REMOVAL OF NATURAL ORGANIC MATTER FOR DRINKING WATER TREATMENT USING ELECTROCOAGULATION AND ULTRAFILTRATION

by

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The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, the thesis entitled:

Removal of Natural Organic Matter for drinking water treatment using electro-coagulation and ultrafiltration.

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Abstract

This work combined iron electrocoagulation (EC) and ultrafiltration (UF) to treat synthetic and natural surface waters to remove Natural Organic Matter (NOM). Fixed EC conditions were applied to the feed water in a continuous flow EC reactor, at a flow rate of 1 LPM and an applied current of 2 A. These test conditions resulted in an average DOC and UVA-254 reduction of 33 ± 4% and 57 ± 8% respectively for the synthetic feed water.

The EC effluent acted as the feed water for the EC/UF systems. Two UF membrane types were tested: (1) a 300kDa ceramic disk membrane; and, (2) a 0.04μm PVDF hollow-fibre membrane. Both systems were operated at a constant flux of 50 LMH. Periodic backwash cycles were applied to evaluate the effect of backwashing on the overall membrane fouling rates. Backwashing with a 30 minute filtration cycle and 5 minute backwash reduced the fouling rate by (50 ± 3)% and (2 ± 6)% in the ceramic and PVDF membranes, respectively. Applying backwash to the EC/UF test with natural feed water resulted in a (95 ± 0.5)% lower fouling rate compared to the EC/UF test with synthetic feed water test under the same conditions. Therefore, water composition has a significant effect on the membrane fouling rates of the EC/UF system.

Air sparging was also applied to the PVDF membrane system and resulted in reducing the overall fouling rate by (64 ± 2)%. Comparatively, the combination of air sparging and backwashing reduced the overall fouling rate by (98 ± 1)%. The EC/UF test with air sparging and backwash also resulted in additional NOM removal of the UF permeate. Air sparging has never been combined with an EC/UF system and these are promising results in the quest to develop a EC/UF drinking water treatment system for small and remote communities.
Lay Summary

Natural Organic Matter (NOM) is often found in drinking water sources. Removal of NOM from drinking water is important because NOM interferes with disinfection processes and can lead to the formation disinfection byproducts, which are heavily regulated. Disinfection is an important part of water treatment, and removal of NOM before disinfection is needed to prevent these byproducts from forming. Electrocoagulation (EC) uses electricity to add particles to the water, which can capture NOM.

The key goal of this work was to combine EC with a membrane filtration step to remove these particles from the water. Two different filters were used and different filtration settings were tested, such as applying air sparging and backwashing to improve filtration performance. These filtration settings have never before been tested when combining filtration with EC pre-treatment for drinking water. Results from these tests indicate that air sparging improves membrane performance and water quality.
Preface

The work presented in this thesis was completed by the author, Emily Froese, under the supervision of Professors Madjid Mohseni (Chemical and Biological Engineering) and Pierre Bérubé (Civil Engineering) at the University of British Columbia.

The author was responsible for literature review, experiment design, data collection and data analysis. Dr Mohseni and Dr Bérubé contributed to development of the experimental plan and provided guidance for development of research objectives and data analysis.
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<th>Description</th>
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<tr>
<td>AMW</td>
<td>Apparent Molecular Weight; the estimated molecular weight of a compound</td>
</tr>
<tr>
<td>BWAs</td>
<td>Boil Water Advisories</td>
</tr>
<tr>
<td>CC</td>
<td>Chemical Coagulation</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>CP</td>
<td>Concentration Polarization</td>
</tr>
<tr>
<td>DBP</td>
<td>Disinfection By-Product</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized Water</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
</tr>
<tr>
<td>EC</td>
<td>Electrocoagulation</td>
</tr>
<tr>
<td>HAAs</td>
<td>Halo-Acetic Acids, a DBP</td>
</tr>
<tr>
<td>HPSEC</td>
<td>High Performance Size Exclusion Chromatography; an analytical method to determine the MWD of an organic sample</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma-Optical Emission Spectroscopy; an analytical method to determine the concentration of metals in an aqueous sample</td>
</tr>
<tr>
<td>IHSS</td>
<td>International Humic Substances Society</td>
</tr>
<tr>
<td>kDa</td>
<td>kilo-Dalton, unit to express molecular weight of organic compounds</td>
</tr>
<tr>
<td>LMH</td>
<td>Litres per Meter squared per Hour (Lm^{-2}h^{-1}); Unit for filtration flux</td>
</tr>
<tr>
<td>LOQ</td>
<td>Limit of Quantification</td>
</tr>
</tbody>
</table>
LPM  Litres Per Minute (L min\(^{-1}\)); Unit for volumetric flow rate
MDL  Method Detection Limit
MF   Microfiltration
MWCO Molecular Weight Cut-Off; The nominal molecular weight above which particles are rejected by a membrane
MWD  Molecular Weight Distribution
NDIR Non-Dispersive Infrared Detection; A method to detect gases such as CO\(_2\)
NF   Nanofiltration
NOM  Natural Organic Matter
OP   Operating Potential
PSD  Particle Size Distribution
RO   Reverse Osmosis
RPD  Relative Percent Difference between the measured value and the true value of the standard.
SHA  Sulfonated Humic Acid
SR-NOM Suwannee River NOM, a standard NOM source provided by the IHSS
SRFA Suwannee River Fulvic Acid
SRHA Suwannee River Humic Acid
STP  Standard Temperature and Pressure (25°C and 1 atm)
SUVA Specific UV-absorbance
THMs Trihalomethanes, a DBP
TMP  Trans-Membrane Pressure
TOC  Total Organic Carbon
UF   Ultrafiltration
UVA  UV-Absorbance
UVA-254 UV-Absorbance at 254nm
### List of Symbols

<table>
<thead>
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<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$A$</td>
<td>The membrane surface area</td>
</tr>
<tr>
<td>$Al$</td>
<td>Atomic symbol, aluminum</td>
</tr>
<tr>
<td>$Al(OH)_{3(s)}$</td>
<td>Aluminum hydroxide, an aluminum precipitate</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration of species</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Inter-electrode gap</td>
</tr>
<tr>
<td>$\Delta E^\circ$</td>
<td>Overall reaction potential</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>Trans-membrane pressure</td>
</tr>
<tr>
<td>$\Delta P_t$</td>
<td>Term for the measurement of TMP as a function of time</td>
</tr>
<tr>
<td>$\Delta z$</td>
<td>Membrane pore length</td>
</tr>
<tr>
<td>$E^\circ$</td>
<td>Standard reduction potential</td>
</tr>
<tr>
<td>$e_x$</td>
<td>Error associated with measured value $x$, calculated from the 95% confidence intervals of replicate measurements</td>
</tr>
<tr>
<td>$%e_x$</td>
<td>Relative error of measured value $x$</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>$Fe$</td>
<td>Atomic symbol, iron</td>
</tr>
<tr>
<td>$Fe^{2+}$</td>
<td>Ferrous iron</td>
</tr>
<tr>
<td>$Fe^{3+}$</td>
<td>Ferric iron</td>
</tr>
<tr>
<td>$Fe(OH)_{3(s)}$</td>
<td>Ferric hydroxide, an iron precipitate</td>
</tr>
<tr>
<td>$I$</td>
<td>Applied current</td>
</tr>
<tr>
<td>$i$</td>
<td>Applied current density</td>
</tr>
<tr>
<td>$J$</td>
<td>Filtration flux</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar mass of compound</td>
</tr>
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</table>
\( m \)  Mass or metal released from electrolytic reaction

\( ML_{\text{measured}} \)  The measured metal loading from EC

\( ML_{\text{theory}} \)  Theoretical metal loading or concentration of iron in the cell effluent

\( \mu \)  Dynamic viscosity of the liquid

\( N \)  Number of samples used in confidence interval calculations and data analysis

\( P_{\text{pore}} \)  Membrane pore density (or porosity)

\( \phi \)  Current efficiency

\( PXR_A \)  The signal output of pressure transducer A

\( PXR_{B, \text{as A}} \)  The output of pressure transducer B, expressed in equivalent units to pressure transducer A

\( q \)  The total charge passed through the electrode

\( Q \)  Volumetric flow rate

\( R \)  Membrane resistance

\( r \)  Membrane pore radius

\( R_{\text{end, } i-1} \)  The fouling resistance at the end of the previous cycle

\( R_{f} \)  The accumulated fouling resistance of a membrane

\( R_{m} \)  The intrinsic hydraulic membrane resistance of a clean membrane

\( R_{r, i} \)  The resistance recovery from backwash at the start of the \( i\)-th cycle

\( R_{\text{start, } i} \)  The resistance measured at the beginning of the current cycle

\( R_{T} \)  Total resistance of the membrane

\( s \)  Standard deviation of replicate measurements

\( s_m \)  Standard deviation of the slope, from linear regression

\( t \)  Time

\( t_{95\%} \)  2-sided t-value for calculation of 95\% confidence intervals

\( \tau \)  Membrane pore tortuosity
z Valence of ion released from anode, or the number of electrons exchanged
I would like to thank my supervisors Madjid Mohseni and Pierre Bérubé for taking me on as a student and providing support over the last 2+ years. I truly appreciate the opportunity to have been part of RES’EAU WaterNET, and this experience has provided me with an education beyond the technical aspects of water treatment and chemical engineering.

I would also like to thank my lab mates for sharing their knowledge and lab equipment. Having someone to chat with in the lab while I watched water drops slowly fill a sample vial always made the process more enjoyable. Thanks to Doug in the CHBE workshop and Scott in the CIVL department workshop for helping me build my setup (and make it work). And thank you to Joerg and Shona, for answering my questions about membranes and pressure transducers as I tried to assemble a setup that was completely new to me.

The team at BQE Water was so supportive of my decision to return to UBC, for which I am very grateful. Thank you to my parents for raising me to love science and encouraging me throughout my education to achieve my goals. And finally – Mark. Your support throughout this degree has been invaluable. Thank you.
This work is dedicated to kids who love science
Chapter 1

Introduction

1.1 Research motivation

The main objective of drinking water treatment is to produce clean water that is safe to drink. Canada is perceived as a country rich in freshwater sources due to the abundant lakes and rivers that cover the country’s surface. These water sources supply potable water for over 90% of Canadian municipalities (Environment Canada, 2011). However, this freshwater is not pristine, and the current methods of treatment and distribution are not perfect. At the time of writing, there are over 700 drinking water advisories in place across the country (see http://www.watertoday.ca/ to access the most recent numbers). Although the majority of these advisories are issued as preventative measures to address equipment and process issues, unacceptable water quality accounted for 16.5% of all Boil Water Advisories (BWAs) issued in 2017 and over 70% of these advisories were issued to small systems that serve communities of 500 people or less (Environment and Climate Change Canada, 2018).

Unacceptable water quality can be caused by insufficient treatment, which may be due to poor or deteriorating source water quality or inadequate operation of the water treatment plant. A review of waterborne disease outbreaks in British Columbia, Canada, between 1980 and 2002 concluded that the most
common outbreak was caused by Giardia, a pathogen commonly found in surface water (Sierra Legal Defense Fund, October 2003). In most cases, the solution implemented to treat for Giardia contamination was an increased chlorine dose, which is not desirable for many reasons. However, in small systems, chlorine is one of the most common methods of disinfection.

Chlorine is inexpensive. It is capable of inactivating many pathogens of concern, and provides a secondary disinfection by maintaining a residual concentration in the treated water through the distribution system until the water reaches the consumer’s tap. However, chlorine is also associated with unwanted taste and odour issues, corrosion of pipes and fittings, and increased risk of forming disinfection byproducts (DBPs). Furthermore, in addition to the higher dosage required to kill pathogenic Giardia cells, chlorine is also ineffective in killing other protozoa, such as Cryptosporidium cells when they are in the oocyst form (Sierra Legal Defense Fund, October 2003). Therefore, chlorine is not an ideal disinfectant.

A reliable water supply and treatment system is important for any community. However, small and remote communities have the added challenge of meeting the needs of the community with limited resources. The motivation behind this research is to investigate a water treatment technology that can be applied to small and remote water systems which rely on surface water as the drinking water source. A successful treatment system would effectively meet treatment targets and would be user friendly, low cost and robust.

1.2 Background and literature review

1.2.1 Drinking water treatment and Natural Organic Matter

There are many different approaches to drinking water treatment, but the overall objective is always the same: produce a safe and reliable supply of drinking water for the consumer. Drinking water regulations are often primarily focused on removal or inactivation of pathogens in water, but there are other chemical
contaminants that can also have adverse health effects on consumers. DBPs are a type of chemical contaminant that are heavily regulated in Canada and around the world but are not the primary focus of drinking water treatment.

DBPs are formed when water containing natural organic matter (NOM) undergoes a disinfection process such as chlorination or chloramination (Rook, 1976). Common DBPs include Trihalomethanes (THMs) and Halo-acetic Acids (HAAs), however, these compounds only represent a small fraction of possible compounds formed during disinfection. DBPs are cause for concern because they are suspected to have negative health effects (Richardson, 2003). Therefore, prevention of DBP formation is a very important part of drinking water treatment. Preventing DBP formation involves removing DBP precursors, like NOM, prior to disinfection.

NOM is a term used to describe the complex organic molecules that are produced by the breakdown of plant and animal matter in water. The chemical and physical properties of NOM will vary, depending on source organic material, and time of year (Thurman (1985) cited in Brinkman and Hozalski (2015)). The molecular weight and character of the NOM can be separated into different classes depending on its variable molecular structure. NOM can be classified based on hydrophilic, transphilic or hydrophobic character as well as its acidity (Leenheer & Croué, 2003). Two common methods for determining the concentration of NOM in water is by measuring the dissolved oxygen concentration (DOC) and the UV-absorbance of a sample at 254nm (UVA-254).

The variable chemical and physical properties of NOM impacts the efficiency of the treatment process applied (Collins et al., 1986). Different fractions of NOM are preferentially removed by the different treatment technologies (Sharp et al., 2006; Aschermann et al., 2016) and different fractions of NOM are correlated to different types of DBP formation (Hua et al., 2015). The hydrophobic, larger molecular weight and aromatic fractions have been cited as more likely to lead to DBP formation (Lin & Wang, 2011; Rook, 1976). Therefore, in the application of drinking water treatment of surface water, removal of these fractions of NOM
prior to disinfection is a priority.

1.2.2 Removal of NOM from drinking water

A typical North American surface water treatment system involves coagulation (and rapid mixing phase), flocculation (and slow mixing phase), some sort of solid/liquid separation, and a final disinfection step. The solid/liquid separation could include sedimentation and granular media filtration of the settled supernatant or direct filtration of the coagulation/flocculation effluent.

Each unit in this process can be studied and described in detail and proper operation of each unit is key to successful process performance. The coagulation/flocculation stage is responsible for removing suspended material, including pathogens such as bacteria and protozoa, from the water. Enhanced Coagulation is the term used to describe coagulation with the objective of removing the NOM dissolved in the water. This is done by adding excess coagulant and following a protocol for flash mixing and flocculation (Crozes et al., 1995). To better understand enhanced coagulation for NOM removal and how it can be improved, it is useful to understand the basic principles of coagulation.

Chemical coagulation and flocculation

Coagulation is an important process in water treatment. In this process, charged species are added to water to remove suspended and dissolved charged particles. Most of these particles have a negative surface charge and this charged layer can be neutralized by adding positively charged ions to the water, which reduces the repulsive forces between the particles and allows them to come together (Crittenden et al., 2012a).

Typical coagulants are aluminum or iron salts, which are added as a liquid reagent to the source water and are hydrolysed to form ferric or aluminum hydroxide species. This is known as chemical coagulation (CC). The coagulant is fully dispersed during a rapid mix phase and then the water is transferred to a
slower, gentle mixing phase that allows particles to grow in size. This is called flocculation. If excess coagulant is added and the solution is at a suitable pH, the hydrolysed iron or aluminum ions will exceed their solution solubility and precipitate in the form of aluminum or ferric hydroxides (Fe(OH)$_3(s)$ or Al(OH)$_3(s)$), which can further capture soluble NOM (Crittenden et al., 2012a). This is known as the ‘sweep floc’ mechanism of coagulation/flocculation and is an important part of enhanced coagulation for NOM removal from surface water.

Enhanced coagulation is a complex process and determination of optimal coagulant dose is best done using lab-scale jar tests with the real water to be treated (Crozes et al., 1995). Technology drawbacks and issues include high sludge production, process requirements for pH adjustment and control, and high reagent consumption compared to regular coagulation processes. Furthermore, reagents such as ferric chloride are classified as dangerous goods, and therefore require regulated handling and storage of the reagent when shipping it to site. The drawbacks of this process has led to the research and development of other technologies to remove NOM.

Electrocoagulation (EC) is a promising alternative to chemical coagulation. Other non-coagulation based technologies capable of NOM removal also exist, including ion-exchange, adsorption, and membrane filtration (or a combination of these processes) (Humbert et al., 2007; Velten et al., 2011; Stoquart et al., 2012; Winter et al., 2017). Each process has its own set of strengths and weaknesses and will not be discussed in detail. It is only important to know that many different approaches exist to solve this complex problem.

### 1.2.3 Electrocoagulation

EC follows the same principles as chemical coagulation however the means of introducing the coagulant species to the water is different. EC has been widely applied to different types of water to remove hardness, chemical oxygen demand (COD), turbidity, viruses, heavy metals, and NOM (Zhao et al., 2014; Tanneru & Chellam, 2012; Nariyan et al., 2017; Vik & Carlson, 1984).
Aluminum and iron are the most common materials used in EC (Dubrawski & Mohseni, 2013; Särkkä et al., 2015); however, iron is preferred due to lower cost and higher durability (Moreno C. et al., 2009). In EC, an electric current is passed through a pair of electrodes immersed in the water to be treated. This results in a set of electrochemical reactions happening on the surfaces of the electrodes. In an iron EC unit, these reactions are:

**Anode:**

\[
\text{Fe}_0 \rightarrow \text{Fe}^{2+} + 2 \text{e}^- \quad E^o = 0.447 \text{V} \tag{1.1}
\]

**Cathode:**

\[
2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{OH}^- \quad E^o = -0.8277 \text{V} \tag{1.2}
\]

The standard reduction potential cited \((E^o)\) is measured at STP (25°C and 1 atm) (Vanysek, 2005). This coupled reaction corresponds to an overall reaction potential of \(\Delta E^o = -0.3807 \text{V}\). In theory, \(\text{Fe}^{3+}\) could also be produced from the anode, but the prediction of ferrous iron production corresponds to observations in literature (Bagga et al., 2008; Tanneru & Chellam, 2012).

Direct formation of \(\text{Fe}^{3+}\) is likely not often observed because the standard reduction potential for ferric iron is much higher than that for ferrous iron, resulting in a greater overall reaction potential. The electrochemical reaction for the direct production of ferric iron on the anode is:

\[
\text{Fe}_0 \rightarrow \text{Fe}^{3+} + 3 \text{e}^- \quad E^o = 0.037 \text{V} \tag{1.3}
\]

which would result in an overall reaction potential of \(\Delta E^o = -0.7907 \text{V}\). This potential may not be in the range of current densities commonly investigated in this application. Lakshmanan et al. (2009) completed an in-depth study on the iron species generated during iron EC. Their results suggested that \(\text{Fe}^{2+}\) was formed directly through electrolysis and was then oxidized to \(\text{Fe}^{3+}\) in solution. How-
ever, these reactions are complex, and are affected by system conditions such as dissolved oxygen (DO) concentration and water matrix (Dubrawski et al., 2015; Dubrawski & Mohseni, 2013).

The amount of Fe\(^{2+}\) added to the system can be predicted by Faraday’s Law of Electrolysis:

$$m = \frac{qM}{Fz}$$

where \(m\) is the mass of material released from the electrode (g), \(q\) is the total charge passed through the electrode (Coulombs), \(M\) is the molar mass of the material (g/mol), \(F\) is Faraday’s Constant (96485 Coulombs/eq), and \(z\) is the number of electrons transferred (eq/mol). In the case of Fe EC, \(M = 55.85\) g/mol and \(z = 2\). When operating under constant current operation, the total charge \((q)\) is proportional to the applied current multiplied by time:

$$q = It$$

where \(I\) is the applied current (Amp) and \(t\) is the time (sec).

In a continuous flow reactor that is operated with a known volumetric flow rate, \(Q\), the theoretical metal loading \((ML_{theory})\) or concentration of iron in the cell effluent can be predicted and controlled using the following equation:

$$ML_{theory} = \frac{I \times M}{Q \times F \times z} = \frac{I \times 55.85\ \text{g/mol}}{Q \times 96485\ \text{C/mol} \times 2}$$

Using this equation, \(ML\) is expressed as the total concentration of iron as mass/volume (mg/L). The actual metal loading \((ML_{measured})\) can be measured by analyzing a sample for concentration of total iron, which can be used to determine the current efficiency \((\phi)\) of the system.

$$\phi = \frac{ML_{measured}}{ML_{theory}}$$

A new anode is expected to operate at 100% current efficiency, however as an an-
ode ages, the current efficiency will decrease if the anode is not cleaned regularly (Lakshmanan et al., 2009).

After \( \text{Fe}^{2+} \) is released into solution, a series of chemical reactions can occur in the bulk, including oxidation and hydrolysis of the iron ions. The oxidation rate of \( \text{Fe}^{2+} \) to \( \text{Fe}^{3+} \) and precipitated iron species solubility in EC experiments depends on pH (Ben-Sasson et al., 2009). Lakshmanan et al. (2009) observed a faster oxidation rate of \( \text{Fe}^{2+} \) in an EC batch reactor compared to a \( \text{Fe}^{2+} \) chemical batch reactor, due to the localized high pH on the cathode. However, the oxidation rate could be affected by mass transfer limitations, caused by the overall current density and charge loading rate in the EC reactor (Dubrawski & Mohseni, 2013). Therefore, depending on the reactor conditions, the final EC-produced species may include other ferric and ferrous (oxy)hydroxides, beyond \( \text{Fe(OH)}_3(s) \). The species formed, and their subsequent transformation as they age, depends on the ions available for complexation in the water, as well as the presence of dissolved oxygen (Dubrawski et al., 2015). Dubrawski and Mohseni (2013) observed many iron species including magnetite, goethite and green rust under different EC conditions, which appeared to influence NOM capture by EC. This is a fundamental difference between CC and EC: iron CC involves hydrolysis of the coagulant species (such as \( \text{Fe}^{3+} \)) but does not typically include oxidation of \( \text{Fe}^{2+} \) in the solution bulk, since iron is not commonly introduced as \( \text{Fe}^{2+} \) for this purpose.

It was thought that the formation of \( \text{Fe(OH)}_3(s) \) flocs drives NOM capture during EC, as it does in CC. Bagga et al. (2008) hypothesized that the presence of NOM inhibits \( \text{Fe}^{2+} \) oxidation, by complexing with the ferrous species and preventing formation of \( \text{Fe(OH)}_3(s) \) and reducing the overall efficiency for NOM removal through EC. However, Timmes et al. (2010) identified an important feature of the system used by Bagga et al.: the batch reactor used did not account for the depletion of oxygen in the system. In the work completed by Timmes et al. (2010), when adequate oxygen was available, there was comparable performance between CC and EC for NOM removal in filtered, EC treated samples.
Further research into the mechanism of NOM removal by EC indicated that the solids produced during EC are able to capture and remove contaminants, either by sweep flocculation or charge neutralization mechanisms, depending on the dose of iron added to solution (Timmes et al., 2010).

The majority of EC NOM removal studies are focused on lab scale or batch reactors. McBeath (2017) investigated a continuous flow pilot scale EC unit for removal of NOM from surface water, up to a flow rate of 10 LPM. He concluded that even with high metal loading (up to 66 mg/L Fe) the energy requirements do not outweigh the benefits of the process. McBeath (2017) was able to achieve an average DOC and UVA-254 reduction of $37.2 \pm 4.2\%$ and $54.7 \pm 0.9\%$, respectively using humic acid as a model NOM reagent.

These are promising results for applying electrocoagulation to drinking water treatment. However, the final product must be a water that meets drinking water quality guidelines, which means that the coagulant added and flocs formed must be removed. Therefore, a method of solid/liquid separation is required if EC is to become a process that can produce clean, safe drinking water.

### 1.2.4 Membrane filtration and the EC/UF hybrid system

A possible method for removing the solids produced in the EC unit is through ultrafiltration (UF), which is one classification in the larger field of membrane filtration. Membrane filtration is a way of physically separating materials from water based on the size or molecular weight of the material. There are many different types, classifications, and configurations for membrane filtration technologies. The following section will provide an overview of membrane filtration and previous research combining EC pre-treatment with membrane filtration. This will provide background information on the membrane filtration setups used in this research. Additional details on the experimental setup are available in Section 2.3.2.
Membrane filtration - basic principles

A key principle of membrane filtration is the relationship between the volumetric flow rate, membrane surface area and the trans-membrane pressure (TMP). The following equation can be used to represent this relationship, which is a modified form of Darcy’s law (Cheryan (1998) cited in American Water Works Association (2008)):

\[ J = \frac{Q}{A} = \frac{\Delta P}{\mu R_T} \]  

(1.8)

Where \( J \) is the filtration flux (m s\(^{-1}\)), \( Q \) is the volumetric flow rate (m\(^3\)s\(^{-1}\)), \( A \) is the membrane surface area (m\(^2\)), \( \Delta P \) is the trans-membrane pressure (Pa), \( \mu \) is the dynamic viscosity of the liquid (kg m\(^{-1}\)s\(^{-1}\)) and \( R_T \) (m\(^{-1}\)) is the total resistance term of the membrane. \( R_T \) accounts for the internal membrane resistance as well as the accumulation of resistance as water is filtered. The accumulated resistance is known as membrane fouling and will be discussed later in this chapter.

Membrane systems can be classified by membrane material, system hydrodynamic properties (such as flow configuration and geometry) and membrane pore size. These classifications are outlined in Figure 1.1.

Polymeric and ceramic materials are two classifications of membrane material. The membrane material may influence physical and chemical interactions between the membrane and the feed water. This may be due to to properties such as hydrophilic or hydrophobic character, surface roughness, surface charge and pore shape (Crittenden et al., 2012b). Polymeric membranes are often used in drinking water treatment because they are considered easy to install and relatively inexpensive. Ceramic membranes were previously considered too expensive due to high capital costs but are gaining attention as the field develops. Research suggests that ceramic membranes are less susceptible to irreversible fouling and would therefore support a system with higher throughput (S. Lee et al., 2013). However, for experimental design of this project it was assumed that
these interactions are minimal and the membrane filtration is purely a physical process of size exclusion. This assumption is discussed further in Section 4.1. Both ceramic and polymeric membranes were used in this research.

The hydrodynamics of a membrane system is affected by the flow configuration and geometry, which in turn, affects the membrane performance. In terms of operation, membrane systems can either be operated under dead-end or cross-flow configuration. Figures 1.2 and 1.3 present a simplified schematic of the two different flow configurations.

Cross-flow operation is beneficial for feed waters that have high concentrations of suspended solids, due to the sweeping movement of flow across the surface of the membrane, preventing a buildup of large cake layer (Crittenden et al., 2012b). Dead-end filtration systems have the benefit of simple design and operation. However, without the tangential force of a cross-flow, severe fouling and concentration polarization are likely to occur, leading to an increase in the force required to filter the water (Belfort et al., 1994). In drinking water applications, the source water is typically low in suspended solids the dead-end configuration is more common. Therefore, a dead-end filtration configuration was used for this
Membranes can also be operated under constant pressure or constant flux configuration. Constant pressure systems are common in the lab scale but constant flux systems are more common for full scale plants. Miller et al. (2014) compared constant pressure and constant flux operation for UF membranes. The threshold flux of the system was identified (the flux above which membrane resistance rapidly increases, as defined by Field et al. (1995)). Tests were completed at fluxes and equivalent pressures above and below this critical flux value. Results indicated that at low flux, constant flux and constant pressure tests demonstrated similar fouling behaviour. However, at high fluxes, results deviated and membrane resistance rapidly increased for constant high flux experiments, but not for constant high pressure experiments. This implies that constant pressure and constant flux systems may not yield the same results when scaling up a filtration system during technology development. A constant, low flux configuration
was used in this project, as it is more likely to resemble a large system.

Membrane geometry defines how the driving force for filtration is applied. Submerged systems are typically operated at constant flux while external geometry typically refers to a pressurized system. Geometry refers to the physical shape of the membrane module. Examples of different module shapes include: hollow-fibre, flatsheet, tubular, or spiral wound systems. The membrane geometry affects the fluid dynamics of the system, which is extremely important in terms of fouling and process design (Belfort et al., 1994). Lab-scale flatsheet (disk) and hollow-fibre membrane modules were used in this research, as these geometries resemble those used in drinking water applications. Schematics of the UF membrane systems used in this project are available in Section 2.3.2.

Membrane pore-size or molecular weight cut off (MWCO) is the most important parameter in membrane classification, as it defines what material is rejected by the membrane. Both terms are used to classify the size of particles or molecules that will be removed from the water (Crittenden et al., 2012b).

Microfiltration (MF) and ultrafiltration (UF) systems are known as low pressure membranes and are designed for suspended particle and colloid removal. The approximate pore-sizes of these membranes are $0.1 - 0.2\mu m$ (nominally 0.2) and $0.01 - 0.05\mu m$ for MF and UF membranes, respectively (Allgeier, November 2005). Nanofiltration (NF) and Reverse Osmosis (RO) systems are known as high pressure membrane systems and are used for small molecule and ion removal to produce ultra-pure water. With respect to the contaminants commonly found in surface water sources, low pressure membrane systems are sufficient for meeting treatment objectives when combined with a subsequent disinfection step to inactivate any bacteria or viruses that may be able to permeate the membrane (Jacangelo et al., 1995). Low pressure membranes require less energy than high pressure membranes to operate, which is favourable when designing a simple system for a small community. In this research, two UF membranes were tested with the EC pre-treatment step.

Selection of membrane pore size has a significant impact on membrane per-
formance in terms of permeate water quality and changes in membrane resistance (known as membrane fouling). NOM has long been identified as a membrane foulant for both high pressure and low pressure membranes. N. Lee et al. (2004) compared UF and MF membranes for filtration of NOM-containing water and concluded that MF membranes are more prone to fouling than UF membranes due to the difference in pore sizes relative to the size of particles removed by the membrane. Therefore, the combination of EC (which increases the average particle size) with a UF membrane system is expected to reduce membrane fouling.

Previous research that has incorporated EC/membrane hybrid systems has primarily focused on MF systems. Bagga et al. (2008), Ben-Sasson et al. (2013), and Gamage and Chellam (2011) all investigated hybrid EC/MF systems for NOM removal. However, very little work has been completed using hybrid EC/UF systems. Han et al. (2015) applied an EC/UF process to investigate sulfonated humic acid (SHA) removal from water and achieved up to 95% SHA removal with a 5kDa UF membrane. This process, however, incorporated sedimentation of the flocs and well as a pre-filtration step with a bag filter prior to ultrafiltration. Han et al. did not consider direct filtration of the EC effluent. Direct filtration is desirable as it may simplify the total footprint of a full-scale treatment plant.

**Membrane fouling**

As mentioned throughout this chapter, membrane fouling is an important consideration in membrane operation and system design. A simplified description of membrane fouling is to characterize it as two types: internal fouling (where molecules will become attached to the inner pores of the membrane structure) and external fouling (where a cake layer of particles build up on the outer surface of the membrane). In both cases, the required pressure to push water through the membrane at a constant flux will be increased.

Recall the resistance term, $R_T$ in equation 1.8. Membrane fouling can be evaluated by treating fouling as a ‘resistance in series’ model, where the total
resistance, $R_T$, is the sum of each factor that contributes to the overall resistance (American Water Works Association, 2008):

$$R_T = R_m + R_f$$  \hspace{1cm} (1.9)$$

$R_m$ is the intrinsic hydraulic membrane resistance of a clean membrane and $R_f$ is the accumulated fouling resistance. $R_m$ is related to physical properties of the membrane, as outlined in equation 1.10

$$R_m = \frac{8 \times \tau \times \Delta z}{\pi \times r^4 \times P_{pore}}$$  \hspace{1cm} (1.10)$$

where $\tau$, $\Delta z$, $P_{pore}$, and $r$ refer to the pore tortuosity, pore length, pore density (or porosity), and pore radius of the membrane, respectively (American Water Works Association, 2008). $R_m$ can be determined by measuring the flux or TMP of the system when filtering deionized water through a clean membrane. This is calculated through the following equation:

$$R_m = \frac{\Delta P_o}{\mu J}$$  \hspace{1cm} (1.11)$$

$\Delta P_o$, $\mu$ and $J$ are the clean water TMP (Pa), dynamic viscosity (Pa.s), and filtration flux (m/s), respectively. $R_m$ may change as the membrane ages and undergoes periodic chemical cleans. Gao et al. (2016) suggested that chemical cleaning of PVDF membranes using NaOCl resulted in irreversible compaction of the membrane material properties, causing sharp changes in $R_m$. However, typically it is $R_f$ that changes as material is filtered out of solution.

$R_m$ and $R_T$ must be used to determine $R_f$. In a constant flux system $R_T$ can be determined by measuring the TMP as a function of time ($\Delta P_t$):

$$R_T = \frac{\Delta P_t}{\mu J}.$$  \hspace{1cm} (1.12)$$
Using equations 1.9, 1.11, and 1.12 we can define an equation and solve for $R_f$:

$$R_f = \frac{\Delta P_t - \Delta P_o}{\mu J}$$

(1.13)

which can be used to evaluate the system in terms of membrane fouling rate and fouling mechanism.

The membrane fouling rate (or, the rate at which $R_f$ increases) depends on many factors such as mass of foulants approaching the membrane, mass of foulants being pushed away from the membrane through back-transport or cross-flow mechanisms, and adsorption of material onto the surface or inner pores.

Four main mechanisms are accepted as the dominant mechanisms for fouling, and a fouling model has been proposed to correspond to each of these mechanisms to express the relationship between resistance accumulation and volume filtered (Hermia, (1983), cited in Bolton et al., (2006)). The four mechanisms are:

- Complete blocking (external): inverse relationship, particles seal pores, area blocked is proportional to area filtered
- Incomplete blocking (external): exponential relationship, particles accumulate on area already covered by other particles, or on remaining pores
- Cake fouling (external): linear relationship, a porous cake accumulates, proportional to the volume filtered
- Standard blocking (internal): power function, material adsorbed onto the inner pore decreases the actual pore radius

It is accepted that membrane fouling may not follow a single mechanism throughout a filtration cycle. Fouling is a complex process, and the dominant mechanism may change over time or more than one mechanism may be occurring during filtration of material (Jermann et al., 2007; Bolton et al., 2006).
As NOM varies in size and structure, different constituents of NOM will foul membranes in different ways. Huber (1998) was able to differentiate between the different fractions of NOM that cause irreversible fouling in RO membranes. Knowledge of which fractions cause fouling helps determine which processes are necessary for treatment prior to membrane filtration. This is important, as different fractions of NOM are preferentially removed by different treatment processes.

In the application of coagulation pre-treatment of membrane filtration, the dominant fouling mechanism observed is often described as cake fouling. Bagga et al. (2008) observed incomplete blocking during raw water filtration and cake fouling when the feed water was pre-treated by chemical coagulation. This implies that coagulation pre-treatment changes the particle properties and affects the fouling mechanism.

Gamage and Chellam (2011) also observed cake fouling as the dominant fouling mechanism during microfiltration of aluminum EC pre-treated feed water, which was an improvement over direct filtration of raw feed water. EC pretreatment improved the overall fouling rate. However, these works did not investigate other means of fouling mitigation.

### 1.2.5 Membrane fouling mitigation

There are three approaches to fouling mitigation during water treatment:

1. Pre-treatment to capture or remove foulants before they reach the membrane;
2. Hydraulic controls, such as backwashing, turbulence or cross-flow, to dislodge foulants from the surface; and,
3. Chemical controls, such as chemical cleans with citric acid or NaOCl to remove internal foulants.
Application of these controls is designed to either prevent fouling from occurring, or temporarily remove the fouling from the membrane before it begins to re-accumulate in later filtration cycles. Fouling that can be removed in this way is known as ‘reversible’. Chemical cleaning is designed to remove ‘irreversible’ fouling, such as adsorbed material or internal foulants that would otherwise not be removed through backwashing.

The EC/UF hybrid system is an example of pre-treatment to remove NOM before it reaches the membrane. In municipal wastewater systems, direct microfiltration is problematic due to the colloidal fraction of particles suspended in the water causing fouling and lowering the overall flux of the system. Pouet and Grasmick (1994) applied aluminum electrocoagulation-flotation as a pre-treatment step in a municipal wastewater MF system, which improved the membrane flux of the system from 20LMH to 350LMH.

Ben-Sasson et al. (2013) investigated the effect of pH and anode type on EC pre-treatment for NOM removal and membrane fouling mitigation. The researchers observed that improved NOM removal did not correlate with improved membrane efficiency, yet both parameters were dependent on initial pH, total metal loading, and type of electrode used (Ben-Sasson et al., 2013).

Gamage and Chellam (2011) applied Al EC to MF for surface water treatment and observed cake fouling in all cases, which exacerbated fouling at high TMPs due to cake compression. The authors suggested that EC pre-treatment requires a balance between total metal loading and large floc generation (Gamage & Chellam, 2011). EC causes higher total filtration resistance, as the total mass of material in the feed water is increased, but the increased particle size decreases the specific resistance of the cake. This agrees with results reported by Ben-Sasson and Adin (Ben-Sasson & Adin, 2010): the researchers claim that the sweep coagulation mechanism is responsible for fouling mitigation, as it changes the particle sizes in such a way that the cake fouling mechanism dominates, instead of the other blocking models.
These examples suggest that EC pre-treatment has the potential to improve membrane efficiency, however very little work has been completed on how hydraulic and chemical controls can be applied to improve fouling mitigation in a hybrid EC/UF system. Timmes et al. (2010) observed high hydraulic recovery of membrane resistance when using EC treated water. However, cyclic backwashing was not investigated. Ben-Sasson and Adin (2010) applied dead end, constant pressure MF to Fe EC treated water. Flux restoration was observed by rinsing the membrane with tap water, due to easy removal of the cake layer. However, the reversible fouling was not investigated further than that observation (Ben-Sasson & Adin, 2010). Reversible fouling can be removed by backwashing or introducing turbulence into the system, yet very little research has been completed on the effect of hydraulic controls for UF membrane mitigation of EC pre-treated water.

A review by Böhm et al. (2012) highlights the importance of fluid dynamics in membrane fouling mitigation. Understanding of the system fluid dynamics help to optimize the hydraulic controls, such as induced turbulence and backwash efficiency. Furthermore, backwash is important but so are other methods of induced turbulence, such as air sparge. The use of air bubbles is common in membrane filtration fouling control as means to introduce turbulence in the system without the expenses of a pressurized cross-flow system (Cui et al., 2003).

In the application of combining EC with membrane filtration for drinking water, the majority of research has focused on pre-treatment and evaluation of permeate water quality, not hydraulic fouling control. There has been no research investigating the use of air sparge on UF feed water or subsequent membrane performance. This is a knowledge gap that is addressed in this research: The effect of cyclic backwash and induced turbulence by air sparging on an EC/UF system.
1.3 Research objectives

The objectives of this research are as follows:

1. Apply iron EC to synthetic surface water containing Suwannee River NOM.
   - Evaluate EC performance by measuring total iron, dissolved organic carbon and UVA-254 in EC-treated water, under fixed EC settings.
   - Analyze the molecular weight distribution of NOM in raw water (untreated) and EC treated water (filtered to 0.45µm).

2. Filter EC pre-treated water using a ceramic disk UF membrane.
   - Analyze membrane fouling rates under different filtration cycle and backwash cycle duration settings. Compare these results to a filtration test without backwash.
   - Analyze DOC, UVA-254 and total iron in the UF permeate, as measurement of permeate water quality. Compare these values to raw water values to determine the effectiveness of the iron EC/UF hybrid system to capture and remove NOM from the source water. Evaluate permeate water quality at the start and end of the filtration test.

   - Analyze membrane fouling rates when air sparging and/or backwashing is applied. Compare these results to filtration test where no fouling mitigation is applied.
   - Analyze DOC, UVA-254 and total iron in the UF permeate, as measurement of permeate water quality. Compare these values to raw water values to determine the effectiveness of the iron EC/UF hybrid system to capture and remove NOM from the source water. Evaluate permeate water quality at the start and end of the filtration test.
4. Apply the EC/UF process to a natural surface water and evaluate the treated water quality (DOC, UVA-254, and Fe) and fouling rate for a single UF operation mode. Compare results to tests using synthetic surface water.

1.4 Scope of research

A set of experiments were designed to address the research objectives outlined above, using two different UF membranes. The membrane fouling and permeate water quality were monitored and analysed. The effect of backwash was investigated with both membranes by evaluating the overall rate of resistance increase across multiple cycles. Air sparging, backwash duration and filter cycle duration were all investigated, however, a complete factorial experimental design was not implemented due to the limited time available to complete a MASc research project.

1.5 Research significance

The benefit of a hybrid EC/UF system is that it can treat water without having to deal with significant reagent addition or pH adjustment. The EC/UF system can capture and remove NOM from surface water prior to chlorination, which reduces the risk of DBP formation. Membrane filtration can remove the flocs produced in the EC unit and has the added benefit of providing disinfection credits by also filtering out some pathogens. These combined processes then decrease the overall demand of chlorine required for disinfection, and decrease the taste and odour issues associated with chlorine disinfection.

The combination of electrocoagulation and ultrafiltration has the potential to have significant impact on the water treatment options available to small communities where reliable, safe drinking water is still a requirement but a high capacity/high volume water treatment system may not be feasible.

This research is significant because little work has been done on this type of
integrated process. Limited research into UF fouling with EC pre-treatment has been completed, and in the research that has been published, the focus has been on water quality and overall membrane performance in dead-end, constant pressure, lab-scale systems. There is very little research into the effect of hydraulic fouling mitigation techniques like cyclic backwashing and induced turbulence through air sparging on EC pre-treated water for drinking water treatment and NOM removal. I will address these gaps and propose additional work to help further the development of an EC/UF process for drinking water treatment.
Chapter 2

Materials and Methods

This chapter describes details of the experimental methods and apparatus used during the project and the methods used to analyse samples and water quality. All tests were completed at room temperature (22°C).

2.1 Preparation of synthetic feed water

To account for the seasonal variability of NOM, a synthetic feed water was used throughout this research, which modeled natural surface water but was prepared using a reference NOM material (Suwannee River NOM). Suwannee River NOM (SR-NOM) is a RO isolate that is used as a reference material for NOM research. SR-NOM can be further separated into Suwannee River Humic Acid (SRHA) and Suwannee River Fulvic Acid (SRFA) fractions.

Her et al. (2002) analyzed the molecular weight distribution of SRHA and SRFA solutions using techniques combining UV-absorbance and DOC with chromatography. In all cases, the signal response curve began at an apparent molecular weight (AMW) less than 30kDa (Her et al., 2002). The MWCO for UF membranes range from 1 - 500kDa (Crittenden et al., 2012b). Therefore, depending on membrane pore size or MWCO, a UF membrane may be able to reject large MW fractions of NOM.
Synthetic surface water was prepared to model a surface water site in British Columbia, Canada. Table 2.1 outlines the parameters of interest and target concentrations in the synthetic feed water used in these tests.

Table 2.1: Target concentrations for SR-NOM synthetic feed water

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Target value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.07 ± 0.42</td>
</tr>
<tr>
<td>UVA-254</td>
<td>0.153 ± 0.010</td>
</tr>
<tr>
<td>Alkalinity, mg/L as CaCO₃</td>
<td>76.8 ± 2.7</td>
</tr>
<tr>
<td>DOC, mg/L C</td>
<td>5.80 ± 0.31</td>
</tr>
<tr>
<td>Chloride, mg/L Cl⁻</td>
<td>2.94 ± 0.11</td>
</tr>
<tr>
<td>Sulphate, mg/L SO₄²⁻</td>
<td>32.5 ± 1.3</td>
</tr>
</tbody>
</table>

The synthetic feed water was prepared using deionized (DI) water (18mS/cm²) and stock solutions of SR-NOM, sodium sulphate, sodium chloride and sodium bicarbonate. Synthetic feed was prepared in small batches as required for the day of use (6L to 10L batches). A graduated vessel was partially filled with DI water, then the sulphate, chloride, and NOM stock solutions were added and mixed. The solution was topped up to the target volume and the pH in the vessel was measured and recorded using a Hanna pH electrode. The sodium bicarbonate stock solution was then added and the solution was once again mixed. The final pH was measured and recorded. All reagents used were ACS or reagent grade. If needed, pH of the feed batch was adjusted to 7.07 ± 0.42 using dilute sodium hydroxide or sulphuric acid solutions. Feed water pH, DOC and UVA was measured for every feed batch prepared.

### 2.1.1 Preparation of NOM stock solution

This work evaluated the removal of soluble organic matter from surface water. A 400mg/L (as C) NOM stock solution was prepared to spike the synthetic water with a known concentration of dissolved organic carbon. IHSS Suwannee Rive
NOM RO isolate (lot 2R101N) was used as the dissolved organic carbon source. The stock was prepared in 500mL batches. 400mg of SR-NOM was accurately weighed and transferred to a 500mL volumetric flask. The flask was filled with deionized water and shaken to fully suspend the material. The solution was then transferred to a 1L Erlenmeyer flask and mixed using a magnetic stir plate at room temperature for 24 hours. The stock was then filtered through a 0.45µm membrane filter to ensure that only dissolved organic carbon was collected in the final stock. Concentration of the NOM stock solution was confirmed using a TOC analyzer (Shimadzu carbon analyzer, non-purgeable organic carbon method).

### 2.2 Collection and properties of natural surface water

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reported value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.40 ± 0.13</td>
</tr>
<tr>
<td>Turbidity, NTU</td>
<td>1.59 ± 0.64</td>
</tr>
<tr>
<td>UVA-254</td>
<td>0.15 ± 0.01</td>
</tr>
<tr>
<td>Alkalinity, mg/L as CaCO₃</td>
<td>36.4 ± 6.0</td>
</tr>
<tr>
<td>TOC, mg/L C</td>
<td>5.31 ± 0.64</td>
</tr>
<tr>
<td>Chloride, mg/L Cl⁻</td>
<td>0.71 ± 0.02</td>
</tr>
<tr>
<td>sulphate, mg/L SO₄⁻²</td>
<td>4.12 ± 0.22</td>
</tr>
<tr>
<td>Nitrate, mg/L NO₃⁻</td>
<td>0.56 ± 0.18</td>
</tr>
</tbody>
</table>

To test the EC/UF process on natural surface water, feed water was collected from a drinking water source in Middle River, British Columbia, Canada. The sample was collected in a 20L jug and delivered to the laboratory within 48 hours of collection. The sample was stored in the dark at 4°C until required for testing. Testing was completed within one week of sample collection. Feed water
properties are listed in Table 2.2. Prior to the start of the test using this water, the water was allowed to warm to room temperature.

2.3 Experimental apparatus

This research evaluated a hybrid electrocoagulation-ultrafiltration (EC/UF) technology for the treatment of drinking water. The EC unit was operated as a continuous flow system, to produce a composite volume of EC effluent, which acted as the feed for the UF unit. Raw feed water was also filtered directly through the UF unit. A general schematic of the overall process is presented in Figures 2.1 and 2.2. Stars in the figure indicate sample points throughout the process. Experiments evaluated permeate water quality and membrane fouling in these systems during filtration and evaluated the effect of cyclic backwash and air sparge.

2.3.1 EC experimental apparatus and procedure

The removal of NOM using EC for drinking water has been extensively studied. In this project, EC conditions were fixed to provide a UF feed water of similar composition. These conditions were selected based on those that were most successful in NOM removal according to previous work (McBeath, 2017). The EC conditions applied are outlined in Table 2.3. See Figure 2.3 for a schematic of the
Table 2.3: EC test conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>inter-electrode gap, $\delta$</td>
<td>2 mm</td>
</tr>
<tr>
<td>Cell flow rate, $Q$</td>
<td>1 LPM</td>
</tr>
<tr>
<td>Anode material</td>
<td>Cold-rolled steel</td>
</tr>
<tr>
<td>Cathode material</td>
<td>Stainless Steel (304)</td>
</tr>
<tr>
<td>Operating current, $I$</td>
<td>2 A</td>
</tr>
<tr>
<td>Operating current density, $i$</td>
<td>6.42 A/m²</td>
</tr>
<tr>
<td>Target metal loading, $ML$</td>
<td>35 mg/L</td>
</tr>
</tbody>
</table>

EC unit. Additional details of EC reactor geometry and design are provided by McBeath (2017).

Prior to the start of each experiment the iron electrode was manually cleaned with dilute sulphuric acid (0.657N) and scrubbed with a steel wool scrub pad. This was to remove any ferric hydroxide from the surface of the anode and maximize current efficiency. The electrode was then rinsed with DI water and placed into the EC apparatus with an inter-electrode gap of 2mm. A DC power supply was used to drive the electrochemical reactions. It was operated in constant current mode, with variable voltage. The continuous flow reactor was operated at 2A and a flow rate of 1LPM to provide a target $ML$ of 35mg/L Fe. Current efficiency and metal loading was confirmed through measurement of Total iron in the EC effluent sample (see Section 2.5.5). A peristaltic pump was used to push water through the EC unit. The volumetric flow rate was measured and adjusted to 1.0±0.1 LPM before the start of each EC experiment using a stopwatch and a 1L graduated cylinder.

At the start of the EC test the system was operated until it reached steady state and the voltage stabilized. Then, the EC effluent composite volume was collected in a single bucket. Once the desired volume of effluent was produced, the process stopped and the effluent composite was sampled. The solution was mixed briefly and allowed to flocculate for approximately 10 minutes prior to
sampling to ensure all of the iron particles were suspended. A 50mL sample was then collected and filtered through a 0.45µm PVDF syringe filter to measure the DOC concentration in the effluent. This mimics direct filtration of EC effluent in a full-scale process. McBeath (2017) was unable to correlate strong evidence of flocculation time with NOM removal while using the same system and it was therefore assumed that the EC effluent could be treated as having constant composition during the UF stage of the test (McBeath, 2017).

2.3.2 UF experimental apparatus and procedure

Two different membrane types were used to meet the objectives of this project. The first was a ceramic disk dead-end membrane and the second was a hollow-
fibre polymeric membrane. Important properties of each membrane type are outlined in Table 2.4.

Table 2.4: UF membrane properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Type 1</th>
<th>Type 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material type</td>
<td>Ceramic</td>
<td>Polymeric</td>
</tr>
<tr>
<td>Membrane material</td>
<td>ZrO₂</td>
<td>PVDF</td>
</tr>
<tr>
<td>Membrane shape</td>
<td>Disk, flat sheet</td>
<td>Hollow-fibre</td>
</tr>
<tr>
<td>Configuration</td>
<td>dead-end, submerged</td>
<td>dead-end, submerged</td>
</tr>
<tr>
<td>Nominal pore size (or MWCO)</td>
<td>(300kDa)</td>
<td>0.04 μm</td>
</tr>
<tr>
<td>Nominal filtration flux, ( J )</td>
<td>50 LMH</td>
<td>50 LMH</td>
</tr>
<tr>
<td>Nominal surface area</td>
<td>13.2 cm²</td>
<td>34 cm²</td>
</tr>
<tr>
<td>Volume of membrane module</td>
<td>3.3 cm³</td>
<td>622 cm³</td>
</tr>
</tbody>
</table>

The nominal pore size or MWCO is listed as provided by the membrane manufacturer. Both membranes were tested using continuous filtration and cyclic backwash, using an automated timer system. The effect of air sparge was also evaluated using UF membrane Type 2. Two membrane units (noted as A or B during testing) were operated in parallel to allow for duplicate tests for each membrane type. Due to the difference in geometry for the two filters, the systems are not identical, as evident by the nominal filtration surface area and volume of the membrane module. See Figures 2.4 and 2.5 for schematic diagrams of the two UF membrane units.

**UF Membrane Type 1**

During filtration tests using UF membrane Type 1, feed water was held in a separate feed tank, which was gently mixed (60rpm) throughout the duration of the experiment to ensure consistent composition of water being fed to the membrane. This was meant to model direct filtration, without a sedimentation step before the membrane.
Filtration using UF membrane Type 1 required re-purposing of a Ceramic Disk Membrane filter holder designed for pressure filtration using lab-scale ceramic disk filters (47mm, Tami Industries). This involved removal of the pressure system and applying suction to the permeate side of the membrane through a peristaltic pump. Through these changes, the system was modified to model a dead-end, flat sheet, submerged membrane system.

UF membrane Type 1 was housed in a module with a 47mm diameter and sealed with a rubber o-ring. The available surface area for the membrane was 13.2cm$^2$. The average available volume in the housing above the membrane was 3.3cm$^3$. The flow rate of solution into the filter was set at 50LMH, which corresponds to a volumetric flow rate of 1.1ml/min. The volumetric flow rate was measured at the beginning, middle and end of each UF test.

Filtration was driven by a peristaltic pump applying suction to the membrane module. Backwash stages used a second peristaltic pump, flowing in the opposite direction. The pumps are labeled as P1 and P2 in Figure 2.4. An au-
tomated timer controlled the timing of filtration and backwash; solenoid valves controlled the direction of flow. During filtration, V1 was open and P1 was ON. During backwash, V2 was open and P2 was ON. Backwash reject was collected in a separate container. Trans-membrane pressure (TMP) was measured using a pressure transducer connected to datalogger (labeled as PT-A/B on Figure 2.4). A pressure gauge was also included in the line to allow for visual confirmation of suction and flow (labeled as PG-A/B on Figure 2.4). UF permeate samples were collected from the effluent line from P1. Ten minute and five minute backwash times were tested. These times are longer than what would typically be used in a full scale process but the extended backwash was selected because it was expected that the configuration of UF membrane Type 1 would require extra time to completely flush the system with backwash water, due to the shape and orientation of the membrane module.

Brand new 300kDa ceramic membranes were cleaned using an adaptation of the manufacturers recommended cleaning procedure. The adapted procedure is as follows: soak the membrane in 0.5N NaOH solution at 70-80°C for 1 hour and rinse the membrane and system with DI until pH runs neutral. Then soak the membrane with 75% w/w phosphoric acid solution at 40-50°C and rinse the membrane and system with DI until pH runs neutral. This was done to remove any residual manufacturing residues.

At the end of each UF test, the membrane was removed from the module, rinsed with DI water and gently wiped with a soft tissue to remove the accumulated cake on the surface of the membrane. The membrane was then re-installed into the module and underwent a chemical clean that is similar to procedures followed in drinking water treatment plants.

The first step in the cleaning cycle was a 1 hour backwash and soak using a 400mg/L NaOCl and 0.1N NaOH solution. The system was then rinsed with DI water until the wash was neutral. Then the system underwent a 1 hour backwash and soak using a 1% (w/v) citric acid solution and rinsed with DI until the rinse ran neutral. Between experiments the system was left at room temperature,
primed with DI water.

Prior to the start of each UF test, the system was rinsed with DI water for a minimum of 2 hours. The TMP was logged during this time and defined at the clean water TMP ($\Delta P_c$, used to calculate the initial membrane resistance, defined as $R_m$).

**UF Membrane Type 2**

![Figure 2.5: Process schematic for UF membrane Type 2 (hollow-fibre)](image)

UF membrane Type 2 used a hollow-fibre membrane module, constructed from commercially available membranes (0.04µm, Suez ZeeWeed membranes, PVDF, non-ionic and hydrophilic). Each module was composed of three 19cm lengths of the hollow fibre membranes, with the top end of the module open for suction and the bottom end sealed. During filtration the module was submerged in a graduated cylinder. Feed solution was pumped into the cylinder at a rate slightly faster than the filtration suction rate to ensure that the solution level (and therefore the hydraulic head) remained constant throughout the test. This is identified as P3 in Figure 2.5.
UF feed water was held in a 20L feed tank, which held graduated cylinders that contained the submerged membrane modules. The feed in the large tank was mixed throughout the test (at 120 rpm) to ensure all iron flocs were suspended and to provide consistent composition of water being fed to the membrane. Due to the geometry of the tank, a higher mixing speed was required to suspend all particles compared to the mixing speed used to test UF membrane Type 1.

The available surface area of each module was 34cm$^2$. The average available volume in the cylinder housing the module was 622cm$^3$. The flow rate of solution into the filter was set at 50LMH, which corresponds to a volumetric flow rate of 2.8ml/min. The volumetric flow rate was measured at the beginning, middle and end of each UF test.

Cyclic filtration and backwash cycles were controlled using an automated timer and peristaltic pumps (P1 and P2 in Figure 2.5). Due to the limited volume of feed water available and simplicity of the UF system design, backwash reject went directly into the feed cylinder and was recombined with the fresh feed. Solenoid valves were not used.

Trans-membrane pressure was measured using a pressure transducer connected to datalogger (labeled as PT-A/B on Figure 2.5). A pressure gauge was also included in the line to allow for visual confirmation of suction and flow (labeled as PG-A/B on Figure 2.5). UF permeate samples were collected from the effluent line from P1.

During air sparging tests, an air line was submerged to the bottom of the graduated cylinder. Air was sparged at a pressure greater than 30cm H$_2$O, which is the height of the column of water. This value was not measured and the air flow rate was set at a pressure high enough to overcome the hydraulic head in the cylinder to provide consistent, vigorous air flow to both cylinders. The compressed air used was provided from the building air system.

At the end of each UF test, the hollow-fibre modules were removed from the system, and rinsed with DI water and gently wiped with a soft tissue to remove any accumulated cake on the surface of the membrane. The modules were then
re-installed and underwent a chemical clean that is similar to procedures followed in drinking water treatment plants.

The first step in the cleaning cycle was a 1 hour backwash and soak using a 50mg/L NaOCl solution. The system was then rinsed with DI water until the rinse ran neutral. Then the system underwent a 1 hour backwash and soak using a 1% (w/v) citric acid solution and rinsed with DI until the rinse ran neutral. Between experiments the system was left at room temperature, primed with DI water.

Prior to the start of each UF test, the system was rinsed with 50mg/L NaOCl solution for 20 minutes and then washed with DI water for a minimum of 20 minutes. The TMP was logged during the DI wash and was defined as the clean water TMP ($\Delta P_c$, used to calculate the initial membrane resistance, $R_m$).

## 2.4 Experimental matrix

A series of experiments were designed to evaluate membrane fouling in EC pre-treated water and compare it to water that had not been pre-treated (called raw water in this text). Two different membrane types were studied (See Section 2.3.2 for details on the UF setup). See Table 2.5 for the conditions tested.

The tests were designed to evaluate the performance in terms of water quality and resistance accumulation with or without the use of EC pre-treatment, backwash or air-sparge. In the table, ✓ denotes with treatment applied, × denotes without treatment applied. Additional tests on the effect of filter cycle duration and backwash duration were also completed for UF membrane Type 1, indicated by a ✓* symbol. Air sparge was only available using UF membrane Type 2. Note: this is not an exhaustive matrix and it could easily be expanded for future research.

The results from these experiments were reviewed and one setting from this matrix was selected and applied to natural surface water collected from Middle River, British Columbia. The setting selected was:
Table 2.5: Experimental matrix: Synthetic feed water using SR-NOM

<table>
<thead>
<tr>
<th></th>
<th>EC pre-treatment</th>
<th>Backwash</th>
<th>Air sparge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td>✓</td>
<td>×</td>
<td>n/a</td>
</tr>
<tr>
<td>Type 1</td>
<td>✓</td>
<td>✓*</td>
<td>n/a</td>
</tr>
<tr>
<td>Type 1</td>
<td>×</td>
<td>×</td>
<td>n/a</td>
</tr>
<tr>
<td>Type 1</td>
<td>×</td>
<td>✓*</td>
<td>n/a</td>
</tr>
<tr>
<td>Type 2</td>
<td>✓</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Type 2</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>Type 2</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Type 2</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
</tr>
<tr>
<td>Type 2</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

- UF membrane Type 2;

✓ With EC pre-treatment;

✓ With backwash;

✗ Without air sparge.

Chapter 5 presents the results from this experiment.

### 2.5 Analytical methods

Water quality and membrane fouling were measured throughout this work. Water quality parameters include: Dissolved Organic Carbon (DOC), UV-absorbance (UVA-254) and total and dissolved iron. Membrane fouling was evaluated by measuring and logging the TMP and using it to calculate the accumulated membrane resistance, $R_f$. These methods are discussed in the following sections.
2.5.1 Total and dissolved organic carbon

In this work, DOC is synonymous with TOC (Total Organic Carbon) as all samples were pre-filtered to 0.45µm or less, prior to analysis.

DOC was analysed using a Shimadzu ASI-V Total Organic Carbon analyser. Reagent blanks, calibration check standards and duplicate samples were run with each batch of samples to ensure reliable results. The non-purgable organic carbon method was used for these samples. This method allows for determination of organic carbon without interference from carbonate species that were part of the feed solution.

In the method, the sample is acidified and sparged with compressed ultra-pure air to convert inorganic carbon to CO₂ which is then purged from the sample. The sample then undergoes combustion over a catalyst heated to 680°C, oxidizing all non-purgeable organic carbon to CO₂, which is then detected using an NDIR sensor.

TOC Method Detection Limit and Accuracy

The method detection limit (MDL) and limit of quantification (LOQ) were determined following the procedure described in (US EPA Office of Water, 2016). Following these guidelines, the LOQ of TOC analysis by the Shimadzu TOC instrument was determined to be 0.20mg/L C. The MDL of the instrument was determined to be 0.21mg/L C.

Standard solutions at different known concentrations were also analyzed at different occasions to determine the precision and accuracy of the TOC method. Table 2.6 outlines the results of these samples. These results indicate that the TOC analysis is accurate at concentrations of 2.5mg/L DOC or higher, which is the working range for this research. At the higher concentrations (2.5mg/L and 5.00mg/L) there is no significant difference between the measured value and the true value of the TOC standard, as calculated based on 95% confidence intervals. Details on how the confidence intervals were calculated is presented in Section 2.6.
Table 2.6: TOC instrument accuracy. Measured value is reported with the calculated 95% confidence intervals. N is the number of samples, RPD is the Relative Percent Difference between the measured value and the true value of the standard.

<table>
<thead>
<tr>
<th>True value mg/L DOC</th>
<th>Measured value mg/L DOC</th>
<th>N</th>
<th>RPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>0.23 ± 0.01</td>
<td>9</td>
<td>6.8%</td>
</tr>
<tr>
<td>0.50</td>
<td>0.52 ± 0.01</td>
<td>9</td>
<td>2.2%</td>
</tr>
<tr>
<td>2.50</td>
<td>2.43 ± 0.15</td>
<td>11</td>
<td>1.3%</td>
</tr>
<tr>
<td>5.00</td>
<td>5.04 ± 0.12</td>
<td>61</td>
<td>0.4%</td>
</tr>
</tbody>
</table>

2.5.2 UVA-254

UV-absorbance was analyzed using a Cary UV-Vis spectrophotometer, at a wavelength of 254nm. A 1cm quartz cell was used to hold each sample during measurement. Method blanks and duplicate samples were run with each batch of 10 samples to ensure reliable results.

The estimated MDL of this method was determined to be 0.0040, which is the value of the 99th percentile of a set of 100 method blank samples analysed by the UV spectrophotometer at 254nm. A detailed MDL and LOQ study was not performed, as UVA-254 was reported as an absolute value and was not used to calculate the concentration or quantify the amount of a substance in the sample.

2.5.3 Specific UV-absorbance

Specific UV-absorbance (SUVA) is a method of relating the ratio of UV-absorbing compounds to the total organic carbon concentration in a sample. The following equation is used to calculate SUVA:

\[ SUVA = \frac{UVA_{254}}{DOC} \times 100 \]  

(2.1)

SUVA is useful because provides an indication of the aromatic character of the
NOM and is correlated to the DBP formation potential of water (Hua et al., 2015). The uncertainty of SUVA measurements were calculated based on propagation of error of UVA-254 and DOC measurements, as discussed in Section 2.6.

2.5.4  Apparent Molecular Weight by HPSEC

The apparent molecular weight (AMW) of NOM was determined using a Waters 2695 XE Separations Module, coupled with a Waters 2487 dual λ absorbance detector at 260 nm, as described by Dubrawski and Mohseni (2013). The carrier solution was a phosphate buffer of 0.01 M KH₂PO₄, 0.01 M K₂HPO₄ and 0.06 M NaCl (Certified A.C.S. reagent, Fisher Scientific). The column flow rate was 0.7 mL/min.

The chromatogram produced by the instrument gives the UVA in relation to elution time. The corresponding molecular weight of the compounds were determined based on a calibration performed using a set of polysulphonate standards, following a procedure described in literature (Sarathy & Mohseni, M., 2007). The following equation was obtained from the calibration and used to relate elution time to the apparent molecular weight of NOM in the sample:

\[
\log(MW) = -0.2857t + 6.9205
\]  

(2.2)

where \( t \) is the elution time (in minutes). The \( R^2 \) value for this equation is 0.9911.

The calibration data used to develop this equation is historical data and a calibration was not performed with each sample batch. Therefore, the calculated AMW is only an estimate of the MWD of NOM samples, and is not expected to represent exact values. Nevertheless, HPSEC chromatograms are useful in helping quantify the fractions of NOM removed from or present in a sample. To gain further insight to the fractionation of NOM during treatment, an analysis of UV chromatogram peaks was performed using Systat Peakfit® v4.12.

Peakfit® was applied to identify different AMW fractions using a deconvolution method assuming symmetrical Gaussian peaks. Five AMW fractions were identified with the purpose of quantifying the change in peak area during treat-
ment. In a HPSEC chromatogram, the low MW compounds (such as protein building blocks) elute first, followed by low MW humics, non-polar humics, and then much larger MW inorganic colloids and biological residues (Chow et al., 2008). The assumed NOM type for each fraction was labeled based on the peak assignment made by Chow et al., in a different body of work (2008). The characteristics and properties of the fractions were not investigated further. Table 2.7 presents the identified AMW range for the different NOM fractions assumed in this research.

Table 2.7: Identified NOM fractions, based on HPSEC results

<table>
<thead>
<tr>
<th>Fraction</th>
<th>AMW range, Da</th>
<th>Assumed NOM type</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>&lt;500</td>
<td>Building blocks</td>
</tr>
<tr>
<td>F2</td>
<td>500-700</td>
<td>Low MW humics</td>
</tr>
<tr>
<td>F3</td>
<td>700-900</td>
<td>Low MW humics</td>
</tr>
<tr>
<td>F4</td>
<td>900-1100</td>
<td>Low MW humics</td>
</tr>
<tr>
<td>F5</td>
<td>&gt;1100</td>
<td>Non-polar humic substances, inorganic colloids, biological residues</td>
</tr>
</tbody>
</table>

These defined fractions are qualitative. The peaks identified may not represent the true nature of elution of NOM fractions, as they may not be symmetrical, Gaussian peaks. NOM varies in chemical and physical properties, and the interactions of each type of NOM with the HPSEC column may vary. Zhou et al. (2000) suggest that UVA determination of MWD can vary from 10-20%, therefore the identified peaks using Peakfit® are most useful in identifying a change, if any, in the MWD of NOM in samples, and not measure accurate concentrations of NOM.
2.5.5 **Total and dissolved iron**

Analysis of iron concentration was performed using ICP-OES. Calibration standards were prepared in the same matrix as the sample to be analyzed within the expected concentration range of the samples (0.100 - 100.0mg/L Fe). Samples were acidified using nitric acid to a final concentration of 2% HNO$_3$ and were held at room temperature for a minimum of 24 hours prior to analysis to ensure that all iron was solubilized. Samples with anticipated high iron concentrations were diluted with acidified matrix blank diluent and held at room temperature until all iron was solubilized.

2.5.6 **Analysis and logging of trans-membrane pressure**

Trans-membrane pressure (TMP) data was logged using a pressure transducer that translated the pressure as a signal (in V). Two different pressure transducers were used when running duplicate tests in parallel. These transducers operated in two different output ranges, therefore, the signal from one had to be converted to match the signal from the other.

A calibration was performed, where the two transducers were connected in series and pressure was applied. The signal from PXR-A was matched to PXR-B and the following equation was obtained:

\[ PXR_{B as A} = PXR_A \times 0.4005 + 0.4025 \]  

(2.3)

The $R^2$ value for this data was 0.9993. These signals were then converted to units of pressure (psi) used to calculated the system TMP ($\Delta P_t$). Pressure Transducer A had a maximum voltage of 2.5V, corresponding to +15 psi. The minimum voltage was 0.0V, which corresponded to -15psi. Using these values, the following equation was obtained to convert signal output values to psi.

\[ \Delta P_t = PXR_A \times 29.9550 - 27.0580 \]  

(2.4)
The TMP data was logged using a HOBO datalogger at 10 second intervals throughout the UF tests. This data was then processed using a Python script to convert the logger output signal (in V) to pressure values (in kPa or psi).

To evaluate the accumulated fouling throughout the test, the $\Delta P_t$ term was converted to the accumulated resistance term, $R_f$, as described in Section 1.2.4, using equation 1.13, repeated here for clarity:

$$R_f = \frac{\Delta P_t - \Delta P_0}{\mu J}$$

The dynamic viscosity, $\mu$, was assumed to stay constant at 0.9544 mPa.s, corresponding to a temperature of 22 $^\circ$C. For the purpose of calculations, the membrane flux, $J$, was assumed to stay constant at the rate measured at the beginning of the test. Using these values, $R_f$ was calculated as a function of time. The time variable was then translated to the more useful term, throughput. Throughput allows for easy comparison between different membrane types and the variation in flow rate to account for changes in surface area at constant flux.

*Throughput* is calculated by calculating the volume filtered as a function of time in relation to the surface area ($SA$) of the membrane.

$$\text{Throughput} = \frac{Q \times t}{SA} = J \times t$$

where $Q$ is the volumetric flow rate and $t$ is time.

Linear regression was performed on the different datasets to evaluate the rate of resistance accumulation for each test. The calculated rate of accumulation was expressed as the slope, $\pm$ the corresponding 95% confidence interval, based on the calculated standard deviation of the slope.

### 2.5.7 Analysis of resistance recovery from backwashing

Backwashing efficiency can be quantified by measuring the resistance recovery between filtration cycles. The following formula was applied to complete this
calculation:

\[ R_{r,i} = 1 - \frac{R_{\text{end},i-1} - R_{\text{start},i}}{R_{\text{end},i-1}} \]  \hspace{1cm} (2.7)

where \( R_{r,i} \) is the resistance recovery from backwash at the start of the \( i \)-th cycle, \( R_{\text{end},i-1} \) is the fouling resistance at the end of the previous cycle and \( R_{\text{start},i} \) is the resistance measured at the beginning of the current cycle.

### 2.6 Data analysis and confidence intervals

Determination of confidence intervals is an important part of data analysis, as it helps identify which test conditions cause significant differences in test results. 95% confidence intervals were calculated for water quality results based on the assumption of a Gaussian distribution of random error for duplicate tests. 2-sided \( t \)-values were used in the calculations, based on the number of samples \( (N) \) and degrees of freedom \((N - 1)\). The general formula used for calculating the 95% confidence interval, \( e \), is:

\[ e = t_{95\%} \times \frac{s}{\sqrt{N}} \]  \hspace{1cm} (2.8)

where \( s \) is the standard deviation of the replicate measurements and \( N \) is the number of measurements. \( t_{95\%} \) is the 2-sided \( t \)-value for 95% confidence. The percent relative error for each measured value is:

\[ \%e = \frac{e}{\text{Measured Value}} \]  \hspace{1cm} (2.9)

In this work, every experiment was completed in duplicate and the results for water quality measurements were determined by calculating the confidence interval for two duplicate tests. Error bars in figures were calculated using 2-tailed \( t \)-values for 95% confidence limits, unless otherwise noted.

Some reported values, such as \( R_f \) or the normalized sample concentrations, \( C/C_0 \), are calculated values and were not based on direct analysis. In these cases,
propagation of error had to be considered to determine the error associated with the calculated value. The following formulas were applied to determine the propagation of error when simple mathematical operations were applied. These steps are outlined in reference material (Harris, 2007a).

**Propagation of error when the operation is addition or subtraction (ie, $y = x_1 + x_2$):**

$$e_y = \sqrt{(e_{x_1})^2 + (e_{x_2})^2}$$  \hspace{1cm} (2.10)

**Propagation of error when the operation is multiplication or division, such as calculation of normalized feed concentration or SUVA (ie, $w = \frac{x_1}{x_2}$):**

$$\%e_w = \sqrt{(\%e_{x_1})^2 + (\%e_{x_2})^2}$$  \hspace{1cm} (2.11)

**Calculation of error from relative percent error:**

$$e_w = \%e_w \times w$$  \hspace{1cm} (2.12)

Propagation of error works under the assumption that systematic error has been detected and corrected. The 95% confidence intervals were calculated for each replicate test and sample, and the error of the ratio was calculated to provide error bars for graphs representing this data.

To determine the error of the calculated accumulated resistance, $R_f$ (from equation 1.13), equations 2.11 and 2.10 were applied. Error bars on the figures presenting $R_f$ data represent the calculation of $R_f$ error of the measured maximum and minimum TMP of parallel systems.

Linear regression was performed to determine the slope and rate of change for resistance increase with respect to throughput. The standard deviation of the slope ($s_m$) was calculated following steps provided in a reference text (Harris, 2007b). The 95% confidence interval was calculated using equation 2.8, with the 2-sided t-value at 95% confidence interval and $N - 2$ degrees of freedom, where $N$ is the number of data points used in the regression. Calculated slopes
were deemed significantly different if the determined confidence intervals did not overlap. It is important to note that the calculated slopes did not account for any uncertainty in the $x$ or $y$ range.
Chapter 3

Results and discussion of synthetic water tests: UF membrane Type 1

Two types of UF membranes were evaluated in this work, however because they vary in material, geometry and pore size (MWCO), they will be discussed separately. This chapter presents water quality and membrane fouling results for UF membrane Type 1.

As described in Section 2.3.2, UF membrane Type 1 is a 300kDa, ceramic disk membrane with dead-end flow configuration. The disk is housed in a module with a working volume of 3.3cm$^3$ and suction is applied to drive filtration and model a submerged, flat-sheet membrane system. The schematic and description of this setup is available in Section 2.3.2. The effect of backwash duration and filtration cycle duration was investigated, using EC pre-treated synthetic feed water.

During the test, the filtration flux was kept constant at 50 ± 2.5 LMH. The initial grab sample began after 90 minutes and finished once the required volume was collected, which is equivalent to a throughput of 60-100L/m$^2$. A second sample was collected after approximately 18-20 hours of filtration, which
is equivalent to a throughput of approximately 650-1100L/m² (depending on the measured flow rate of the test and the time of the sample).

### 3.1 Filtration of raw water

Raw water filtration tests were completed to set a baseline for filtration of the feed water without EC pre-treatment. Tests with continual filtration and a 60 minute filtration cycle with a 10 minute backwash were performed. The MWCO of the membrane used in this test is 300kDa. Therefore, given the SR-NOM MWD upper limit of 30kDa (as discussed in Section 2.1), removal of DOC by the membrane was not expected.

During the test, DOC, UVA-254 and Fe were measured in the feed and permeate samples. Table 3.1 presents the feed and permeate water quality for the UF membrane Type 1 continual filtration test using raw water. Unfortunately, the feed sample for the raw water filtration test with backwash was contaminated with EC effluent from other tests and water quality results for this test are not reported.

<table>
<thead>
<tr>
<th></th>
<th>DOC mg/L C ± 95% CI</th>
<th>UVA-254 mg/L ± 95% CI</th>
<th>Fe - total mg/L ± 95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw feed 5.50 ± 0.20</td>
<td>0.228 ± 0.005</td>
<td>&lt; 0.10</td>
<td></td>
</tr>
<tr>
<td>Initial sample 5.54 ± 0.09</td>
<td>0.231 ± 0.010</td>
<td>&lt; 0.10</td>
<td></td>
</tr>
<tr>
<td>Final sample 5.52 ± 0.18</td>
<td>0.230 ± 0.003</td>
<td>&lt; 0.10</td>
<td></td>
</tr>
</tbody>
</table>

These results indicate that there is no significant difference between the feed and permeate samples in terms of the measured water quality parameters. This supports the assumption that NOM will not be removed by the membrane and
any observed NOM removal in UF tests using EC pre-treated feed water is due to the EC capture of NOM and not this membrane.

The TMP was also monitored throughout the tests to determine whether the SR-NOM feed water would cause any fouling. It was hypothesized that fouling would not be observed, as the MWCO of the membrane is much larger than the expected MWD of SR-NOM and it was assumed that membrane filtration was purely a physical process.

The accumulated membrane resistance was calculated as described in Section 2.5.6. The fouling resistance during the raw SR-NOM water filtration tests is presented in Figure 3.1. The rate of fouling resistance accumulation with respect to throughput is referred to as the ‘fouling rate’ in this text.

![Figure 3.1: UF membrane Type 1 fouling resistance accumulation for raw water filtration tests with and without backwash. Error bars represent calculated maximum and minimum $R_f$ for duplicate tests.](image)

Despite the overlap of the error bars of the calculated $R_f$ values, these results indicate that resistance is increasing during filtration of raw water for both tests, at different rates. Although fouling was not expected during filtration of...
the synthetic feed water, the apparent resistance may be due to the fraction of dissolved or ‘soluble’ NOM that passed through the 0.45 \( \mu \)m filter during solution preparation, but was rejected by the 300kDa membrane.

Examining the results of these two tests, backwashing appears to reduce the overall fouling rate. Linear regression analysis was performed on the resistance results to determine if this difference was significant. Determination of the slope in the linear region of filtration provides information on the relative fouling rate to compare the two experiments. For the test with backwash, regression was performed with data points collected at the end of each filtration cycle, as this is the point at which maximum fouling would occur. Table 3.2 presents the results from this analysis.

Table 3.2: Linear regression of raw water filtration using UF membrane Type 1, with 95% confidence intervals calculated based on the slope

<table>
<thead>
<tr>
<th>Test setting</th>
<th>slope, ( \frac{m^{-1}}{L.m^{-2}} )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>without backwash</td>
<td>((6.18 \pm 0.30) \times 10^8) 0.9644</td>
<td></td>
</tr>
<tr>
<td>with backwash</td>
<td>((2.37 \pm 0.63) \times 10^8) 0.7769</td>
<td></td>
</tr>
</tbody>
</table>

These results suggest that the backwash is reducing the overall fouling rate for the raw water filtration tests with UF membrane Type 1, as there is no overlap of confidence intervals between the calculated slopes. However, as noted in Table 3.1, the difference in DOC and UVA-254 between feed and permeate samples is not significant, which implies that despite this increase in resistance, the 300kDa membrane does not significantly remove NOM from feed water.

Given the \( R^2 \) value for the two test conditions and the spread of data points from the parallel tests, linear regression may not be an appropriate method to evaluate the fouling rate for these tests conditions. A true evaluation of the fouling rate for the tests with backwash would be to identify the fouling rate for each individual filtration cycle, instead of collecting data points at the end of each cy-
cle. However, the purpose of this exercise was to evaluate the overall increase in membrane resistance as water is filtered. A detailed evaluation of the fouling mechanism was not within the scope of this research.

3.2 Filtration of EC treated water

UF tests were completed with EC pre-treated feed water to evaluate the effect of filtration cycle duration and backwash duration on membrane performance in terms of permeate water quality and accumulation of membrane resistance. Results of EC pre-treated feed water preparation are presented in Section 3.2.1 and UF test results are presented in Sections 3.2.2 and 3.2.3.

3.2.1 Preparation of EC pre-treated feed water

The EC performance for NOM removal depends on a number of factors such as metal loading, current density and concentration of dissolved oxygen. To try and mitigate variability of results, EC experimental conditions were fixed, and selected based on results observed by McBeath (2017).

This report will not provide a detailed discussion of NOM removal results or mechanism as it was not part of the scope of the project. Nevertheless, understanding the EC effluent water quality is valuable as this water is the incoming feed for the UF system. Table 3.3 outlines the EC test performance and results for treatment of SR-NOM synthetic surface water. EC effluent samples were filtered through a 0.45 µm filter after approximately 10 minutes of flocculation.

These test conditions resulted in an average DOC and UVA-254 reduction of 33 ± 4% and 57 ± 8% respectively. The decrease in SUVA indicates that the aromatic fraction is preferentially removed by EC, which is similar to results reported in literature for EC and CC treatment using iron for NOM removal (Bagga et al., 2008). The average metal loading for all EC tests was 34.2 ± 1.3 mg/L Fe, corresponding to a average current efficiency of 95%. In all cases an increase
Table 3.3: EC test results, with an operating current density of 6.43mA/cm\(^2\) and target metal loading of 35mg/L Fe

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved Organic Carbon, mg/L C</td>
<td>5.50 ± 0.20</td>
<td>3.66 ± 0.37</td>
</tr>
<tr>
<td>UV absorbance at 254 nm</td>
<td>0.225 ± 0.004</td>
<td>0.097 ± 0.014</td>
</tr>
<tr>
<td>pH</td>
<td>7.32 ± 0.17</td>
<td>8.54 ± 0.24</td>
</tr>
<tr>
<td>Total iron, mg/L Fe</td>
<td>&lt;0.10</td>
<td>34.2 ± 1.3</td>
</tr>
<tr>
<td>Dissolved iron (0.45µm)</td>
<td>&lt;0.10</td>
<td>0.25 ± 0.10</td>
</tr>
<tr>
<td>SUVA</td>
<td>4.08 ± 0.17</td>
<td>2.65 ± 0.46</td>
</tr>
</tbody>
</table>

in pH was observed, which was expected given the anticipated reaction on the cathode.

HPSEC analysis was also performed to determine the AMW and change in MWD of NOM in the EC pre-treated water. Results of HPSEC analysis are presented in Figure 3.2.

Figure 3.2: AMW of untreated water and EC effluent for tests using synthetic SR-NOM feed water
These results appear to agree with results reported in literature that the larger MW faction of NOM is removed using EC (Dubrawski et al., 2013). Table 3.4 presents the percent removal of the different fractions identified using Peakfit®. Results indicate that increasing percent removal occurs with increasing AMW,

<table>
<thead>
<tr>
<th>Fraction</th>
<th>AMW range, Da</th>
<th>Average % removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>&lt;500</td>
<td>(13 ± 18)%</td>
</tr>
<tr>
<td>F2</td>
<td>500-700</td>
<td>(37 ± 4)%</td>
</tr>
<tr>
<td>F3</td>
<td>700-900</td>
<td>(53 ± 5)%</td>
</tr>
<tr>
<td>F4</td>
<td>900-1100</td>
<td>(71 ± 5)%</td>
</tr>
<tr>
<td>F5</td>
<td>&gt;1100</td>
<td>(91 ± 3)%</td>
</tr>
</tbody>
</table>

with over 90% removal of the higher AMW fraction (F5) and only (13 ± 18)% of the low MW fraction (F1).

An analysis of the particle size distribution (PSD) of the EC effluent was also completed, to confirm whether UF is an appropriate method to remove the flocs produced. A sample of EC effluent was measured for PSD directly, as well as a sample that was allowed to settle in a beaker for 22 hours. Table 3.5 presents the water quality for the two samples. The reported values for Dissolved iron and Dissolved Organic Carbon are based on filtration of the samples with a 0.45μm syringe filter. As this was only an exploratory test, it was not performed in duplicate and strong conclusions cannot be made from the resulting water quality data. Nevertheless, the high concentration of total iron and particle concentration by % volume in the Settled supernatant sample suggests poor settleability of the EC produced flocs. Although both the total iron and particle concentration decreased after 22 hours of settling, over 20mg/L total Fe and a detectable level of particles remained in the supernatant sample. This is unacceptable for treated drinking water.
Table 3.5: Water quality results for EC effluent settling test of SR-NOM feed water.

<table>
<thead>
<tr>
<th></th>
<th>EC effluent</th>
<th>Settled supernatant (22h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total iron, mg/L Fe</td>
<td>32.4</td>
<td>21.1</td>
</tr>
<tr>
<td>Dissolved iron, mg/L Fe</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Dissolved Organic Carbon, mg/L C</td>
<td>2.65</td>
<td>3.30</td>
</tr>
<tr>
<td>UV absorbance at 254 nm</td>
<td>0.082</td>
<td>0.117</td>
</tr>
<tr>
<td>pH</td>
<td>9.06</td>
<td>8.88</td>
</tr>
<tr>
<td>SUVA</td>
<td>3.09</td>
<td>3.53</td>
</tr>
<tr>
<td>Particle concentration by % volume</td>
<td>0.086</td>
<td>0.019</td>
</tr>
</tbody>
</table>

Furthermore, the observed increase in DOC and UVA-254 in the filtered samples may indicate possible changes to floc stability and filtered water quality with respect to time. However, further analysis would be required to understand floc formation and stability for a specific water sample, as these behaviours vary depending on the water matrix (Crittenden et al., 2012a). EC was also applied to natural surface water, which had a different matrix than the synthetic SR-NOM feed water. The results of this test are discussed in Chapter 5.

Particle size distribution analysis provides insight into what happened to the flocs produced from EC. The PSD results for the EC effluent and the Settled supernatant are presented in Figure 3.3. The PSD results are reported as the % volume of each fraction, normalized to the particle concentration by % volume. Therefore, although the relative peak height of the supernatant sample is higher than that of the non-settled EC effluent sample, the total concentration is still lower. The distribution reported through the PSD analysis suggests that only particles greater than 724µm settled out of solution. These results indicate that given these test conditions, settling is insufficient as means of solid-liquid separation of EC treated water.

A bi-modal distribution of particle size diameters is also observed. This may be due to the breakup and regrowth of floculated aggregates during the PSD analysis (Maguire, 2009). The aggregate particle size during filtration may be
larger than the diameter detected, which is useful when combining EC pre-treatment with membrane filtration.

Furthermore, all particles detected were reported as greater than 2µm and less than 2200µm in diameter. Therefore, the membranes selected for this research (with MWCO or pore size of 300kDa and 0.04µm) are appropriate, as the smallest detected particle size is around two orders of magnitude greater than the pore size of the membranes used.

### 3.2.2 Membrane fouling during filtration of EC pre-treated feed

UF tests were completed with and without backwash and at different filtration cycle and backwash cycle durations. The test without backwash was used to determine the upper limit of fouling during filtration of EC pre-treated feed. Three different backwash and filtration cycle duration settings were tested, as defined in Table 2.5. The remainder of this section will discuss membrane fouling from
these tests. Permeate water quality results will be discussed in Section 3.2.3.

Figure 3.4 presents a snapshot of the accumulated resistance data, $R_f$, for these tests between 200-400L/m$^2$. Each filtration cycle is connected by a line, with points plotted at the beginning, middle and end of each cycle. The continual filtration tests (without backwash) is one continuous line.

![Figure 3.4: Snapshot of resistance accumulation for filtration of EC pre-treated feed using UF membrane Type 1, from 200-400L/m$^2$. Each filtration cycle is represented by its own line. Error bars represent calculated maximum and minimum $R_f$ for duplicate tests.](image)

In the test without backwash (Figure 3.4a), accumulated resistance appears to increase linearly with increasing throughput, indicating that the dominant foul-
The fouling mechanism is through cake formation. Resistance accumulation rates for all four tests appear to be of the same magnitude. However, the absolute resistance accumulation does not appear to differ significantly between the different tests with backwash. Linear regression and analysis of the overall fouling rates provides more information as to whether there is a significant difference in overall fouling rate between the different treatments.

For the tests that included backwash, linear regression was performed on data points collected at the beginning, middle and end of each filtration cycle. Analysis of the variance was performed on these results to compare the calculated slopes. Results from this analysis indicate that there is no significant difference between the calculated overall rates of fouling, regardless of the point at which the slope was measured (i.e. at the beginning, middle, or end of the filtration cycle. ANOVA results for this comparison are: $F_{calc} = 0.21, p = 0.81; F_{crit} = 5.15, \alpha = 0.05$. In terms of practical applications of this data, the data point collected at the end of the filtration cycle provides useful information for determining the maximum rate of resistance accumulation. The linear regression results, calculated based on the accumulated resistance at the end of the filtration cycle are presented in Table 3.6, along with the results from the test without backwash, for comparison. These results indicate that membrane filtration with backwash.

Table 3.6: Linear regression of EC pre-treated SR-NOM water filtration using UF membrane Type 1, presented with 95% confidence intervals. For tests with backwash, linear regression was performed on data points collected at the end of each filtration cycle.

<table>
<thead>
<tr>
<th>Test setting</th>
<th>slope, $\frac{m^{-1}}{L.m^{-2}}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>without backwash</td>
<td>$(5.11 \pm 0.05) \times 10^9$</td>
<td>0.9987</td>
</tr>
<tr>
<td>30 min filtration &amp; 5 min backwash</td>
<td>$(2.57 \pm 0.15) \times 10^9$</td>
<td>0.9666</td>
</tr>
<tr>
<td>60 min filtration &amp; 5 min backwash</td>
<td>$(1.67 \pm 0.27) \times 10^9$</td>
<td>0.8968</td>
</tr>
<tr>
<td>60 min filtration &amp; 10 min backwash</td>
<td>$(3.96 \pm 0.22) \times 10^9$</td>
<td>0.9739</td>
</tr>
</tbody>
</table>
using UF membrane Type 1 is able to reduce the total rate of resistance accumulation, as every test including backwash had a significantly lower slope compared to the test without backwash. Therefore, we can conclude that cyclic backwash significantly reduces the overall fouling rate during filtration of EC pre-treated water using a dead-end, ceramic membrane. The overall fouling rate was reduced by \((23 \pm 4)\%\), \((67 \pm 5)\%\), and \((50 \pm 5)\%\) for the 30-5, 60-5 and 60-10 filtration and backwash cycle settings, respectively.

The test with 60 min filtration cycle and 10 min backwash had a higher fouling rate than the 30-5 and 60-5 tests. This may be due to the initial conditions of the test; the membrane module contained an air bubble for the first 4 hours of filtration, which resulted in a higher initial TMP at the start of the test. Perhaps this high TMP caused a change within the cake, making it more compact and cause increased overall resistance. This work combined iron electrocoagulation (EC) and ultrafiltration (UF) to treat synthetic and natural surface waters to remove Natural Organic Matter (NOM). Fixed EC conditions were applied to the feed water in a continuous flow EC reactor, at a flow rate of 1 LPM and an applied current of 2 A. These test conditions resulted in an average DOC and UVA-254 reduction of \(33 \pm 4\%\) and \(57 \pm 8\%\) respectively for the synthetic feed water.

The EC effluent acted as the feed water for the EC/UF systems. Two UF membrane types were tested: (1) a 300kDa ceramic disk membrane; and, (2) a 0.04μm PVDF hollow-fibre membrane. Both systems were operated at a constant flux of 50 LMH. Periodic backwash cycles were applied to evaluate the effect of backwashing on the overall membrane fouling rates. Backwashing with a 30 minute filtration cycle and 5 minute backwash reduced the fouling rate by \((50\pm3)\%\) and \((2\pm6)\%\) in the ceramic and PVDF membranes, respectively. Applying backwash to the EC/UF test with natural feed water resulted in a \((95\pm0.5)\%\) lower fouling rate compared to the EC/UF test with synthetic feed water test under the same conditions. Therefore, water composition has a significant effect on the membrane fouling rates of the EC/UF system.

Air sparging was also applied to the PVDF membrane system and resulted in
reducing the overall fouling rate by \((64 \pm 2)\%\). Comparatively, the combination of air sparging and backwashing reduced the overall fouling rate by \((98 \pm 1)\%\). The EC/UF test with air sparging and backwash also resulted in additional NOM removal of the UF permeate. Air sparging has never been combined with an EC/UF system and these are promising results in the quest to develop a EC/UF drinking water treatment system for small and remote communities. This may also be a trait of EC produced flocs. Harif et al. (2012) observed that aluminum EC generated flocs were more prone to compaction and restructuring, compared to those produced from CC. However, additional testing would be required to confirm these results.

ANOVA was also applied to compare each test setting to determine if there was a significant difference between the different backwash settings. To do this, the slopes calculated from early, middle and end points of the filtration cycles were averaged and compared. ANOVA results for the comparison of the different backwash test results are as follows: \(F_{\text{calc}} = 16.0\), \(p = 0.004\); \(F_{\text{crit}} = 5.15\), \(\alpha = 0.05\). This analysis supports the conclusion that all three backwash and filtration cycle timing conditions tested resulted in significantly different overall fouling rates, as \(F_{\text{calc}}\) is less than \(F_{\text{crit}}\) and \(p\) is less than \(\alpha\).

However, this conclusion may not represent the true effect of backwash and filtration cycle duration, as other confounding variables may be influencing the overall fouling rate. Ye et al. (2011) studied fouling and mitigation in hollow-fibre filtration with periodic backwash. They found that short periodic backwash only expanded the foulant cake, which re-compressed after filtration began. Furthermore, changes in cake height, composition and structure were affected by the hydrodynamics of the backwash (Ye et al., 2011). Therefore, given the limited conditions tested, a clear conclusion regarding the optimal backwash and filtration cycle durations for this system cannot be made. Further research would be required to confidently optimize the fouling rate for UF of EC pre-treated water.

Another parameter of filtration performance is determination of the resistance recovery between backwash cycles. This approach allows us to quantify
whether the filter cake is effectively removed or merely expanded. The average resistance recovery from backwashing was calculated for the period of 200-400L/m² for the UF membrane Type 1 filtration tests with EC pre-treated feed. These results are presented in Figure 3.5.

![Figure 3.5: Average resistance recovery measured during cycles between 200-400L/m² throughput for UF membrane Type 1 tests with EC pre-treated feed and backwash](image)

These results indicate that there is no significant difference in the relative resistance recovery between the three different settings tested. This is further supported by the results of ANOVA analysis. Comparing the mean resistance recoveries for the three backwash settings for this system resulted in a calculated F-value of 1.39 and a p-value of 0.28. The F-critical value for this analysis was 3.63 (assuming 95% confidence, α = 0.05). Therefore, these calculated means are not significantly different and the backwash and filtration cycle times tested did not affect the resistance recovery between cycles.

An important part of fouling mitigation is the hydrodynamics of the system and the degree of back-transport at the membrane surface. To improve the recovery during backwash, a couple of things could be done. First, increase the intensity of the backwash. For these tests, the backwash intensity was fixed at
approximately 120% of the filtration flux, however higher backwash intensities may provide improved fouling control (Shi et al., 2014). Varying the intensity of the backwash will change the hydrodynamics of the backwash cycle and may improve fouling mitigation. Second, introduce some sort of additional shear force or cross-flow into the system, such as an air sparge. As mentioned earlier, Ye et al. (2011) studied periodical backwash in a hollow-fibre membrane system. They found that air scouring during backwash assisted in membrane cleaning and introduced forces necessary to carry foulants away (Ye et al., 2011). Limitations of the UF membrane Type 1 setup did not allow for investigation into this type of turbulence for this membrane, but it was studied using UF membrane Type 2 (presented in Chapter 4).

### 3.2.3 Permeate water quality

The permeate water quality was monitored throughout each test. The initial grab sample began after 90 minutes of filtration and finished once the required volume was collected, which is equivalent to a throughput of 60-100L/m². A second sample was collected after approximately 18-20 hours of filtration, which is equivalent to approximately 650-1100L/m² (depending on the measured flow rate of the test and the time of the sample).

DOC, UVA-254 and Fe were measured in the feed and permeate samples. Results for DOC and UVA-254 are presented in Figure 3.6. DOC and UVA-254 values are expressed with respect to the initial value of the raw feed water, prior to EC pre-treatment. The measured concentrations of Fe in the permeate were all below 0.100mg/L Fe, indicating complete removal of iron from the feed water. Results do not conclusively demonstrate a significant difference in water quality between the initial and final permeate samples for the UF membrane Type 1 tests.

It was hypothesized that the formation of a filter cake may enhance NOM removal through formation of a dynamic membrane, as observed in literature (Chellam & Sari, 2016), however this does not appear to happen in this case. A
dynamic membrane is formed when particles are deposited on the membrane surface and assist in additional particle removal through interception and Brownian motion (Wiesner et al., 1989).

There is no significant difference in DOC results between initial and final permeate samples. There appears to be a difference between initial and final UVA-254 values for the test with continual filtration and the 60 minute filtration cycle with 5 minute backwash. However, recall that the (60-5) test had the lowest rate of resistance accumulation, which would imply that filter cake was the most porous.

If the filter cake had a significant impact on floc and NOM removal, then it would be expected that the final UF permeate sample in the continuous filtration test would have a significantly lower DOC and UVA-254 than all other tests, given that a continual filtration test would result in the most significant cake layer. As there is no strong pattern regarding additional NOM removal, this was not the case and these results are inconclusive.

There was also no detectable difference in water quality in the permeate when comparing continuous filtration tests and tests with backwash. This indicates that backwash does not cause significant changes to floc properties or perme-
ate water quality. The results of these tests indicate that within the parameters tested, all significant NOM removal occurs in the EC pre-treatment step and is not affected by backwash and filtration cycles settings.

Finally, SUVA was calculated for the permeate samples. SUVA is an expression of the ratio of DOC and UVA-254 in a water sample and is a measure of the DBP formation potential of the water (Hua et al., 2015). SUVA results for the initial and final permeate samples are presented in Figure 3.7.

These results suggest that there is no significant difference in SUVA between the initial and final UF permeate samples for these tests. The SUVA of the untreated, raw feed water was $4.08 \pm 0.17$, which is significantly higher than the reported permeate values. Therefore, the EC/UF system is able to produce water with a significantly lower SUVA than the initial value, and thus, with an expected lower DBP formation potential.

![Figure 3.7: SUVA of permeate samples in UF membrane Type 1 filtration tests](image)
Chapter 4

Results and discussion of synthetic water tests: UF membrane Type 2

Two types of UF membranes were evaluated in this work, however because they vary in material, geometry and pore size (MWCO), they will be discussed separately. This chapter presents water quality and membrane fouling results for UF membrane Type 2. A brief discussion comparing the test results for the two membrane types is presented in Section 4.3. A detailed comparison between the two membranes is not feasible as the differences in hydrodynamics and pore size and material prevent accurate or representative conclusions to be made.

UF membrane Type 2 is a 0.04µm, PVDF membrane with hollow-fibre geometry and outside-in flow configuration. Each membrane module consisted of 3 fibres, 19cm in length, that were submerged in a 500mL graduated cylinder kept at constant level throughout the duration of the test. The average working volume of the cylinder was 622cm³. Suction was applied to the module with a peristaltic pump to drive filtration through the membrane. The schematic and description of this setup is available in Section 2.3.2.

The effect of backwash and cross-flow through air sparging was investigated,
using EC pre-treated SR-NOM feed water. Natural surface water was also tested using UF membrane Type 2, with these results being presented separately in Chapter 5.

During the tests, the filtration flux was kept constant at $50 \pm 2.5$ LMH. The initial grab sample began after 90 minutes and finished once the required volume was collected, which is equivalent to a throughput of 60-100L/m$^2$. A second sample was collected after approximately 18-20 hours of filtration, which is equivalent to a throughput of approximately 650-1100L/m$^2$ (depending on the measured flow rate of the test and the time of the sample).

### 4.1 Filtration of raw water

As with UF membrane Type 1, an initial test was completed using UF membrane Type 2 to evaluate membrane performance and fouling rate during filtration of Raw water. The Raw water filtration test was completed to identify whether any NOM was removed by the filters themselves, without EC pre-treatment. The membrane pore size used in these tests was 0.04µm. As mentioned in Section 2.1, the synthetic feed was prepared using a stock solution of Suwannee River NOM (SR-NOM), that had been pre-filtered with a 0.45µm filter. Therefore, because UF membrane Type 2 had a pore size that was an order of magnitude smaller than that of the filter used to prepare the solution, it was expected that some of the higher MW fractions of NOM may be rejected by the membrane. Table 4.1 presents the water quality results for the direct filtration of Suwannee River NOM feed solution. These results indicate that there is no detectable significant difference in DOC for feed and permeate samples. UVA-254 values, however, suggest that the membrane is removing a small portion of the UV-absorbing compounds, as there appears to be a difference between the feed and permeate samples for UVA-254. HPSEC analysis of the feed and permeate samples is able to provide further insight to this observation, as presented in Figure 4.1.

There appears to be a difference in the permeate peaks in the higher MW
Table 4.1: Feed and permeate water quality for raw water filtration using UF membrane Type 2. Reported as average ± 95% confidence interval.

<table>
<thead>
<tr>
<th></th>
<th>DOC mg/L C</th>
<th>UVA-254 -</th>
<th>Fe - total mg/L Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw feed (batch)</td>
<td>4.94 ± 0.20</td>
<td>0.232 ± 0.004</td>
<td>&lt; 0.10</td>
</tr>
<tr>
<td>Initial UF permeate @75-100L/m²</td>
<td>4.66 ± 0.25</td>
<td>0.193 ± 0.015</td>
<td>&lt; 0.10</td>
</tr>
<tr>
<td>Final UF permeate @900-1100L/m²</td>
<td>4.84 ± 0.09</td>
<td>0.198 ± 0.005</td>
<td>&lt; 0.10</td>
</tr>
</tbody>
</table>

Figure 4.1: MWD of Suwannee River NOM feed water and UF permeate using UF membrane Type 2, by HPSEC.

fractions F4 and F5. Calculation of the % reduction in AMW fraction area (calculated as the sum of the areas of peaks assigned to each fraction) suggests a 11% removal of F4 and 17% removal of F5. These results suggest that the membrane may be able to remove a small fraction of the larger MW NOM, according to the MWD from HPSEC analysis. This was not observed during the raw water filtration using UF membrane Type 1. The difference in UVA-254 during filtration
with UF membrane Type 2 may be due to the difference in membrane pore size or MWCO. Both membrane types are classified as UF membranes. However, they vary in terms of nominal MWCO and pore size. UF membrane Type 1 is reported as having a MWCO of 300kDa; UF membrane Type 2 has a reported pore size of 0.04µm. The relationship between MWCO and pore size is non-linear and the actual MWCO may differ from the manufacturer stated value depending on NOM characteristics and properties (Cho et al., 2000). Therefore, pore size and MWCO would need to be measured directly to allow for direct comparison between the two membrane types. However, given the difference in permeate UVA-254, the possible difference in pore size between these two membranes may explain the difference in performance during filtration of raw water.

Another possibility is the membrane material. Gray et al. (2007) suggest that hydrophobic compounds are more likely to adsorb onto the inner pores of the membrane while hydrophilic compounds will form a gel layer and cause surface fouling. S. Lee et al. (2013) completed research comparing ceramic and polymeric membranes during filtration of NOM from source water. Part of the analysis was to compare the adsorption of Suwannee River Humic acid (SRHA) onto the membrane material in a batch test. Results indicated that the ceramic membrane had a much lower tendency to adsorb SRHA compared to the polymeric membranes used (S. Lee et al., 2013). Therefore, although it was assumed that NOM removal by membrane filtration was only based on size exclusion, the chemical and physical properties beyond MWCO may also play a role in membrane performance. Further investigation into these properties was beyond the scope of this project.

The TMP was also monitored throughout the raw water UF test to determine the extent of membrane fouling without EC pre-treatment during filtration of SR-NOM feed. The measured TMP and the initial membrane resistance were used to calculate the accumulated fouling resistance, as described in Section 1.2.4.

Experiments were completed at room temperature (22±2°C) and the dynamic viscosity was assumed constant at 0.9544mPa.s. The measured volumetric flow rate from each individual test was used to determine the membrane flux, J. The
accumulated fouling resistance during the raw water filtration tests is presented in Figure 4.2.

Figure 4.2: Fouling resistance during filtration of Raw water using UF membrane Type 2. Error bars represent calculated maximum and minimum $R_f$ for duplicate tests. Variation in first 150L/m$^2$ is due to changes in water level of membrane module cylinder, before automated water level was applied.

These results suggest that some degree of fouling is occurring during filtration of Raw SR-NOM feed water, as the general trend of fouling resistance is increasing. Linear regression of the UF membrane Type 2 SR-NOM raw water filtration test resulted in a calculated fouling rate of $(3.34 \pm 0.17) \times 10^8$ m$^{-1}$/Lm$^{-2}$ with an $R^2$ value of 0.9678. This slope is $(46 \pm 4)\%$ less than the calculated fouling rate of UF membrane Type 1 (a ceramic membrane). This was unexpected as ceramic membranes are reportedly less prone to fouling compared to polymeric membranes (S. Lee & Kim, 2014; S. Lee et al., 2013). Additional replicate raw water filtration tests are recommended to confirm these observations. However, a detailed analysis of the raw water filtration mechanism was beyond the scope of the experimental design.
4.2 Filtration of EC treated water

UF tests were completed with EC pre-treated feed water to evaluate the effect of filtration cycle backwash and air sparging on permeate water quality and UF membrane fouling rates. The procedure for preparing EC treated feed was discussed in Section 3.2.1. The only difference between preparation of EC pre-treated feed for UF membrane Type 2 tests was that a larger volume was required. Table 4.2 outlines the EC performance and results for EC pre-treated feed tests, presented and discussed previously in Section 3.2.1.

Table 4.2: EC treated UF feed water quality, presented previously in Section 3.2.1

<table>
<thead>
<tr>
<th></th>
<th>EC treated UF Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved Organic Carbon, mg/L C</td>
<td>3.66 ± 0.37</td>
</tr>
<tr>
<td>UV absorbance at 254nm</td>
<td>0.097 ± 0.014</td>
</tr>
<tr>
<td>pH</td>
<td>8.54 ± 0.24</td>
</tr>
<tr>
<td>Total iron, mg/L Fe</td>
<td>34.2 ± 1.28</td>
</tr>
<tr>
<td>Dissolved iron (0.45µm)</td>
<td>0.25 ± 0.10</td>
</tr>
<tr>
<td>SUVA</td>
<td>2.65 ± 0.46</td>
</tr>
</tbody>
</table>

Given the results from previous tests, it was expected that the DOC and UVA concentrations would not change significantly through UF membrane Type 2 filtration tests. The particulate iron was expected to be completely removed.

4.2.1 Membrane fouling during filtration of EC pre-treated feed

UF tests were completed using EC pre-treated feed to determine the effect of air sparging as a fouling mitigation technique. The combination of backwash and air sparge was also investigated.

Figure 4.3 presents the resistance accumulation data from the continual filtration tests using UF membrane Type 2. The resistance of raw water filtration using the same membrane is included in the graph for reference.
These results indicate that air sparging has a significant effect during continual filtration in terms of fouling mitigation. EC pre-treatment causes a significant increase in resistance accumulation compared to filtration of raw water, which agrees with results observed in the tests with UF membrane Type 1. Again, this is to be expected, given the concentration of iron particles in the EC treated water.

After approximately 700 L/m² of throughput, there appears to be a zone where the resistance accumulation rate seems to decrease for the test with EC pre-treated water (without air sparge). This is the point of system failure. The membrane had exceeded the TMP limit for suction of water and was unable to continually filter water at the defined flux of 50LMH.

The effect of backwash was also investigated. UF membrane Type 2 filtration tests were completed using backwash with and without air sparge. The TMP was monitored throughout the test and the accumulated resistance, $R_f$, was calculated according to the method described in Section 2.5.6. The resistance accu-
mulation results for UF membrane Type 2 tests using EC pre-treated SR-NOM feed is presented in Figure 4.4.

Figure 4.4: Fouling resistance during filtration of EC pre-treated water using UF membrane Type 2, with and without backwash, in presence and absence of air sparge. Filtration cycle was 30 minutes with period of 5 minute backwash. Total cycle duration was 35 minutes. Error bars have been omitted for clarity.

Results indicate that backwash improves fouling mitigation in cases with and
without air sparge. In the case without air sparge (Figure 4.4a), the use of backwash appears to successfully mitigate fouling for the first 100L/m², but then the accumulated resistance begins to increase at a rate similar to that of the continuous test without backwash. After this point, the degree of reversible hydraulic fouling appears to increase: the final $R_f$ point is increasingly greater than the point at the start of the cycle, for each subsequent cycle. However, the overall rate of resistance accumulation follows the same trend as the test without backwash. This suggests that the filter cake that accumulated on the membrane during filtration was released from the membrane during the backwash stage, but was re-established once the next filtration cycle began. This suggests that the cake fouling with EC pre-treated feed is reversible, but another process may be required to sweep the cake away from the membrane before the next filtration cycle begins.

The effect of this sweeping force is evident in the tests with air sparging (Figure 4.4b). The overall fouling rate for both tests with air sparge is much lower than the tests without air sparge. However, the combination of backwash and air sparge effectively eliminates fouling compared to the other test conditions. This improved mitigation with air and backwash could be because air bubbles from the sparge were ineffective at removing small particles that may have been attracted to the membrane. The backwash step may be responsible for dislodging particles that were stuck to the membrane surface, improving the overall fouling mitigation for the process.

Linear regression was performed on the linear portion of the data for all tests. Results from linear regression are presented in Table 4.3. Examination of these results suggest that the optimal method of fouling mitigation for this system is a combination of backwash and air sparge. Backwash resulted in minimal fouling rate decrease compared to the test without backwash ($2 \pm 6\%$). Air sparging alone resulted in a $(64 \pm 2)\%$ decrease in overall fouling rate (slope) while air sparging combined with backwash resulted in a decrease of $(98 \pm 1)\%$.

Air sparging is effective in fouling mitigation but it may also have an effect
Table 4.3: Linear regression for UF membrane Type 2 filtration tests reported with 95% confidence interval. For tests with backwash, regression is performed on data point logged at the end of the filtration cycle.

<table>
<thead>
<tr>
<th>Test Setting</th>
<th>Slope, $\frac{m^{-1}}{L.m^2}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC, No backwash, no air</td>
<td>$(5.47 \pm 0.30) \times 10^9$</td>
<td>0.9599</td>
</tr>
<tr>
<td>EC, With backwash, no air</td>
<td>$(5.30 \pm 0.16) \times 10^9$</td>
<td>0.9923</td>
</tr>
<tr>
<td>EC, No backwash, with air</td>
<td>$(1.97 \pm 0.03) \times 10^9$</td>
<td>0.9961</td>
</tr>
<tr>
<td>EC, With backwash, with air</td>
<td>$(0.09 \pm 0.032) \times 10^9$</td>
<td>0.4598</td>
</tr>
<tr>
<td>Raw water, no backwash, no air</td>
<td>$(0.33 \pm 0.017) \times 10^9$</td>
<td>0.9678</td>
</tr>
</tbody>
</table>

on the size and properties of the flocs. Vigorous air sparging may introduce enough turbulence in the UF feed to break apart the EC flocs. Jarvis et al. (2005) investigated floc strength and regrowth of NOM flocs using different kinds of chemical coagulants. The authors concluded that the type of coagulant used may affect floc properties such as size, resistance to breakage, and ability to regrow after breakage occurs (Jarvis et al., 2005). Floc size, breakage, and regrowth was not investigated here, but given the chemical complexity of EC produced flocs, it would be valuable to investigate this topic further.

Nevertheless, these results are promising as they suggest that a water treatment system using conventional fouling mitigation techniques would be able to operate for a long time without stopping to perform more intensive chemical cleaning. There does not appear to be any fatal flaws in the process when pre-treating with iron EC. However, in this work, only one sparge condition was tested. More research could be done to optimize the conditions for fouling mitigation for EC pre-treated feed using air sparging. For example, pulse bubble sparging may be even more effective than continuous bubble sparging (Jankhah & Bérubé, 2014). Furthermore, introducing air to a system with EC pre-treated solids may cause chemical and physical changes in the properties of the flocs. This is discussed further in Section 4.2.2.
4.2.2 Permeate water quality

The permeate water quality was monitored throughout each test. The initial grab sample began after 90 minutes of filtration and finished once the required volume was collected, which is equivalent to a throughput of 60-100L/m$^2$. A second sample was collected after approximately 18-20 hours of filtration, which is equivalent to approximately 650-1100 L/m$^2$ (depending on the measured flow rate of the test and the time of the sample). DOC, UVA-254 and Fe were measured in the feed and permeate samples. Results for DOC and UVA-254 are presented in Figures 4.5a and 4.5b respectively. DOC and UVA-254 values are expressed with respect to the initial value of the raw feed water, prior to EC pre-treatment. The measured concentrations of Fe in the permeate were all below 0.100mg/L Fe, indicating complete removal of iron from the feed water.

![Normalized DOC and UVA-254 for UF Membrane Type 2 permeate samples during filtration of EC pre-treated SR-NOM feed.](image)

For the tests without air sparge, there is no observable trend in changes to DOC between the initial and final UF permeate samples. There does appear to be a difference between initial and final UVA-254 values for the test with continual filtration. This was also observed during the continual filtration test using UF membrane Type 1. This suggests that the filter cake may be contributing to improved removal of UV-absorbing compounds. However, additional replicate
tests would be required to make a stronger conclusion.

As for the tests with air sparge, results suggest a significant increase in DOC and UVA-254 in the UF permeate between the initial and final samples. The results from these two tests are very interesting. The average UF feed DOC $C/C_0$ was $0.72 \pm 0.11$. The average UVA-254 $C/C_0$ was $0.45 \pm 0.18$. These values are much higher than the respective measurements for the initial UF permeate samples for the tests with air sparge. This suggests that the air sparge has an additional effect on NOM removal at the start of the test.

The additional initial NOM removal may be due to two possible explanations. First, the turbulence from the air sparge may cause improved mixing of the flocs in the UF feed cylinder, allowing for better mixing and adsorption of NOM by the produced EC solids. However, floc strength and size was not measured. The second possibility is that the air sparge is introducing additional oxygen to the system, oxidizing any ferrous iron in the feed water to ferric iron. This would induce formation of ferric hydroxide species. As mentioned in Chapter 1, previous researchers have suggested that a steady flow of oxygen is required for an effective electrocoagulation process (Timmes et al., 2010). This could be further investigated by studying the speciation of iron in the UF feed over time and repeating the test with a nitrogen sparge, isolating the UF feed from oxygen and observing the results of performing the test under an inert atmosphere.

The error bars for the tests with air sparge are large, indicating high variability in the measured results. An improvement of this test would be to repeat the test conditions but with better control on the degree of air sparging and improved purity of the air line, to better control systematic error.

The low permeate concentrations do not stay constant throughout the tests, as the final UF permeate samples for the tests with air sparge are much higher than the initial values. This trend is exhibited in both DOC and UVA-254 data, suggesting that although additional NOM removal is initially occurring, with time, the captured NOM is either re-released into solution or the rejected NOM is building up in the feed cylinder and ends up permeating the membrane.
To understand this change in water quality throughout the filtration tests, the UF feed samples were analysed. HPSEC analysis of the feed and permeate samples was used to understand this change in NOM in the feed and permeate concentrations. The apparent molecular weight of the feed and permeate samples was examined for UF membrane Type 2 tests with and without air sparge. These results are presented in Figure 4.6.

Figures 4.6a and 4.6b confirm the observations made for the tests without air sparge: there does not appear to be a significant difference between the UF feed and UF permeate samples. Figures 4.6c and 4.6d, however, suggest a different
story for the tests with air sparge. The initial sample (presented in Figure 4.6c) appears to have a significant difference between the early UF feed and the UF permeate samples, across all AMW fractions. However, at the end of the test, the results indicate that the NOM fractions that are causing the increased feed and permeate concentrations are the lower MW fractions. The fraction captured by the EC treatment is not released back into solution. Therefore, the lower MW fractions are building up in the feed concentration and permeating the membrane. Because this was not observed in the tests without air sparge, we must conclude that the air sparge is the source of this change in behaviour.

DOC and UVA-254 as a function of throughput is presented in Figure 4.7 for UF membrane Type 2 tests with air sparge. Additional samples, beyond the initial and final samples, were collected for the test with backwash to track the feed and permeate water quality in greater detail throughout the test. These results highlight a number of interesting features. First, the feed sample for the test without backwash had higher reported DOC and UVA-254 than the test with backwash. This is likely due to the inherent dilution of the backwash setup. Backwash was performed with permeate water, that was pumped directly into the feed cylinder without a bleed and refill step between each filtration cycle. Therefore, the feed for the test with backwash would have a lower concentration than the test with backwash.

Second, the DOC and UVA-254 increased in the feed and permeate throughout both tests and there is a significant difference between the feed and permeate concentrations for both tests. Therefore, in this case, UF membrane Type 2 is removing additional NOM compared to the standard 0.45 µm syringe filter used to prepare the UF feed/EC effluent samples. As discussed previously, the air sparge may be causing a chemical change in the flocs, allowing them to capture more NOM. However, because the enhanced NOM removal is only detected in the permeate samples, the particles responsible for capturing the additional NOM must be small enough to permeate the standard syringe filter, but too large to escape the 0.04 µm membrane.
Therefore, the EC/UF system with air sparge appears to successfully improve NOM removal compared to other filtration systems without air. Operation of the system at a pilot scale with continual bleed from the UF cylinder would provide more information about the changes in the UF feed and permeate composition. Further analysis of the system and investigation into the effect of air sparge is recommended.
4.3 Comparison of UF membrane systems

A comparison of the two UF membrane systems was also performed, to evaluate the difference in performance between the two membrane types.

4.3.1 Membrane fouling comparison

Figure 4.8 presents the accumulated resistance data for the filtration tests with matching conditions using UF membranes Type 1 and Type 2. These matching conditions include: continual filtration of raw water, continual filtration of EC pre-treated water, and filtration with 30 minute filtration cycle and 5 minute backwash for EC pre-treated water.

![Figure 4.8: Resistance accumulation comparing UF membranes Type 1 and 2 for Raw and EC pre-treated feed water for cases without backwash (a) and with backwash (b). Error bars represent the calculated $R_f$ error, based on the maximum and minimum value of the parallel tests.](image)

The result of linear regression analysis of these six tests is presented in Table 4.4. According to the 95% confidence intervals for the calculated values, the fouling rates for each of these test settings is uniquely different and there is a significant difference in the fouling accumulation rates of UF membranes Type 1
and Type 2. The fouling rate for UF membrane Type 1 is \((5.1 \pm 0.3)\%\) less than that of UF membrane Type 2 for the continuous filtration tests (without backwash). The fouling rate for UF membrane Type 1 is \((51 \pm 3)\%\) less than that of UF membrane Type 2 for the tests with backwash.

Table 4.4: Linear regression and \(R^2\) values for resistance accumulation for filtration with UF membranes Type 1 and Type 2.

<table>
<thead>
<tr>
<th></th>
<th>Slope, (\frac{m^{-1}}{L.m^{-2}})</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF1-EC-continuous</td>
<td>((5.11 \pm 0.05) \times 10^9)</td>
<td>0.9987</td>
</tr>
<tr>
<td>UF2-EC-continuous</td>
<td>((5.47 \pm 0.30) \times 10^9)</td>
<td>0.9599</td>
</tr>
<tr>
<td>UF1-raw-continuous</td>
<td>((0.62 \pm 0.03) \times 10^9)</td>
<td>0.9487</td>
</tr>
<tr>
<td>UF2-raw-continuous</td>
<td>((0.33 \pm 0.02) \times 10^9)</td>
<td>0.9678</td>
</tr>
<tr>
<td>UF1-EC-BW(30-5)</td>
<td>((2.57 \pm 0.15) \times 10^9)</td>
<td>0.9666</td>
</tr>
<tr>
<td>UF2-EC-BW(30-5)</td>
<td>((5.30 \pm 0.16) \times 10^9)</td>
<td>0.9923</td>
</tr>
</tbody>
</table>

The difference between the two membrane types could be explained by a number of factors. First, the membrane material is different, and different membrane materials have different fouling tendencies (S. Lee & Kim, 2014). Second, the pore sizes are different; UF membrane Type 2 has a tighter pore size than UF membrane Type 1, which would result in a higher overall membrane resistance. Third, the hydrodynamics of the two modules are completely different, which will affect membrane fouling and backwash efficiency (Shi et al., 2014).

UF membrane Type 1 is a small chamber that holds approximately 3.3mL of feed water. Water is fed through a \(1/4\)" diameter opening from the centre top of the module and the flow then rapidly expands to the full diameter of the module, approximately 41mm. Rapid expansion, even at low flow rate, results in a turbulent flow pattern. The flow would not be considered fully developed until a distance of 60X the initial pipe diameter. This turbulence induces shear and back-transport on the surface of the membrane, which would lower the overall fouling rate.

UF membrane Type 2 is housed in a large cylinder that holds approximately
622mL of water. Feed water was fed through a 1/4” hose immersed approximately 10cm below the water level in the cylinder. Without the use of induced shear through air sparge or mechanical agitation, hollow fibre dead-end membranes have very poor back-transport (Belfort et al., 1994; Ye et al., 2011). The inertial lift caused by particles and turbulent flow in the UF membrane Type 1 module may be the cause of the lower fouling rates during filtration of EC pre-treated feed, but a more in-depth study on the properties of the membranes is required to make strong conclusions.

These factors may help explain the overall difference in performance between the two membranes. However, complete calculation and characterization of the fluid dynamics of these membrane systems is beyond the scope of this project.

### 4.3.2 Permeate water quality comparison

The difference in permeate water quality was presented previously when each membrane type was discussed individually. Comparison here is made to highlight the differences, if any, in membrane performance in terms of water quality.

Water quality for raw water filtration tests is presented in Figure 4.9. Results

![Figure 4.9: Permeate water quality during raw water filtration: comparison of UF membranes Type 1 and Type 2](image)
indicate that there is no significant difference between the two membranes in terms of DOC removal but there appears to be a slight difference in terms of UVA removal between UF membranes Type 1 and Type 2. This difference was discussed previously, in Section 4.1, this could be due to the differences in the chemical properties of the membranes. However, further analysis of these properties would be required to make a stronger conclusion.

Water quality for EC pre-treated UF tests is presented in Figure 4.10. Here, there does not appear to be a significant different between the two types, however there does appear to be a difference between the initial and final UVA-254 values for the tests with continual filtration. This was already discussed in Section 4.2.2. Comparison of the permeate results for EC pre-treated feed to the raw water permeate (Figure 4.9) suggests that the fraction of UV-absorbing material that was removed by UF membrane Type 2 is captured in the EC pre-treatment step. There is no significant difference in the permeate water quality of these membranes under the conditions tested.

![Figure 4.10: Permeate water quality during EC pre-treated water filtration: comparison of UF membranes Type 1 and Type 2, during filtration with and without backwash (30 min cycle + 5 min backwash)](image)

Finally, SUVA was calculated for the permeate samples. SUVA results for the initial and final permeate samples are presented in Figure 4.11. These results
suggest that there is no significant difference in SUVA between the initial and final UF permeate samples for these tests. The SUVA of the untreated, raw feed water was $4.08 \pm 0.17$, which is significantly higher than the reported permeate values. Therefore, regardless of membrane type, the EC/UF system is able to produce water with a significantly lower SUVA than the initial value, and thus, with a potentially lower DBP formation potential.

![Graph showing SUVA comparison](image)

(a) UF membrane Type 1  
(b) UF membrane Type 2

Figure 4.11: SUVA of UF permeate: comparison of UF membranes Type 1 and Type 2, during filtration with and without backwash (30 min cycle + 5 min backwash)

The results from these tests are important because they suggest that the EC pre-treatment step is the more important step in the hybrid EC/UF process. There is no significant difference in membrane permeate water quality, and therefore when designing a drinking water treatment system, the decision for which membrane to use does not have to be based on permeate water quality for NOM removal. It should instead be based on membrane fouling rates and simplicity of fouling control. In order to optimize the membrane system, other EC settings would need to be investigated as well as further study to optimize backwash.
Furthermore, these results are based on treatment of a synthetic surface water, that was prepared using only the soluble fraction of Suwannee River NOM. As the chemical and physical properties of NOM vary significantly depending on water source, it is also important to observe how the system responds to real water samples. One EC/UF test was completed using natural surface water. The results from this test are presented in Chapter 5.
Chapter 5

Results and Discussion of natural surface water test

Natural surface water was collected from Middle River, British Columbia and was treated with the EC/UF hybrid system. A single test condition was applied to evaluate the general performance of the EC/UF process using natural surface water as the feed water. See Section 2.2 for a description of the feed water collection and source water quality results. A summary of the results for EC pre-treatment of natural surface water are presented in Table 5.1, alongside the synthetic surface water results for comparison.

These results indicate that the EC settings used were not optimal for this type of water, as the DOC removal was low for the natural surface water feed (approximately 12%). McBeath (2017) observed (33.7 ± 4.8)% reduction in DOC and a (48.1 ± 2.7)% reduction in UVA-254 when treating surface water with the same continuous flow EC reactor as the one used in this work, at a flow rate of 10 LPM. The OP for McBeath’s system was 7V to 14V and the current density was 7.35 mA/cm². The DOC removal of the natural surface water is less than the removal achieved by McBeath, however UVA-254 removal was significantly higher. High UVA-254 removal indicates that there may be variation in the NOM structure and properties, which affect NOM removal by EC.
Table 5.1: EC test result summary for treatment of natural surface water, with an operating current density of 6.43mA/cm² and target metal loading of 35mg/L Fe

<table>
<thead>
<tr>
<th></th>
<th>Synthetic surface water</th>
<th>Natural surface water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final DOC, mg/L C</td>
<td>3.66 ± 0.37</td>
<td>4.89 ± 0.20</td>
</tr>
<tr>
<td>% removal DOC</td>
<td>33%</td>
<td>12%</td>
</tr>
<tr>
<td>Final UVA-254</td>
<td>0.097 ± 0.014</td>
<td>0.063 ± 0.044</td>
</tr>
<tr>
<td>% removal UVA-254</td>
<td>57%</td>
<td>67%</td>
</tr>
<tr>
<td>Final pH</td>
<td>8.54 ± 0.24</td>
<td>7.07</td>
</tr>
<tr>
<td>Initial SUVA</td>
<td>4.08</td>
<td>3.38</td>
</tr>
<tr>
<td>Final SUVA</td>
<td>2.65</td>
<td>1.28</td>
</tr>
<tr>
<td>EC current efficiency, (\phi)</td>
<td>95%</td>
<td>89%</td>
</tr>
</tbody>
</table>

The natural surface water EC test had a lower current efficiency than the synthetic surface water. The measured operation potential (OP) during the EC test with the natural surface water was in the range of 11.9V to 12.5V. The OP for the synthetic surface water EC tests ranged from 5.7V to 9.4V. Therefore, the resistance in the natural surface water EC test was much higher than the synthetic surface water tests.

An important difference between the two water sources is the water matrix. The synthetic surface water was prepared using only sodium salts of sulphate, chloride and bicarbonate. The natural surface water likely contained other cations such as magnesium and calcium (not measured). The natural surface water also contained significantly lower sulphate and chloride concentrations, which would explain the higher OP during the EC test; the operation potential (or voltage) is inversely related to resistance (as defined by Ohm’s Law). High ion concentrations imply higher ionic strength, which would result in reduced repulsive forces between molecules (\(\zeta\)-potential) and improved flocculation (Crittenden et al., 2012a). The composition of the two different feed waters are available in Tables 2.1 and 2.2.

Other compounds found in surface water may also affect NOM removal by EC. For example, Dubrawski et al. (2013) observed reduced NOM removal with
increasing carbonate concentration in EC tests with an iron anode and Suwannee River NOM. Nevertheless, the EC effluent from the natural surface water feed underwent filtration by UF membrane Type 2, which is discussed in the next section.

5.1 Membrane fouling

One UF test setting was completed to investigate the general effect of feed water on the EC/UF system performance. UF membrane Type 2 was used, with a 30 minute filtration cycle and 5 minute backwash. Figure 5.1 presents the membrane resistance accumulation for the natural surface water test, compared to UF membrane Type 2 tests completed with EC pre-treated synthetic feed water and backwash.

These results highlight the significant difference between the flocs produced with the different feed types. When only backwash was applied, the natural feed water had significantly lower fouling compared to the synthetic feed water. Membrane fouling for the natural surface water test with only backwash was comparable to the synthetic surface water results that incorporated both backwash and air sparge. Table 5.2 reports the linear regression results for determining the rate of resistance increase during filtration of EC pre-treated synthetic and natural feed water.

Table 5.2: Linear regression of EC pre-treated synthetic and natural feed water filtration using UF membrane Type 2, with 95% confidence intervals. Linear regression is based on data points collected at the end of each filtration cycle.

<table>
<thead>
<tr>
<th>Water source</th>
<th>Slope, $m^{-1} L.m^{-2}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic feed water SR-NOM, EC + BW</td>
<td>$(5.30 \pm 0.16) \times 10^9$</td>
<td>0.9923</td>
</tr>
<tr>
<td>Synthetic feed water SR-NOM, EC + BW + air</td>
<td>$(0.089 \pm 0.032) \times 10^9$</td>
<td>0.4598</td>
</tr>
<tr>
<td>Natural Surface Water, EC + BW</td>
<td>$(0.239 \pm 0.024) \times 10^9$</td>
<td>0.9197</td>
</tr>
</tbody>
</table>
These results suggest that feed water quality has a significant impact on UF fouling rates. The fouling rate of the natural surface water test was $(95 \pm 0.5)\%$ lower than the synthetic feed water test, under identical conditions. The test with synthetic feed water and air sparge (Synthetic feed water, SR-NOM, EC + BW + air) still had the lowest fouling rate of the three tests, suggesting that air sparge is still required to optimise fouling minimisation.

During the experiment, the foulant layer was observed as a large fluffy layer of flocs that accumulated on the surface of the membrane. At the end of the filtration cycle the flocs were adhered to the fibre, however the cake must have been extremely permeable because the resistance accumulation rate of the synthetic surface water was significantly higher than the natural surface water. This could be due to the structure of the flocs, causing a more permeable cake. Ad-
ditional tests with the natural surface water and air sparge would provide more information on the effect of air sparge to help optimise fouling mitigation.

Resistance accumulation for the natural surface water is presented in Figure 5.2. These results indicate that both reversible and irreversible fouling is occurring. The calculated average resistance recovery for this test was (22 ± 4)%, which is significantly higher than the calculated recovery of the synthetic feed water tests. The resistance recovery results of the UF membrane Type 2 backwash tests are presented in Figure 5.3. These results support the observation that there is a significant difference in the relative resistance recovery between the three different settings tested. Comparing the mean resistance recoveries for the three backwash settings for this system resulted in a calculated F-value of 13.0 and a p-value of < 0.001. The F-critical value for this analysis was 3.42 (assuming 95% confidence, α = 0.05). Therefore, these calculated means are sig-
significantly different and feed water matrix and floc properties have a significant impact on membrane recovery during filtration of EC pre-treated feed.

The higher relative resistance recovery for the natural surface water test indicated that backwash efficiency is also affected by floc characteristics and feed water matrix. These results imply that complicated air sparge systems may not be necessary depending on the type of floc produced. To further expand this research and understand the effect of source water quality on EC/UF process performance, it is recommended to investigate further the floc properties such as $\zeta$-potential and particle size distribution in the UF feed water and how these properties affect membrane fouling.

Ulu et al. (2014) evaluated floc formation through measurement of $\zeta$-potential and particle size distribution measurements in a 50ppm humic acid solution treated with iron and aluminum EC. They concluded that the floc size evolution does not only depend on solution chemistry, but also on flocculation conditions such as shear and flocculation time. For iron EC produced flocs, a maximum floc size was observed, at which point the $\zeta$-potential underwent reversal and the shear
force exceeded floc strength and led to breakage (Ulu et al., 2014). A valuable contribution to the field would be to further examine the effect of EC-produced floc size and characteristics on UF process efficiency.

5.2 Permeate water quality

The permeate water quality was monitored throughout the test. The initial grab sample began after 90 minutes of filtration and finished once the required volume was collected, which is equivalent to a throughput of 60-100L/m². A second sample was collected after approximately 18-20 hours of filtration, which is equivalent to approximately 650-1100L/m² (depending on the measured flow rate of the test and the time of sampling).

DOC, UVA-254 and Fe were measured in the feed and permeate samples. Results for DOC and UVA-254 are presented in Figure 5.4. DOC and UVA-254 values are expressed with respect to the initial value of the raw feed water, prior to EC pre-treatment. The measured concentrations of Fe in the permeate were all below 0.100mg/L Fe, indicating complete removal of iron from the feed water. Results are presented alongside the EC pre-treated synthetic feed permeate water quality results for comparison.

These results indicate that there is no significant difference in permeate water quality when comparing the two source feed waters. The filter cake does not appear to contribute to NOM removal, as there is no significant difference between initial and final DOC or UVA-254 for either test.

However, recall that the DOC removal by EC pre-treatment was 12% (as measured in a 0.45µm filtered sample immediately after EC treatment). This would indicate that NOM removal is enhanced through membrane filtration. As noted in Figure 5.4a, the DOC removal in the permeate samples was approximately 44% (compared to DOC in raw feed water). However, a feed sample was taken during the final permeate sample and the measured concentration was 3.89 ± 0.20. The DOC of the corresponding permeate sample was 3.12 ± 0.20 mg/L. This suggests
Figure 5.4: Normalised DOC and UVA-254 for UF Membrane Type 2 permeate samples during filtration of EC pre-treated natural surface water feed and synthetic feed water

that the UF feed DOC may be decreasing with time, but since only one UF test condition was evaluated with this feed, additional tests should be completed to confirm these results.

Nevertheless, the source feed water type does not seem to affect the UF permeate water quality when comparing synthetic and natural surface water sources. This is indicative of a robust system, however it is recommended that additional EC and UF conditions be tested with natural surface water sources to better understand the system.
Chapter 6

Conclusion

This research combined iron electrocoagulation (EC) and ultrafiltration (UF) to treat synthetic and natural surface waters in order to remove Natural Organic Matter (NOM). This work is especially valuable for the development of small water systems for remote communities, which have historically been subject to drinking water advisories due to poor water quality or insufficient treatment. The EC/UF system has the potential to effectively treat surface water, however, very little research has been completed on the effect of hydraulic controls for UF membrane fouling mitigation of EC pre-treated water. This knowledge gap has been addressed in this work.

6.1 Summary of results

Fixed EC conditions were applied to the feed water in a continuous-flow EC reactor, at a flow rate of 1 LPM and an applied current of 2 A. The EC effluent acted as the feed water for the UF systems. The membranes types used were: (1) A 300kDa ceramic disk membrane, operated in a dead-end flow configuration; and, (2) a 0.04μm PVDF hollow-fibre membrane operated as a submerged membrane system with outside-in flow. Both systems were operated at a constant flux of 50 LMH. Periodic backwash cycles were applied to evaluate the effect of back-
washing on the overall membrane fouling rates. The backwash intensity was kept constant at approximately 120% of the filtration flux. Air sparging was also applied to the hollow-fibre PVDF membrane as a method of fouling mitigation.

EC treatment of synthetic surface water resulted in average DOC removal of $33 \pm 4\%$ and UVA-254 removal of $57 \pm 8\%$. Average SUVA went from $4.08 \pm 0.17$ in the feed to $2.65 \pm 0.46$ in the permeate. The decrease in SUVA is due to removal of the UV-absorbing fraction of NOM, which could reduce the disinfection byproduct formation potential of the treated water. The average concentration of total iron in the EC effluent was $34.2 \pm 1.3$mg/L, corresponding to a 95% current efficiency.

For the ceramic disk membrane, periodic backwash was demonstrated to decrease the overall fouling rate during filtration of EC pre-treated feed, compared to tests without backwash. Filtration of raw water indicated that NOM was not removed by the membrane, and instead was captured by EC flocs, which were then filtered out. There was no significant difference between the initial and final UF permeate samples, indicating that the development of a filter cake layer did not contribute to additional floc or NOM removal.

For the PVDF hollow-fibre membrane, both backwashing and air sparging were applied as fouling mitigation techniques. Backwashing on its own resulted in minimal fouling rate decrease. However, air sparging resulted in reducing the overall fouling rate by $(64 \pm 2)\%$. The combination of air sparging and backwashing reduced the overall fouling rate by $(98 \pm 1)\%$. The EC/UF test with air sparging and backwash also resulted in additional NOM removal from the UF feed by the membrane (not observed in the tests without air sparging). DOC in the treated water was reduced from $4.69 \pm 0.20$mg/L in the UF feed (EC effluent) sample to $1.24 \pm 0.11$mg/L in the UF permeate. UVA-254 was reduced from $0.170 \pm 0.04$ to $0.020 \pm 0.008$. Therefore, air sparging appears to have a significant effect on membrane fouling and permeate water quality.

A single test condition using natural surface water was also completed. Applying backwash to the EC/UF test with natural surface water resulted in a $(95 \pm 92$
0.5)\% lower fouling rate compared to the EC/UF test with synthetic feed water test under the same conditions. Therefore, water composition has a significant effect on the membrane fouling rates of the EC/UF system.

6.2 Recommendations for future work

This research provides promising results for the development of a EC/UF water treatment system. However, this research can be expanded to better understand the system. The effects of air sparging on the feed water chemistry should be investigated further. This could be done by examining floc size and strength as well as changes in $\zeta$-potential during air sparge of Fe EC treated water. It is recommended that compressed air, high purity air and nitrogen sparging be investigated to evaluate the effect of oxygen on the sparging process.

Development of a pilot scale UF system is also recommended. The EC unit used in this work has already been investigated at the pilot scale (McBeath, 2017). Addition of a UF module to the pilot system would provide the opportunity to evaluate the EC/UF process in a mode more closely resembling real-life applications. A pilot-scale EC/UF unit would also provide more information on the effect of feed water quality on process performance, as the pilot would be applied to natural feed water sources. The membrane type did not appear to have an effect on the permeate water quality, therefore selection of the membrane to be used in the pilot system should be motivated by the ability to easily implement hydraulic controls such as air sparging.

Finally, remote communities often have unreliable power supplies, and may rely on diesel generators for power production. Investigation into using alternative energy sources to power the EC unit and methods of low-energy, passive filtration may make this process more attractive to remote communities.
References


Humbert, H., Gallard, H., Jacquemet, V., & Croué, J. P. (2007). Combination of coagulation and ion exchange for the reduction of UF fouling properties of


