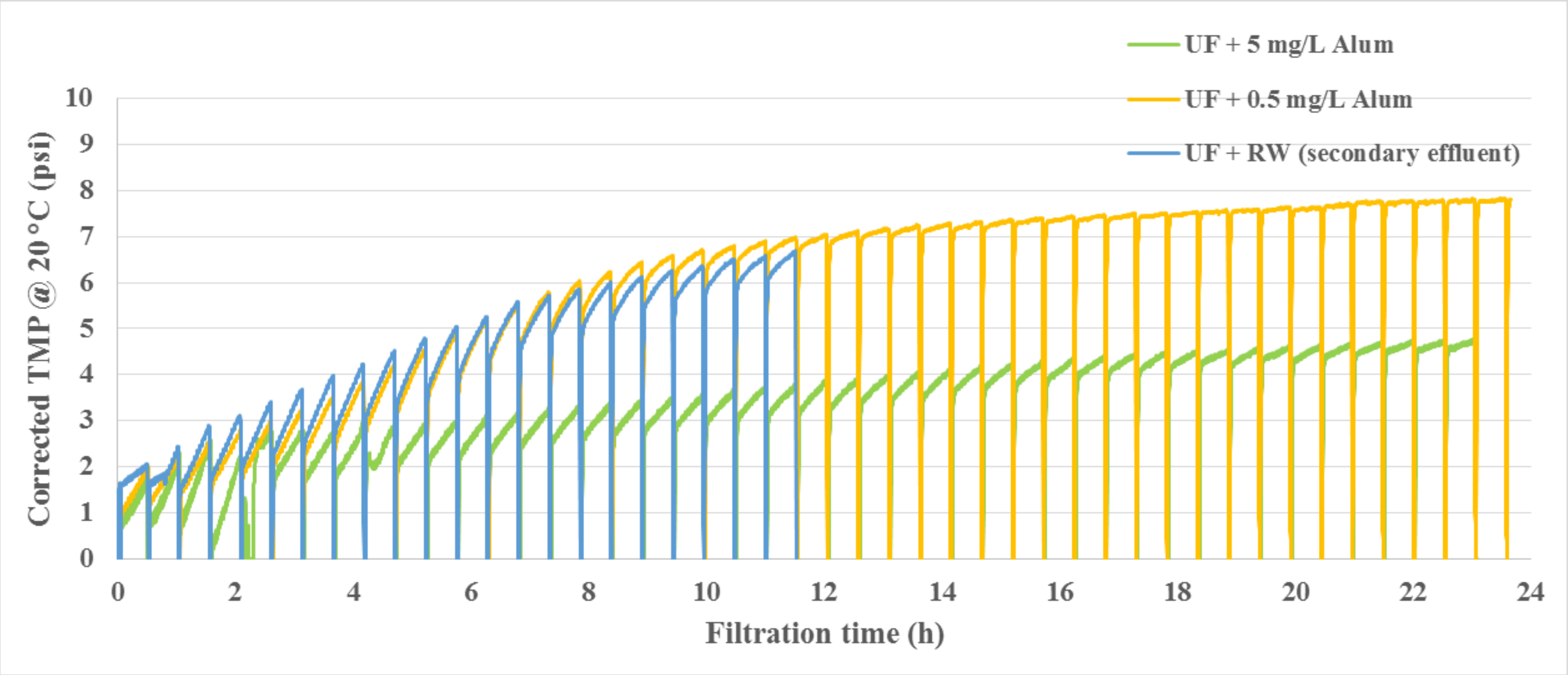


Figure H. 1 UF transmembrane pressure when fed with raw water (secondary effluent) vs. transmembrane pressure when fed with 0.5 and 5.0 mg/L of alum (experiment conducted from Jan. 15 to 22, 2015)

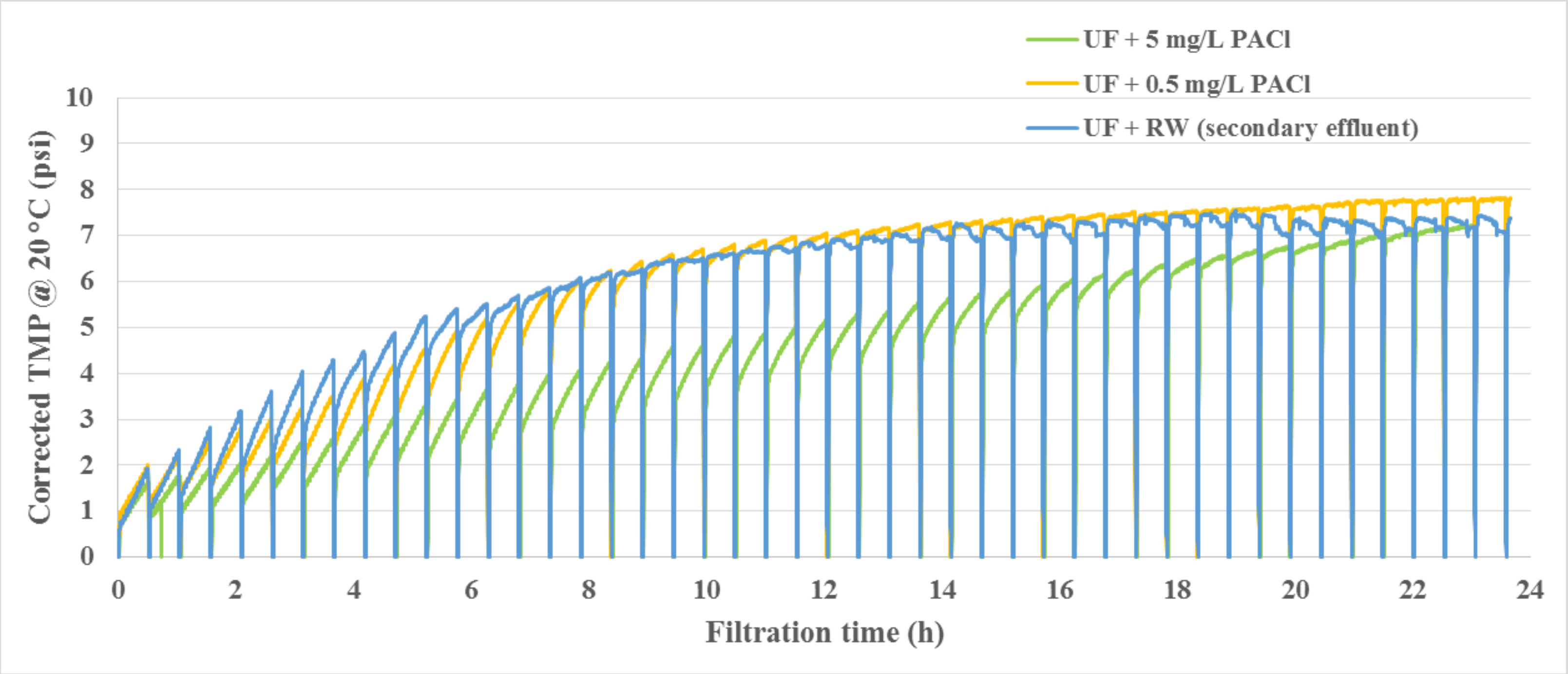


Figure H. 2UF transmembrane pressure when fed with raw water (secondary effluent) vs. transmembrane pressure when fed with 0.5 and 5.0 mg/L of PACl (experiment conducted from Jan. 26 to 30, 2015)

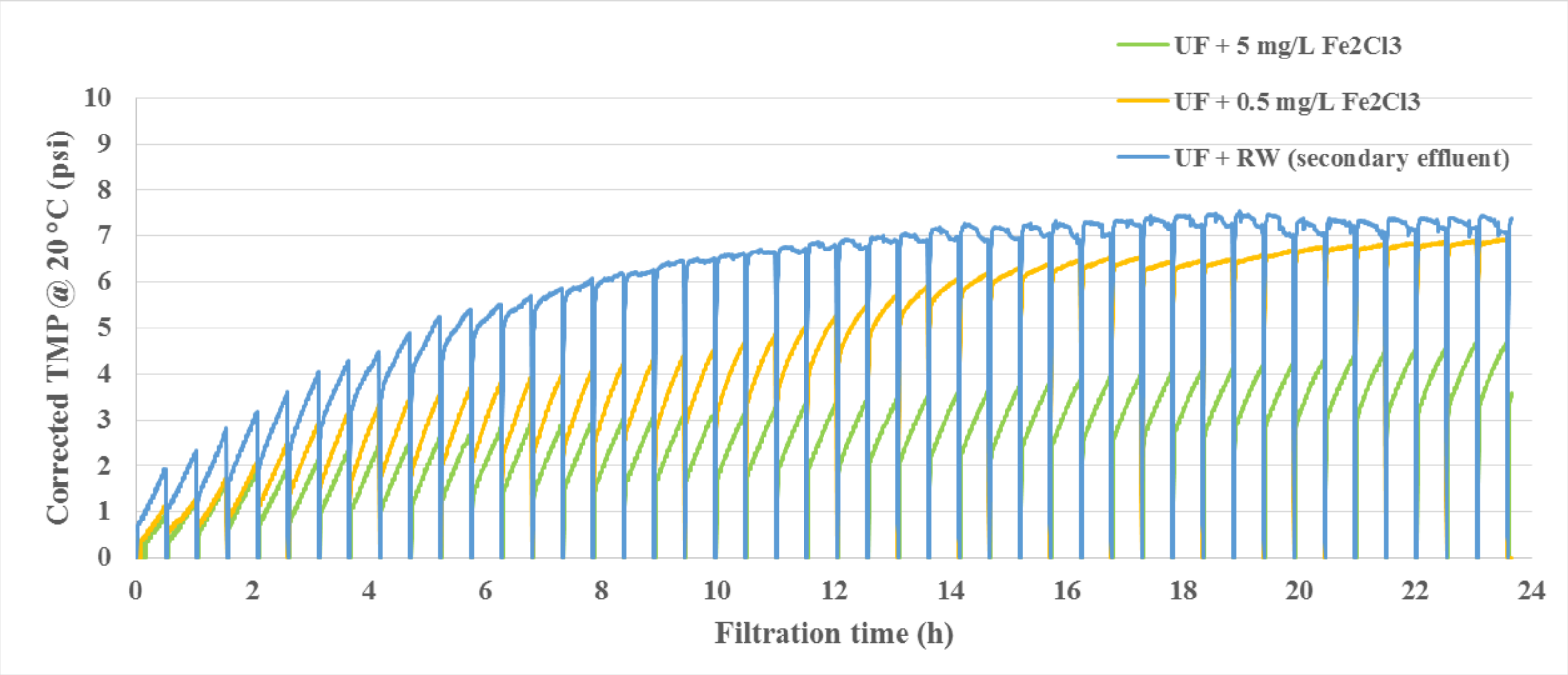


Figure H. 3 UF transmembrane pressure when fed with raw water (secondary effluent) vs. transmembrane pressure when fed with 0.5 and 5.0 mg/L of ferric chloride (experiment conducted from Feb. 03 to 07, 2015)

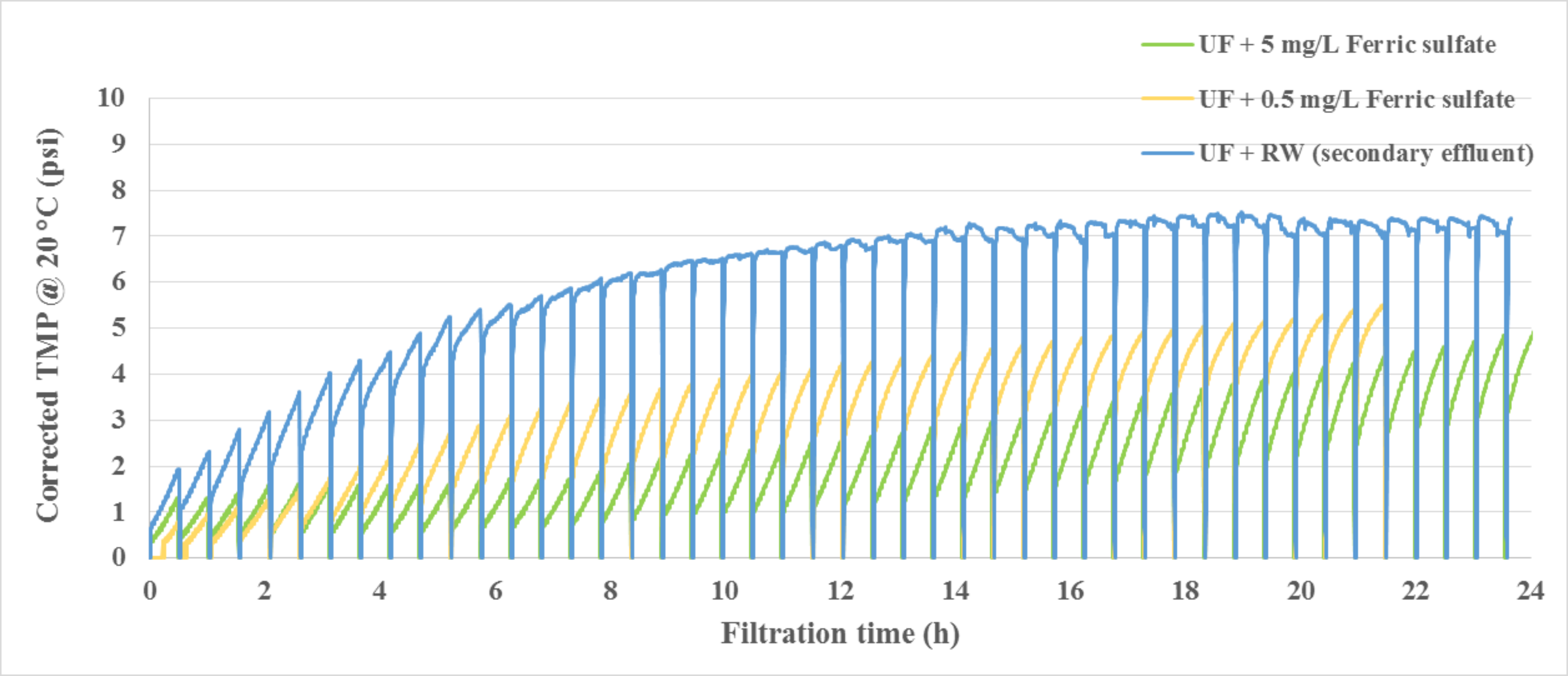


Figure H. 4 UF transmembrane pressure when fed with raw water (secondary effluent) vs. transmembrane pressure when fed with 0.5 and 5.0 mg/L of ferric sulfate (experiment conducted from Feb. 09 to 13, 2015)

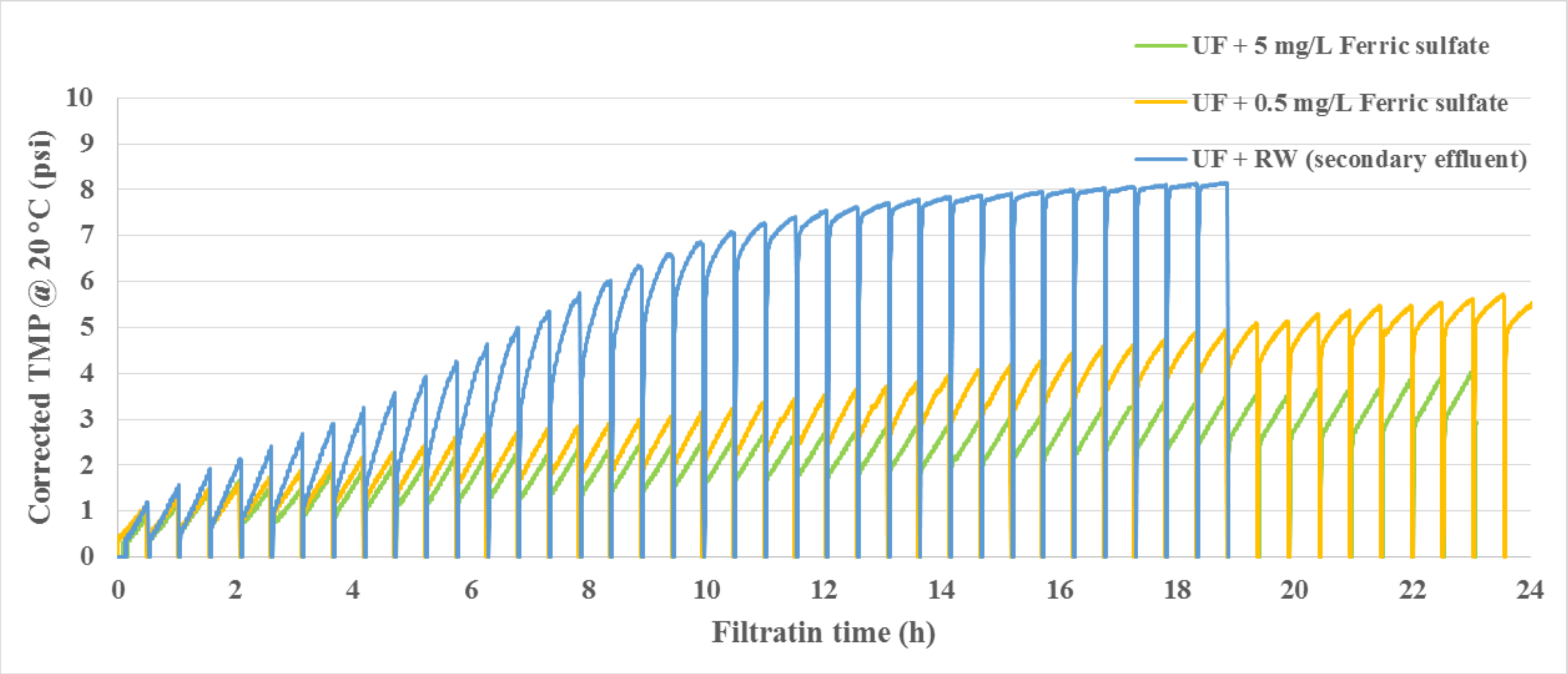


Figure H. 5 UF transmembrane pressure when fed with raw water (secondary effluent) vs. transmembrane pressure when fed with 0.5 and 5.0 mg/L of ferric sulfate (experiment conducted from Mar. 09 to 13, 2015)

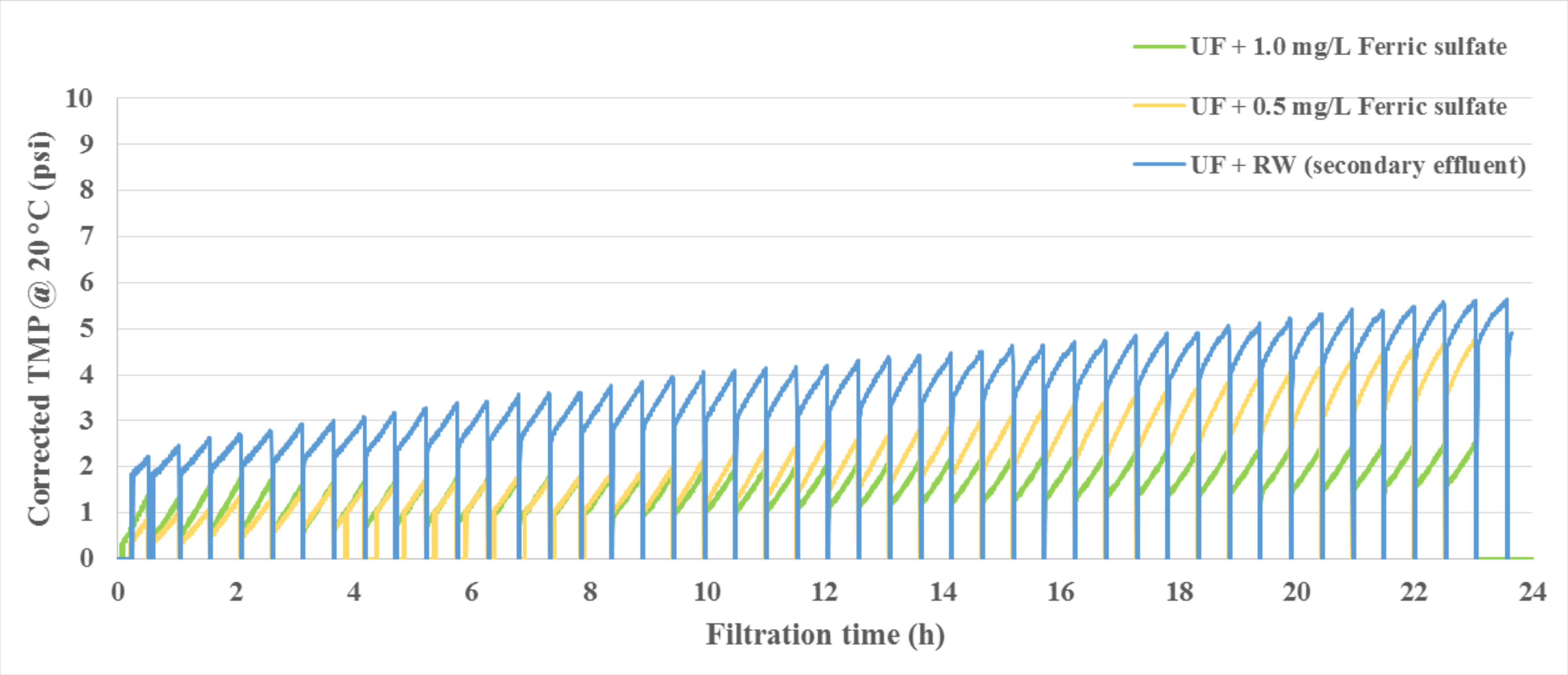


Figure H. 6 UF transmembrane pressure when fed with raw water (secondary effluent) vs. transmembrane pressure when fed with 0.5 and 1.0 mg/L of ferric sulfate (experiment conducted from Mar. 25 to 29, 2015)

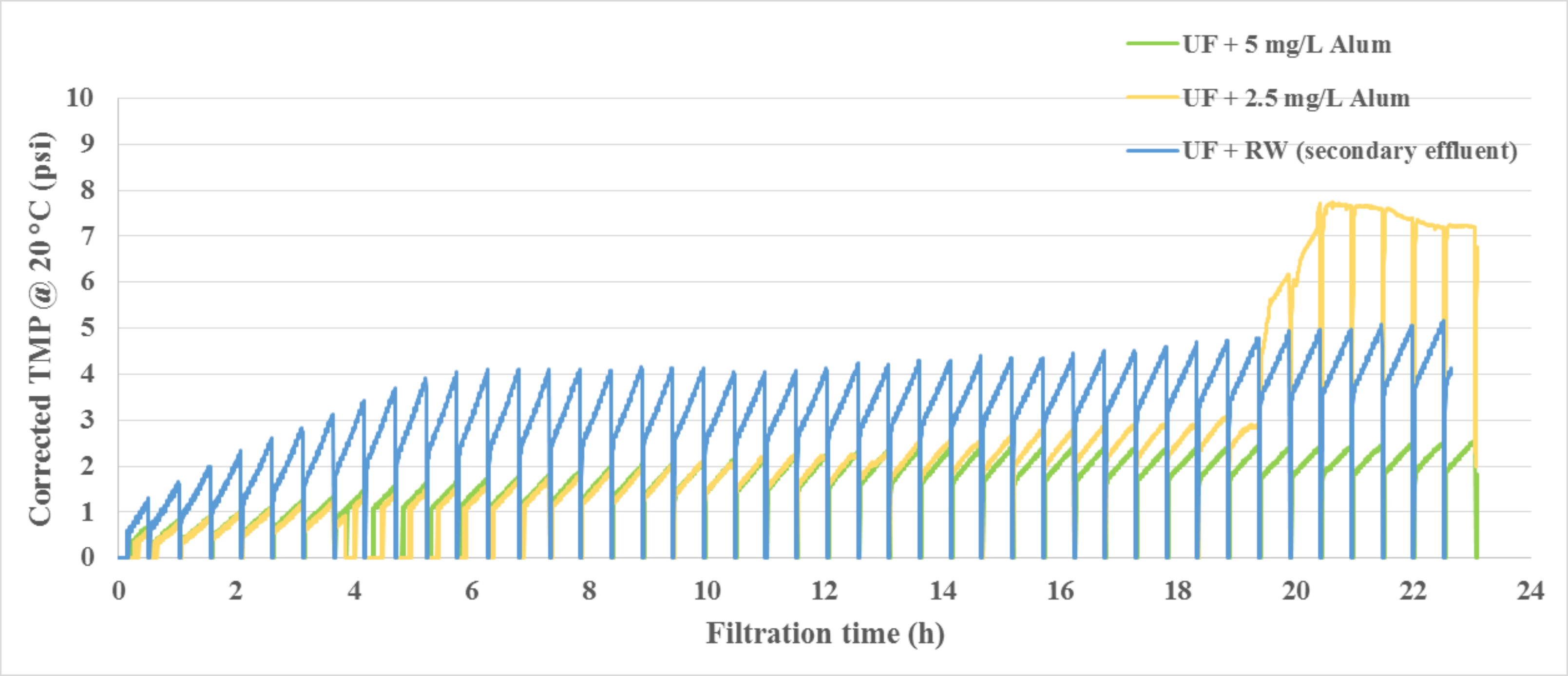


Figure H. 7 UF transmembrane pressure when fed with raw water (secondary effluent) vs. transmembrane pressure when fed with 2.5 and 5.0 mg/L of alum (experiment conducted from Mar. 30 to Apr. 03, 2015)

Appendix I

Raw Data for In-line Coagulation Prior to Biofiltration Experiment

Date	Sample ID	Analysis											LC-OCD									
		TOC		DOC		UV		SUVA		Turbidity		pH	biopolymer		humics		building blocks		LMW neturals		LMW acids	
		mg/L	Rem. %	mg/L	Rem. %	cm-1	Rem. %	L/mg. m	Rem. %	NTU	Rem. %		mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %	mg/L	Rem. %
13-Apr-15	UF in (BF2)	28.6		8.9		0.1185		1.33		0.55		8.04	1.23		3.02		2.20		1.90		0.55	
	UF out	20.8	27.3	6.4	28.7	0.1111	6.2	1.7	-31.4	0.13	76.4	7.81	0.80	35.0	2.68	11.3	1.85	15.9	1.08	43.2	0.20	63.6
15-Apr-15	UF in (RW)	32.1		10.0		0.1354		1.35		3.35		7.5	1.89		4.00		1.90		1.94		0.26	
	UF out	24.2	24.6	7.5	25.3	0.1400	-3.4	1.9	-38.5	0.16	95.2	7.54	0.33	82.5	2.90	27.5	0.75	60.5	1.06	45.4	0.19	26.9
17-Apr-15	UF in (coaulant+BF	18.7		9.2		0.1176		1.28		0.43		7.68	1.20		3.30		1.30		3.10		0.26	
	UF out	16.2	13.4	6.7	27.2	0.1089	7.4	1.6	-27.2	0.14	67.4	7.55	0.80	33.3	2.40	27.3	1.25	3.8	2.06	33.5	0.19	26.9
20-Apr-15	UF in (coaulant+BF	18.4		6.7		0.1056		1.58		0.64		7.61	1.00		2.90		0.75		1.80		0.29	
	UF out	15.7	14.7	4.6	32.1	0.0890	15.7	2.0	-24.1	0.13	79.7	7.44	0.30	69.9	2.30	20.7	0.73	2.7	1.04	42.2	0.18	37.9
22-Apr-15	UF in (RW)	20.6		8.4		0.1384		1.65		5.5		7.39	1.66		2.92		1.30		1.80		0.32	
	UF out	19.2	6.8	7.3	13.1	0.1249	9.8	1.7	-3.8	0.13	97.6	7.37	0.40	75.9	2.80	4.1	1.60	-23.1	2.10	-16.7	0.30	6.3
24-Apr-15	UF in (BF2)	22		6.9		0.1258		1.8		1.44		7.56	1.30		2.80		1.00		1.30		0.34	
	UF out	17.2	21.8	5.2	24.6	0.1213	3.6	2.3	-27.9	0.13	91.0	7.39	0.23	82.3	2.77	1.1	0.92	8.0	1.20	7.7	0.31	8.8
25-May-15	UF in (BF2)			7.1		0.1482		2.09		1.7		7.55	1.50		3.40		1.50		3.20		0.60	
	UF out			5.5	22.5	0.1437	3.0	2.6	-25.2	0.17	90.0	7.33	0.47	68.7	2.90	14.7	0.90	40.0	1.80	43.8	0.37	38.3
27-May-15	UF in (RW)			7.9		0.1499		1.9		2.2		7.11	1.60		2.95		1.50		1.60		0.33	
	UF out			6.1	22.8	0.1351	9.9	2.2		0.13	94.1	7.13	0.40	75.0	2.50	15.3	1.20	20.0	1.50	6.3	0.34	-3.0
29-May-15	UF in (coaulant+BF2)			6.5		0.1380		2.12		1.2		7.2	1.05		2.60		1.50		1.40		0.38	
	UF out			5.4	16.9	0.1107	19.8	2.1	3.4	0.12	90.0	7.3	0.34	67.6	2.40	7.7	1.44	4.0	1.30	7.1	0.32	15.8
Long run experiment																						
7-May-15	UF in (coaulant+BF	17.9		7.7		0.0966		1.25		0.7		7.74	1.50		3.40		1.02		1.34		0.19	
	UF out	16.2	9.5	11.8	-53.2	0.0830	14.1	0.7	43.9	0.13	81.4	7.62	0.33	78.0	3.10	8.8	2.20	-115.7	4.80	-258.2	1.10	-478.9
4-May-15	UF in (BF2)	19.2		5.2		0.1389		2.67		1.7		7.61	1.00		2.60		0.86		1.10		0.19	
	UF out	18	6.3	6.3	-21.2	0.1317	5.2	2.1	21.7	0.16	90.6	7.5	0.26	74.0	2.10	19.2	0.92	-7.0	1.30	-18.2	0.18	5.3

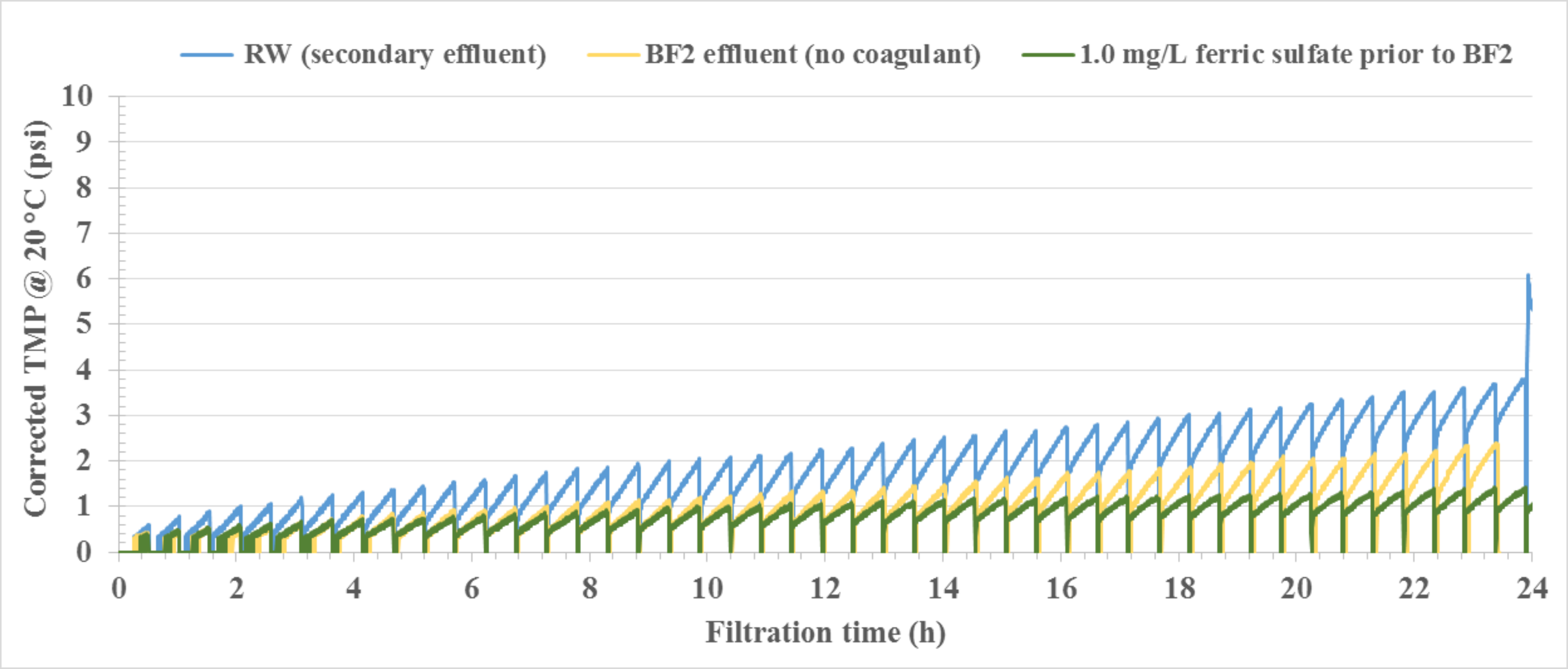


Figure I.1 UF transmembrane pressure when fed with raw water (secondary effluent) vs. transmembrane pressure when fed with BF2 (anthracite) effluent and in-line coagulation prior to BF2 (experiment conducted from Apr. 13 to Apr. 17, 2015)

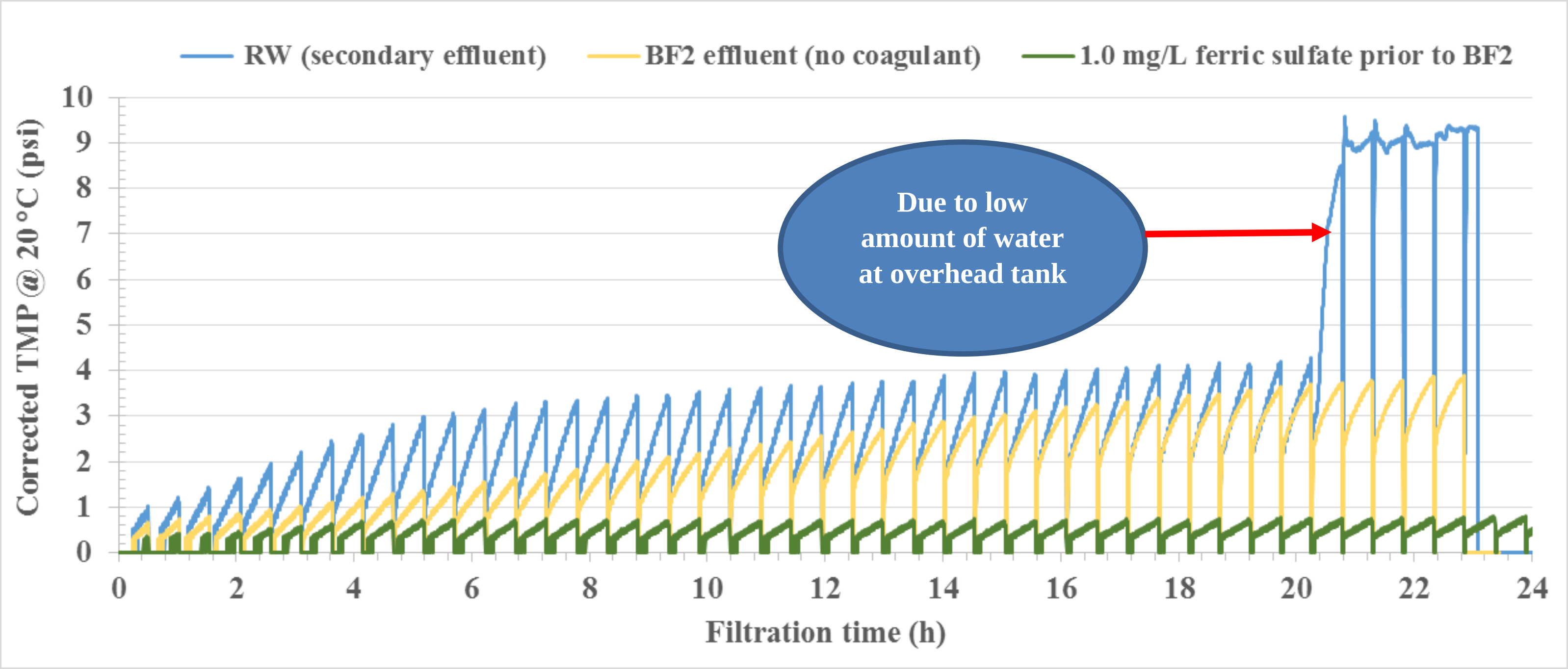


Figure I.2 UF transmembrane pressure when fed with raw water (secondary effluent) vs. transmembrane pressure when fed with BF2 (anthracite) effluent and in-line coagulation prior to BF2 (experiment conducted from May 25 to May 29, 2015)

Appendix J

Calculations of Normalized ATP (ng ATP/cm^2)

In this study biomass concentrations were measured per unit volume of biofilter media as (ng ATP/cm^3). The following calculations were used to normalize ATP data per surface area of sand or anthracite. In this part, the shape of sand and anthracite particles was assumed to be spherical and the same porosity value (0.3) was assumed for both biofilter media.

Table J. 1 Normalized ATP input/output data

Parameter	Sand	Anthracite
Effective size	0.5 mm	1.0 mm
Surface area (mm^2)	0.78	3.14
Volume of voids (cm^3)	0.3	0.3
Volume of each (mm^3)	0.065	0.52
Total surface area (mm^2/ cm^3)	8400	4227
Normalized ATP (top, mid, bottom as (ng ATP/cm^2)	6.2, 4.2, 3.6	9.8, 6.0, 4.6

Appendix K

Integrity Testing and UF Chemical Cleaning

Pressure decay test (integrity testing)

This test was performed before each experiment.

1. Plug the air supply port of membrane module with a stainless steel pipe end cap
2. Connect the permeate port of membrane module with a hand pump
3. Submerge membrane module into a DI water bath
4. Remove any air bubbles from membrane module by supplying pressure to the permeate side of the membrane up to 10 psi using hand pump. The supplied pressure should be maintained for at least 2 min
5. Suppling pressure is stopped after 2 min and drop in pressure over time is monitored using digital pressure calibrator (Meriam DP2000I Digital Manometer / Pressure Calibrator)
6. The allowable drop in pressure is 0.3 psi over 2 min (based on the manufacturer's recommendation)

Membrane chemical cleaning

After each experiment, membrane module was chemically cleaned as described in the following steps.

1. A hydraulic backwashing was performed on membrane module to remove any reversible fouling
2. The membrane module was soaked in a 200 mg/L sodium hypochlorite solution for at least 5 h
3. The module was rinsed with DI water to remove any remaining sodium hypochlorite
4. The membrane module was soaked in a 5 g/L citric acid solution for another 5 h
5. The module was rinsed again with DI water and was kept at DI water tank at 4°C until being placed back into service

Appendix L

Clean Water Permeability Data

Clean water permeability test was performed before each experiment to confirm the membrane cleaning efficiency, and it is described as follows:

- The membrane module was fed with deionized water at five different flow rates (25, 35, 45, 55 and 65 ml/min) and change of TMP was recorded
- The average of TMP at each flow rate was calculated
- The TMP values were corrected for temperature using the following equation

$$\textbf{Corrected TMP @ 20°C = TMP X 1.025^ (T – 20)}$$

Where T: is the recorded temperature during the experiment in °C

- The relationship between corrected average TMP values and the fluxes values was drawn to find the clean water permeability of the membrane which is defined as the slope of the line

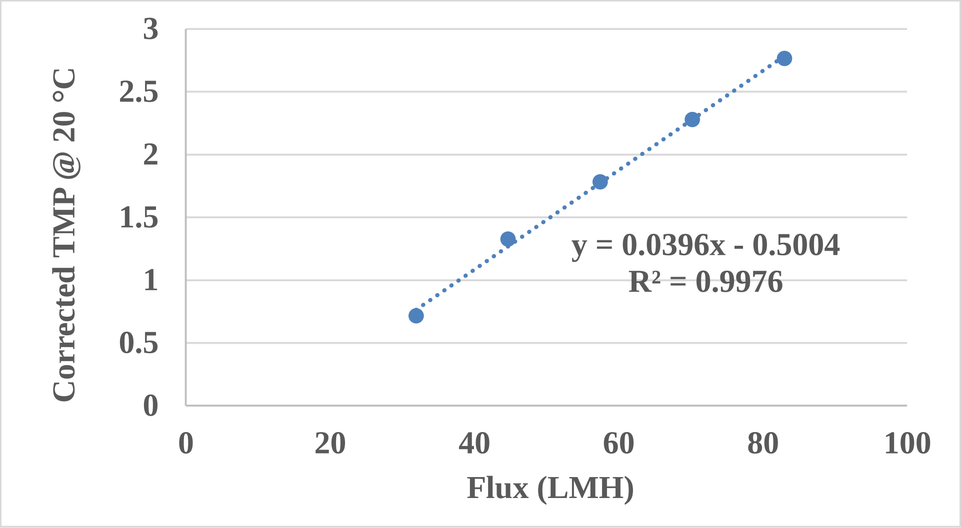


Figure L.1 An example of clean water permeability data conducted on January 26, 2015