

ANION EXCHANGE RESIN TECHNOLOGY FOR NATURAL ORGANIC MATTER
REMOVAL FROM SURFACE WATER

by

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Abstract

Natural organic matter (NOM) is present in all surface waters as a result of decaying vegetation, biological activity, and organic soil. Alternative NOM removal processes such as anion exchange resins (AERs) have shown NOM removals typically ranging between 50 to 90%, with up to 99% removal achieved in some cases.

The first portion of this study evaluated the performance of two AERs; a conventional Type 1 AER and magnetic ion exchange resin (i.e. MIEX[®]) for NOM removal from surface water quantified by UV254, dissolved organic carbon (DOC), and specific UV absorbance (SUVA). Samples were also characterized for chloride, sulphate, and chloride-to-sulphate mass ratio (CSMR) to provide additional information on water quality characteristics of AER treated waters. Overall, the results showed that both AERS were effective for removing NOM. However, the MIEX[®] resin provided greater removal of NOM with shorter contact times compared to the conventional resin investigated. Water treated with MIEX[®] resin showed significantly higher chloride and lower sulphate concentrations than the conventional AER. Higher CSMR values were found with MIEX[®] treated water compared to conventional AER system, although both resins showed CSMR much greater than 0.5, which can increase galvanic corrosion effects with lead.

Bench-scale jar tests were conducted to investigate the impact of temperature on the efficacy of three NOM removal treatment technologies; enhanced coagulation with alum, MIEX[®] and a combined MIEX[®] treatment followed by coagulation with a low dose of alum. Higher settled water turbidity was observed during cold water operating conditions for all three processes. At cold-water operating conditions, DOC removal was reduced with combined MIEX[®]-Alum treatment, and UV254 removal was impacted for both MIEX[®] and MIEX[®]-Alum processes. The combined MIEX[®]-Alum process was found to provide the lowest THMFP and HAAFP at both temperatures to concentrations lower than current regulatory maximum acceptable concentration (MAC) guidelines in Canada.

Surface charge analysis experiments were performed at bench-scale using synthetic water containing humic acid to determine the relationship between NOM and the charge of AER-treated waters. Further bench and pilot-scale studies were performed to investigate the use of surface charge measurements to monitor and optimize NOM removal during treatment with AER systems. Strong correlations were observed between UV254 and respective charge measurements (i.e. ZP, SC) of AER-treated synthetic and raw waters. The results of this research has shown that it is possible to use charge to optimize the MIEX[®] process for NOM removal. Additionally, it was found that SC measurements could be used as an operational tool for AER processes, where deviations in SC from optimum treatment would indicate the requirement for fresh resin addition or resin regeneration.

List of Abbreviations and Symbols Used

AER – Anion Exchange Resin

Al – Aluminum

Al₂(SO₄)₃ – Aluminum Sulphate (Alum)

Al(OH)₃ – Aluminum Hydroxide

Br₂CHCO₂H – Dibromoacetic Acid

BV – Bed Volume

CaCO₃ – Calcium Carbonate (alkalinity)

Ca²⁺ - Calcium

CCl₃CO₂H – Trichloroacetic Acid

CDWQG – Canadian Drinking Water Quality Guidelines

CH₃ – Methyl Group

CHBr₃ – Bromoform

CHBr₂Cl – Dibromochloromethane

CH₂BrCO₂H – Monobromacetic Acid

CHCl₃ – Chloroform

CHCl₂Br – Dichlorobromomethane

CHCl₂CO₂H – Dichloroacetic Acid

CH₂ClCO₂H – Monochloroacetic Acid

CH₃CH₂OH - Ethanol

Cl⁻Chloride Ion

CSMR – Chloride to Sulfate Mass Ratio

CSTR – Continuously Stirred Tank Reactor

CTAB - Cetyl Trimethylammonium Bromide

Da – Dalton

DAF – Dissolved Air Flotation

DBP – Disinfection By-Product

DBPFP – Disinfection By-Product Formation Potential

DLVO – Derjaguin and Landau, Verwey and Overbeek

DOC – Dissolved Organic Carbon

DVB - Divinylbenzene

ES – Effective Size

GAC – Granular Activated Carbon

H_2SO_4 – Sulfuric Acid

HAA – Haloacetic Acid

HAAFP – Haloacetic Acid Formation Potential

HCl – Hydrochloric Acid

HIA – Hydrophilic Acid

HIB – Hydrophilic Base

HIN – Hydrophilic Neutral

HMW – High Molecular Weight

HOA – Hydrophobic Acid

HOB – Hydrophobic Base

HOCl – Hypochlorous Acid

HON – Hydrophobic Neutral

IC – Ion Chromatography

IMW – Intermediate Molecular Weight

IX – Ion Exchange

L - Litre

LMW – Low Molecular Weight

MAC – Maximum Acceptable Concentration

MCL – Maximum Contaminant Level

meq – Milliequivalents

mg/L – Milligrams per Litre

MIEX® – Magnetic Ion Exchange

min - Minute

mL – Millilitre

μm – Micrometer

MW – Molecular Weight

mV - Millivolts

NaCl – Sodium Chloride

Na₂CO₃ – Sodium Carbonate (Soda Ash)

NaHCO₃ – Sodium Bicarbonate

NaOH – Sodium Hydroxide

NH₄OH – Ammonium Hydroxide

NOM – Natural Organic Matter

NTU – Nephelometric Turbidity Unit

OCl⁻ – Hypochlorite Ion

OH⁻ - Hydroxide Ion

PACl – Polyaluminum Chloride

pH – Potential Hydrogen

pKa – Acid Dissociation Constant

polyDADMAC - Polydiallyldimethylammonium chloride

RO – Reverse Osmosis

RSO₃⁻ - Sulfonate Functional Group

RCOO^- - Carboxylate Functional Group

$\text{R}(\text{CH}_3)_3\text{N}^+$ - Quaternary Amine Functional Group

rpm – Revolutions Per Minute

SAC – Strong Acid Cation Exchange Resin

SBA – Strong-Base Anion Exchange Resin

SC – Streaming Current

SCM – Streaming Current Meter

SCD – Streaming Current Detector

SO_4^{2-} - Sulfate Ion

SUVA – Specific UV Absorbance

THM - Trihalomethane

THMFP – Trihalomethane Formation Potential

TOC – Total Organic Carbon

UC – Uniformity Coefficient

UF - Ultrafiltration

UFC – Uniform Formation Conditions

USEPA – United States Environmental Protection Agency

USGPM – US Gallons Per Minute

UV - Ultraviolet

UV254 – Ultraviolet Absorbance at 254 nm

WAC – Weak Acid Cation Exchange Resin

WBA – Weak Base Anion Exchange Resin

WTP – Water Treatment Plant

ZP – Zeta Potential

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Chapter 1: Introduction

1.0 Project Rationale

Natural organic matter (NOM) is ubiquitous in all waters as a result of biological degradation of organic matter. It is of concern due to its adverse impact on treatment processes. NOM causes taste, color, and odour issues in raw drinking water (Thurman, 1985) and increases chemical costs for coagulation and disinfection (White et al., 1997). Most importantly, NOM reacts with chlorine to form disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs).

Coagulation, flocculation, clarification, and filtration is the conventional and most common treatment design for the removal of NOM. Anion exchange resins (AERs) can be used for NOM removal in ion exchange (IX) process designs as they contain functional groups that specifically target negatively charged NOM compounds. Strong-base AERs have shown to remove more NOM than other types of anion exchange resins (Bolto et al., 2002). The development of a magnetic strong-base AER (i.e. magnetic ion exchange - MIEX®), which was designed specifically to target NOM removal in drinking water treatment has shown excellent removal (35 to 95%) of DOC and UV254 absorbing substances compared to coagulation (Johnson and Singer; Wert et al., 2005). It has also been shown to remove a wider range of NOM molecular weight (MW) fractions and it allows for a substantially lower chlorine demand compared to conventional coagulation processes. MIEX® treatment has been used to overcome many of the challenges associated with conventional fixed bed resins as it is used in a continuous stirred tank reactor (CSTR) process. CSTR allows for continuous regeneration of the MIEX® resin,

which in turn avoids the high capital cost of having multiple IX columns to avoid process interruptions during regeneration. It also eliminates the requirement for pre-treatment for the removal of suspended solids that clog traditional fixed bed columns as the MIEX® - CSTR design allows for the treatment of high turbidity waters (Nguyen et al., 1997).

While it is clear that AERs show promising removal of NOM, there are several aspects of treatment with AERs that remain unclear. For example, the majority of published literature on AER treatment has been conducted at room temperature, leading to questions regarding the efficacy of AER treatment technology in climates where surface waters can approach 2 °C. Secondly, the use of charge measurements (i.e. zeta potential and streaming current) for process monitoring NOM removal during coagulation and other processes (i.e. granular activated carbon (GAC) adsorption) has been well documented (Anielak et al., 2011). However, there is a noticeable gap in this area of research with respect to application to AER processes.

1.1 Research Objectives

The aim of this research was to examine the anion exchange process and its ability to remove NOM from an Atlantic Canadian surface water with low turbidity (<2 NTU), low alkalinity (< 10 mg/L as CaCO₃), and moderate organic concentrations (~5 mg/L DOC).

This research was conducted in three sub-objectives described below;

- 1) To compare two commercially available AERs (i.e. MIEX® and Resin #1) for NOM removal and to quantify residual mineral ion concentrations (i.e. chloride and sulphate) and chloride to sulphate mass ratio (CSMR) in the AER treated waters.

- 2) To evaluate NOM removal via enhanced coagulation with alum, MIEX® as a single unit operation, and a combined MIEX® -alum treatment process at both warm (20 °C) and cold (5 °C) water operating conditions.
- 3) To investigate the ability of surface charge measurement devices (i.e., zeta potential and streaming current meters) to provide monitoring and system optimization capacity in AER treatment systems.

1.2 Thesis Organization

Chapter 2 provides a literature review of topics relevant to this research. Specifically, NOM, DBPs, coagulation, ion exchange, and surface charge are covered. Chapter 3 contains a description of materials and methods used throughout this study. Chapter 4 presents results of a study that evaluated two AERs for NOM removal as well as the secondary effects of AER treatment such as chloride release and sulphate uptake. Chapter 5 presents and discusses the impacts of temperature on the efficacy of magnetic ion exchange and enhanced coagulation as single unit and combined processes. Chapter 6 investigates the use of alternative process monitoring tools for AER treatment of surface waters for NOM removal. Chapter 7 recaps conclusions of this study and provides recommendations and suggestions for further research.

1.3 Originality of Research

Several studies (Bolto et al., 2002; Humbert et al., 2005; Tan and Kilduff, 2007; Cornelissen et al., 2008; Drikas et al., 2011) have focused on the use of Type 1 strong-base anion exchange resins for the removal of NOM from surface waters at bench and pilot-scale. However, the majority of that research has been conducted at room

temperature. This research evaluated enhanced coagulation with alum, MIEX®, and a combined MIEX®-alum process at warm and cold water conditions for NOM removal and DBP formation. This would provide valuable information to utilities interested in MIEX® treatment or a combined MIEX®-coagulation treatment for NOM removal in colder climates.

The use of charge measurements for optimization of conventional coagulation processes is well documented. Specifically, zeta potential and streaming current have been used to monitor and evaluate the charge neutralization of NOM during coagulation treatment. As AER treatment is an alternative treatment to coagulation for NOM removal, it is expected that charge measurements could be used to improve AER treatment efficiency. Currently, there is a lack of published literature on the use of charge analysis as a tool to monitor AER treatment processes. This research investigates the use of charge measurement as a tool to optimize and monitor NOM removal during treatment with AERs at bench and pilot-scale using synthetic and raw surface waters.

Chapter 2: Literature Review

2.2 NOM

NOM is ubiquitous in all surface waters as a result of decaying vegetation, biological activity, and organic soils (Edzwald, 1993). NOM is generally known for its ability to cause taste, color, and odour issues, and more importantly for its potential to react with chlorine to form a harmful group of compounds known as DBPs namely THMs and HAAs (Beckett and Ranville, 2006; Cornelissen et al., 2008). It is a heterogeneous, complex mixture of aromatic and aliphatic hydrocarbons, varying spatially and temporally within a water source (Leenheer and Croué , 2003). NOM generally exhibits a seasonal trend. In terms of its properties, NOM molecules are generally large and contain various functional groups, including amides, carboxyls, hydroxyls, ketones (Croué et al., 2000), all of which affect their chemical behaviour in water.

2.2.1 Characteristics of NOM

2.2.1.1 NOM Composition

NOM contains both hydrophobic and hydrophilic compounds, which can be further classified into acid, base, and neutral fractions. The hydrophobic acid fraction has gained the most attention in research as it was estimated that it accounts for nearly half of the dissolved organic carbon (DOC) in rivers (Thurman, 1985), and that it provides the greatest contribution to DBP formation (Croué et al., 2000).

NOM can be further characterized by MW where high molecular weight (HMW) (>1000 Da), intermediate molecular weight (IMW) (500 to 1000 Da) and low molecular weight (LMW) (<500 Da) classifications are typically used. The size of NOM compounds can also impact the formation of DBPs and the effectiveness of coagulation, as it is well known that lower MW compounds are more difficult to remove via coagulation (El-Rehaili and Weber, 1987; Reckhow et al., 1990).

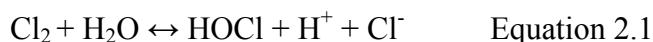
2.2.1.2 Charge of NOM

The surface charge of NOM is commonly estimated using measurements such as zeta potential (ZP). Generally, the ZP of organic material is negative at neutral pH, ranging from -12 to -40 mV (Chandrakanth et al., 1996; Duan et al., 2002). The importance of charge in treatment processes is significant. The objective of most treatment processes is to make the overall charge balance of the water more positive, implying that NOM has been removed. In general, zeta potential is reduced as treatment efficiency of NOM removal processes increases.

The charge density of NOM functional groups is typically 10 to 100 times greater than the charge density of inorganic particulate matter (Edzwald and VanBenschoten, 1990; Pernitsky, 2003). The negative charge is thought to be a result of the dissociation of carboxylic functional groups ($\text{R}-\text{COO}^-$) present on the surface of NOM. Previous research has suggested that humic substances can contribute to the charge of clay particles, resulting in a more negative surface charge than pure clay minerals (O'Melia et al., 1987; Murphy et al., 1990). Hydrophobic NOM is thought to be dominant in terms of most raw water characteristics (Malcolm, 1985), and is therefore responsible for the majority of the charge balance of the water.

2.2.2 Disinfection By-Products

While NOM compounds present in raw water do not pose a risk to human health on their own, their reaction with chlorine based disinfectants form DBPs that have been linked to various health problems such as cancers and birth defects. The typical reaction between chlorine and water to form hypochlorous acid, which can break down further into hypochloric acid, depending on pH. These reactions depicted in Equations 2.1 and 2.2, respectively.



While the exact reactions between NOM, HOCl and/or OCl⁻ are not completely understood, it is known that the oxidation of NOM and the incorporation of Cl⁻ into NOM forms DBPs (Li et al., 2000). Although there are many types of chlorinated DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) are currently the only regulated

species in Canada and the United States. Currently the maximum acceptable concentration (MAC) for DBPs according to the Canadian Drinking Water Quality Guidelines (CDWQG) are 100 and 80 µg/L for THMs and HAAs, respectively (Health Canada, 2012). The United States Environmental Protection Agency (USEPA) has a maximum contaminant level (MCL) of 80 µg/L for THMs and 60 µg/L for HAAs (USEPA, 2006).

The formation of DBPs is directly related to the concentration of disinfectant and humic material as well as pH, temperature, contact time and bromide concentration (Stevens et al., 1976; Amy et al., 1987). Currently, four THMs are regulated in most guidelines: chloroform, bromoform, chlorodibromomethane, and bromodichloromethane. The most prevalent is chloroform, as the presence of naturally occurring bromide is required for the formation of brominated species (Richardson et al., 2007). A total of nine HAAs are known to occur during disinfection in drinking water systems. However only five HAAs are regulated; monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid, and dibromoacetic acid. Table 2.1 depicts regulated THMs and HAA species and their chemical formulas.

Table 2.1. Chemical formulas of regulated THMs and HAAs.

Disinfection By-Product	Chemical Formula
<i>Trihalomethanes (THMs)</i>	
Chloroform	CHCl ₃
Dichlorobromomethane	CHCl ₂ Br
Dibromochloromethane	CHBr ₂ Cl
Bromoform	CHBr ₃
<i>Haloacetic Acids (HAAs)</i>	
Monochloroacetic Acid	CH ₂ ClCO ₂ H
Dichloroacetic Acid	CHCl ₂ CO ₂ H
Trichloroacetic Acid	CCl ₃ CO ₂ H
Monobromoacetic Acid	CH ₂ BrCO ₂ H
Dibromoacetic Acid	Br ₂ CHCO ₂ H

Not all NOM fractions form DBPs when in contact with chlorine. Research has suggested that aromatic organics and humic acid are principal DBP precursors (Edwards 1997). In general, more hydrophobic and acidic fractions tend to be precursors to DBPs (Croué et al., 2000). However, several contrasting studies have been conducted to correlate NOM fractions with THM and HAA formation potentials. In terms of THMs, Panyapinyopol et al., (2005) discovered that HIN and HOA fractions provided the greatest contributed to the THMFP of water from a WTP in Bangkok. Croué et al., (2000) partially agreed, indicating that HOA fractions resulted in the highest THMFP over all other fractions. Conversely, Kitis et al., (2002) found that both hydrophobic and hydrophilic fractions contributed greatly to THMFP. Owen et al., (1993) also found that hydrophobic fractions provided the greatest contribution to THMFP.

2.2.2.1 DBP Surrogate Parameters

As heterogeneous NOM is difficult to predict, several surrogate parameters have been developed for predicting and quantifying DBP precursors. Specifically, TOC, DOC, ultraviolet absorbance at 254 nm (UV254) and specific UV254 absorbance (SUVA). A summary of these parameters is listed below.

2.2.2.1.1 TOC and DOC

Total organic carbon (TOC) and dissolved organic carbon (DOC) are two measurements for quantifying organic carbon compounds in water. TOC is the gross concentration of organic carbon found in natural water, with units of mg/L. Included in the TOC measurement are suspended particulate, colloidal, and dissolved organic carbon. DOC concentrations consist of all dissolved and colloidal organic carbon species that can pass through a 0.45 μm filter paper (USEPA, 2009). It is evident that there is a strong correlation between DBP formation and DOC concentrations as shown by Shorney et al., (1999). However, in practice this has not always been the case. White et al., (2003) and Chowdhury and Champagne (2008) both found good correlations between DOC and DBPPFP. Conversely, Owen et al. (1993) observed a negligible relationship between the two.

2.2.2.1.2 UV254 Absorbance and Specific Ultraviolet Absorbance

Organic substances absorb UV light at wavelengths between 100 and 400 nm. Specifically, DBP precursors (i.e. humic acids) absorb light very strongly at 254 nm. Ultraviolet absorbance at 254 nm is known as UV254 and is commonly used as a surrogate measurement for the concentration of both NOM and DBPFP (Crittenden et al.,

2005; Edzwald et al., 1985). Several researchers have demonstrated the correlation between UV254 and DBPFP. For example, Ben Amor (1988) observed that UV254 was more correlated with DBPFP than any other parameter. In addition, White et al., (2003) performed a study to determine the influence of NOM on DBPFP and found strong correlations between THMFP and UV254 (r^2 0.89 to 0.99) as well as HAAFP and UV254 (r^2 between 0.59 and 0.99). Chowdhury and Champagne (2008) referred to several studies that found good correlations with models using parameters such as UV254 to predict THMFP. Conversely, Semerjian et al., (2008) observed weak correlations ($r^2 < 0.5$) between THMs and UV254 concentrations during experiments modeling DBP formation in distribution systems at lab and field scale. Nguyen et al., (2002) found better correlations with HAAFP ($r^2=0.91$) than for THMFP ($r^2=0.69$).

SUVA is a concept that was introduced by Edzwald (1993) and is the normalized UV absorbance of a water sample with respect to DOC, according to equation 2.3.

$$SUVA = \frac{UV254(cm^{-1})}{DOC(\frac{mg}{L})} * 100. \quad \text{Equation 2.3}$$

Similar to UV254 and DOC, SUVA is often used as a surrogate parameter for DBPFP (Van Benschoten and Edzwald, 1990). Krasner et al., (1996) demonstrated that waters with higher SUVA showed higher THMFP. Kitis et al., (2002) found strong correlations between SUVA and THMFP and HAAFP (r^2 between 0.86 to 0.92) after fractionation with UF and adsorption with a non-ionic macroporous resin. Alternatively, Shorney et al. (1999) found weak correlation between SUVA and both THMFP (r^2 between 0.05 to 0.10) and HAAFP (r^2 between 0.43 and 0.70).

2.3 Coagulation and Flocculation

Coagulation and flocculation are commonly used for the removal of colloidal particulates and NOM present in all surface waters. Coagulation involves the addition of chemical coagulants in order to destabilize dissolved or colloidal matter and to react with NOM, and has been applied since the early 20th century (Cohen and Hannah, 1971). Flocculation involves the aggregation and precipitation of destabilized matter, commonly referred to as “flocs” which are subsequently removed via sedimentation or dissolved air flotation (DAF) (Droste, 1997; Crittenden et al., 2005). Hydrolyzing metal salts are extensively used in the water treatment industry due to their multivalent characteristics allowing them to attract oppositely charged matter. Specifically, aluminum-based coagulants such as aluminum sulphate (alum) and ferric-based (ferric chloride, ferric sulphate) are commonly used in the water treatment industry (Duan and Gregory, 2003). Prehydrolysed coagulants such as polyaluminum chloride (PACl) are also widely used (Duan and Gregory, 2003). The coagulation of colloidal particulates with aluminum-based coagulants involves charge neutralization/destabilization and enmeshment, while the coagulation of NOM (i.e. humic and fulvic acids) generally involves complexation/precipitation and adsorption (Edzwald and Van Benschoten, 1990; VanBenschoten and Edzwald, 1990a; VanBenschoten and Edzwald, 1990b). A more detailed description of coagulation mechanisms, coagulant types, and the factors affecting coagulation are described below.

2.3.1 Aluminum-Based Coagulants

2.3.1.1 Alum

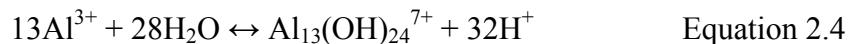
Aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$) otherwise known as “alum” is the predominant coagulant used in both municipal and industrial water treatment due to its low-cost and abundance, as well as its ability to coagulate NOM and particulates as a result of its highly charged aluminum (Al) species (Pernitsky, 2003; Bratby, 2006). The chemistry of Al in water is complex, and therefore multiple reaction pathways are possible. Depending on water characteristics, the formation of multiple Al monomers and amorphous Al ($\text{Al}(\text{OH})_3$) may occur (Van Benschoten and Edzwald, 1990). These hydrolytic reactions have been researched extensively to explain coagulation mechanisms of humic and colloidal species (Hundt and O’Melia, 1988; Dempsey et al., 1984; Edwards and Amirtharajah, 1985; Mangavite et al., 1975). The presence of Al^{3+} , $\text{Al}(\text{OH})^{2+}$, and $\text{Al}(\text{OH})_4^-$ in equilibrium with amorphous $\text{Al}(\text{OH})_3$ (s) have been shown to provide good explanation of the reactions that occur during coagulation with alum, where specific reactions depend on pH and raw water characteristics such as NOM concentration, turbidity, and alkalinity (Van Benschoten and Edzwald, 1990). The impact of these characteristics will be explained in further detail below in section 2.3.3. Table 2.2 portrays these hydrolytic reactions.

Table 2.2. Typical reaction pathways that occur during coagulation with Alum.

Chemical Reaction	Species Formed
$\text{Al(OH)}_{3(\text{am})} \leftrightarrow \text{Al}^{3+} + 3\text{OH}^-$	Amorphous precipitate, Monomeric Al
$\text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})^{2+} + \text{H}^+$	Monomeric Al
$\text{Al}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_2^+ + 2\text{H}^+$	Monomeric Al
$\text{Al}^{3+} + 4\text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_4^- + 4\text{H}^+$	Monomeric Al

2.3.1.2 Polyaluminum Chloride

In recent years, polymerized forms of Al have been used water treatment, with PACl being the most extensively used (Van BenSchoten and Edzwald, 1990). The chemistry of PACl is similar to that of alum; however, PACls contain highly charged polymeric Al species as well as monomers involved with Alum coagulation, previously discussed on table 2.5. Equation 2.4 below demonstrates the hydrolytic reaction producing the most dominant polymeric Al species, often referred to as Al_{13}^{7+} (Van Benschoten and Edzwald, 1990).



There are several differences that exist between PACl and alum. For example, PACl requires less time to form coagulant species when added to water, which can be attributed to the fact that PACl is pre-hydrolyzed and these species have been pre-formed. Additionally, the surface of PACl flocs have a higher charge density than that on alum flocs due to the presence of the highly charged Al_{13}^{7+} species. PACl also has a higher pH of minimum solubility than alum, indicating that PACl can be used at a higher pH value without resulting in dissolved Al.

2.3.2 Coagulation Mechanisms

The four primary mechanisms that are believed to be involved during the coagulation of colloidal particles and NOM in drinking water are charge neutralization and destabilization, enmeshment, complexation and precipitation, and adsorption. Generally, charge neutralization, destabilization, and enmeshment apply to colloidal particles while complexation, precipitation and adsorption mechanisms apply to NOM.

Figure 2.3 below demonstrates these mechanisms. Sections 2.2.1.1 to 2.2.1.4 explain these mechanisms in further detail.

2.3.2.1 Charge Neutralization and Destabilization

Most particulate matter present in natural waters (i.e. colloids) is negatively charged at neutral pH (6 to 8) and therefore remains discrete and stable in solution. Repulsive electrostatic forces create an energy barrier between colloids that must be overcome in order to allow for Van der Waal's forces of attraction to hold them together (Crittenden et al., 2005). The addition of chemical coagulants reduces this energy barrier to near zero, resulting in facilitated collisions and agglomeration of particles, allowing for flocculation to occur. The mechanisms of electrostatic repulsion and Van der Waal's forces exhibited by colloids in suspension are often referred to as the DLVO theory (Deryagin and Landau, 1941; Verway and Overbeek, 1948). This coagulation mechanism can also apply to humic species if they are colloidal in nature (Bratby, 2006).

2.3.2.1.1 DLVO Theory

The electrostatic repulsive and Van der Waal's attractive forces exhibited by dispersed colloids in suspension are described as a part of the double layer theory which was established by Gouy (1910) and Chapman (1913). In natural waters, a colloid carrying a negative accumulates positively charged counter ions (i.e. positive charge), which are tightly bound to the surface known as the Stern layer. Beyond the Stern layer is an area of net negative charge, which attracts cations and repels anions, known as the diffuse layer. There is a point at the boundary of the stern layer called the shear plane, as counter ions in the diffuse layer can be removed via shear forces at this point. The

difference in charge across the layers results in a negative electric potential which is greatest at the colloid surface and decreases to zero as the distance from the colloid increases (Edney, 2005). Figure 2.1 depicts the double layer.

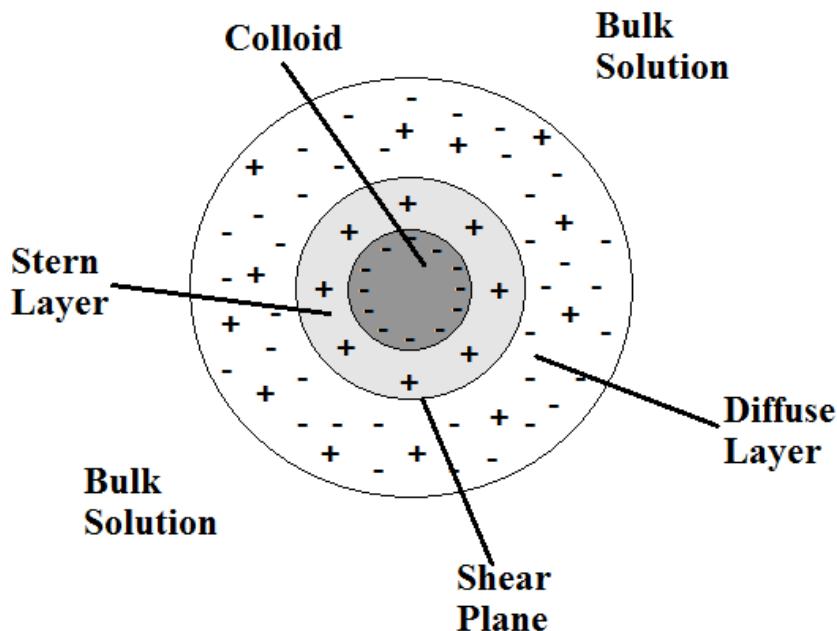


Figure 2.1. A schematic portraying the double layer theory.

During coagulation with aluminum based coagulants, highly charged Al^{3+} and other positively charged aluminum species alter or reduce the charge at the stern layer, reducing the electric potential near the colloid surface (Duan and Gregory, 2003). Coagulation via charge neutralization occurs below pH of minimum solubility.

2.3.2.2 Enmeshment

A secondary mechanism for the coagulation of colloidal matter is enmeshment, or sweep floc. At higher coagulant dosages, suspended particles are removed by enmeshment as they become entrapped in amorphous precipitates (i.e. $\text{Al(OH)}_{3(s)}$) and

settle with them (Stumm and O'Melia, 1968; Van Benschoten and Edzwald, 1990). This mechanism predominates in applications where pH ranges between 6 and 8 (i.e. range maximum amorphous aluminum hydroxide precipitate, optimally at pH of minimum solubility).

2.3.2.3 Complexation and Precipitation

The complexation and precipitation mechanisms are used to describe the coagulation of negatively charged NOM molecules (Edzwald and VanBenschoten, 1990). First, complexation reactions involving the chemical bonding of positively charged Al species and functional groups present on NOM molecules occur until the negative charge exhibited by NOM is satisfied. The direct precipitation of Al-NOM particles (commonly known as Al-humates) follows these compelxation reactions (Edzwald, 1993). The combination of these two mechanisms is known as complexation-precipitation and is the basis for coagulation of NOM in drinking water under a pH lower than minimum solubility where the prevalence of highly charged Al species are the greatest.

2.3.2.4 Adsorption

The adsorption mechanism is generally subdivided into two categories – adsorption-destabilization and bridging. Adsorption of NOM on Al(OH)_3 particles which precipitate following coagulant addition typically occurs at a pH near minimum solubility. The adsorption of humic substances to metal hydroxide surfaces occurs by Van der Waal's interactions, which consequently reduce the surface charge of NOM (Bratby, 2006). The bridging mechanism is a result of the polymerization of metal coagulants during hydrolysis reactions. A coagulant bridge between particles is formed

during adsorption of polymeric species to particles, which promotes destabilization (Bratby, 2006).

2.3.3 Factors affecting Coagulation

2.3.3.1 pH and Alkalinity

The pH during coagulation is one of the most important parameters for proper coagulation performance. Specifically, pH directly impacts coagulant solubility and charge of dissolved Al-species, surface charge of colloids and of NOM functional groups, and the surface charge of floc particles (Pernitsky, 2003). The pH of coagulation is linked to alkalinity, which is the capacity of water to neutralize acid, and is also termed as the “buffering capacity” of water. Metal-based coagulants are acidic and therefore consume alkalinity available in raw water. Therefore, raw water alkalinity is very important in choosing a coagulant type (Pernitsky, 2003). Ideally, the raw water pH should be as close to the pH of minimum solubility of a coagulant, resulting in the least amount of chemical required for pH adjustment (Pernitsky and Edzwald, 2006). Generally, the range of minimum solubility for alum and PACl are 6.0 to 6.4 at 20 °C, respectively and 6.2 to 6.9 at 25 °C (Pernitsky and Edzwald, 2006). Waters with high alkalinity may require the addition of acid when coagulating with alum or low basicity PACl in order to operate near pH of minimum solubility. High basicity PACls may not require acid addition due to their higher pH of minimum solubility (Pernitsky and Edzwald, 2006). Medium alkalinity waters are best suited for alum, medium, or low basicity PACl, all of which are able to bring pH near their respective minimum solubilities at sufficient dosages without pH adjustment (Pernitsky and Edzwald, 2006). Low alkalinity waters often require pH adjustment (i.e. caustic) when alum is the coagulant of choice. However, high basicity

PACls may not require as much pH adjustment in low alkalinity waters due to their wider operating range for minimum solubility (pH 6.4 to 6.7 at 20 °C) and their reduced consumption of alkalinity compared to other PACls (Pernitsky and Edzwald, 2003).

Figure 2.2 depicts a typical solubility diagram for aluminum-based coagulants.

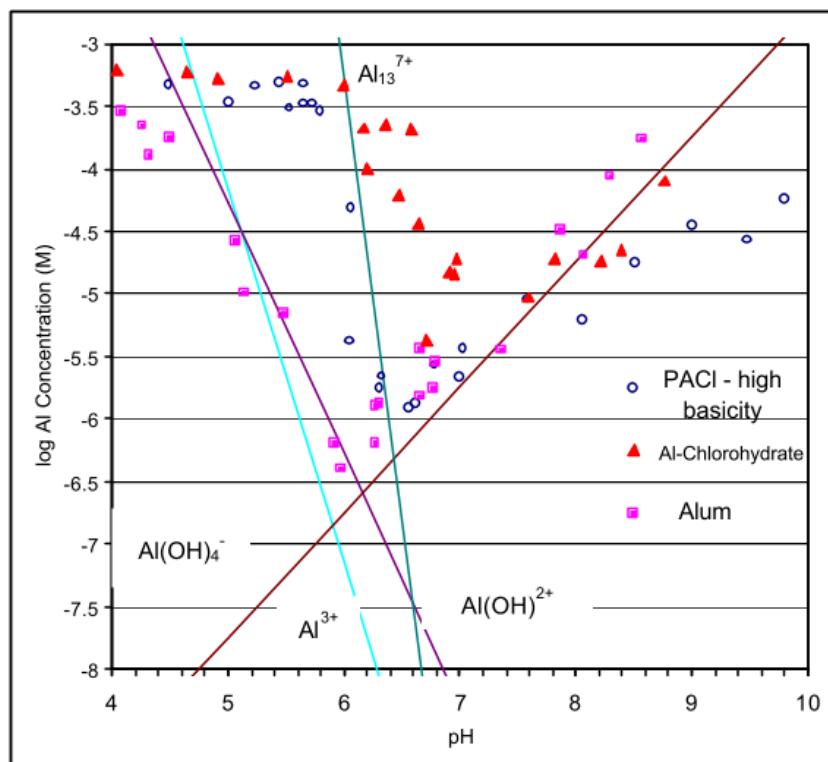


Figure 2.2. Typical solubility diagram for aluminum based coagulants (Pernitsky, 2003).

The pH of minimum solubility is directly impacted by temperature. As the water temperature decreases, the pH of minimum solubility increases. This is crucial for operating during the colder fall and winter months experienced in Canada. Table 2.3 depicts the pH of minimum solubility for various aluminum based coagulants at 20 and 5 °C.

Table 2.3 pH of minimum solubility for various aluminum based coagulants at 5 and 20 °C (Pernitsky and Edzwald, 2003).

Coagulant	20 °C	5 °C
Alum	6.0	6.2
PACl low basicity non sulfated	6.2	6.7
PACl medium basicity sulfated	6.3	6.5
PACl high basicity non sulfated	6.4	6.8
PACl high basicity sulfated	6.4	6.9
Aluminum chlorohydrate	6.7	7.6

From Table 2.3, it can be observed that the pH of minimum solubility is different for each coagulant type. PACls are more soluble than alum and therefore have a higher pH of minimum solubility. As temperature decreases the pH of minimum solubility increases, which is crucial for operating during the colder fall and winter months.

2.3.3.2 NOM

The charge density of NOM functional groups can be 10 to 100 times greater than the charge density of inorganic particles (i.e. colloids, clays) (Edzwald and Van Benschoten, 1990). Additionally, when NOM is present in waters containing inorganic particulates, there is a tendency for the charge density to be dominated by NOM due to its adsorption onto particulate surfaces (Chandrakanth and Amy, 1998). Therefore, in waters where NOM is present, sufficient coagulant must be added in order to ensure that the charge demand of raw water NOM is satisfied (Pernitsky, 2003). SUVA guidelines established by Edzwald and Tobiason (1999) can be used to determine whether NOM will impact coagulant dosages. These guidelines generally indicate that in waters where

SUVA > 4, coagulation is controlled by NOM concentrations and in cases where SUVA <2, NOM does not influence coagulation.

2.3.3.3 Turbidity

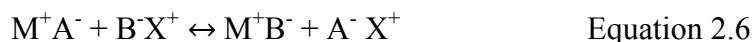
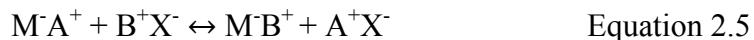
Coagulation of waters with low TOC and DOC are generally controlled by turbidity rather than NOM. In this case, sufficient coagulant dosages are required to destabilize negatively charged suspended colloids (Pernitsky, 2003; Pernitsky and Edzwald, 2006). SUVA values <2 generally indicate that coagulation is controlled by turbidity. Raw water turbidity is related to coagulant dosages (i.e. high turbidity requires a higher coagulant dosage), but this relationship is not linear. Overall, raw water turbidity is less important than NOM and alkalinity of raw waters (Pernitsky, 2003; Pernitsky and Edzwald, 2006).

2.3.3.4 Temperature

Temperature is an important parameter for effective coagulation of both NOM and particulates. Coagulation performance can be hindered under cold-water conditions due to decreased kinetics of hydrolysis reactions, higher water viscosity, and altering coagulant solubility (i.e. pH of minimum solubility increases at lower temperatures) (Pernitsky, 2003; AWWA, 2011). This results in decreased performance in terms of sedimentation (Pernitsky, 2003). Therefore, the proper selection of coagulant dosages under cold temperatures is important.

2.4 Ion Exchange

Electrostatic interaction is known as the dominant exchange mechanism for ion exchange processes. The ion exchange mechanism is a reversible interaction between a solid phase (i.e the ion exchange resin) and a liquid phase, where the resin is an insoluble medium on which the ion exchange reaction is carried out (Harland et al., 1994; Crittenden et al., 2005). Equations 2.5 and 2.6 represent cation and anion exchange reactions, respectively.



In both anionic and cationic exchange processes described above, “M” represents the insoluble fixed component of the resin, containing a negative charge for cation exchange, and a positive charge for anion exchange, both as a result of charged functional groups. Ions that bear the opposite charge of “M” are called counter ions (A and B). Ions in solution that contain the same charge as “M” are called co-ions present in solution. When a cationic exchange resin saturated with “ A^{+} “ is submersed into solution, cation “ A^{+} “ will diffuse into solution and co-ion in solution “ X^{-} “ will migrate into the resin. This causes a net negative charge on the resin and a net positive charge in the solution resulting in a difference in electric potential between the resin and the solution. This potential causes a shortage of anions in the solution and cations within the resin. As a result, cation “ B^{+} “, the target ion in solution will migrate into the resin to replace “ A^{+} “ and co-ion “ X^{-} “ is repelled back into the positively charged solution. In order for this exchange to occur, the resin has to have a higher affinity for B than it does A, so that it

will readily give up A^+ in the presence of co-ion B^+ (Harland et al., 1994; Crittenden et al., 2005). This process is the same with anion exchange however the charges are reversed. Figures 2.3 and 2.4 portray cation and anion exchange processes in solution.

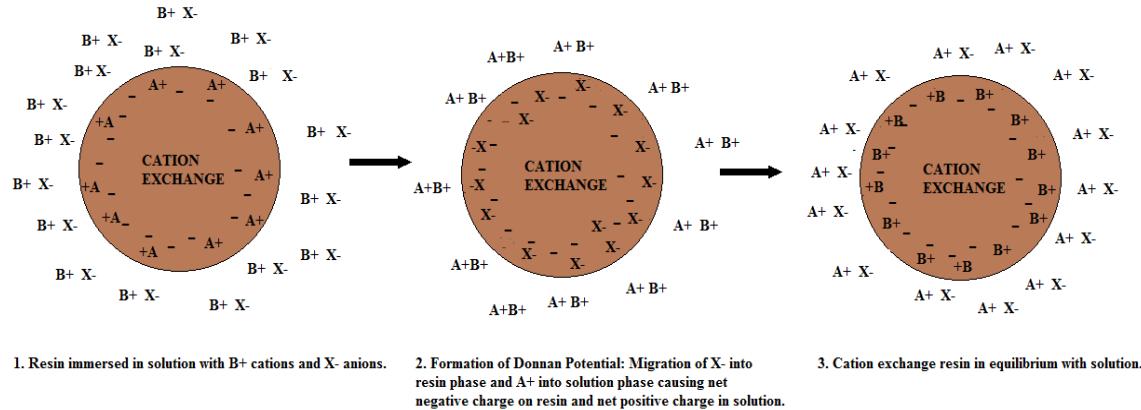


Figure 2.3. Cation exchange process with counter ion A^+ in resin phase submersed in a solution containing target cation B^+ (Adapted from Harland et al., 1994).

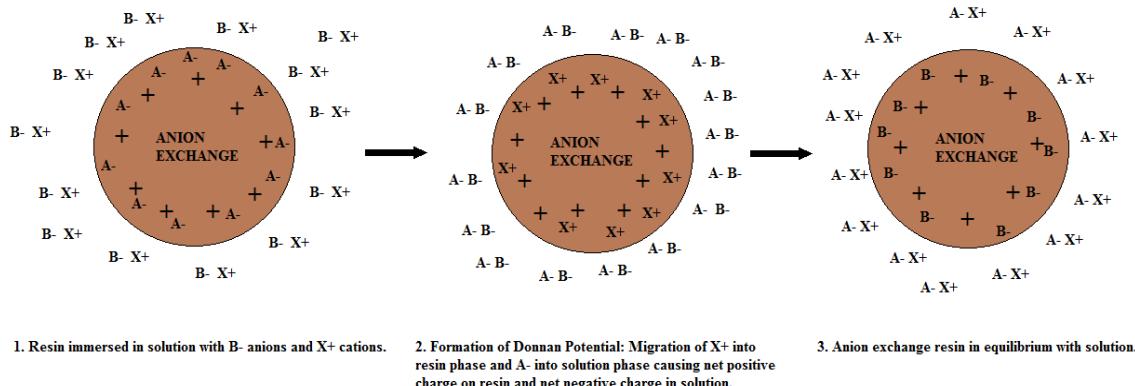


Figure 2.4. Anion exchange process with counter ion A^- in resin phase submersed in a solution containing target cation B^- (Adapted from Harland et al., 1994).

2.4.1 Types of Ion Exchange Resins

Based on the type of functional group bonded to the resin backbone, synthetic ion exchange resins are categorized into four groups – strong acid cation exchange (SAC), weak acid cation exchange (WAC), weak base anion (WBA) and strong-base anion exchange (SBA).

2.4.1.1 Strong Acid Cation Exchange Resins

SAC exchange resins typically contain a sulfonate group (RSO_3^-) as the exchange site within the resin backbone. These resins perform well at any pH due the resin's low pKa. Typical mobile counter exchange cations are hydrogen (H^+) or sodium (Na^+). SACs have a low affinity for the mobile counter ions H^+ and Na^+ , therefore will readily exchange them for another cation present in the solution (Harland et al., 1994; Crittenden et al., 2005). The general exchange reaction is seen in Equation 2.7 below.



Where X^+ is the counter ion associated with the resin before exchange (i.e. H^+ , Na^+), M^{n+} is the counter ion in solution being exchanged (i.e. target cation), and n is the charge of the counter ion in solution. The reverse reaction applies for the regeneration process. Typical regenerant solutions are HCl or NaCl. SAC resin types are typically used for water softening purposes (Harland et al., 1994).

2.4.1.2 Weak Acid Cation Exchange Resins

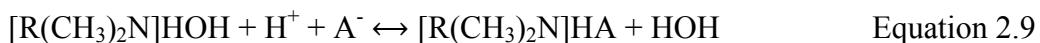
The functional group for weak acid cation exchange resins (WAC) is typically a carboxylic group (RCOO^-). WACs typically use H^+ as their mobile counter ion. Unlike the SAC exchange resins, the performance of WACs depend on pH. They are commonly used at $\text{pH} > 6$, where a pH range of 10 to 11 provides maximum capacity. At a $\text{pH} < 6$, the WACs will not exchange their mobile counter ion (H^+) for another cation in solution as the affinity for H^+ increases at $\text{pH} < 6$. The exchange reaction for WACs is listed below in equation 2.8.



Where X^+ is the ion associated with the resin (H^+) before exchange and after regeneration, M^{n+} is the counterion in solution that is being removed (i.e. exchanged into the resin), and “n” is the charge of the counterion in solution. The reverse reaction applies to the regeneration process. Typical regenerants used for WAC resins are HCl or H_2SO_4 .

2.4.1.3 Weak Base Anion Exchange Resins

WBAs generally have a tertiary amine functional group ($(\text{RCH}_3)_2\text{N}$), which differ from other ion exchange resins because their functional groups do not have a fixed positive charge (Crittenden et al., 2005). WBAs are available in chloride or free base form, where free base indicates that the tertiary amine functional group contains a water molecule rather than being ionized. Equation 2.9 demonstrates the exchange reaction for a WBA resin in free base form.

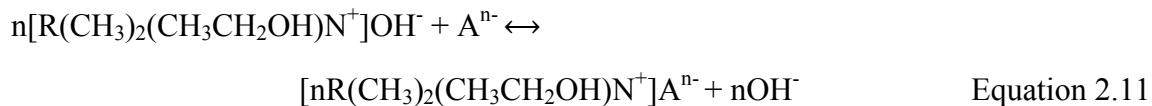
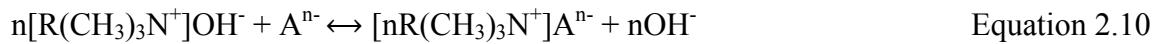


WBAs will not readily give up an OH^- ion unless the pH is between 6.7 to 8.3 at 25 °C (Crittenden et al., 2005). In many cases, the tertiary amine functional group will adsorb target ions without releasing a counter ion (i.e. the resin will act as an adsorbent rather than an ion

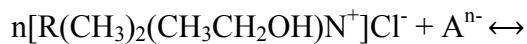
exchanger) (Crittenden et al., 2005). They are commonly regenerated with NaOH, Na₂CO₃, or NH₄OH.

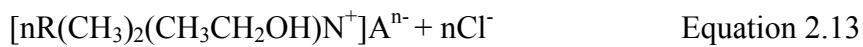
2.4.1.4 Strong-Base Anion Exchange Resins

Strong-base anion exchange resins (SBA) typically contain a quaternary amine ($R(CH_3)_3N^+$) functional group as the anion, or positive charge, that lies fixed within the resin structure. There are two main groups of SBA resins, Types 1 and 2. The main difference between type 1 and 2 is the amine used during the resin activation process. Type 1 resins have three methyl groups (CH₃), while an ethanol (CH₃CH₂OH) replaces one of the methyl groups in type 2 (Harland et al., 1994; Crittenden et al., 2005). Equations 2.10 and 2.11 portray the reactions for Type 1 and 2 anion exchange, where OH⁻ is the mobile counter ion, Aⁿ⁻ is the target anion in solution, and n is the charge on the counter ion in solution. The reverse reactions represent the regeneration process.



Both type 1 and 2 SBA resins operate at a pH range <13 indicating that they work independent of solution pH. SBA resins are commonly regenerated with NaCl or NaHCO₃, and are typically used for demineralization processes (Harland et al., 1994; Crittenden et al., 2005). Equations 2.12 and 2.13 portray the reactions for Type 1 and Type 2 SBA in chloride form.





However, SBAs are being used more frequently for the removal of NOM from surface waters for drinking water treatment. Anion exchange has been effective for NOM removal due to the fact that many NOM fractions are considered anionic due to the presence of phenolic functional groups (Thurman, 1985).

2.4.2 Relevant Properties of Synthetic Ion Exchange Resins

2.4.2.1 Moisture Content

Water is an essential component of ion exchange resins for many purposes. It has an influence on the porosity and selectivity of the resin, as higher moisture content leads to increased porosity and therefore the active exchange sites are spaced further apart (DeSilva, 1999). The water content of a resin is inversely related to the degree of crosslinking. Therefore, a drastic increase in water content is indicative of a reduction in crosslinking (Harland et al., 1994).

2.4.2.2 Exchange Capacity

The exchange capacity of an ion exchange resin determines the quantity of a counter ion that can be exchanged onto the resin (Harland et al., 1994; Crittenden et al., 2005). Generally, the ion exchange capacity is expressed in terms of total exchange capacity, which depends on the quantity of functional groups in the resin bead (Crittenden et al., 2005). Exchange capacities are used in the form of a wet volume capacity in milliequivalents per milliliter (meq/mL). As the exchange capacity of a resin is measured in a wet volume form, the water content of the resin impacts the capacity where greater water content generally indicates a higher exchange capacity.

(Cornelissen et al., 2008). Typically exchange capacities increase as the amount of DVB in the structure of the resin increases. A higher exchange capacity indicates that a greater amount of counter ion can be exchanged by the resin (Crittenden et al., 2005).

2.4.2.3 Selectivity

The selectivity of an ion exchange resin indicates the affinity or preference towards certain anions in terms of anion exchange and cations for cation exchange. Selectivity depends on various properties of the resin bead such as moisture content and functional group (De Silva, 1999; Crittenden et al., 2005). In general, the magnitude of valence and the atomic number of the ion impact the selectivity of a resin. Ion exchange resins have greater affinity or selectivity for ions with increasing charge. In cases where multiple ions carry the same charge, selectivity is based on the atomic number of the ion, where a higher atomic number is more selective (Harland et al., 1994; DeSilva, 1999;

2.4.2.4 Particle Size

Particle size has two influences on ion exchange processes. The rate of exchange for a resin decreases with increasing particle size due to the lower surface area available for exchange. Head loss through ion exchange beds increases as a result of decreasing particle size. As a result, smaller beads are more likely to fracture (Crittenden et al., 2005). Particle size and distribution of resins are typically determined by mechanical sieving. The bead size of conventional resins is 300 to 1200 μm . In industry, particle sizes are usually reported in terms of an effective size (ES) and a uniformity coefficient (UC) (Harland et al., 1994; Crittenden et al., 2005). The ES is defined as the mesh size (μm) that retains 90% of the sieved sample, while the UC is the ratio of the mesh size (μm) retaining 40% of the sieved sample to the effective size (Harland et al.,

1994). In other words, the ES is the mesh size that passes 10% of the sample (d_{10}), while the UC is the ratio of d_{10} to d_{60} (Crittenden et al., 2005).

2.4.3 Ion Exchange Process Configurations

2.4.3.1 Co-current

In the concurrent ion exchange configuration, the regenerant is passed through the fixed bed in the same flow direction (usually downward) as the water or solution being treated (Crittenden et al., 2005). Co-current configuration can lead to leakage (i.e. target or unwanted ions in the treatment effluent), however, this depends on the location of unwanted ions in the bed. Co-current operations are ideal for situations where small amounts of leakage are acceptable (Crittenden et al., 2005).

2.4.3.2 Counter-current

In counter-current operations, service flow is in the upward direction while regeneration is downward (Crittenden et al., 2005). Counter-current configurations typically result in lower leakage levels and higher chemical efficiencies than concurrent operations. This configuration is ideal in situations where high treatment rates and minimal chemical consumption are required. It must be noted that counter-current configurations with up flow treatment is only effective if fluidization of the resin is prevented, as fluidization can destroy the exchange front and thus preventing effective exchange. In order to prevent fluidization, the resin bed must be lifted in the compacted form (Crittenden et al., 2005).

2.4.3.3 Completely Stirred Tank Reactor

The most common application for completely stirred tank reactor (CSTR) configuration is MIEX® for the selective removal of DOC. The process consists of a contactor where the resin

and raw water are mixed and then separated in an up flow clarifier. In this process, about 5 to 10% of the loaded resin is sent to regeneration, while the remainder of the resin is recycled back into the contactor in addition to 5 to 10% fresh resin to replace the volume sent to regeneration. This configuration allows for continuous treatment, and keeps the concentrations of DOC in the contactor consistent and predictable (Crittenden et al., 2005; Boyer et al., 2010). Another advantage of this configuration is that the high surface area of the beads is maximized in CSTR form, as the entire surface of the resin comes into contact with water (Boyer et al., 2010). Figure 2.5 shows a schematic of the CSTR configuration.

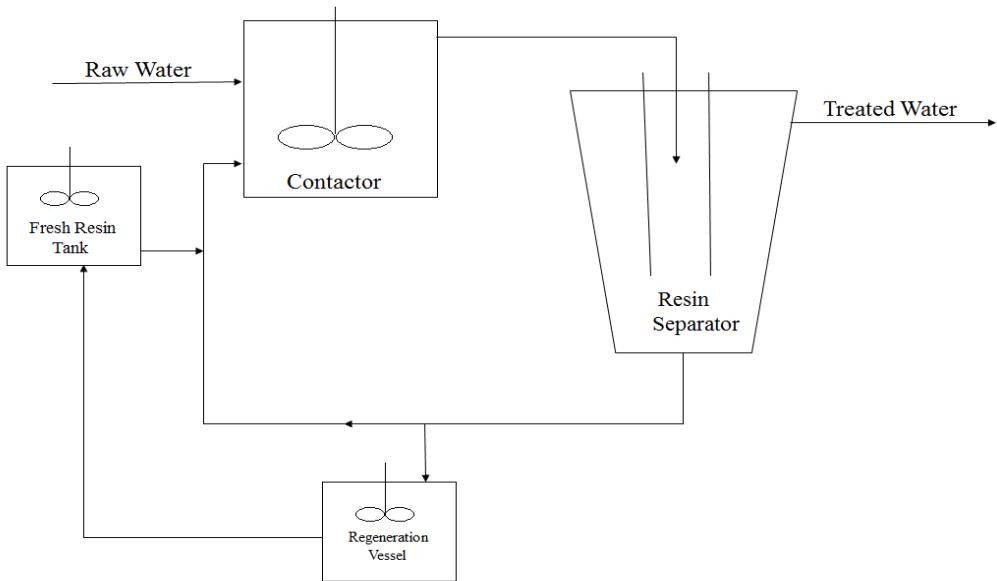


Figure 2.5. MIEX® CSTR Process Configuration.

2.5 NOM Removal with AERs

The first uses of IX technology for NOM removal occurred in the late 1970's (Anderson and Maier, 1979; Boeing et al., 1980; Brattebo et al., 1987; Fu and Symons, 1990; Kim and Symons, 1991; Fettig, 1999; Hongve et al., 1999; Bolto et al., 2002; Humbert et al., 2005; Tan

and Kilduff, 2007; Cornelissen et al., 2008). Specifically, quaternary ammonium, (i.e. strong-base) resins that typically come in chloride form are most commonly used for NOM removal in drinking water treatment.

More recent literature has compared various AERs have shown the effectiveness of strong-base AERs at removing DBP precursor material. Bolto et al. (2002) performed a bench-scale study that investigated 19 commercially available strong-base AERs in terms of UV254 removal and found 59 to 99% reduction in UV254 from raw water. Humbert et al. (2005) compared four strong-base AERs for the removal of NOM from high DOC content surface water at bench-scale. It was found that resins with a smaller particle size provided more rapid kinetic removal than those with larger particle sizes. Cornelissen et al., (2008) comparatively evaluated 9 AERs, both strong and weak-base, for NOM removal at bench-scale. Cornelissen et al. discovered that highest removals (38 to 44% TOC) were achieved by the resins with the smallest size and the highest water contents.

2.6 Charge Analysis

2.6.1 Zeta Potential

Based on electrophoresis, zeta potential is the electric potential produced across the diffuse layer of a negatively charged colloid and the surrounding positively charged atmosphere. It is generally a good approximation of the surface potential, with most natural colloids surface waters acquiring a ZP typically in the range of -5 to – 40 mV (Sharp, 2005). Figure 2.6 demonstrates the location of ZP with regards to the double layer theory.

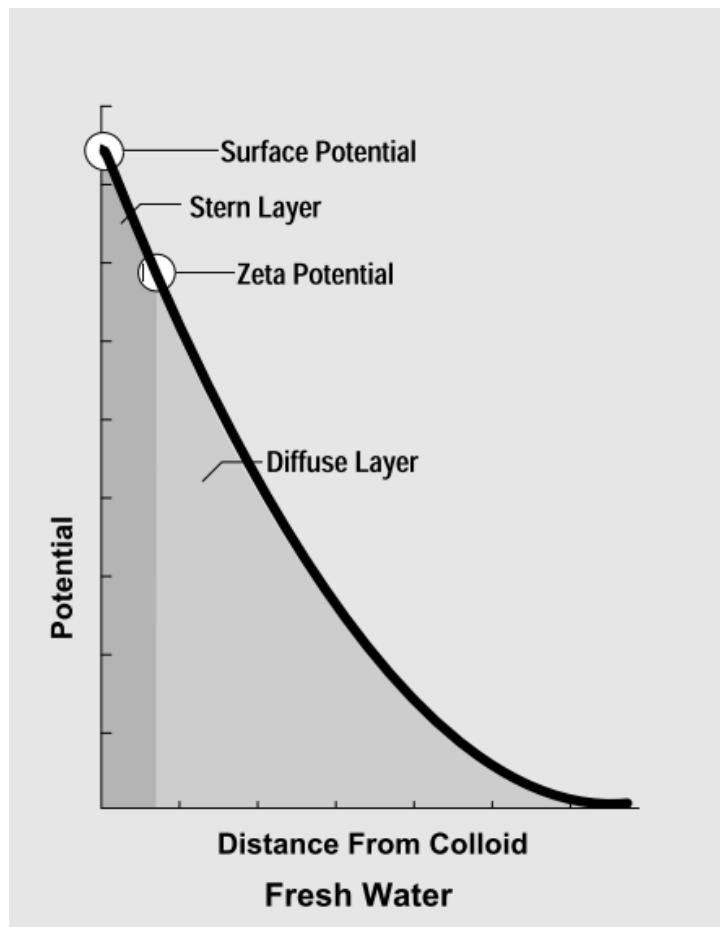


Figure 2.6. The location of zeta potential with regards to the double layer theory (Zeta-Meter Inc. 1993).

Several studies have effectively demonstrated the use of ZP for the selection of optimum coagulant conditions (i.e. dose and pH) for the removal of colloidal matter (Riddick, 1961; Bean et al., 1964; Gupta et al., 1975).

As the charge of NOM is much greater than that of colloidal matter (Edzwald, 1993), it is expected that Zetameters would be capable of estimating the net negative charge exhibited by NOM molecules in water. Hydrophobic NOM is thought to be the dominant fraction in most raw waters having the most influence on the charge balance and coagulant demand of water

(Malcolm, 1985). Generally, the zeta potential of raw waters containing hydrophobic NOM (i.e. humic acid) at ambient pH ranges from -12 to -40 mV (Chandrakanth et al., 1996; Duan et al., 2002). Previous research has been conducted to link the removal of NOM via coagulation to the charge characteristics of coagulated water. Dentel (1991) provided reference to several studies that found zeta potentials of -4 to +3, -5 to +5, and -13 to +13 mV for NOM removal via coagulation. Other researchers have concluded that a ZP range of -10 to +10 mV provided optimal NOM removal (Ratnaweera et al. 1999; Duan and Gregory, 2003; Gregory and Carlson, 2003; Sharp et al., 2004; Sharp et al., 2005; Sharp et al., 2006a; Sharp et al., 2006b).

2.6.2 Streaming Current

In addition to ZP, streaming current measurements have also been used as a continuous, on-line tool for monitoring and control of coagulant dosages (Dentel and Kingery, 1989). Streaming current is an approximation of the net surface charge of small, suspended particles in liquid and is the only instrument that can measure coagulated particle stability for the on-line control of coagulant dosages (Edney, 2005). In theory, streaming current is a measurement of the alternating current generated by mobile counter ions in solution when charged particles are momentarily bound to cylinder and piston walls during reciprocation (Edney, 2005). Figure 2.7 shows a conceptual diagram of the streaming current meter.

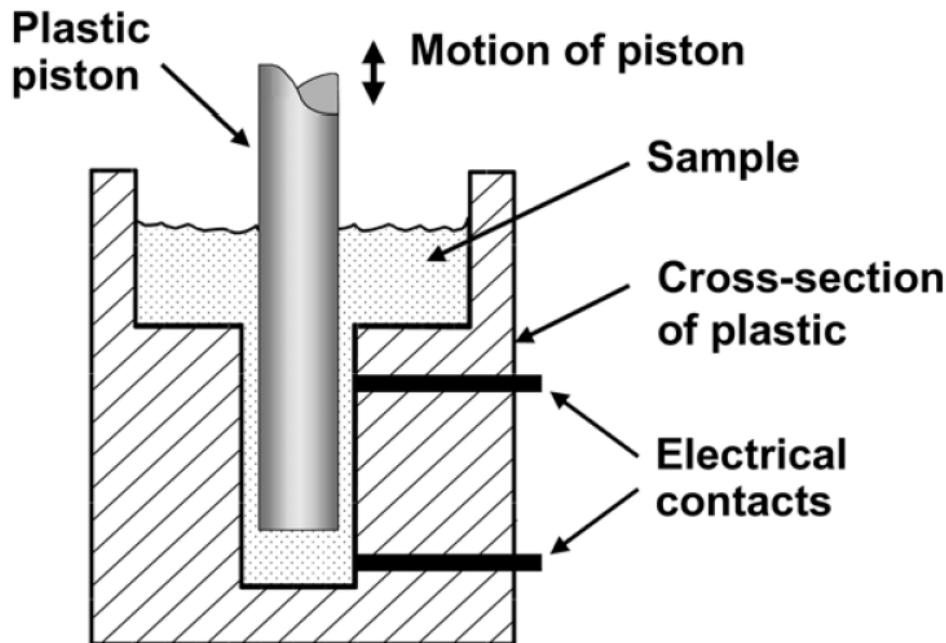


Figure 2.7. A schematic diagram of a streaming current device (Hubbe and Chen, 2004).

Research has been conducted on the use of streaming current as a tool for optimizing NOM removal via coagulation. There is strong evidence that required coagulant doses for the removal of organic impurities is related to their charge carried by these organic impurities (Bernhardt and Schell, 1993; Kam and Gregory, 2001), which forms the basis for the SCD method of determining optimum coagulant dosages. Bernazeau and Hubele (1990) evaluated the response of SCD to the coagulation of water with fluctuating NOM concentrations and observed that an SC window near zero resulted in maximum reductions in UV254. This was further verified by other researchers who found similar results (Kam and Gregory, 2001; Bridley et al., 2002; Xia et al., 2007). These results all showed that streaming current could be used as an effective tool for maintaining optimum coagulation conditions for the removal of organic matter.

Chapter 3: Materials and Methods

The purpose of this chapter is to outline materials, bench-scale equipment, analytical, and data analysis methods that are common throughout Chapters 4, 5, and 6. An average of the raw source water characteristics will also be described in this chapter, however source water characteristics for the water used for each phase of this study will be described within each chapter. Chapter specific materials, methods will be described within their respective chapters.

3.1 Source Water Characteristics

All raw water samples were taken from a source water representative of Atlantic Canadian surface waters characterized by low turbidity (<5 NTU) and alkalinity (<10 mg/L as CaCO₃), an average DOC of 4.5 mg/L and UV254 of 0.162 cm⁻¹. Table 3.1 depicts average raw water characteristics taken over the period of this study (2011 to 2013).

Table 3.1. Source water quality.

Analyte	Average	Standard Deviation
pH	6.7	0.3
Turbidity (NTU)	0.91	0.4
True Color (PtCo)	22	1.7
UV254 (cm ⁻¹)	0.162	0.008
TOC (mg/L)	4.5	0.3
DOC (mg/L)	4.5	0.3
THMFP (µg/L)	349.9	74.6
HAAFP (µg/L)	153.8	9.80
Cl ⁻ (mg/L)	4.7	1.8
SO ₄ (mg/L)	1.7	0.6
SUVA (mg/L·m)	3.6	0.1

3.2 Anion Exchange Resins

A magnetic Type 1 strong-base Anion Exchange Resin (AER) (Orica Watercare, Dry Ridge, KY, USA) was obtained for bench-scale use in all chapters of this study. In addition, a commercially available conventional AER (Purolite A860) was obtained in order to compare

NOM removal capabilities of both resins in Chapters 4 and 6. Both resins were used in chloride form and were regenerated using NaCl. The Purolite A860 resin will be referred to as “Resin #1” for the remainder of this thesis. Table 3.2 summarizes the characteristics of each resin sample based on manufacturer data.

Table 3.2. Characteristics of strong-base AERs studied

Property	MIEX®	Resin #1
Exchange Capacity (meq/L)	0.52 ± 0.02	0.80
Water Content (%)	64 – 66	66 – 72
Structure	Macroporous with iron oxide	Macroporous
Matrix	Polyacrylic	Polyacrylic
Functional Group	Quaternary Ammonium $R(CH_3)_3N^+$	Quaternary Ammonium $R(CH_3)_3N^+$
Particle size (μm)	150 to 180	300 to 1200
Selectivity (Descending order)	Perchlorate > Chromate > DOC > Sulfate > Nitrate > Carbonate > Hydroxide > Phosphate > Arsenate > Bromate > Nitrite > Bromide > Chloride > Bicarbonate > Fluoride	Not Available
Counter Ion	Chloride	Chloride

3.3 Bench-Scale Methods

A standard six paddle jar test apparatus with 2-L jars (Phipps and Bird, Fisher Scientific) was used in all anion exchange experiments in Chapters 4, 5, and 6 as well as for all alum coagulation experiments in Chapter 5. Specific procedures (i.e. coagulant and resin doses, pH, mixing speeds, and settling times) regarding each of the bench-scale experiments are outlined in their respective chapters. The multi-loading MIEX® procedure was used in Chapters 4, 5, and 6 and is explained below. MIEX® is applied in water treatment with an operating parameter known

as Bed Volume (BV) which is defined as the ratio between the volume of water treated and the volume of resin applied as depicted in Equation 3.1.

$$BV = W_{ater}/R_{esin} \quad \text{Equation 3.1}$$

For the multi-loading procedure, 5 mL resin was applied to 1 L raw water and mixed for 15 minutes followed by a 4 minute settling period, based on procedures presented in other studies (Singer and Bilyk, 2002; Johnson and Singer, 2004; Boyer and Singer, 2005). Treated water was decanted and additional increments of 1 L raw water were added to the same resin, equating 400 BV. This was repeated up to 1000 BV. This process is depicted on Figure 3.1 below.

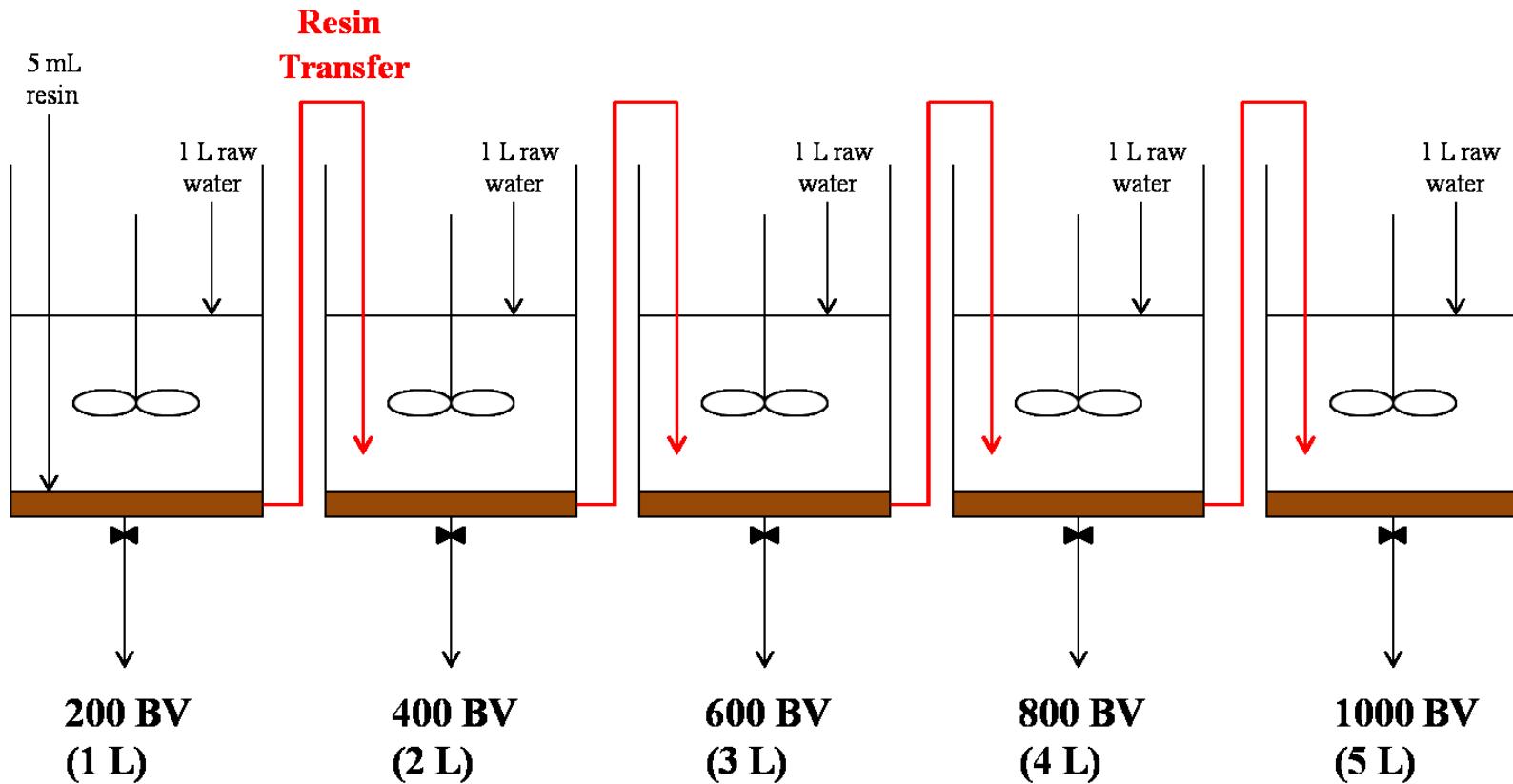


Figure 3.1. A schematic of the multi loading MIEX® treatment process.

3.4 Analytical Methods

All laboratory procedures used in this study were performed in accordance with Standard Methods for the Examination of Water and Wastewater (APHA, 2012). Procedures unavailable in this text were executed in accordance to the equipment manufacturer description. Experimental parameters that were measured throughout this research include pH, turbidity, TOC, DOC, UV254, THMFP, HAAFP, true color, chloride, and sulphate.

3.4.1 General Water Quality Parameters

During the period of this research, RO water from a Milli-Q purification system was used for all chemical stock preparations and cleaning procedures. All jars and glassware were cleaned, followed by thorough rinsing with Milli-Q RO water. Turbidity was measured using a HACH 2100AN laboratory turbidimeter that was zeroed with Milli-Q water prior to use. pH and temperature were monitored using an Accumet XL50 meter (Fisher Scientific). True color was measured on samples filtered through a 0.45 µm polysulfone filter membrane (GE Water and Process Technologies) that was pre-rinsed with 500 mL Milli-Q water. A HACH DR/4000 UV/VIS spectrophotometer (Hach Company, Loveland, CO) was used to measure true color.

3.4.2 Organic Matter

TOC and DOC samples were collected head-space free in 40 mL pre-cleaned glass vials and preserved with concentrated phosphoric acid to pH <2. DOC samples were filtered through 0.45 µm polysulfone filter membrane (GE Water and Process Technologies) that were primed with 500 mL Milli-Q water to prevent leaching of organics from filter papers into the sample. TOC and DOC measurements were performed using a TOC-V CPH analyzer with a Shimadzu ASI0-V autosampler and a catalytically aided combustion oxidation non-dispersive infrared detector (NDIR) having a method detection limit of 0.08 mg/L (Shimadzu Corporation, Kyoto

Japan. UV absorbance at 254-nm (UV254) was measured using a HACH DR/4000 UV/Vis spectrophotometer (Hach Company, Loveland, CO) at a wavelength of 254 nm. UV254 samples were filtered through 0.45 μ m polysulfone filter membrane (GE Water and Process Technologies) that had been pre-rinsed with 500 mL of Milli-Q water.

3.4.3 Disinfection By-Products

THM and HAAFP were analyzed using Standard Method 5710 (APHA, 2012). Samples were buffered to pH 8 with borate and were incubated for 24h following chlorination under uniform formation conditions (UFC) where a chlorine residual of 1 ± 0.4 mg/L was desired.

3.5 Data Analysis

All error bars on graphs represent one standard deviation from the mean from three separate tests unless explained otherwise. Paired t-tests were used to determine if treated samples were significantly different. Statistical analysis was done using Minitab 16 software (Minitab, Inc.). Specific details on data analysis for each phase of this study will be described in their respective chapters.

Chapter 4: Evaluation of Anion Exchange Resins for the Removal of Natural Organic Matter and their Secondary Effects

4.1 Introduction

The ubiquitous nature of NOM and its potential to form DBPs has resulted in improvements in the performance of both chemical and physical NOM removal processes in addition to the development of new technologies. In particular, strong-base AERs have shown NOM removals upwards of 80% (Bolto et al., 2002; Humbert et al., 2005; Cornelissen et al., 2008). Treatment with AERs has been shown to outperform adsorption with GAC (Snoeyink et al., 1979), and it has been established that AER treatment can provide NOM removal efficiencies comparable to coagulation (Cook et al., 2001).

An increase in research on NOM removal with MIEX® resin has shown promising results. NOM removal rates with MIEX® treatment have been reported between 40 to 75% for DOC and 50 to 85% for UV254. However, MIEX® does not remove turbidity, therefore post-MIEX® treatment (i.e. coagulation) is recommended. The use of MIEX® prior to coagulation has shown a reduction in coagulant demand by up to 80% (Singer and Bilyk, 2002).

MIEX® treatment is based on the stoichiometric substitution of chloride in the resin phase for DOC in solution. As a result, there is increase in chloride and a decrease in other ions, including sulphate in finished waters (Humbert et al., 2005; Ishii and Boyer, 2011). This can give rise to a potential increase in CSMR, although CSMR is dependent on raw water characteristics such as chloride, DOC, and sulphate, in addition to resin concentrations. That being said, CSMR serves as an indicator of lead corrosion potential and site-specific corrosion studies would be necessary to make decisive conclusions regarding lead corrosion as a result of AER treatment.

The objective of the experiments presented in this chapter was to evaluate the performance of two strong-base anion exchange resins (AER) for NOM removal quantified by UV254, DOC and SUVA measurements. The first AER product evaluated (A860, Purolite) is used in conventional packed bed IX columns. The second AER evaluated was magnetic ion exchange (MIEX®), which is applied in a continuous stirred-tank reactor (CSTR) process. The AER treated waters were also characterized for chloride and sulphate concentrations to calculate chloride-sulphate mass ratios (CSMR) and provide additional information on typical characteristics of AER treated water. Bench-scale experiments were conducted using a surface water typical of Atlantic Canada (i.e. low turbidity (<2 NTU) low alkalinity (<10 mg/L as CaCO₃) and moderate DOC concentrations (~5 mg/L).

4.2 Materials and Methods

4.2.1 Source Water

Raw water collected over a period from November 2012 to January 2013 from a municipality located in New Brunswick, Canada was used for all experiments in this study. Like many surface waters in Atlantic Canada, this source water is characterized by low turbidity (<2 NTU) and alkalinity (<10 mg/L as CaCO₃), with moderate NOM content (DOC ~ 5 mg/L). Raw water samples were characterized throughout this study and are summarized in Table 4.1.

Table 4.1. Raw water characteristics from November 2012 to January 2013 (N=3).

Analyte	Number of samples	Average	Standard Deviation
pH	3	6.8	0.25
Turbidity (NTU)	3	0.7	0.10
True Color (PtCo)	3	22	1.70
UV254 (cm ⁻¹)	3	0.166	0.001
TOC (mg/L)	3	4.7	0.20
DOC (mg/L)	3	4.7	0.20
SUVA	3	3.5	0.10
Chloride (mg/L)	3	3.7	0.70
Sulfate (mg/L)	3	1.3	0.10
CSMR	3	2.8	0.30

4.2.2 Bench-Scale Experiments

Bench-scale experiments were conducted using a standard jar tester (Phipps and Bird, Fisher Scientific) to comparatively evaluate the efficacy of two strong-base type 1 AERs using batch and dose-response experiments. Resin #1 is a AER used in conventional IX column designs, and MIEX® is a strong-base AER that contains iron oxide, which provides magnetic properties allowing application in continuous stirred-tank reactor designs due to faster settling properties. Table 3.2 (Chapter 3) summarizes the characteristics of the two AERs used in this study. Prior to their use, both fresh resin samples were rinsed with Milli-Q water for 30 minutes as recommended in the manufacturer's procedure. The efficacy of the two resins was evaluated based on preliminary dose-response experiments, where varying resin doses in increments of 2 mL/L were mixed with 1-L raw water samples at 150 rpm for 60 minutes based on previous experiments by Humbert et al., (2005). Samples of treated water were taken in 50 mL aliquots over the 60 minute period at 5, 15, 30, and 60 minutes and were filtered through pre-rinsed 0.45 µm filter paper (GE PES Membrane, GE Water Systems, Inc.) and analyzed for UV254 in order to assess the minimum dosage of resin required to obtain maximum UV254 removal with contact

times under an hour. The minimum resin dosage and contact time chosen from the preliminary dose-response experiments discussed above were used for batch experiments to further evaluate the removal efficacies of both resin samples in terms of NOM removal, as well as chloride release and sulphate uptake. In batch experiments, resin samples were mixed for up to 30 minutes at 150 rpm and treated aliquots of 100 mL were taken at 5, 10, 15, and 30 minutes and analyzed for UV254, DOC, chloride, and sulphate based on the method presented by Humbert et al., (2005).

4.2.3 Analytical Methods

All relevant materials and methods are explained in Chapter 3. Ion chromatography is unique to this chapter and therefore its method is explained. Unpreserved chloride and sulphate samples were stored at 4°C for up to 5 days until analysis using ion chromatography (IC) (Metrohm 761 Compact IC, Metrohm Ltd.). During the IC procedure, wash (Milli-Q water) and quality control samples (Milli-Q water spiked with known concentrations of chloride and sulphate) were used at the beginning of each run and every 10 samples in order to validate precision and accuracy.

4.3 Results and Discussion

4.3.1 Dose-Response Kinetic Tests

4.3.1.1 Impact of Resin Dose and Contact Time on UV254 Removal

Dose-response tests were performed on both Resin #1 and MIEX® AERs to evaluate the impact of both time and resin dose on organic removal in terms of UV254 concentrations. Figure 4.1 demonstrates average UV254 removal over a 1-hour period for Resin #1 at dosages ranging from 2 to 10 mL/L.

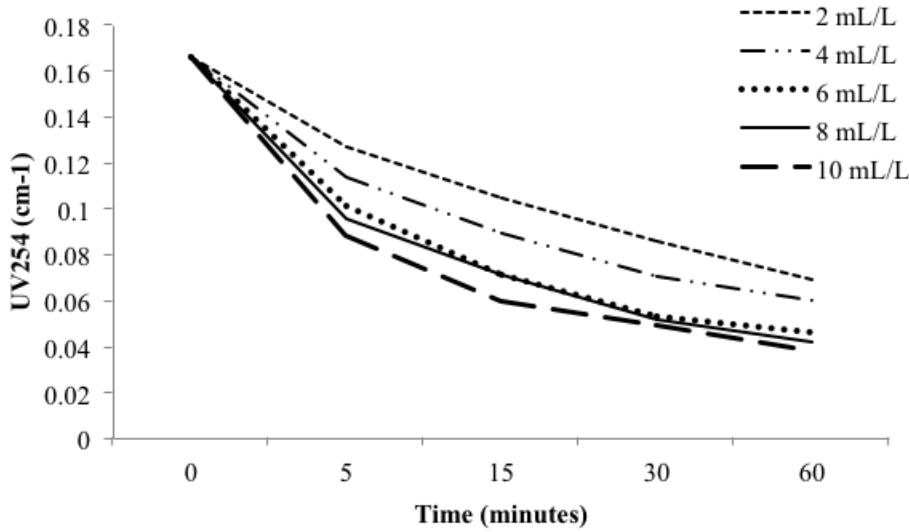


Figure 4.1. Results of dose-response experiments with resin #1 (N=3).

For all resin dosages investigated in this experiment, the majority of UV254 removal occurred in the first 30 minutes. Increasing the contact time to 60 minutes did not result in further removal of UV254. Significant differences ($p < 0.05$) in UV254 removal were seen from 2 to 4 mL/L. However, dosages beyond 6 mL/L did not show any significant ($p > 0.05$) further UV254 removal. The desired level of treatment was to obtain maximum UV254 removal while minimizing resin use. Therefore, 6 mL/L was chosen as the optimum dose for the conventional resin type based on a point of diminishing returns standpoint, which resulted in 68% UV254 removal from raw water levels (0.166 to 0.053 cm^{-1}).

Dose-response experiments were repeated with the MIEX® resin and are presented in Figure 4.2.

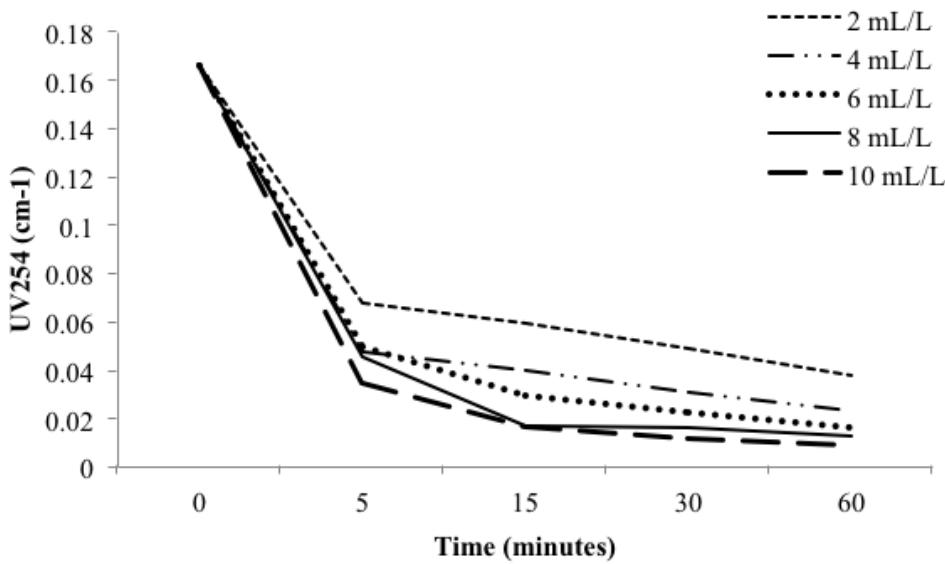


Figure 4.2. Results of dose-response experiments with MIEX® (N=3).

For all of the MIEX® doses evaluated, the majority of UV254 removal was observed within the first 5 minutes of contact time. The MIEX® resin showed a similar trend to Resin #1 where doses beyond 6 mL/L (i.e. 8 and 10 mL/L) did not result in any further significant ($p > 0.05$) UV254 removal with contact times greater than 5 minutes. At a dose of 6 mL/L, UV254 was reduced by 70% from raw water levels (0.166 to 0.050 cm^{-1}). Increasing the contact time to 30 minutes only resulted in an additional 16% reduction in UV254. It can be observed that a 4 mL/L MIEX® resin dose was comparable to the 6 mL/L MIEX® dosage at a 5 minute contact time, however, as the contact time increased beyond 5 minutes, the 4 mL/L MIEX® dosage resulted in significantly higher UV254 concentrations than the 6 mL/L dose.

Based on the results of the dose-response experiments, a minimum resin dose of 6 mL/L provided maximum UV254 removal in contact times of 5 to 30 minutes depending on the resin. These results show that MIEX® resin can be used at lower dosages and contact times than the Resin #1. A consistent dosage of 6 mL/L and a contact time of 30 minutes were chosen for both

resins to use in batch studies for a comparative evaluation in terms of organic removal. This dosage is also close to the dosage of 5 to 10 mL/L suggested by manufacturers of MIEX® to give optimum organic removal (Slunjski et al., 2000). Humbert et al. (2005) conducted a similar dose-response study comparing four strong-base type 1 AERS for UV254 removal and found a minimum resin dosage of 8 mL/L provided maximum UV254 removal in less than one hour. The difference (i.e. 6 mL/L vs. 8 mL/L) in optimal resin dosages were attributed to higher DOC (~6 to 7 mg/L) concentrations in raw water studied by Humbert et al., (2005) as well as the use of similar, but not identical AERs.

4.3.2 Batch Experiments

4.3.2.1 DOC and UV254 Removal

Batch experiments were performed using the resin dose and contact time chosen based on results in section 4.3.1. Figure 4.3 and 4.4 present UV254 and DOC removal, respectively for both Resin #1 and MIEX® at a dose of 6 mL/L and 30 minute contact time.

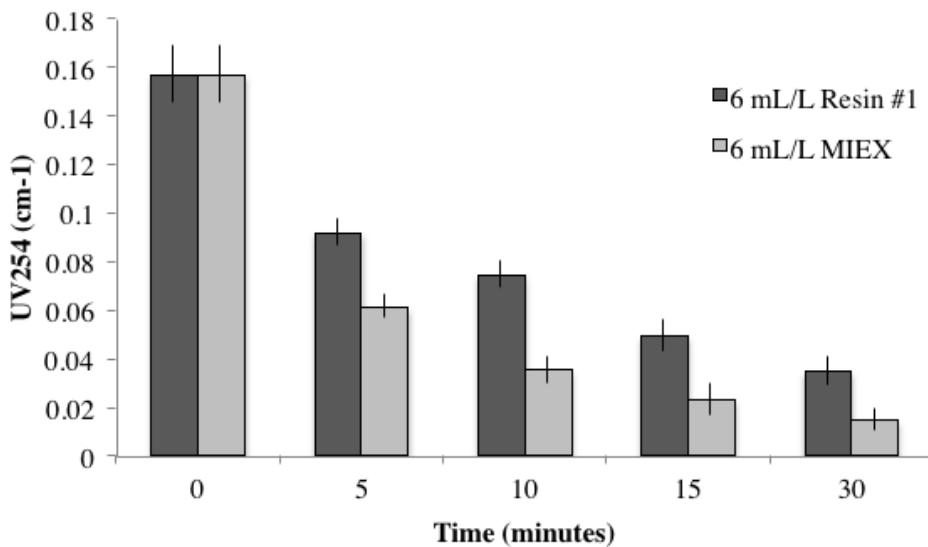


Figure 4.3. Removal of UV254 by both resins at a dose of 6 mL/L (N=3).

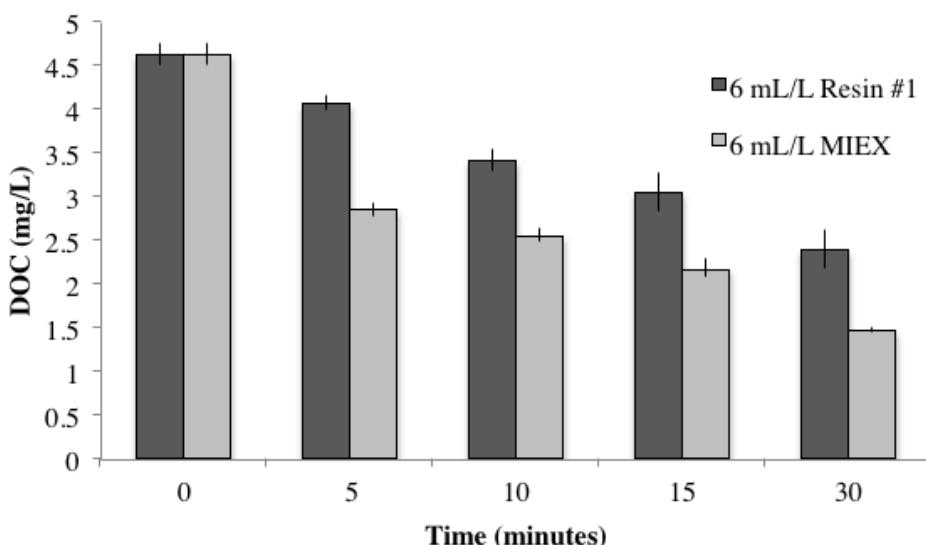


Figure 4.4. Removal of DOC by both resins at a dose of 6 mL/L (N=3).

In all of the experiments, increasing the contact time from 5 to 30 minutes lead to decreasing UV254 and DOC values. After 30 minutes of contact time, UV254 was reduced from 0.166 cm^{-1} to less than 0.050 cm^{-1} (69% removal) for both resins, and DOC decreased from 4.7 mg/L to less than 2.5 mg/L (47% removal). MIEX[®] demonstrated more rapid removal of DOC and UV254 when compared to Resin #1, which was attributed to the smaller bead size and magnetic component, allowing for increased surface area for the exchange and rapid settling rates. Approximately 63% (0.166 to 0.061 cm^{-1}) of UV254 and 40% (4.7 to 2.8 mg/L) of DOC was eliminated after 5 minutes of contact time with 5 mL/L MIEX[®], while the conventional resin resulted in 44% (0.166 to 0.092 cm^{-1}) and 15% (4.7 to 4 mg/L) removals for UV254 and DOC, respectively for the same dosage. The level of organic matter removal in terms of UV254 and DOC achieved by MIEX[®] in 10 minutes of contact time was equivalent to those achieved by Resin #1 in 30 minutes. This indicates that the MIEX[®] resin provides more rapid removal by a factor of three compared to the same dose of Resin #1.

Similar results were observed by Humbert et al. (2005), who observed approximately 74% reduction in DOC after 3 minutes of contact time with a MIEX® resin dose of 8 mL/L, while non-magnetic resins (i.e. conventional) with a larger bead size (i.e. >180 µm) resulted in removals ranging from 10 to 21% for the same contact time. Research by Less (2011) showed a similar trend where DOC and UV254 removals of 68 and 80% were achieved in 15 minutes with 5 mL/L MIEX®, while other Type 1 AERs only achieved up to 44 and 54% in the same amount of time. In that study, DOC and UV254 concentrations reached steady state for the MIEX® treated samples between 5 and 10 minutes, while those from the conventional resin decreased more gradually. In order for the conventional resin to reach the low UV254 and DOC concentrations exhibited by treatment with MIEX® resin, a contact time greater than one hour was required. These results also agree with those of Humbert et al. (2005) who found that equilibrium was reached by MIEX® after less than 15 minutes, while it took approximately one hour for a non-magnetic resin with larger bead size to reach the same concentrations. Less (2011) also found that MIEX® treatment reached equilibrium sooner (i.e. less than 30 minutes) than the conventional AERs investigated, which appeared to reach equilibrium after 30 minutes of contact time.

Figure 4.5 demonstrates specific UV absorbance (SUVA) for both resins at contact times of 0, 5, and 30 minutes.

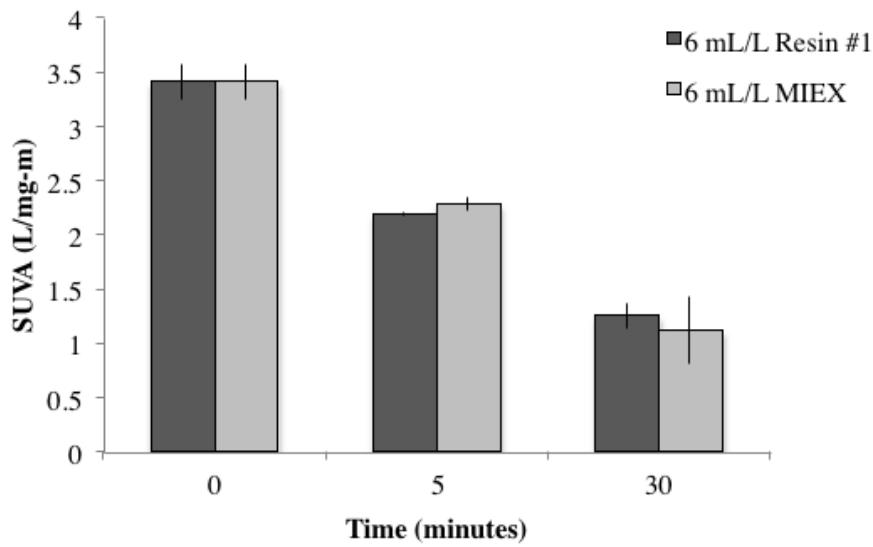


Figure 4.5. SUVA values for raw and treated water using a 6 mL/L resin dose (N=3).

The SUVA concept was developed by Edzwald (1993) and is known to be correlated with the humic and aromatic content of the water, which is linked to DBP formation. After 5 minutes, both resins showed significant reductions in SUVA of more than 33% from raw levels of 3.4 to 2.2 L/mg-M. No significant ($p > 0.05$) difference in SUVA values of the treated waters was observed between both resins. Similarly, a contact time of 30 minutes resulted in up to 65% (3.4 to 1.2) reduction of SUVA from raw water to treated water samples for both resins, which did not show significant differences ($p > 0.05$) when compared against each other.

Humbert et al. (2005) found similar results using 8 mL/L MIEX®, with observed 23 to 56% reductions in SUVA after 3 minutes, and 55 to 65% SUVA reductions after 30 minute. A SUVA value of 4 or higher is said to be indicative of waters with NOM that is generally composed of humic substances, and a SUVA value of 2 or less is correlated with NOM compositions that are non-humic (Edzwald, 1993). The results from this research indicate that both resins removed the majority of humic substances (i.e. SUVA ~ 2) after 5 minutes of contact

time, and that 30 minutes of contact time provided SUVA values lower than 1.5, which would be assumed to be correlated with low DBP formation.

4.3.2.2 Secondary Effects of Strong-Base AERs

In general, the removal of NOM using strong-base anion exchange resins involves the selective exchange of chloride ions (Cl^-) with DOC present in the water. In addition to DOC, some resins have an affinity for sulphate ions (SO_4^{2-}). The increase in chloride and decrease in sulphate concentrations can potentially result in elevated CSMR values. A resin dose of 6 mL/L for both resins was used with a contact time of up to 30 minutes, and samples were analyzed for chloride and sulphate. The impact of resin type on the removal of mineral ions is displayed in Figure 4.6.

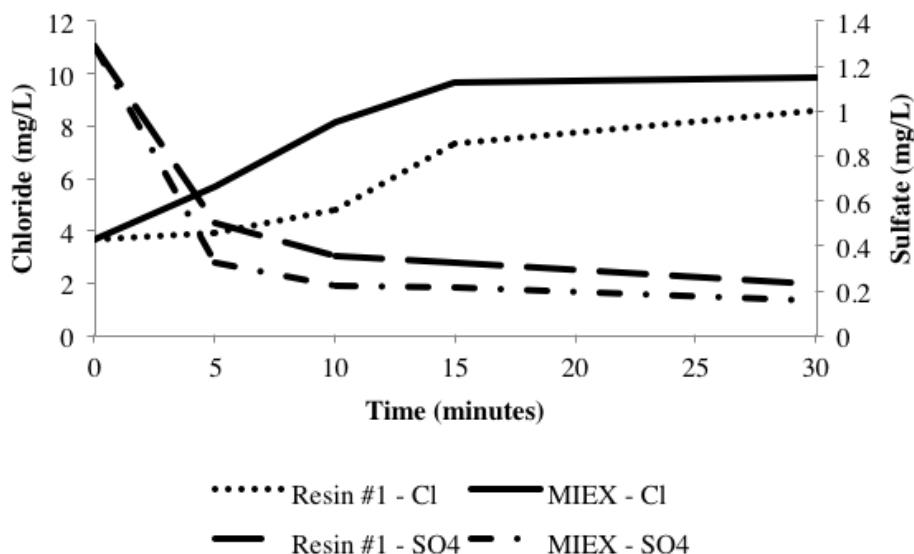


Figure 4.6. Impact of resin type on Chloride and Sulphate concentrations over time (N=3).

As expected, chloride concentrations increased from 3.7 to 9.8 mg/L for MIEX® after 30 minutes of treatment. However, a steady state or equilibrium was reached with MIEX® resin

after 15 minutes. The same trend was seen with the Resin #1, however, concentrations continued to increase beyond 15 minutes. For example, after 15 minutes of treatment with Resin #1, chloride levels increased from 3.7 to 7.3 mg/L and increased to 8.6 mg/L after 30 minutes of treatment. Chloride concentrations in MIEX® treated waters were significantly higher ($p < 0.05$) than those exhibited by water treated with Resin #1 at contact times up to 15 minutes, however, there were no significant differences ($p > 0.05$) between the two at 30 minutes. Like the UV254 and DOC concentrations explained in Section 4.3.2.1, the chloride concentrations resulting from 10 minutes of treatment with 6 mL/L MIEX® were nearly identical to those from 30 minutes of treatment with 6 mL/L Resin #1. This finding further verifies that MIEX® resin provides more rapid removal of organic matter by a factor of three compared to Resin #1.

The opposite trend was observed with sulphate, where increasing contact time resulted in decreasing sulphate concentrations. As expected, the water treated with MIEX® showed higher chloride and lower sulphate concentrations than water treated with Resin #1. This may be attributed to the smaller bead size and increased surface area available for exchange on the MIEX® resin compared to the surface of Resin #1. In addition, MIEX® resin has been shown to have a high affinity for sulphate. Sulphate concentrations follow the same trend as organic matter (UV254 and DOC) and chloride concentrations where the levels achieved by MIEX® in 10 minutes were nearly identical to those as a result of treatment with Resin #1 for 30 minutes.

Similar results were found by Humbert et al. (2005), who observed a sharp increase in chloride and decrease in sulphate with 8 mL/L MIEX® compared to more conventional AERs within the first 5 minutes of contact time. The higher chloride concentrations and lower sulphate concentrations resulting from AER treatment with both resins resulted in rapid increases in CSMR over time.

Figure 4.7 demonstrates the finished water CSMR for both resins used over a 30 minute period.

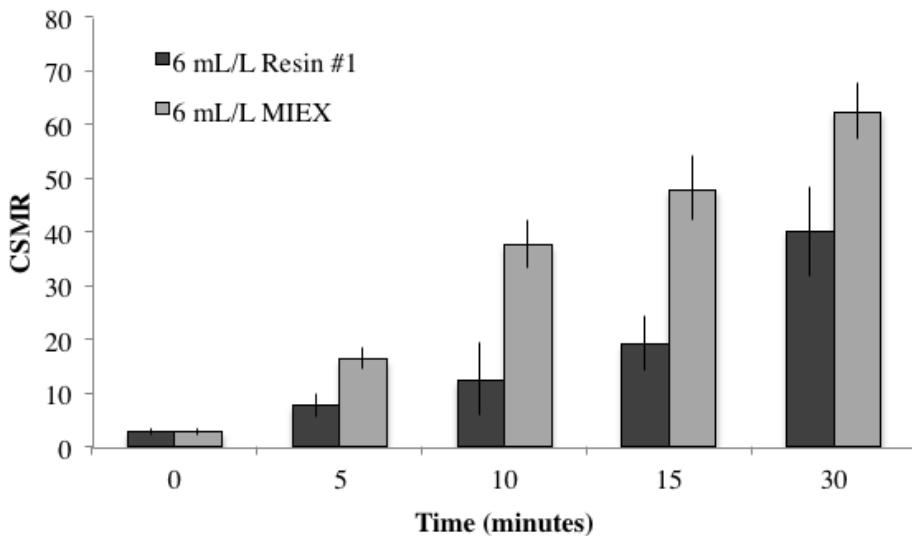


Figure 4.7. Impact of resin type and time on CSMR (N=3).

Although the CSMR values for MIEX[®] treated samples were significantly higher than those exhibited by Resin #1, all CSMR values were above 0.5, which Oliphant (1983) and Gregory (1990) concluded was indicative of higher corrosion currents between lead and water. As expected, the CSMR results follow a similar trend to organic matter concentrations where those achieved by 6 mL/L MIEX[®] within 10 minutes of treatment were nearly identical to those as a result of treatment with 6 mL/L Resin #1 for 30 minutes. Based on these results, it is expected that the finished water CSMR in full-scale AER treatment using either MIEX[®] or Resin #1 would be similar due to the differences in contact time required to achieve similar finished water quality in terms of UV254 and DOC concentrations.

Additional research has also shown that the use of strong-base AERs for NOM removal resulted in elevated CSMR (Boyer and Singer, 2006; Ishii and Boyer, 2011; Willison and Boyer, 2012). However, previous research by Ishii and Boyer (2011) demonstrated that when AER treated waters are coagulated with low-dose (i.e. 7 mg/L) alum; CSMR was reduced to the raw water value. As the CSMR parameter serves only as an indicator for lead corrosion, a full corrosion study using the source water outlined in section 4.2.1 would be required in order to provide conclusive information regarding the actual corrosivity of the raw and AER treated waters.

4.4 Conclusions

The objective of this chapter was to evaluate two strong-base AERs, one magnetic (MIEX®) and one conventional (Resin #1) using dose-response and batch experiments for DBP precursor (i.e. UV254 and DOC) removal, and for their secondary effects (i.e. chloride, sulphate, and CSMR). The results of this study showed the following:

- A 6 mL/L resin dose for both MIEX® and conventional resins was found to be optimum for contact times up to 30 minutes based on UV254 removal, resulting in 68 and 90% reductions in UV254 for Resin #1 and MIEX®, respectively.
- Both AERs were effective at removing organic matter. However, the 6 mL/L MIEX® resin outperformed Resin #1 significantly ($p < 0.05$) in terms of UV254 and DOC removal at all contact times investigated. A 6 mL/L MIEX® dose resulted in 90 and 68% UV254 and DOC removal, respectively. Water treated with both MIEX® and Resin #1

showed similar SUVA values (i.e. ≤ 2), which was indicative of low DBP formation potential.

- Chloride concentrations in MIEX® treated samples were higher than those in water treated by Resin #1 at all contact times except for 30 minutes. Sulphate concentrations followed the opposite trend, where Resin #1 exhibited higher sulphate concentrations. This was attributed to the fact that MIEX® has a high affinity for sulphate. Treatment with both resins resulted in chloride concentrations of at least 8 mg/L, while sulphate concentrations were reduced to less than 0.3 mg/L, both after 30 minutes of contact time.
- Waters treated with MIEX® exhibited significantly higher CSMR values (up to 63) than those treated by a conventional AER (up to 40), however, CSMR for both were $>>0.5$ and a corrosion study is recommended in order to make specific conclusions regarding the actual corrosivity of the treated water.
- MIEX® treatment for 10 minutes at a dose of 6 mL/L resulted in nearly identical concentrations of UV254, DOC, chloride, sulphate, and CSMR, as treatment with 6 mL/L Resin #1 for 30 minutes. Based on these results, it was suggested that the MIEX® resin should be used for organic removal from surface water.

Chapter 5: Evaluation of Temperature Impacts on Drinking Water Treatment Efficacy of Magnetic Ion Exchange and Enhanced Coagulation

A version of this chapter has been published in the Journal of Water Supply: Research and Technology – AQUA*.

5.1 Introduction

Natural organic matter (NOM) is present in all surface waters and is the result of the biological degradation of organic material (Sharp et al., 2006c). NOM can be problematic in drinking water treatment due to aesthetic and operational issues, as well as providing precursor material for the formation of chlorinated disinfection by-products (DBPs) (Beckett and Ranville, 2006; Cornelissen et al., 2008). Coagulation processes have shown to be very effective in the removal of significant amounts of NOM from source waters prior to chlorine disinfection (Liu et al., 2011). However, coagulation can generate large volumes of concentrated solid waste residuals that can be problematic to water utilities from an operational and economic perspective (Cornwell, 1999; Walsh et al., 2008). Coagulation processes can also be impacted during the winter months, as alum in particular has been known to perform poorly for NOM and turbidity removal in cold-water conditions (i.e. < 5 °C) (Morris and Knocke, 1984; Knocke et al., 1986; Haarhoff and Cleasby, 1988; Exall and Vanloon, 2000; Braul et al., 2001).

Ion exchange technology is based on the reversible exchange of oppositely charged ions between a solid phase (e.g., IX resin) and target contaminants in the water phase. The use of anion exchange resins (AER) for the treatment of humic-rich waters is well published (Brattebø et al. 1987; Symons et al. 1995) and generally involves the selective exchange of chloride ions (Cl^-) with dissolved organic carbon (DOC) to occupy the active side of the resin. The recent

development of magnetic ion exchange resins (MIEX®) that can be used in continuous stirred tank reactor (CSTR) designs has been shown to achieve upwards of 90 % NOM removal (Singer and Bilyk, 2002; Fearing et al., 2004; Boyer and Singer, 2005; Humbert et al., 2005; Jarvis et al., 2008; Drikas et al., 2011).

Collectively, these previous studies have shown the effectiveness of MIEX® at removing NOM and DBP precursor material. However, most of the studies to date have been conducted at room temperature, or for applications in warm climates. A study conducted by Humbert et al. (2005) evaluated the efficacy of MIEX® at water temperatures ranging from 6 to 36 °C and concluded that MIEX® had a more significant impact on organic removal at the warmer operating temperatures. There is a lack of information on the efficacy of MIEX® technology in cold water operating conditions, and therefore the performance of this technology in colder climates where surface water temperatures can approach 2 °C seasonally is unknown. The overall objective of this study was to evaluate enhanced coagulation with alum, MIEX® and a combined MIEX® -alum process at warm (20 °C) and cold water (1 °C) operating conditions. Settled water quality was evaluated in terms of pH, turbidity, true color, DOC, UV254, specific UV absorbance (SUVA), trihalomethane formation potential (THMFP) and haloacetic acid formation potential (HAAFP).

5.2 Materials and Methods

5.2.1 Source Water

Lake water from a municipality located in New Brunswick, Canada was used for this study. The raw water used in the experiments is representative of other surface waters in Atlantic Canada, with low turbidity (< 2 NTU) and alkalinity (< 10 mg/ L as CaCO₃), and

moderate NOM content (DOC = 3 to 5 mg/ L). Water samples were taken quarterly during the period of May 2010 to May 2011 and were stored at 4 °C. The raw water samples were characterized various times throughout the study, and are summarized in Table 5.1. DOC concentrations ranged from 3.7 to 4.0 mg/ L, which were nearly identical to the total organic carbon (TOC) concentrations, demonstrating that the organics in the source water are mostly in the dissolved form.

Table 5.1. Raw water characteristics.

Analyte	Number of Samples	Average	Standard Deviation
pH	6	6.3	0.01
Turbidity (NTU)	6	1.5	0.05
True Color (TCU)	6	20	2
UV 254 (cm ⁻¹)	6	0.150	0.010
TOC (mg/L)	6	4.1	0.2
DOC (mg/L)	6	4.1	0.2
SUVA (mg/L·m)	6	3.6	0.5
THMFP (µg/L)	3	349.9	74.6
HAAFP (µg/L)	3	153.8	9.80

5.2.2 Bench-Scale Experiments

Bench-scale experiments were conducted using a standard jar test apparatus (Phipps and Bird, Fisher Scientific) to evaluate (1) enhanced coagulation with alum, (2) MIEX® and (3) a combination of MIEX® followed by coagulation with a low dose of alum. Each treatment process was evaluated at warm (20 °C) and cold (1 °C) water temperature conditions in replicates (N=5).

For the coagulation experiments, alum dosages ranging from 10 to 60 mg/ L were evaluated. A pH of 6.2 was maintained during the coagulation experiments at both cold and warm water conditions through the addition of soda ash (0.1 N Na₂CO₃). This pH was selected for this study based on typical coagulation pH targets practiced by surface water treatment plants in Atlantic Canada using aluminum-based coagulants for the treatment of highly colored water. The jars were rapid mixed for 1 minute at 300 rpm followed by two-stage flocculation of 10 minutes at 40 rpm then 10 minutes at 20 rpm. The jars were then allowed to settle for one hour before settled water samples were taken for analysis.

All MIEX® experiments were conducted using the multi-loading BV procedure explained in Chapter 3.

For both the enhanced coagulation and MIEX® experiments, optimum dose and BV treatment level were determined based on UV254 measurements of the settled water during the warm water (20°C) experiments. The optimum alum dose and MIEX® BV were then evaluated at the cold water (1°C) experiments to examine the impact of variable operating temperatures on treatment performance. For the combined MIEX® -alum treatment, the water was treated with MIEX® at the optimum BV followed by the addition of a low dose of alum (5 mg/ L) using the same methodology for the enhanced coagulation trials. No pH adjustment was required in the MIEX® and combined MIEX® -alum treatments due to the pH of the MIEX® treated water (6.3 ± 0.1) and low dose of alum evaluated. For the cold water trials, the raw water samples were refrigerated at 1 °C overnight prior to testing during which the test jars were tightly insulated with crushed ice to maintain the cold water temperature. For the warm water temperature trials, a second refrigerator was set at 20 °C and the raw water samples were left to temperature adjust overnight prior to testing.

Throughout all experiments, temperature and pH were monitored. Settled water samples were analyzed for pH, turbidity, true color, DOC and UV254. A composite sample of 6 L of treated water was generated for each process at the determined optimum dose at 1 and 20 °C to perform DBP formation potential testing (THMFP , HAAFP).

5.2.3 Analytical Methods

All analytical methods used in this chapter are explained in Chapter 3: Materials and Methods.

5.2.4 Statistical Methods

Paired t-testing ($\alpha = 5\%$) was performed to determine the significance of temperature on treatment efficacy at cold and warm water conditions, and to evaluate the difference between each treatment technology at equivalent operating temperatures. Standard error was calculated and is portrayed on each figure via error bars from five replicates.

5.3 Results and Discussion

5.3.1 Determination of Optimum Coagulant Dose and MIEX® Bed Volume

Jar tests were run at alum dosages from 10 to 60 mg/ L at 20 °C to determine the optimum coagulant dosage to achieve maximum reduction in DBP precursor material as quantified with UV254 measurements (Figure 5.1). From a diminishing returns perspective, the most favourable alum dosage was determined to be 40 mg/L, which achieved a 74% reduction in UV254 measurements from raw water levels. Beyond the 40 mg/L alum dosage, minimal improvements in UV254 removals were observed in the settled water samples. A similar trend was seen for DOC removal with varying alum dosages (Figure 5.1).

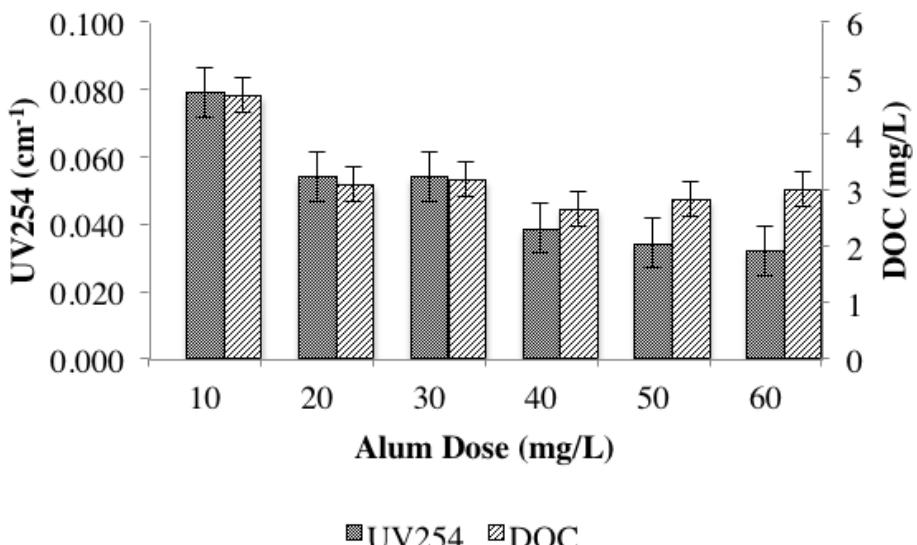


Figure 5.1. Settled water DOC and UV254 for optimum alum dose determination (20°C operating temperature).

The dosage of 40 mg/L alum resulted in the lowest DOC concentration, with a 35% reduction in DOC concentrations from raw water levels. Beyond 40 mg/L, DOC concentrations reached a plateau; therefore further addition of alum did not significantly reduce the concentration of dissolved organics.

Fair to good DOC removal with NOM influencing coagulation processes is generally accepted for source waters with SUVA values between 2 and 4 mg/ L·m (Edzwald and VanBenschoten 1990; Edzwald 1993). The results of the enhanced coagulation experiments with alum showed moderate DOC removal ranging from 24 to 35%. The calculated SUVA value of the source water was 3.3 mg/ L·m (Table 5.1), indicating a mixture of aquatic humics, hydrophobic/hydrophilic NOM and molecular weights. NOM fractionation was not conducted in this study, and it is possible that the organics in the source water used in this study is comprised of a higher fraction of hydrophilic and low molecular weight NOM compounds which are more

difficult to remove with coagulation processes. However, further study would be required to verify this theory.

Settled water DOC and UV254 measurements versus the MIEX® BV treatment rate at 20°C are shown in Figure 5.2.

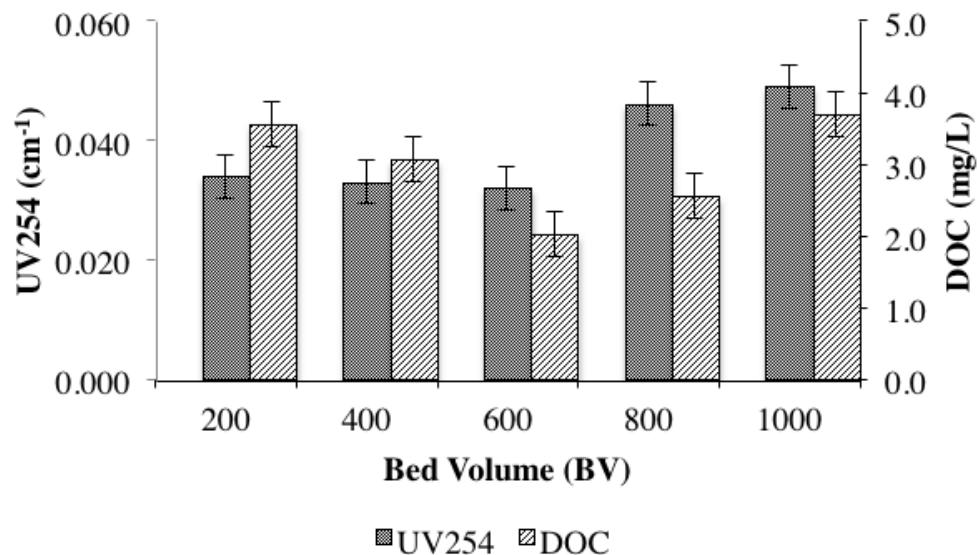


Figure 5.2. Settled water DOC and UV254 for optimum bed volume treatment determination (20°C operating temperature).

The 600 BV treatment rate was chosen as optimum, with DOC and UV254 reduced by 51 and 79%, respectively, from the raw water levels. At the higher treatment rates of 800 and 1000 BV corresponding to increased water to resin contact time, UV254 and DOC removal were shown to be impeded. From 200 to 600 BV, UV254 measurements were found to be relatively constant, but 600 BV was chosen as the optimum treatment rate due to the fact that it represented the longest water to resin contact time, above which the test results indicated that the resin had reached full capacity on the exchange sites to achieve further removal of UV254. As expected, settled water DOC concentrations followed a similar pattern as the UV254 measurements. The

600 BV treatment rate resulted in the lowest DOC concentration of approximately 2.0 ± 0.1 mg/L, increasing to approximately 2.5 ± 0.4 and 3.7 ± 0.05 mg/L at the 800 and 1000 BV rates, respectively.

5.3.2 Impact of Operating Temperature on Treatment Performance

5.3.2.1 Settled Water Turbidity

Figure 5.3 presents settled water turbidity at 1 and 20 °C for all three treatments investigated in this study.

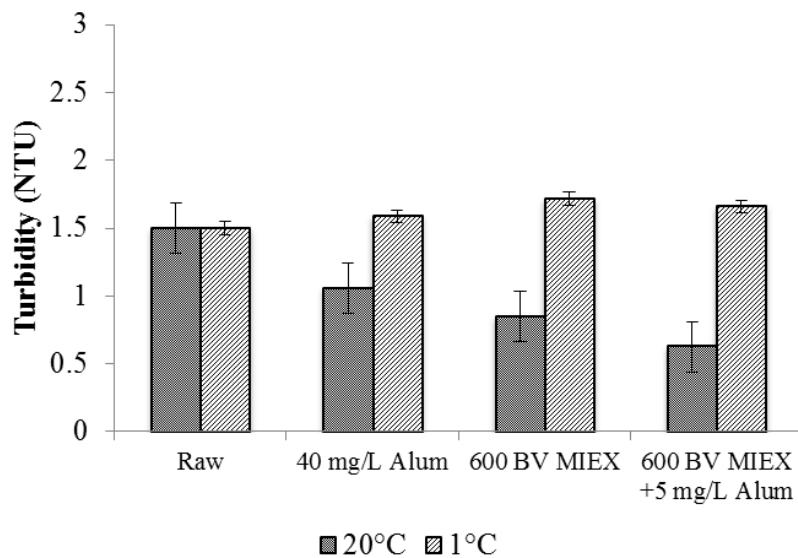


Figure 5.3. Average settled water turbidity at 1 and 20 °C operating temperatures (N=3).

Due to the low turbidity (< 5 NTU) of the source water used in this study, the settled water turbidity (i.e., residual turbidity) results of the bench-scale testing can be viewed as representing the removal efficiency of floc formed in coagulation with alum or the combined process (MIEX®-Alum), or that of the ion exchange resin in the MIEX® experiments. Settled

water turbidity measurements can provide an indication of floc or resin carryover that may impact downstream filtration operations, and in this study were evaluated to determine potential differences under warm and cold water operating conditions. It has been shown in other studies that turbidity removal in coagulation-sedimentation processes using inorganic coagulants can be hindered by cold-water temperatures (Morris and Knocke, 1984; Exall and Vanloon, 2000; Braul et al., 2001).

Paired t-testing at the 95% confidence interval was conducted for all three treatments to determine if there was a significant impact on residual turbidity in the settled water samples under cold water temperature conditions. For the enhanced coagulation experiments conducted at a dosage of 40 mg/ L alum, paired t-testing showed that operating at the colder water temperature had a significant impact ($p < 0.05$) on residual turbidity after settling. Residual turbidity was 33% higher in the cold-water trial compared to the warm water experiments. Similar results have been reported in previous studies. Morris and Knocke (1984) found that residual turbidity measured at 1 and 20 °C after coagulation with alum was a direct function of solution temperature. A similar study that evaluated turbidity removal at 2 and 22 °C with alum dosages ranging from 20 to 100 mg/ L demonstrated that the operating temperature had a significant impact on turbidity removal efficacy (Knocke et al. 1986).

It has been reported in other studies that MIEX® treatment results in elevated turbidity in the treated water due to resin carryover (i.e., suspended resin beads) (Cook et al., 2001; Singer and Bilyk, 2002; Humbert et al., 2005; Kitis et al., 2007). However, water sampling protocols for turbidity measurements in those studies were not reported. In this study, the first 50 mL of water sample collected after MIEX® treatment was discarded in order to remove any resin particles that may have collected in the jar test apparatus sample port during mixing. This

methodology follows those used by Boyer and Singer (2005) in bench-scale MIEX® studies. Paired t-testing of the MIEX® treated settled water samples showed that residual turbidity in the samples generated under cold operating conditions was significantly higher ($p < 0.05$) than levels generated under warm water operating conditions.

The combined treatment (600 BV MIEX® followed by a 5 mg/L dosage of alum) was also shown to be impacted by cold-water conditions in terms of turbidity removal (Figure 5.3). Paired t-testing demonstrated a highly significant difference ($p < 0.05$) in mean turbidity values between the 1 and 20 °C operating temperatures. Specifically, the combined MIEX®-Alum treatment resulted in settled water turbidity levels that were 62 % higher at the 1 °C operating temperature compared to 20 °C. Although settling of the coagulated floc and/or resin in all of the experiments was demonstrated to be impacted by the colder operating conditions, it is important to note that the residual turbidity levels for all treatments were below 2.0 NTU.

5.3.2.2 Removal of NOM and DBP Precursors

The removal of dissolved organic material with alum coagulation was not found to be impacted under colder operating conditions (Figure 5.4).

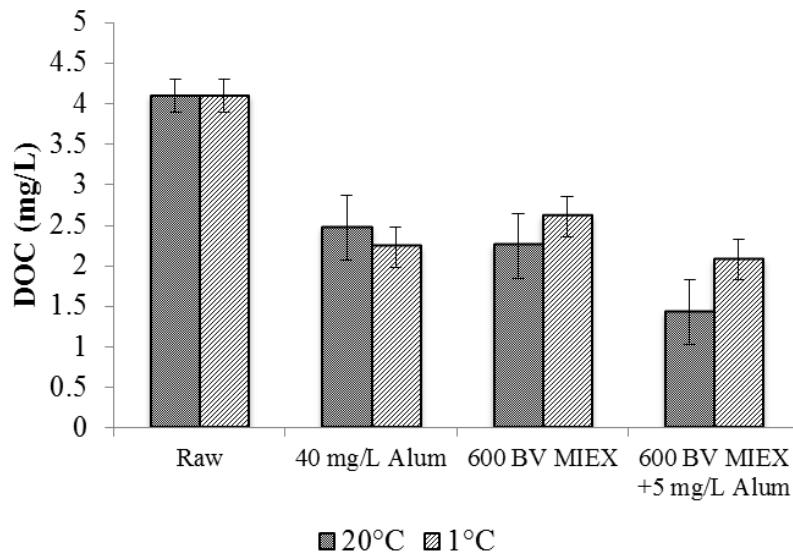


Figure 5.4. Average settled water DOC concentrations at 1 and 20 °C operating temperatures (N=3).

Paired t-test results showed that there was not a significant difference ($p > 0.05$) in DOC removal between the two operating temperatures evaluated for alum coagulation at 40 mg/L. It has been previously noted that DOC removal is not as sensitive as turbidity, or may not be impacted at all by cold-water conditions (Knocke et al., 1986; Randtke, 1988; Hanson and Cleasby, 1990; Braul et al., 2001). Overall DOC concentrations were reduced by up to 46% via coagulation with 40 mg/L alum.

Paired t-testing showed no significant difference ($p > 0.05$) between MIEX® treatment at 1 °C compared to 20 °C in terms of DOC removal. In a bench-scale study, Humbert et al. (2005) found that DOC removal with MIEX® was not impeded at cold water conditions (6 °C) compared to warm water conditions (36 °C). In that study, with a resin dose of 8 mL/ L and a contact time of 15 minutes, minimal difference between settled water DOC concentrations at both temperatures were observed. Semmens et al. (2000) evaluated the NOM removal capability of

MIEX® at temperatures ranging from 5.5 to 24.2 °C using a 6 mL/ L resin dose and found a 12% decrease in TOC removal at the cold temperature condition. Semmens et al. attributed this change in performance to a combination of cold temperature and changes in NOM chemistry. Overall, DOC concentrations were reduced by up to 45% after 600 BV MIEX® treatment.

In contrast to the results of the alum and MIEX® treatments alone, DOC removal with the combined MIEX®-Alum process was found to be impacted at cold operating temperatures. Paired t-testing results showed that there was a significant impact ($p < 0.05$) of operating temperature on the DOC removal capabilities of the combined process, with DOC removal reduced by approximately 31% at 1°C versus 20 °C. Several studies have investigated the use of combined MIEX®-Alum treatment and its ability to significantly reduce DOC concentrations as well as coagulant demand (Singer and Bilyk, 2002; Boyer and Singer, 2005; Kitis et al., 2007; Drikas et al., 2011). However, none of these previous studies evaluated potential impacts of cold water operating conditions. The results of this study demonstrate that although DOC removal with a combined MIEX®-coagulation process can be significantly ($p < 0.05$) hindered at cold operating conditions, the overall DOC removal achieved is still higher compared to alum coagulation or MIEX® treatments as single unit operations. Reductions in DOC from raw water achieved by the combined MIEX®-Alum process were 50 and 65% at 1 and 20 °C, respectively.

Figure 5.5 presents the settled water UV254 measurements for each treatment evaluated at 1 and 20 °C.

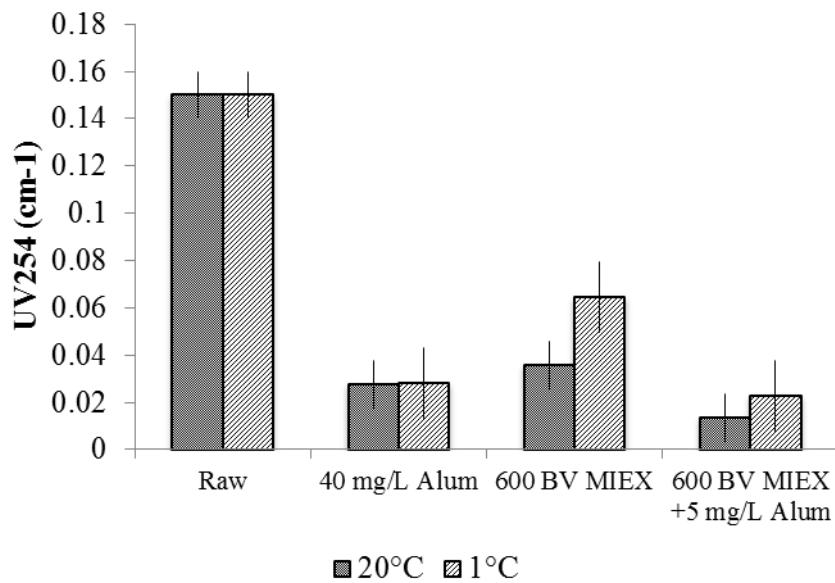


Figure 5.5. Average settled water UV254 at 1 and 20 °C operating temperatures (N=3).

The results of the enhanced coagulation with alum experiments showed there was no significant difference ($p > 0.05$) between the settled water UV254 measurements obtained during the cold and warm operating temperatures. Similar results were reported by Braul et al. (2001) who found that temperature did not affect UV254 absorbance reduction at 1.5 °C compared to 20 °C. A reduction in UV254 of up to 82% was observed after treatment with enhanced coagulation.

The MIEX® treatment was found to perform significantly better ($p < 0.05$) in terms of UV254 removal at the warmer operating temperature than under cold water conditions, as the treatment efficacy was reduced by 45 % at 1 °C. Overall reductions in UV254 from raw water after 600 BV MIEX® treatment were 57 and 77% at 1 and 20 °C, respectively. Semmens et al. (2000) evaluated the changes in settled water UV254 from 5.5 to 24.2 °C using a 6 mL/ L MIEX® dose and a 45 minute contact time, observing nearly identical UV254 measurements at both temperatures. Humbert et al. (2005) evaluated UV254 absorbance at an 8 mL/ L MIEX®

resin dosage with operating temperatures ranging from 6 to 36 °C, and found minor effects of temperature on UV254 removal. In that study, a slight temperature impact on UV254 removal for the first 10 minutes of contact time was observed, which diminished as contact time increased to 30 minutes. The significant impact of temperature on UV254 removal observed in this study may be linked to the lower temperatures investigated (i.e., 1 °C vs 6 °C), the lower MIEX® dosage evaluated (5 mL/ L vs. 6 to 8 mL/ L) and/or the lower resin contact time (15 min vs. 30 – 45 min) compared to the other studies.

Although the combined MIEX®-Alum treatment process showed reductions UV254 removal by 40% at 1 °C compared to 20 °C, no significant differences were observed ($p > 0.05$). Operation of the combined MIEX®-Alum process in cold water conditions still resulted in an 85 % reduction in UV254 from raw water levels.

5.3.2.3 Disinfection By-Product Formation Potential

Figure 5.6 presents the mean THM formation potential results for each treatment at both 1 and 20 °C.

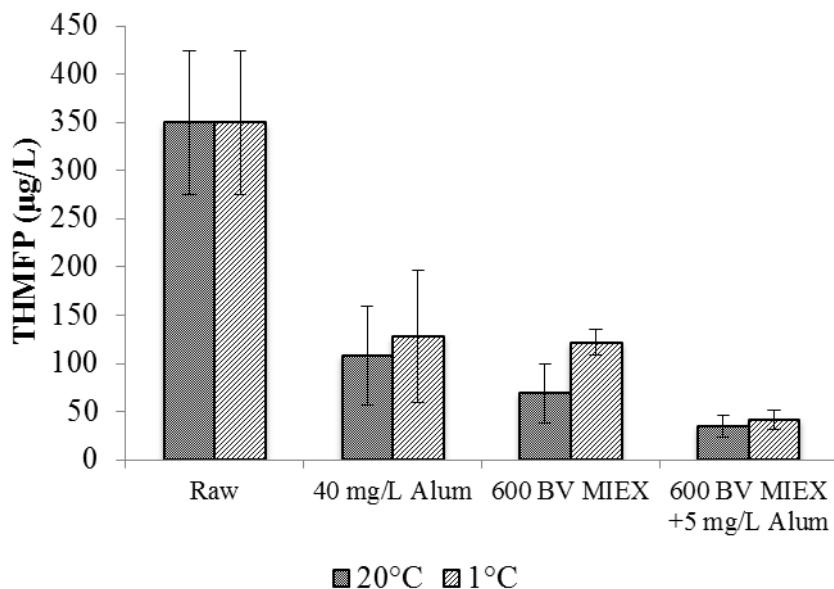


Figure 5.6. Average trihalomethane formation potential at 1 and 20 °C operating temperatures (N=3).

Paired t-test results showed that operating temperature did not significantly ($p > 0.05$) impact THMFP of the alum treated water. As UV254 removal with enhanced coagulation was not found to be impacted at cold water operating temperatures, these results were expected. Up to 69% reductions in THMFP were observed after treatment with enhanced coagulation. In drinking water treatment, it has been shown that UV254 is a good surrogate parameter for predicting THMFP in source or treated water (Edzwald et al., 1985). THM formation with the MIEX® treatment was found to be significantly ($p < 0.05$) impacted by cold water operating temperatures, with a 43% increase in THMFP concentrations at 1°C compared to water generated at 20 °C. These results agree with the reduced UV254 removal observed with MIEX® treatment in cold water conditions (Figure 5.5). UV254 concentrations were reduced by 65 and 80% from raw water at 1 and 20 °C, respectively after MIEX® treatment. The combined treatment did not show any significant impacts of cold-water temperatures on THMFP ($p >$

0.05), as expected based on settled water UV254 values, resulting in up to 90% reductions UV254 reductions from raw water.

For the HAAFP results shown in Figure 5.7, paired t-testing results showed that there was no significant impact ($p > 0.05$) of operating temperature on HAAFP with enhanced coagulation with alum and the combined MIEX® -Alum processes, as their means were nearly identical.

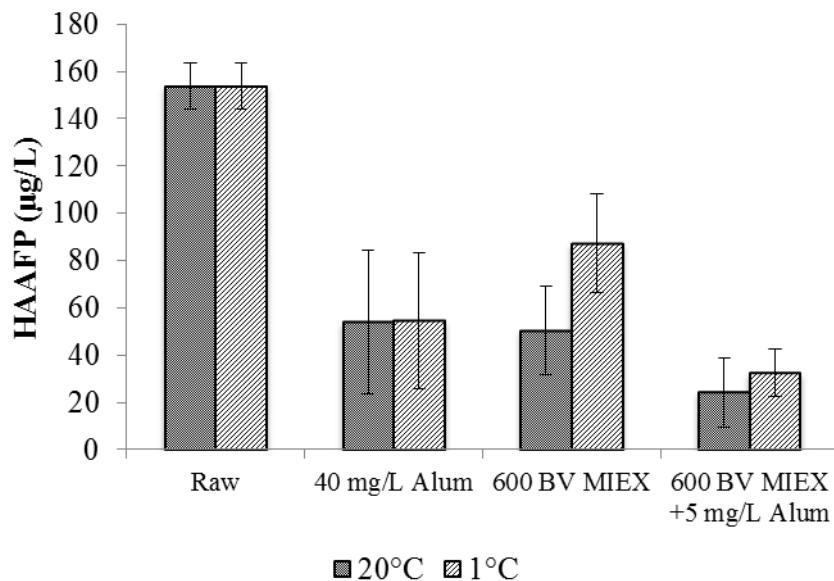


Figure 5.7. Average haloacetic acid formation potential at 1 and 20 °C operating temperatures (N=3).

This was in agreement with the THMFP and UV254 removal results found with both of these processes, which were not found to be impacted by cold-water conditions. The overall HAAFP concentrations were reduced by up to 65 and 84% for enhanced coagulation with alum and the combined MIEX®-Alum treatment, respectively. The MIEX® treatment showed HAAFP concentrations were significantly higher ($p < 0.05$) in the cold temperature trials compared to warm water conditions. These results are also consistent with the THMFP and UV254 removal

results for the MIEX® treatment as a single unit operation. The MIEX® process provided 43 and 67% reductions in HAAFP at 1 and 20 °C, respectively.

Specific UV absorbance (SUVA), a concept developed by Edzwald (1993) and calculated as the ratio of UV254 to DOC, has been correlated with DBP formation, as it serves as a good indicator of the humic and aromatic content of the water linked to greater DBPFP (Liang and Singer, 2003, Weishaar et al., 2003, Kitis et al., 2004, Ates et al., 2007, Kitis et al., 2007). Figure 5.8 presents SUVA values for each treatment evaluated in this study at both 1 and 20 °C operating conditions.

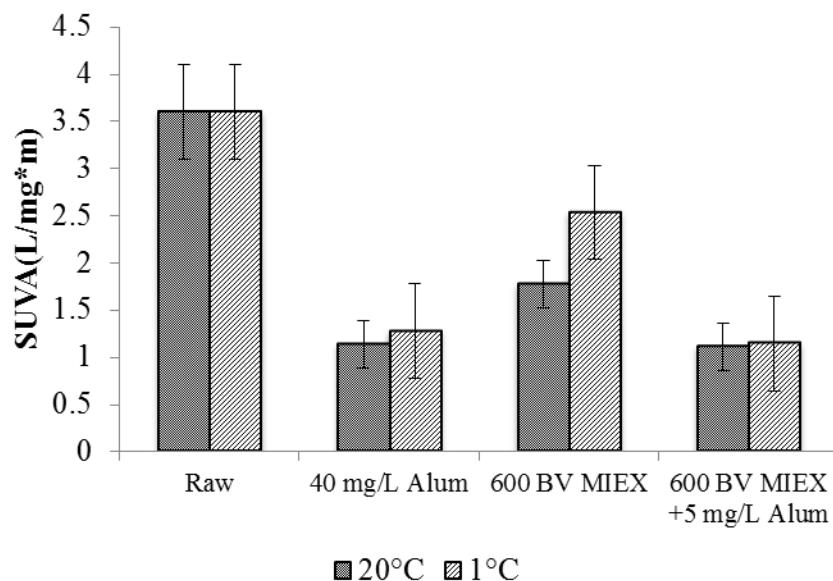


Figure 5.8. Average specific UV absorbance at 254 nm at 1 and 20 °C operating temperatures (N=3).

Paired t-testing showed that temperature did not have a significant ($p > 0.05$) impact on SUVA reduction with the enhanced coagulation and combined MIEX®-Alum treatments. MIEX® treatment as a single unit operation showed a significantly higher ($p < 0.05$) SUVA value at 1 °C compared to at 20 °C. These results with SUVA analysis present the same correlation

with the THMFP and HAAFP results, reinforcing the idea of SUVA serving as an indicator for THMFP.

5.3.2.3.1 Operational Window for Minimizing Disinfection By-Product Formation Potential

Raw and treated water UV254, THMFP and HAAFP concentrations at both 1 and 20 °C were evaluated using regression analysis in order to determine an operational window in terms of UV254 for targeting DBPFP concentrations of 100 and 80 µg/L respectively, regardless of treatment technology used. It must be noted that THMFP and HAAFP concentrations were formed under UFC conditions. THMFP and HAAFP concentrations can be an over-estimate compared to actual THM and HAA concentrations formed due to the elevated chlorine dosages and contact time (target residual 1±0.4 mg/L after 24h), as well as the warmer incubation temperature (20 °C) used under UFCs. Table 5.2 below summarizes the regression analysis results.

Table 5.2. Regression analysis for UV254 and formation potential at 1 and 20 °C.

Parameters	Regression Equation	
	20 °C	1 °C
UV254, THMFP	THMFP = 2139.7(UV254)+14.892 $r^2=91\%$	THMFP = 2024(UV254)+19.322 $r^2=78\%$
Target UV254 to Achieve 100 µg/L	0.03 to 0.05 cm ⁻¹	0.02 to 0.06 cm ⁻¹
UV254, HAAFP	HAAFP = 921.35(UV254)+17.515 $r^2=84\%$	HAAFP = 911.81(UV254)+21.142 $r^2=77\%$
Target UV254 to Achieve 80 µg/L	0.05 to 0.08 cm ⁻¹	0.05 to 0.08 cm ⁻¹

Strong correlations between UV254 and THMFP or HAAFP were observed for all regression equations depicted in Table 5.2, indicating that UV254 serves as a good surrogate for DBPFP in this source water. The operational window for UV254 concentrations that allowed for THMFP and HAAFP concentrations less than or equal to 100 and 80 µg/L at 20 °C was determined to be 0.03 to 0.08 cm⁻¹. This indicates that any treatment technology that can maintain a finished water UV254 concentration within this range will most likely have THM and HAA concentrations below 100 and 80 µg/L, respectively, as regression analysis was based on formation potential under UFC conditions and is likely a conservative estimate. Similarly, a UV254 range of 0.02 to 0.08 cm⁻¹ was determined to provide THMFP and HAAFP concentrations below 100 and 80 µg/L at 1 °C. Figures 5.9 and 5.10 below portray the relationship between UV254, and THMFP or HAAFP at both 20 and 1 °C.

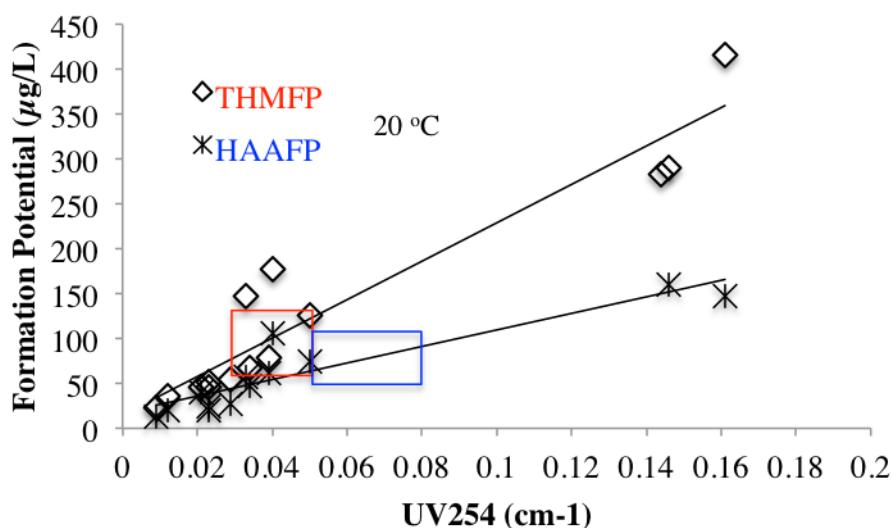


Figure 5.9. Relationship between UV254 and formation potential at 20 °C.

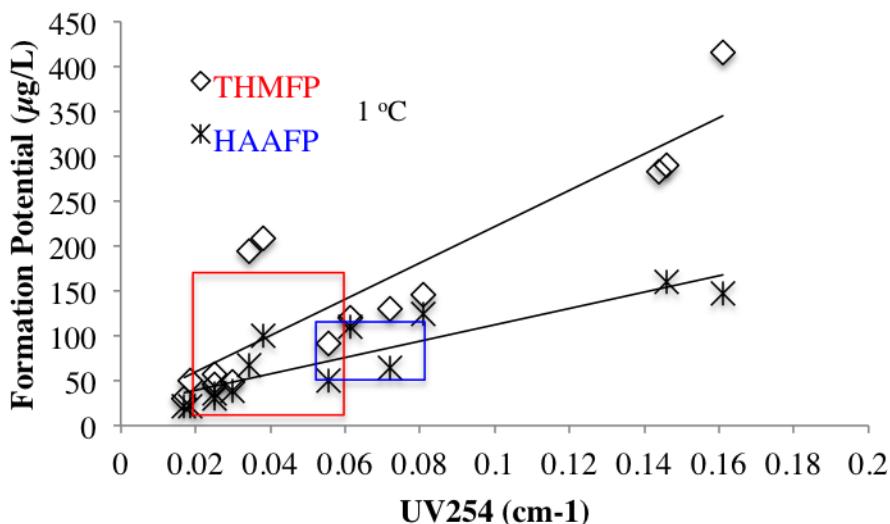


Figure 5.10. Relationship between UV254 and formation potential at 1 °C.

It can be observed on Figures 5.9 and 5.10 that the relationships between UV254, THMFP and HAAFP are similar at both 1 and 20 °C. A slightly wider operating range was achieved under at 1 °C. (Figure 5.10), which can be attributed to slower formation of DBPs in cold water.

5.3.3 Process Treatment Efficacy at Equivalent Temperatures

Statistical analysis using paired t-testing was used to compare the treatment efficacy of the three treatment technologies at equivalent operating temperatures. With warm water operating conditions (20°C), no significant difference ($p > 0.05$) was found between the enhanced coagulation and MIEX® treatments in terms of all of the water quality parameters measured in this study. Under reduced operating temperature (1°C), significantly higher ($p < 0.05$) DOC and UV254 measurements were observed in the MIEX® versus coagulated settled water. However, overall reductions in UV254 (0.065 cm⁻¹) and SUVA (2.5 mg/ L·m) from raw water levels (0.150 cm⁻¹ and 3.6 mg/ L·m, respectively) with the MIEX® treatment resulted in

DBP formation potential concentrations that were not found to be significantly different ($p > 0.05$) from those formed after coagulation treatment in cold water.

Overall, the combined MIEX®-alum treatment provided equal or greater removal of DBP precursors compared to the treatments as single unit operations at both operating temperatures. DBP formation potential concentrations, however, were not found to be statistically significantly different ($p > 0.05$) between the three technologies at 20°C. At both operating temperatures, the combined process resulted in the lowest mean THMFP and HAAFP concentrations in the settled water, well below the maximum acceptable concentrations (MAC) outlined in the Canadian drinking water quality guidelines (TTHM MAC $< 100 \mu\text{g/L}$ and HAA MAC $< 80 \mu\text{g/L}$) (Health Canada 2012), compared to the technologies operated as single unit operations.

5.4 Conclusions

The objective of this study was to investigate the treatment efficacy of three NOM removal technologies: enhanced coagulation with alum, MIEX® and a combined process of MIEX® followed by a low dose of alum (MIEX®-Alum), at warm and cold operating temperatures (20 vs. 1 °C). The results of this study showed that:

- Cold water operating conditions resulted in significantly higher settled water turbidity for all three of the processes evaluated in this study. However, the residual turbidity measurements were all lower than 2.0 NTU.
- NOM removal as quantified by settled water DOC concentrations was not found be significantly impeded by cold water conditions for the enhanced coagulation and MIEX® treatments. DOC removal in the MIEX®-Alum process was found be significantly

reduced under colder operating conditions, however this combined process was found to result in greater DOC reductions compared to the individual treatments as single unit operations at both operating temperatures.

- DBP precursor removal as quantified by settled water UV254 measurements was not found to be significantly impacted by cold-water conditions for the enhanced coagulation treatment. In contrast, results of the study found that the colder operating temperature significantly reduced UV254 removal in the MIEX® process as a single unit operation. The combined process resulted in the greatest reduction in UV254 compared to the technologies operated as single unit operations and was not significantly impacted by temperature.
- Disinfection by-product formation potential as quantified by THM and HAA concentrations measured under uniform formation conditions were not significantly impacted by water temperature changes in the enhanced coagulation and combined MIEX®-Alum experiments. The combined process was found to provide the lowest THM and HAA formation potential concentrations at both operating temperatures.
- MIEX® treatment was found to be impacted by the lower 1°C operating temperature in terms of DBP precursor removal which corresponded to THMFP and HAAFP concentrations greater than current DBP guidelines. These results indicate that operating at a lower bed volume rate may be warranted in cold-water conditions, although further study would be required to determine if the colder water conditions would concurrently result in reduced DBP formation rates.
- Based on regression analysis of UV254 and DBPFP of raw and treated samples, the target UV254 window that would provide THMFP and HAAFP under 100 and 80 µg/L,

respectively ranged from 0.03 to 0.08 cm⁻¹ at 20 °C and 0.02 to 0.08 cm⁻¹ at 1 °C. As these UV254 concentrations were based on THMFP and HAAFP under UFC as opposed to actual THM and HAA concentrations in the distribution system, these target ranges are conservative.

Chapter 6: Process Monitoring Tools for Anion Exchange Treatment of Surface Waters for NOM Removal

6.1 Introduction

Negatively charged colloidal particles are present in all surface waters and are often considered the contaminants that control coagulation dosages. Coagulation processes are often used to destabilize this charge, allowing for effective precipitation. However, several researchers have shown that the charge of NOM is 10 to 100 times greater than that exhibited by colloidal matter, therefore coagulation dosages are likely to be controlled by NOM concentrations rather than turbidity (Edzwald, 1993; Edzwald and VanBenchhoven, 1990; Pernitsky, 2003).

Surface charge measurements such as zeta potential and streaming current have been shown to be capable of estimating the surface potential on colloids and NOM and have been used to optimize the coagulation process for charge neutralization. Specifically, streaming current has been used as a tool to monitor the performance of coagulation for NOM removal. It has also been used for automatic dose control of coagulants based on deviations due to plant upsets, from an SC set-point based on optimal treatment conditions.

An alternative process to conventional coagulation/sedimentation for NOM removal is ion exchange (IX), through the use of anion exchange resins (AERs). The anion exchange process involves the removal of negatively charged organic matter through the selective exchange of DOC for a mobile counter ion on the resin surface such as chloride (Cl^-). The use of AERs for the removal of NOM is well researched (Brattebo et al., 1987; Symons et al., 1995; Bolto et al., 2002; Singer and Bilyk, 2002; Boyer and Singer, 2005; Boyer and Singer, 2006; Humbert et al., 2005; Cornelissen et al., 2008).

As AER treatment has been shown to remove NOM to a great extent, there is an opportunity to monitor the treatment efficacy of AER processes in the removal of negatively charged NOM species via measurements such as ZP and SC. To date, there has been a lack of published literature on this subject. Therefore, the objectives of this chapter were to 1) investigate the relationship between ZP and SC and NOM in terms of UV254 of AER treated waters, 2) to evaluate the use of charge analysis to optimize and monitor the MIEX® treatment process in terms of NOM removal, and 3) to use the overall charge demand of AER treated waters as a tool for determining optimum coagulation dosages for downstream treatment processes.

6.2 Materials and Methods

6.2.1 Source Water

A synthetic water containing 5 mg/L humic acid (Sigma Aldrich) was used in preliminary bench-scale experiments to simulate an Atlantic Canada source water with low turbidity (< 2 NTU) and moderate DOC (4 to 6 mg /L). Surface source water was also sampled from a municipality in New Brunswick from May to September, 2013 to be used in applied experiments to simulate full-scale treatment. Raw and synthetic waters were characterized throughout this study and are summarized in Table 6.1.

Table 6.1. Average raw and synthetic water characteristics May – September, 2013 (N=3).

Analyte	Raw Water	Synthetic Water
pH	6.70 ± 0.5	5.5 ± 0.05
Turbidity (NTU)	0.80 ± 0.20	1.6 ± 0.2
True Color (PtCo)	20.00 ± 2.7	44 ± 1
UV254 (cm⁻¹)	0.15 ± 0.01	0.137 ± 0.004
TOC (mg/L)	5.9 ± 1.3	3.2 ± 0.4
DOC (mg/L)	5.8 ± 1.2	2.5 ± 0.2
SCM	-337.3 ± 2.5	-795 ± 12
ZP (mV)	-21 ± 1	-53.5 ± 2.7

6.2.2 Bench-Scale Experiments

6.2.2.1 Baseline Experiments

A set of baseline jar tests were conducted on a synthetic water with two strong-base anion exchange resins, Resin #1 (conventional, typically used in packed bed) and MIEX® (magnetic AER used in CSTR processes), to investigate the application of charge measurements (ZP, SC) to evaluate the removal of NOM. A synthetic water was used in order to ensure that no interfering contaminants (i.e. clay turbidity particles) were present that may affect charge readings. Therefore, these experiments are representative of the actual relationship between NOM removal with AERs and charge readings in terms of ZP and SC. A set of five jars were prepared each with 1 L synthetic water and 5 mL resin and were mixed for 60 minutes at 150 RPM. A 250 mL sample was taken from each consecutive jar at 0, 5, 15, 30 and 60 minute intervals, respectively. All samples were analyzed for streaming current, zeta potential, and UV254. Prior to analysis, resin carryover was removed from using a 500 µm sieve and/or and a

magnet in order to prevent the altering of readings by resin charged resin beads. Experiments were repeated in triplicate.

6.2.2.2 Optimization Experiments

A second set of jar tests were carried out on both synthetic and raw waters using MIEX® to evaluate the use of charge analysis to determine the BV treatment rate that would provide the greatest reductions in organics (UV254, DOC). The multi-bed loading procedure described in Chapter 3 was used to simulate treatment which has been shown to model full scale MIEX® treatment (Slunjski et al., 2000; Semmens et al., 2000; Kitis et al., 2007; Mergen et al., 2008; Anderson and Walsh, 2012). Each composite BV sample was analyzed for UV254, DOC, ZP, and SC. These experiments were further repeated using raw water. All experiments were repeated in triplicate to ensure consistency of results.

6.2.3 Pilot-Scale Trials

A 10 USGPM (0.63 L/s) high rate MIEX® pilot plant was operated from June to August 2013 in a municipality New Brunswick, Canada with raw water characteristics similar to those listed in Table 6.1. A full characterization of raw water during this period is listed in Table 6.2.

Table 6.2. Raw water characteristics during pilot-scale trials, June – August, 2013.

Analyte	Number of Samples	Average	Standard Deviation
pH	27	6.8	0.2
Turbidity (NTU)	27	0.95	0.2
True Color (PtCo)	27	22	2.5
UV254 (cm-1)	27	0.158	0.006
DOC (mg/L)	27	4.3	0.3
SCM	6	-372	11
ZP (mV)	6	-19	0.8

The pilot system was operated with MIEX® at 400 to 1150 BV treatment rates, using UV254 removal as an indicator for optimum NOM removal and treatment. Samples were collected from the 400 to 1150 BV treatment runs and were analyzed for UV254, DOC, ZP, SC, and charge demand in order to determine if charge measurements would be able to predict optimum removal of organic matter. A schematic of the pilot system is demonstrated below in Figure 6.1. Figure 6.2 portrays a photo of the actual pilot system. Operating specifications during the pilot study are presented in Table 6.3.

Table 6.3. MIEX® 10 USGPM pilot specs.

Parameter	
Flow Rate	10 USGPM (0.63 L/s)
Contactor Flow	5.4 L/m ² s
Contactor Concentration	200-250 mL/L
Contact Time	4-8 minutes
Regen Rate	1.0 liter resin regenerated/1,000 liters water treated
Regenerant	Sodium Chloride
Regenerant Concentration	10%

Pilot Scale: MIEX High Rate Treatment System

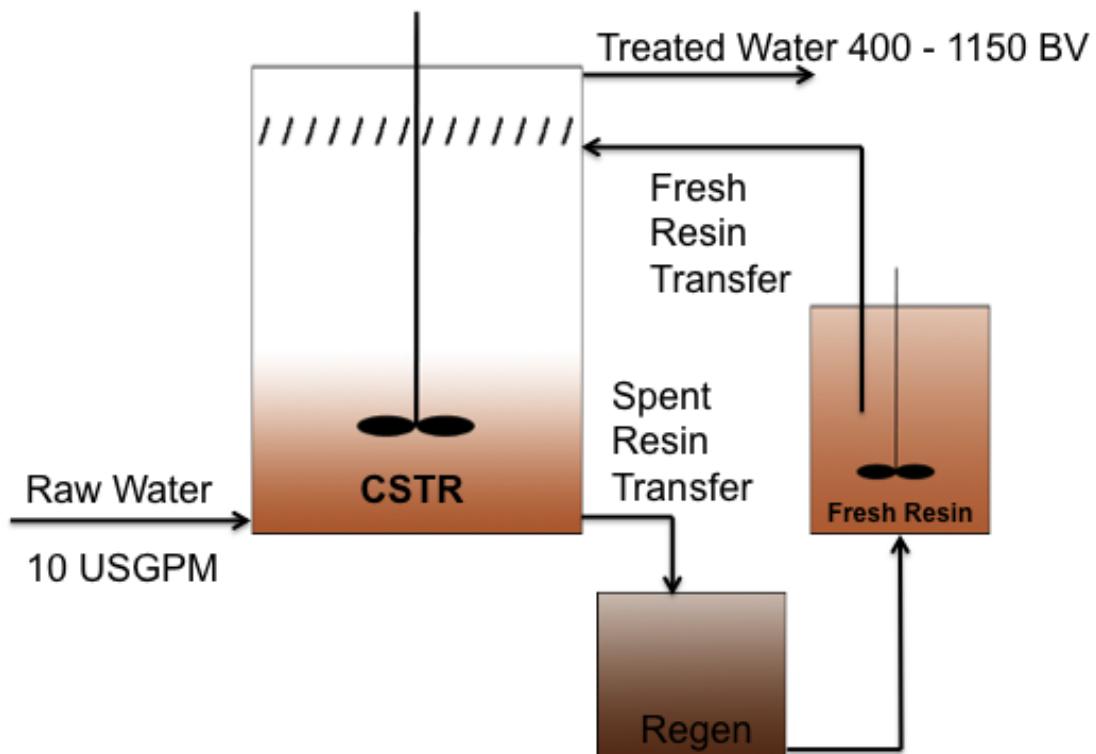


Figure 6.1. Schematic of 10 USGPM MIEX® pilot system.



Figure 6.2. On-site photo of 10 USGPM MIEX® high rate system.

6.2.4 Analytical Methods

Analytical methods for general water quality parameters (i.e. UV254 and DOC) are explained in Chapter 3. Streaming current analysis was performed in duplicate on 150 mL samples. A bench-scale streaming current meter (ECAT 2011, Chemtrac Inc.) with a 0.001 N cationic polymer (polyDADMAC, Nalco TM) was used to measure streaming current on all samples (unfiltered). A bench-scale Zetasizer Nano ZS (Malvern Instruments) was used to measure zeta potential in triplicate on unfiltered samples using a folded capillary cell. Samples were injected with a 10 mL syringe, and extreme caution was taken to ensure that bubbles were not injected into the capillary cell.

6.2.5 Statistical Methods

All relationships between parameters investigated in this study were correlated using the Pearson's product-moment correlation coefficient, (r) which is a measure of the strength and direction of a linear relationship. Paired t-testing was conducted on the mean of triplicate samples to comparatively evaluate the significance of results in terms of UV254, DOC, ZP, SC, and charge demand over a variety of contact times and BV treatment rates.

6.3 Results and Discussion

6.3.1 Baseline Experiments

A series of baseline experiments were conducted with synthetic water treated with 5 mL/L of both MIEX® and Resin #1 for up to 60 minutes in order to determine if there was a correlation between NOM removal and charge measurements in terms of ZP and SC. Figure 6.3 presents the UV254 and zeta potential results from the baseline experiments.

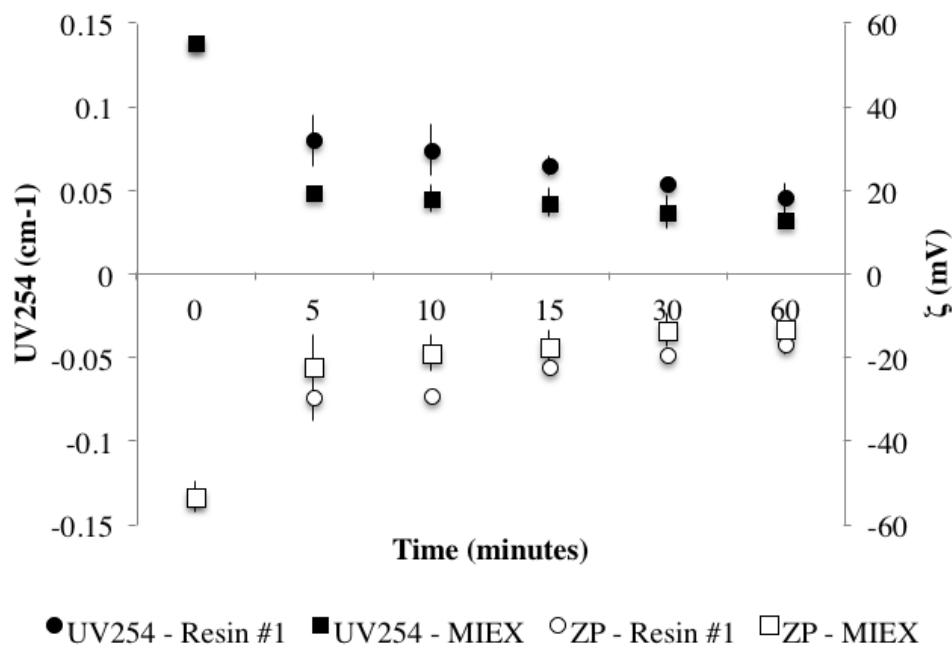


Figure 6.3. UV254 and zeta potential (ζ) for synthetic waters treated with 5 mL/L MIEX® and Resin #1 for 60 mintues (N=3).

It was expected that the removal of NOM in terms of UV254 absorbance would result in an increasingly positive ZP. Both resins showed good correlation with zeta potential and UV254 of AER treated waters ($r=-0.99$ for both MIEX® and Resin #1). While there is a lack of published literature on the use of charge measurements to monitor and optimize AER treatment, previous

studies have documented the relationship between charge and the concentration of organic matter during conventional treatment such as coagulation. While the mechanisms of NOM removal with coagulation and AER treatment processes differ, the residual NOM concentrations from treatment with AERS have shown to be comparable and thus should exhibit similar charge measurements in the treated water. Rebhun and Lurie (1993) demonstrated that electrophoretic mobility (related to ZP by the Henry equation for electrophoretic mobility) became more positive as more humic acid was removed via coagulation with cationic polyelectrolyte at dosages ranging from 1 to 16 mg/L on a synthetic humic solution (10 mg/L). Zouboulis et al. (2003) discovered a similar relationship when monitoring the removal of humic acid (100 mg/L) from landfill leachate via column flotation with positively charged cetyl trimethylammonium bromide (CTAB) surfactant (40 to 120 mg/L). It was observed that zeta potential became more positive as humic acid concentrations were reduced by increasing the amount of surfactant (Zouboulis et al., 2003).

After 30 minutes of treatment with MIEX®, zeta potential was reduced from -53.4 mV in the raw water to -13.5 mV, resulting in an overall reduction of 75%. Reductions in ZP with Resin #1 were not as high (64% at 30 minutes), which was attributed to higher residual UV254 in water treated with Resin #1. No significant differences ($p > 0.05$) were observed beyond 30 minutes of contact time for both UV254 and ZP with Resin #1 treatment (i.e. ZP at 30 and 60 minutes were not statistically different). However significant differences were observed between 15 and 30 minutes, where 30 minutes resulted in significantly better reduction in UV254. With MIEX® treatment, there were no significant differences in both UV254 and ZP beyond 5 minutes, as the majority of removal UV254 occurred within the first 5 minutes of treatment.

Figure 6.4 displays UV254 and streaming current results for synthetic water treated with 5 mL/L of both resins.

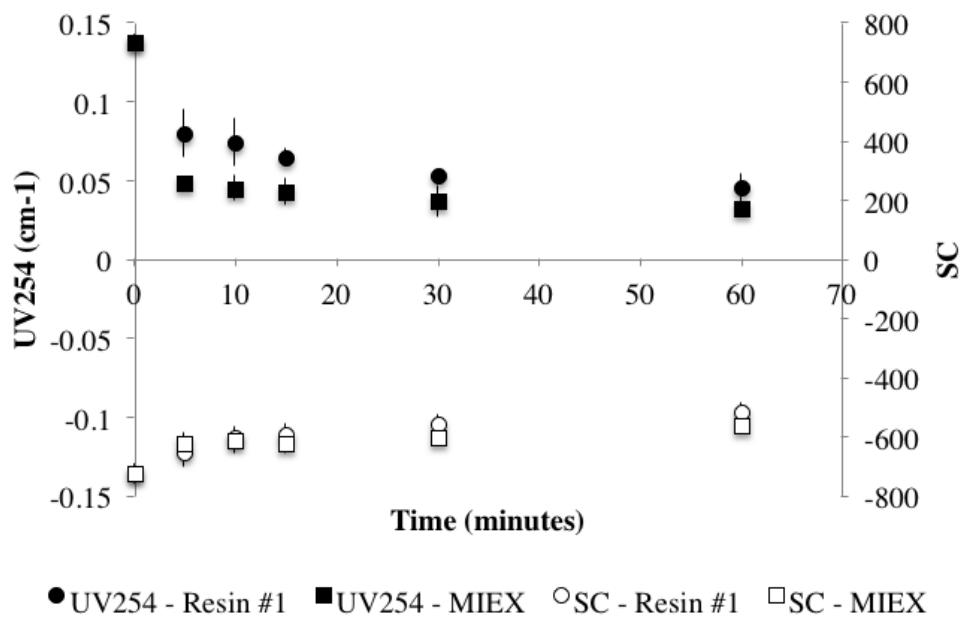


Figure 6.4. UV absorbance at 254 nm and streaming current for synthetic waters treated with 5 mL/L MIEUX® and Resin #1 for 60 mintues (N=3).

The relationship between streaming current and zeta potential is well documented (Dentel et al., 1989; Erickson and Li, 2001). Therefore it was expected that the trend of streaming current and UV254 of AER treated samples would be similar to that of ZP. This was validated by the good correlations observed between UV254 and SC for both resins ($r=-0.95$ for both MIEUX® and Resin #1), where decreasing UV254 measurements resulted in a less negative SC measurement. These results were similar to those found with ZP measurements. Previous research by Juhui (1997) using streaming current to monitor alum coagulation of synthetic water (10 to 50 mg/L humic acid) also found a similar relationship where reductions in humic acid concentrations corresponded with increases in SC. Streaming current did not approach zero as rapidly as

expected, however, the most positive SC values did correlate with the lowest UV254 measurements. For water treated with Resin #1, there were no significant differences ($p > 0.05$) observed between individual SC measurements at contact times up to 30 minutes. However, the SC at 60 minutes was significantly lower than at 30 minutes. A similar trend was observed with MIEX[®] resin.

The charge demand of the AER treated waters was also measured using the streaming current meter. Figure 6.5 presents charge demand and UV254 measurements for synthetic waters treated with MIEX[®] and Resin #1.

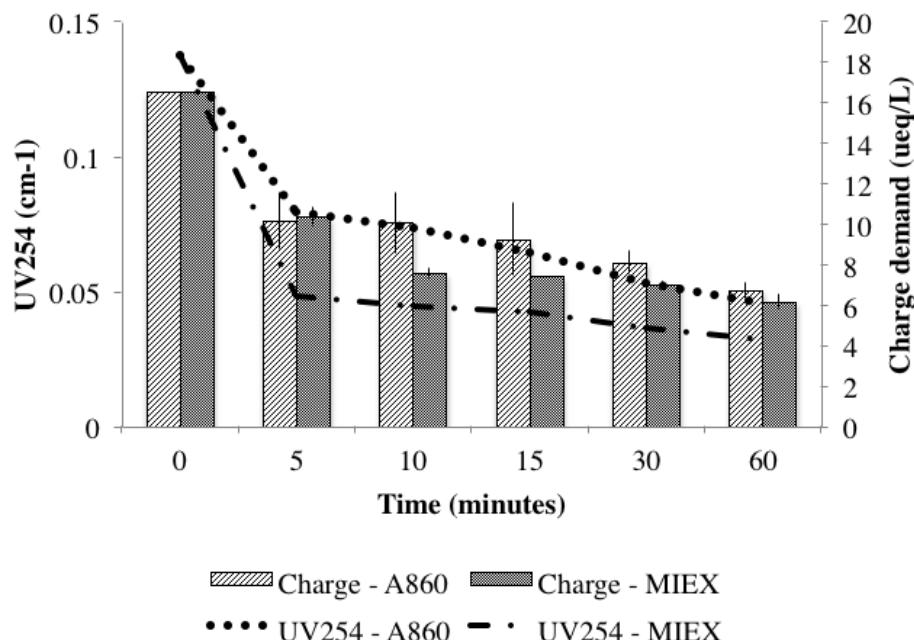


Figure 6.5. UV absorbance at 254 nm and charge demand for synthetic waters treated with 5 mL/L MIEX[®] and Resin #1 for 60 mintues (N=3).

Again, both resins showed good correlation of UV254 and charge demand ($r=0.99$ and 0.97 for MIEX[®] and Resin #1, respectively), which was anticipated due to the relationship between charge demand and streaming current (charge demand (meq/L) = (normality of titrant x

SC x 10⁶/volume of sample)). These results indicate that increased UV254 removal corresponds with a decrease in charge demand, which would be beneficial in determining the coagulant requirements to obtain charge neutralization (i.e. net charge near zero) during combined AER-coagulation treatment. Paired t-testing of charge demand for both resins showed that for Resin #1, the most significant ($p < 0.05$) reduction in charge demand was observed between 30 and 60 minutes, while it occurred between 5 and 10 minutes for MIEX®. In other words, within 10 minutes of MIEX® treatment, the charge demand was reduced to an equivalent amount by 60 minutes with Resin #1. This corresponded directly with UV254 removal, where after 10 minutes of MIEX® treatment, UV254 was reduced to 0.044 cm⁻¹ which was nearly identical to the UV254 value after 60 minutes of treatment with Resin #1.

The relationship between organic matter and charge measurements (i.e. ZP, SC, charge demand) is evident for both resins investigated in this study. Overall, the results demonstrate that the charge measurements investigated were able to detect changes in UV254 in the test water during AER treatment, and would be beneficial for use at full-scale in terms of optimizing treatment for the removal of organic matter by providing an optimum set point (i.e. most positive charge) for AER treatment. These findings also suggest that charge measurements can be used for optimization of NOM removal with treatment processes other than coagulation. For AER applications, treatment would be offset by a predetermined value rather than at zero as it is with charge neutralization during coagulation. Since MIEX® resin showed more promising removal of organic matter, it was used for other application experiments to simulate full-scale treatment throughout the remainder of this study.

6.3.2 Using Charge Analysis for Optimization and Monitoring of AER Treatment for NOM Removal

6.3.2.1 Synthetic Water Experiments

A second set of experiments was performed in order to determine if the MIEX® multi-loading process could be optimized and monitored using charge measurements. Specifically, bench-scale experiments were conducted to try to identify the point of MIEX® treatment where the resin becomes fully loaded and would require regeneration. Determining point of minimal charge would provide a set-point that could be used as an indicator for the requirement of resin regeneration which would be beneficial in situations where fluctuating raw water conditions cause variable and/or unpredictable regeneration frequencies.

Figure 6.6 presents UV254 and ZP values for synthetic water treated with 200 to 1000 BV treatment rates of MIEX®.

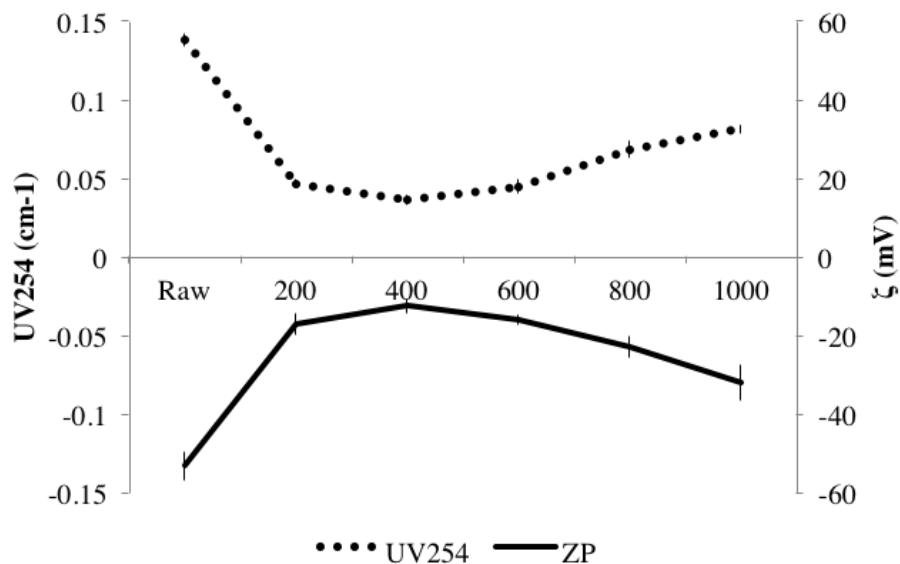


Figure 6.6. UV absorbance at 254 nm and zeta potential (ζ) for synthetic waters treated with 200-1000 BV MIEX® (N=3).

Good correlation ($r=-0.99$) was observed between UV254 and ZP measurements, where decreasing UV254 values corresponded with a less negative ZP, as seen with baseline experiments explained in section 6.3.1. UV254 removal was observed at all treatment rates, however, 400 BV was selected as optimum based on the fact that it was significantly lower ($p < 0.5$) than all treatment rates in terms of UV254 and ZP. At 400 BV, UV254 and ZP were from 0.137 to 0.036 cm⁻¹ and -53.4 to -13.3 mV, respectively, which were also the lowest UV254 and most positive ZP values. Beyond 400 BV (i.e. 600 to 1000 BV), UV254 measurements in the treated water began to increase and ZP values became significantly more negative, approaching synthetic water values. This was attributed to the exchange sites becoming saturated with DOC indicating that exchange was no longer occurring and that regeneration would be required. A similar trend was observed between DOC and ZP ($r=-0.98$), which is portrayed in Figure 6.7.

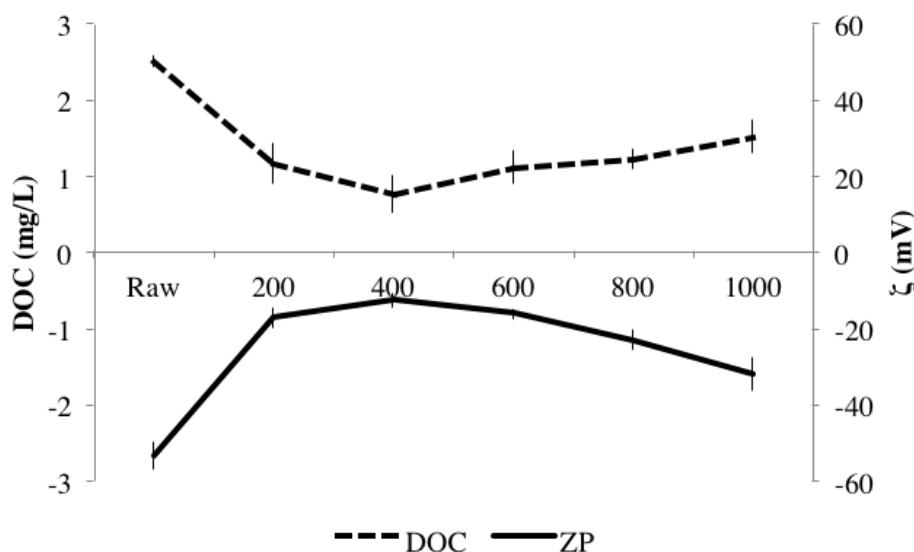


Figure 6.7. DOC and zeta potential (ζ) for synthetic waters treated with 200-1000 BV MIEX® (N=3).

Paired t-testing of DOC values suggested that all treatment rates performed equally, however, ZP results clearly demonstrate that treatment beyond 400 BV resulted in a more negative ZP which indicate reduced treatment efficacy in terms of NOM removal.

Like ZP, SC measurements were also well correlated with UV254 ($r=-0.98$) as expected due to similar results from the preliminary experiments, where increasing UV254 values led to more negative SC readings. Figure 6.8 demonstrates this trend and it was observed that SC readings at 400 BV were significantly more positive than at the 600 to 1000 BV.

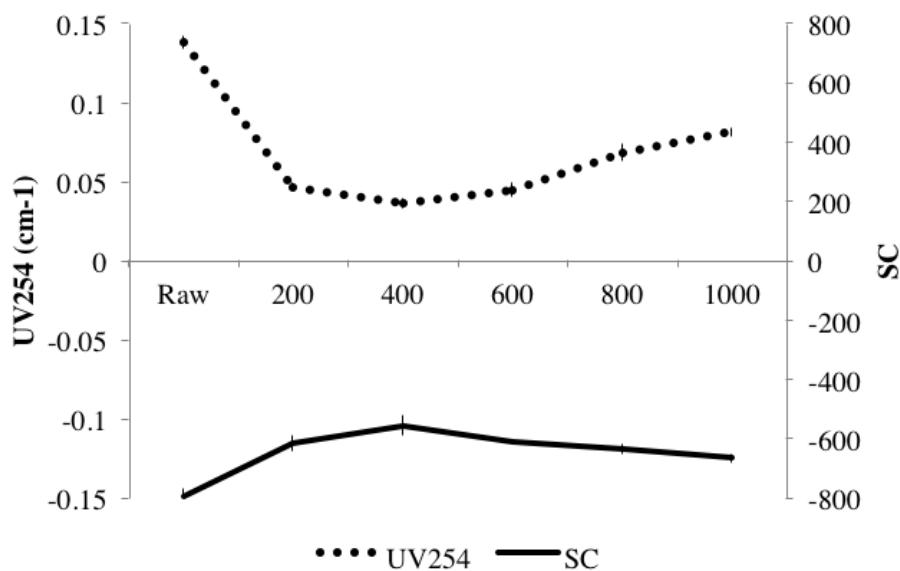


Figure 6.8. UV absorbance at 254 nm and SC for synthetic waters treated with 200-1000 BV MIEX® (N=3).

It was concluded based on statistical analysis of SC readings via paired t-testing that 400 BV was the optimum treatment rate, which agreed with UV254 values. Figure 6.9 demonstrates DOC and SC results, which also followed a similar trend to UV254 and SC with good correlation ($r=-0.99$) as reductions in DOC corresponded with more positive SC readings. Paired

t-testing validated that DOC at 400 BV was optimum as it showed significantly lower ($p < 0.05$) DOC than all other treatment rates.

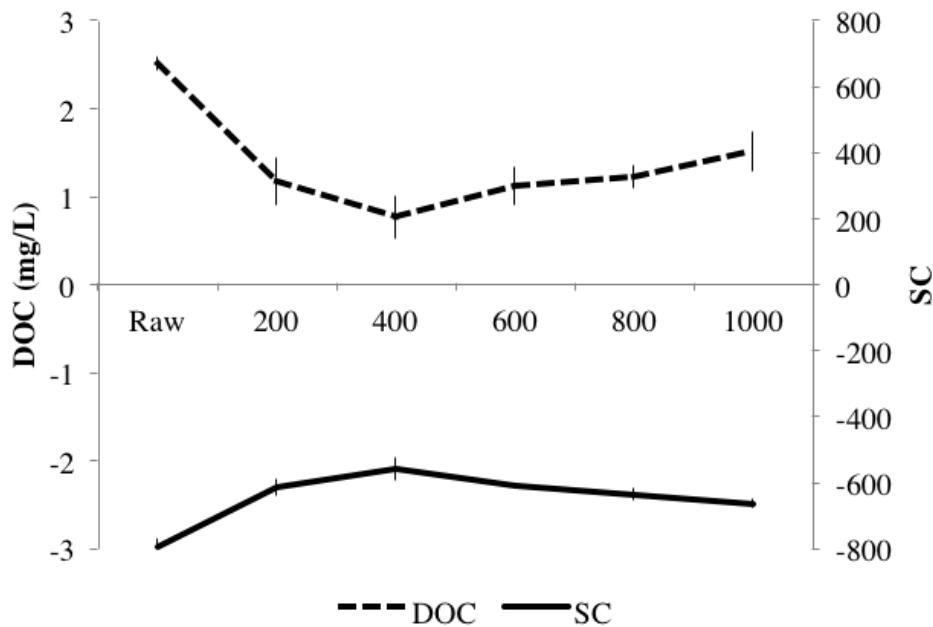


Figure 6.9. DOC and SC for synthetic waters treated with 200-1000 BV MIEX® (N=3).

Previous research has demonstrated the importance of monitoring the charge demand exhibited by NOM for optimizing coagulant dosages (Garcia, 2005; Edzwald et al., 2009). MIEX® treatment followed by coagulation with a low dose of alum (i.e. 5 to 10 mg/L) has been shown to provide superior treatment an NOM removal compared to MIEX® or coagulation processes used as single unit operations (Singer and Bilyk, 2002; Drikas et al., 2011; Anderson and Walsh 2012). The use of charge demand measurements for monitoring AER treated waters could be beneficial in determining appropriate downstream coagulant doses.

Charge demand measurements taken on synthetic water treated with 200 to 1000 BV MIEX® are presented with UV254 and DOC measurements in Figures 6.10 and 6.11,

respectively. These results demonstrate that there is good correlation (0.99 and 0.97 for UV254 and DOC, respectively) between the charge demand of AER treated water and organic removal. Specifically, the 400 BV treatment rate resulted in a significantly lower charge demand ($p<0.05$), corresponding with the lowest DOC and UV254 values. These results also agree with previous ZP and SC values that also showed that 400 BV provided the most positive charge of MIEX[®] treated water.

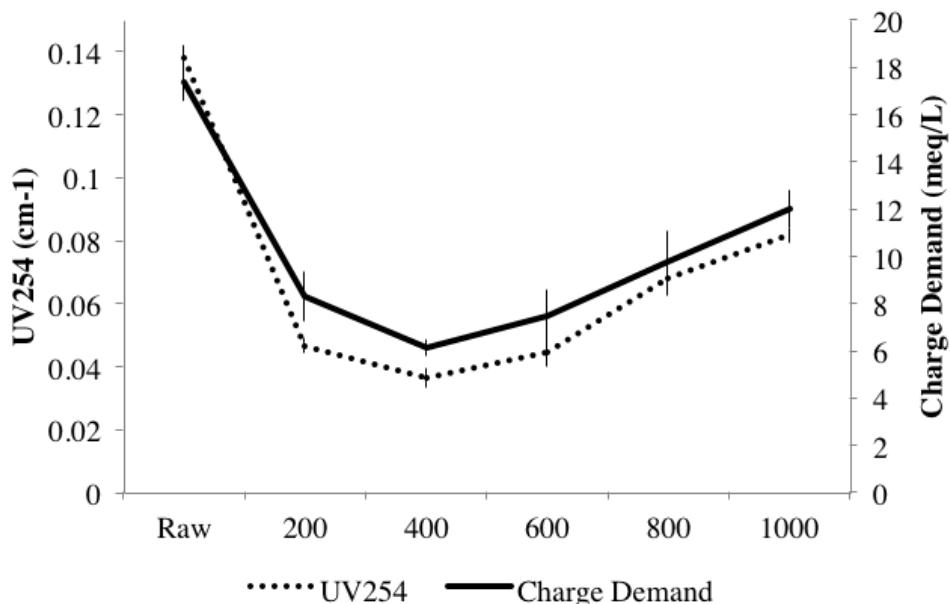


Figure 6.10. UV254 and charge demand for synthetic waters treated with 200-1000 BV MIEX[®] (N=3).

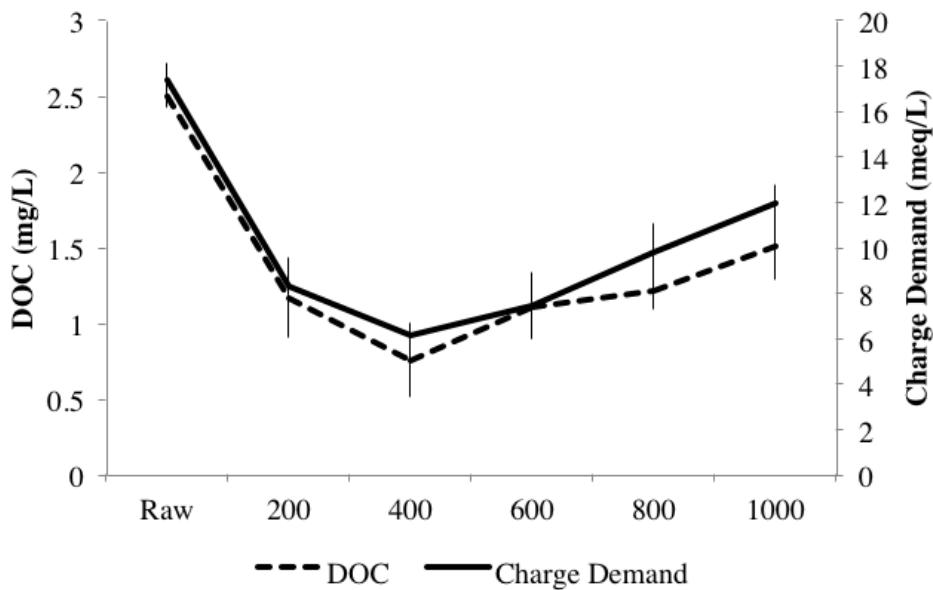


Figure 6.11. DOC and charge demand for synthetic waters treated with 200-1000 BV MIEX® (N=3).

From these results, it was concluded that a 400 BV treatment rate was chosen as optimum for organic removal in terms of UV254 and DOC, based on the most positive ZP and SC readings and lowest charge at this treatment rate. At 400 BV, UV254 and DOC concentrations were reduced by 74 and 70% from raw water, respectively. ZP and SC were reduced by 75 and 30% from raw, while the overall charge demand at 400 BV was reduced by 57%. All charge measurements showed good correlation with organic matter in terms of UV254 and DOC, indicating that these measurements show potential for application during MIEX® treatment on a non-synthetic surface water source. Therefore, these experiments were repeated using a surface water and are explained in section 6.3.2.2.

6.3.2.2 Raw Water Experiments

Surface water sampled from a local municipality in Atlantic Canada (5 to 6 mg/L DOC, <2 NTU) was treated with a 200 to 1000 BV treatment rate of MIEX® and was analyzed for UV254, DOC, ZP, SC and charge demand in order to evaluate the application of charge measurements for treatment optimization. Figure 6.12 and 6.13 demonstrate UV254, DOC and ZP for 200 to 1000 BV MIEX® treated water.

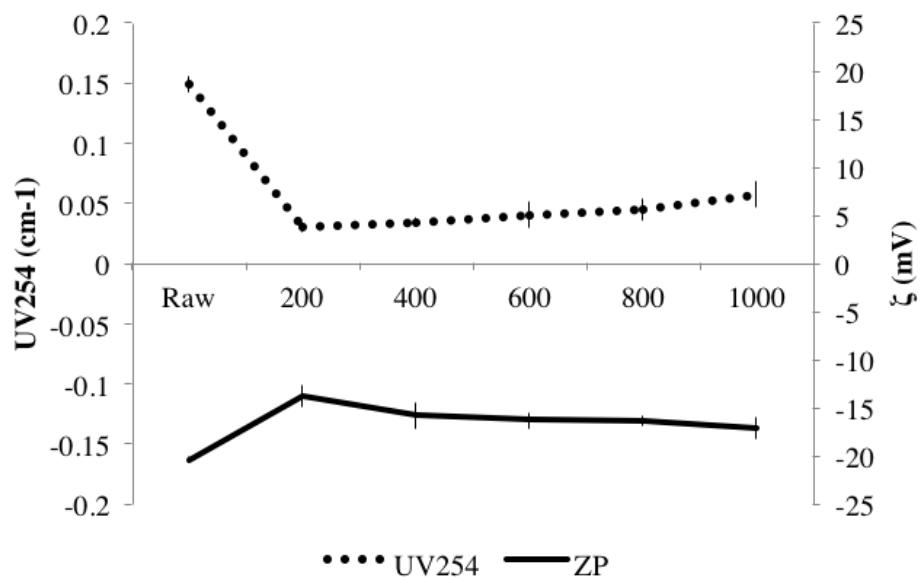


Figure 6.12. UV absorbance at 254 nm and zeta potential (ζ) for raw water treated with 200-1000 BV MIEX® (N=3).

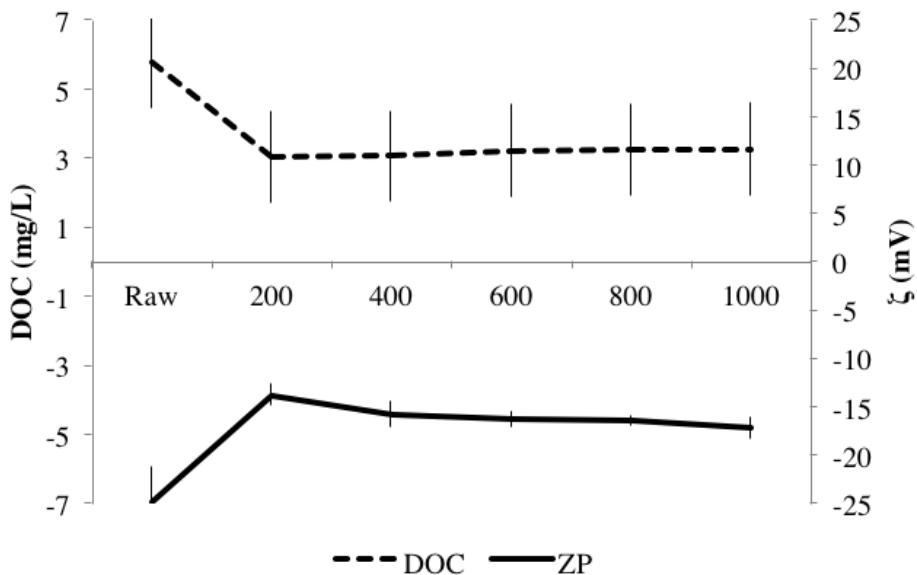


Figure 6.13. DOC and zeta potential (ζ) for raw water treated with 200-1000 BV MIEX® (N=3).

Good correlations were observed between UV254, DOC and ZP ($r=-0.98$ and -0.97 for UV254 and DOC, respectively), as found with similar experiments using synthetic water. This trend is in agreement with previous literature that used ZP to evaluate conventional coagulation with alum (Duan and Gregory, 2003), ferric sulphate (Edwards, 2002), and PACl (Zhang et al., 1998) where an increasingly positive ZP as residual NOM decreased was also observed.

From 200 to 1000 BV ZP decreased from -13 to -17 mV while UV254 and DOC increased from 0.029 to 0.056 cm^{-1} and 0.029 to 0.056 cm^{-1} and 3.03 to 3.2 mg/L, respectively. It was observed that 200 BV provided the lowest UV254, DOC and highest ZP values (81%, 47% and 38% reduction in UV254, DOC and ZP, respectively). However, no significant differences ($p > 0.05$) were observed between UV254, DOC, and ZP at 200 to 1000 BV, indicating that 1000 BV could be

used as optimum. The choice of 1000 BV also corresponds with longer resin use and less frequent regeneration as 5x the amount of water is treated with 1000 BV compared to 200 BV.

A similar trend was observed with SC, UV254, and DOC values, where increasing organic concentrations in the treated water lead to a more negative SC reading. Correlations between UV254 and SC were good ($r=-0.94$) as well as with SC and DOC ($r=-0.91$). This relationship has been well documented (Bridley et al., 2002; Knappe, 2004) where an increase in SC readings corresponded with lower concentrations of NOM. Figures 6.14 and 6.15 portray the relationships between SC, UV254, and DOC for 200 to 1000 BV MIEX[®] treated raw water.

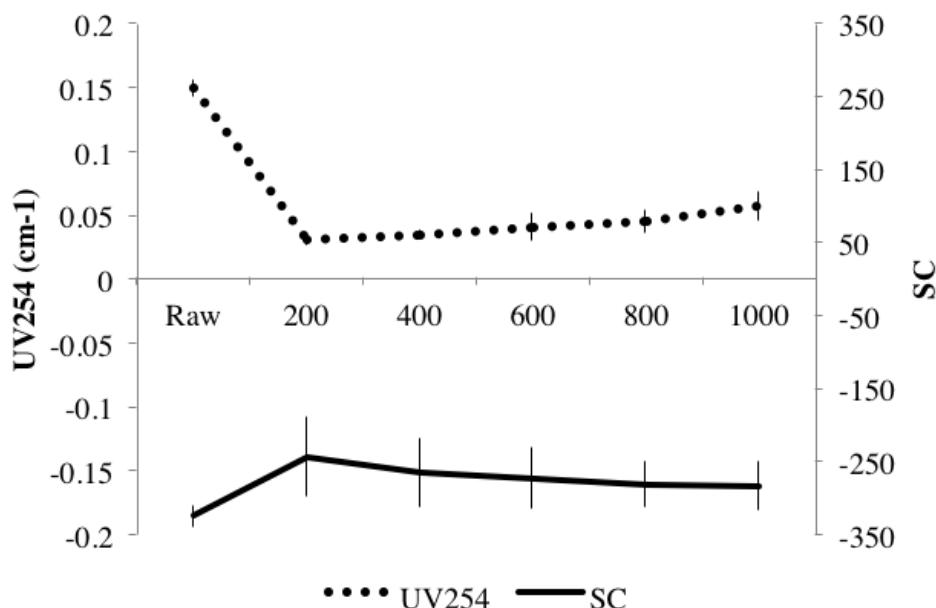


Figure 6.14. UV254 and SC for raw water treated with 200-1000 BV MIEX[®] (N=3).

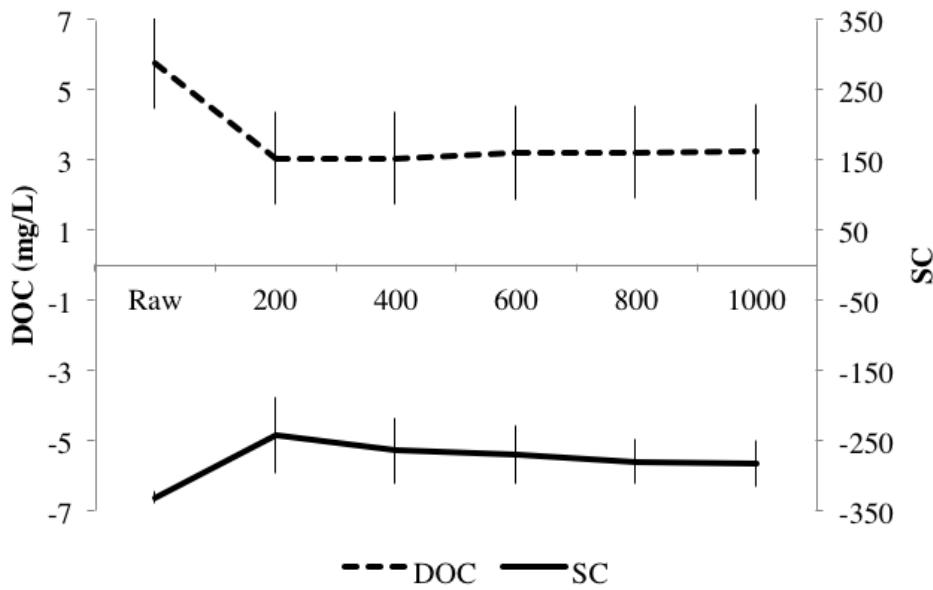


Figure 6.15. DOC and SC for raw water treated with 200-1000 BV MIEX® (N=3).

As previously demonstrated with ZP results, a more positive SC corresponded with small decreases in UV254 and DOC. For example, 200 BV resulted in 0.029 cm^{-1} , 3.03 mg/L DOC, and -244 SC, while 1000 BV UV254 and DOC measurements of 0.056 cm^{-1} and 3.2 mg/L DOC, corresponding with an SC value of -284. There were no significant differences in SC readings from 200 to 1000 BV ($p > 0.05$), which indicated that increasing the treatment rate to 1000 BV would provide similar results as 200 BV. Although 1000 BV did not provide further removal of organic matter or more positive SC readings, this treatment rate maximizes resin use and in turn leads to regenerating less often.

The overall charge demand on MIEX® treated raw water was evaluated in order to observe the treatment rate that would provide minimal coagulant demand in downstream processes. Figures 6.16 and 6.17 portray the relationships between the charge demand and organic matter in terms of UV254 and DOC for 200 to 1000 BV MIEX® treated raw water.

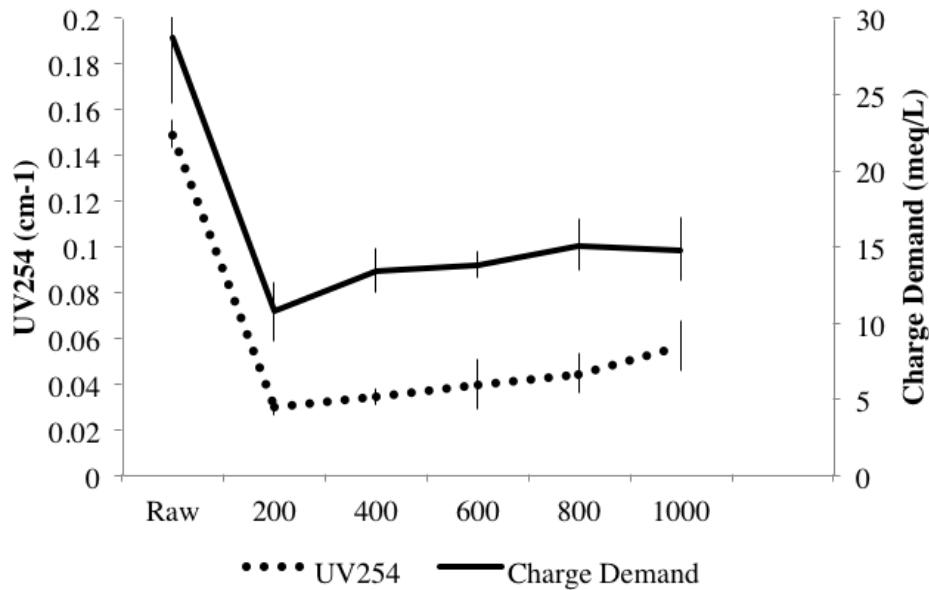


Figure 6.16. UV254 and charge demand for raw water treated with 200-1000 BV MIEX® (N=3).

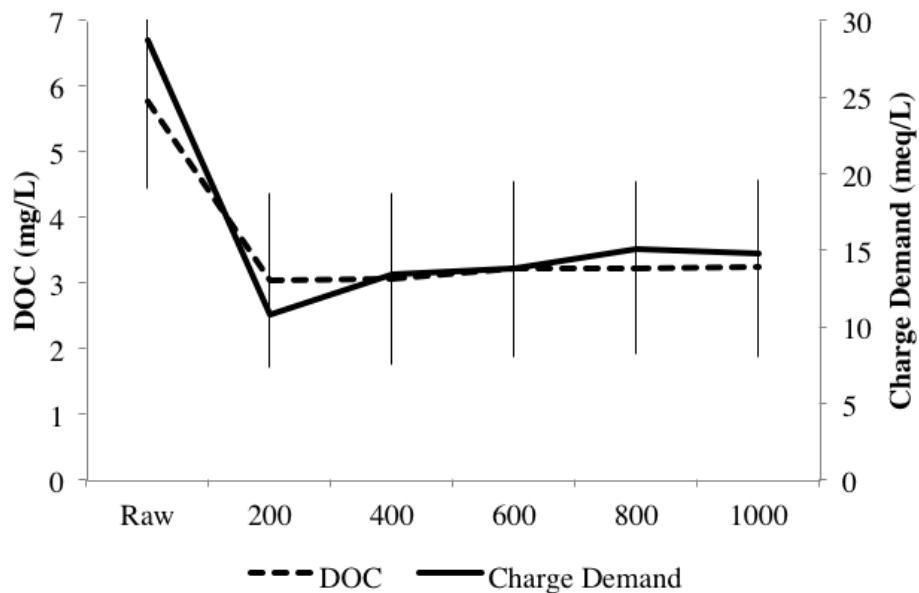


Figure 6.17. DOC and charge demand for raw water treated with 200-1000 BV MIEX® (N=3).

Both UV254 and DOC resulted in good correlation ($r=0.98$ each) with the charge demand exhibited by the MIEX[®] treated waters. These results agree with previous charge demand readings on synthetic humic water and with ZP and SC measurements on raw water treated with MIEX[®]. No significant differences ($p > 0.05$) were observed between the charge demand from 200 to 1000 BV (11 to 14 meq/L). Therefore it was concluded that 1000 BV would provide optimum removal of organic matter resulting in minimal charge demand exhibited. The 1000 BV treatment rate reduced charge demand from 29 to 14 meq/L.

Overall, results from bench-scale MIEX[®] treatment with the surface source water samples showed good correlation between organic matter in terms of UV254 and DOC, and charge measurements in terms of ZP, SC and charge demand. At 1000 BV, reductions in UV254 and DOC from raw water were 62 and 44%, respectively. In addition, ZP and SC readings at 1000 BV were reduced by 32 and 27% from raw water, respectively. The overall charge demand at 1000 BV was reduced by 52% from raw water. These results of this study demonstrate the possibilities for using charge measurements as tool for monitoring and optimizing the AER treatment process, as well as for evaluating post AER coagulation treatment requirements. Specifically, SC readings at the optimum treatment rate could be used as a set-point for optimum treatment performance and deviations from this treatment would indicate a requirement for resin regeneration. To further the understanding of these process monitoring tools, samples from pilot scale treatment were evaluated using charge measurement and are explained in section 6.3.2.3.

6.3.2.3 Pilot Results

As standard jar testing does not always provide an accurate representation of full-scale treatment, it was concluded that samples from pilot-scale treatment would provide a better

representation of the concentrations of organic matter and therefore charge of full-scale MIEX® treated water. Bulk samples during extended runs at 400 to 1150 BV treatment rates were taken from a 10 USGPM pilot-scale MIEX® plant in order to evaluate the relationship between organic matter (UV254, DOC) and charge measurements in terms of ZP, SC and charge demand Figures 6.18 and 6.19 portray the relationship between UV254, DOC, and zeta potential for pilot-scale treatment at 400 to 1150 BV.

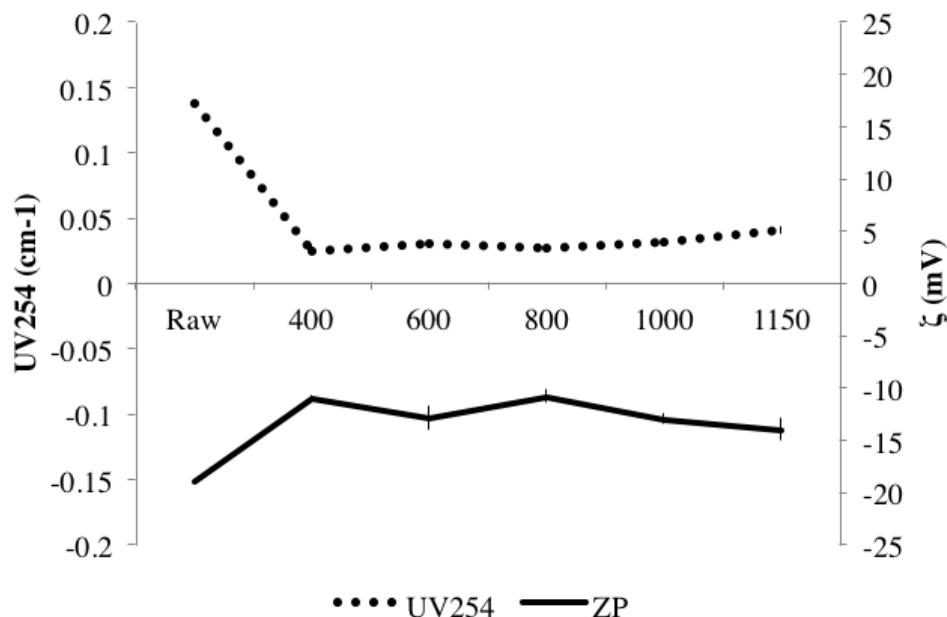


Figure 6.18. UV254 and zeta potential for pilot-scale MIEX® treatment (N=3).

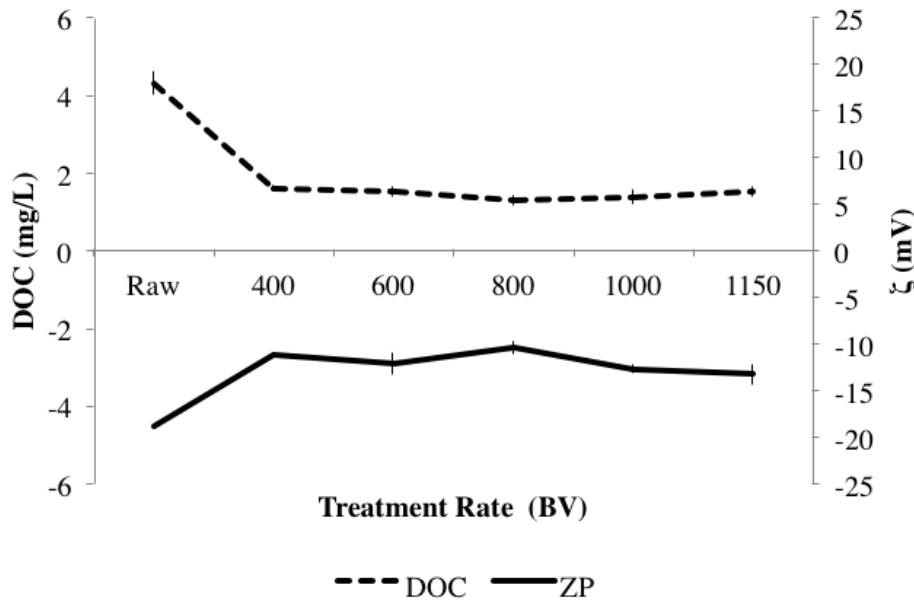


Figure 6.19. DOC and zeta potential for pilot-scale MIEX® treatment (N=3).

As expected, a high correlation coefficient ($r=-0.98$) was observed between UV254 and ZP on pilot treatment from 400 to 1150 BV. Sharp et al. (2005) also demonstrated the direct relationship between reductions in organic matter correlating with zeta potential, although treatment evaluated was conventional coagulation with ferric sulphate and alum. However, the residual DOC and their ZPs were comparable to those found in this study with MIEX® treatment.

There were significant differences found ($p < 0.05$) between UV254 at 800 to 1150 BV, indicating that 800 BV was optimum for the removal of organic matter. A similar trend was observed between DOC and ZP measurements ($r=-0.95$), portrayed on Figure 6.19. Like UV254, DOC at 800 BV was also significantly lower than the other treatment rates investigated. Statistical analysis on ZP measurements agreed with UV254 and DOC, where 800 BV treatment rate was optimum (i.e. significantly more positive than treatment rates 1000 to 1150 BV). These results demonstrate how zeta potential can be used as a tool to optimize treatments other than

coagulation, where the most positive charge indicates optimum, rather than charge neutralization (i.e. ZP of zero).

The relationships between SC, UV254, and DOC of pilot-scale MIEX® treatment are depicted in Figures 6.20 and 6.21.

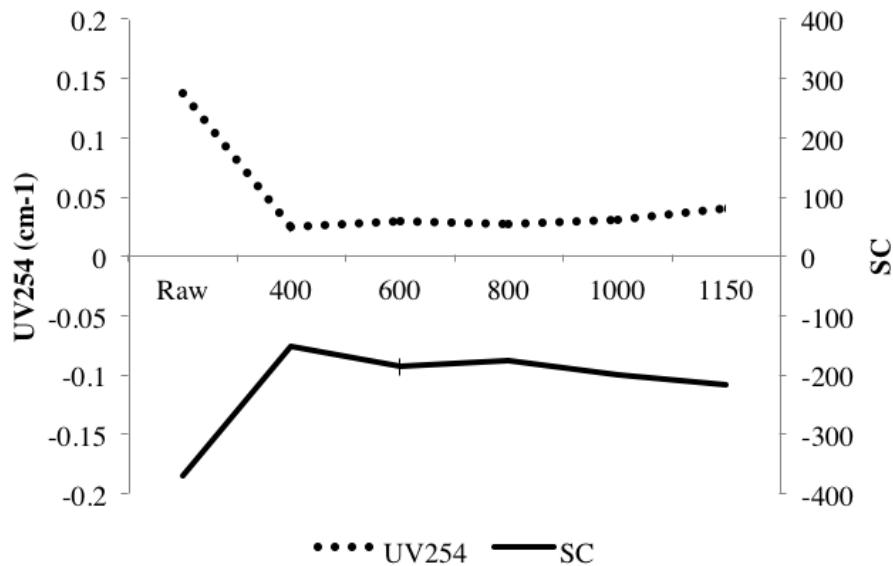


Figure 6.20. UV254 and streaming current for pilot-scale MIEX® treatment (N=3).

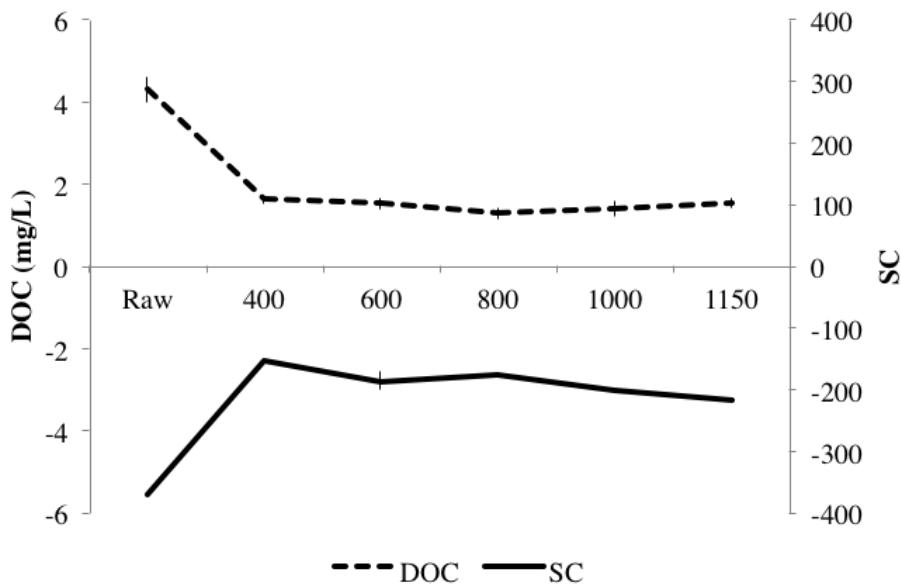


Figure 6.21. DOC and streaming current for pilot-scale MIEX[®] treatment (N=3).

From these figures, it is evident that there is a strong correlation between UV254 and streaming current ($r=-0.98$), where decreases in UV254 led to a more positive streaming current reading. A similar correlation was observed between SC and DOC ($r=-0.95$). Xia et al. (2007) also demonstrated this relationship at pilot-scale using SC to monitor alum dosages prior to membrane treatment, while Bernazeau and Hubele (1990) portrayed it at full-scale using SC readings for coagulant dose control of river water coagulated with alum.

Statistical analysis of SC readings showed that 800 BV was significantly more positive than those of further treatment rates (i.e. 1000 to 1150 BV). This agrees with the previous discussion on ZP, UV254 and DOC. Based on these findings, it was concluded that 800 BV would serve as an optimum treatment rate for organic removal. The 800 BV treatment rate resulted in a 52% reduction in SC (-371 to -177).

The charge demand of pilot-scale 400 to 1150 BV MIEX[®] treated samples agreed with streaming current results, where increased removal of organic matter corresponded with a lower charge demand. Good correlation ($r=0.98$) was observed between UV254 and charge demand as well as with DOC ($r=0.96$). Figures 6.22 and 6.23 depict the relationship between UV254, DOC, and charge demand, respectively.

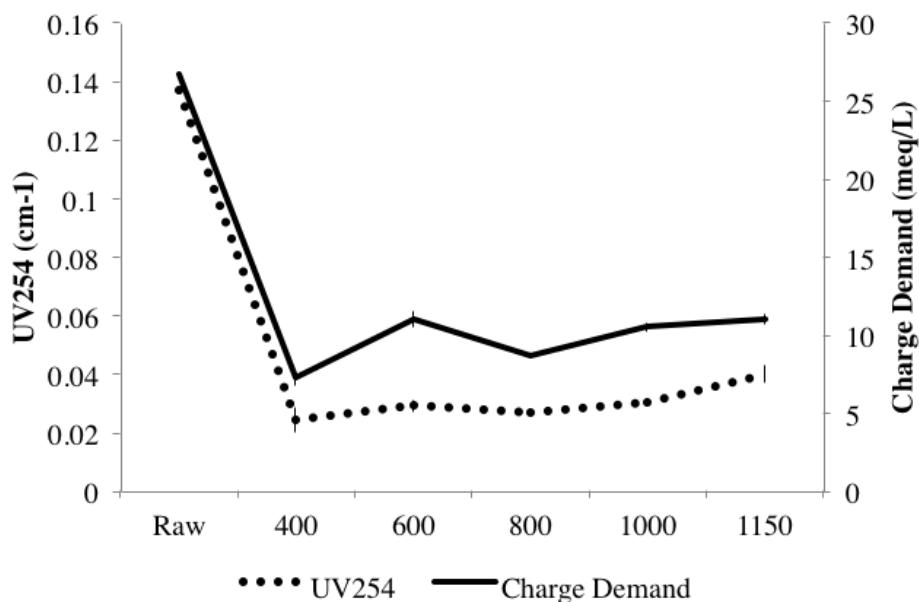


Figure 6.22. UV254 and charge demand for pilot-scale MIEX[®] treatment (N=3).

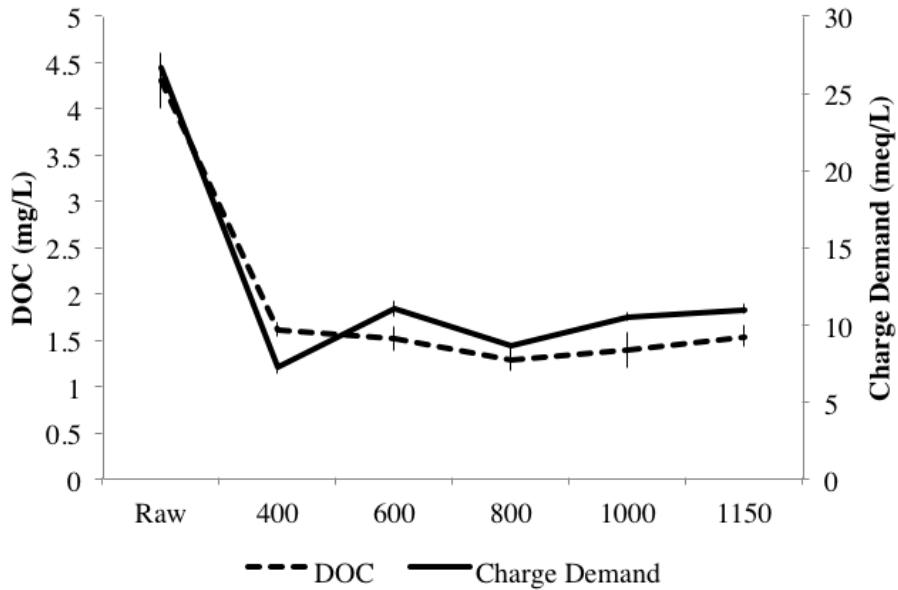


Figure 6.23. DOC and charge demand for pilot-scale MIEX® treatment (N=3).

These results agree with previous pilot-scale results in terms of the good correlations observed between charge readings (i.e. ZP and SC) and organic matter (UV254 and DOC). Although 400 BV provided the lowest charge demand (7.2 meq/L), increasing the treatment rate to 800 BV only resulted in a charge demand of 8.6 meq/L, which was significantly lower than charge demand at 1000 to 1150 BV. Therefore 800 BV maximizes resin use while exhibiting low charge demand, which would be beneficial for downstream coagulation processes.

Overall, the use of charge measurement as a tool for monitoring of organic removal during the AER process is promising. Based on these pilot-scale results, it is evident that there is a strong relationship between organic matter and charge of AER treated waters. Charge measurements at 800 BV showed significantly higher ZP, SC, and lower charge demand, which corresponded with optimum reductions in UV254 and DOC. This indicates that 800 BV would

serve as an optimum MIEX® treatment rate that produced finished water with minimal organic matter while maximizing resin use. Reductions at 800 BV from raw water values were 81 and 70% for UV254 and DOC, and 43 and 52% for ZP and SC, respectively. The charge demand at 800 BV was reduced by 68% from raw water. The streaming current value at 800 BV (-177 SC units) could serve as an optimum treatment set-point for an on-line SC system. Deviations from this set-point would indicate a requirement for the removal of a portion of spent resin from the contactor and the addition of enough fresh resin to bring treatment back to the optimum set-point.

6.4 Conclusions

The objectives of this chapter were to 1) investigate the relationship between ZP and SC and NOM in terms of UV254 of AER treated waters, 2) to evaluate the use of charge analysis to optimize and monitor the MIEX® treatment process at bench and pilot-scale in terms of NOM removal, and 3) to use the overall charge demand of AER treated waters as a tool for determining optimum coagulation dosages for downstream treatment processes. Major conclusions drawn from this research were that:

- Preliminary bench-scale experiments with two AERs (MIEX® and Resin #1) on a synthetic water containing 5 mg/L humic acid both demonstrated good correlation between organic matter in terms of UV254 and charge measurements (ZP and SC). These findings agreed with previous research that used charge instrumentation to evaluate NOM removal via conventional coagulation, where charge measurements became more positive

as removal of NOM increased. As expected, the most positive ZP and SC readings corresponded with the lowest charge demand on AER treated waters.

- Optimization of the multi-loading MIEX® treatment process (200 to 1000 BV) with charge instrumentation on both synthetic and raw waters also demonstrated this relationship with excellent correlations between UV254, DOC, ZP, SC, and charge demand. The optimal treatment rate based on charge measurements was 400 BV for MIEX® treated synthetic waters, which resulted in 74 and 70% removal of UV254 and DOC, respectively. The 400 BV treatment rate resulted in maximum reductions in charge (75 and 30% reductions in ZP, SC) and corresponded with the lowest charge demand (57% reduction from raw), which would result in minimal coagulant requirements in downstream treatment.
- The application of charge analysis for the optimization of the multi-loading MIEX® process on raw water provided similar results as experiments using synthetic water. The treatment rate that resulted in the lowest charge measurements and maximum removal of organic matter was 1000 BV (62 and 44% removal of UV254 and DOC as well as 32% and 27% reductions in ZP and SC). At 1000 BV, the charge demand was minimized by 52%.
- Pilot-scale results were comparable to bench-scale, with an optimum treatment rate of 800 BV based on the most positive charge and corresponding low residual organic matter concentrations. At 800 BV, ZP and SC were reduced by 43 and 52% respectively, while UV254 and DOC showed 81 and 70% reductions. The net charge demand of samples treated with 800 BV MIEX® was reduced by 68% (26.6 to 8.6 meq/L).

This research shows that charge instrumentation may be of benefit for utilities using technologies other than conventional coagulation (i.e. AER processes). The importance of the relationship between NOM removal and charge demand was also highlighted, indicating that post-AER coagulant demand can be optimized on-line rather than with bench-scale jar testing, potentially resulting in a reduction of coagulant dosage and chemical costs for utilities using a combined treatment process. However, further research should be conducted at pilot-scale using on-line charge instrumentation such as streaming current meters to further validate these results.

Chapter 7: Conclusions and Recommendations

7.1 Conclusions

A comparative evaluation of two strong-base AERs, MIEX® and a conventional resin (Resin #1) for NOM removal bench-scale showed that both resins provided significant reductions in UV254 from raw water. Batch experiments with 6 mL/L of each resin resulted in 90 and 68% reductions in UV254 for MIEX® and Resin #1, respectively. However, it took Resin #1 30 minutes to reach equivalent removals achieved by MIEX® in 10 minutes of treatment. Both resins showed similar SUVA values (i.e. <2), which was indicative of low DBP formation potential. Elevated chloride concentrations and lower sulphate concentrations were observed in MIEX® treated waters. This was attributed to the larger surface area for exchange and the affinity for sulphate exhibited by MIEX® resin. Treatment with the MIEX® resin resulted in significantly higher CSMR values than Resin #1 after 30 minutes of treatment, however, the CSMR for MIEX® at 10 minutes was nearly identical to that of water treated with Resin #1 after 30 minutes.

The evaluation of the treatment efficacy of three NOM removal technologies (i.e. MIEX®, enhanced coagulation with alum, and a combined process of MIEX® followed by a low dose of alum) at warm (20 °C) and cold (1 °C) operating temperatures showed that cold water operating conditions resulted in higher settled water turbidity for all processes evaluated, however all settled water turbidities were <2 NTU. Temperature was not a significant factor for DOC removal with coagulation and MIEX® treatment as single unit operations. The combined process was significantly impacted at cold operating temperatures; however, it resulted in the greatest reduction in DOC compared to the processes operated as single unit operations. Similar results were observed with UV254 removal; however, it was found that the cold water operating

conditions had a significant impact on UV254 removal for the MIEX® process as a single unit operation and as a combined treatment with alum. DBPFP concentrations were not impacted by changes in temperature for coagulation and combined treatment processes. The combined process provided the lowest THM and HAA formation potential concentrations at both operating temperatures. The target UV254 concentrations based on DBPFP under UFC that would provide treated water DBP concentrations below 100 and 80 µg/L are 0.03 to 0.08 cm⁻¹ at 20°C and 0.02 to 0.08 cm⁻¹ at 1°C. These operating windows are independent of treatment technology and can be used by utilities with surface waters similar to those in Atlantic Canada (i.e. low turbidity (<2 NTU), low alkalinity (<10 mg/L as CaCO₃) and moderate organic matter concentrations (~ 5 mg/L DOC)) to achieve THM and HAA concentrations below the CDWQG MACs of 100 and 80 µg/L, respectively.

Strong correlations were observed between the finished water UV254 of AER treated samples and their respective charge measurements (i.e. ZP and SC) for both synthetic and raw waters. A decrease in UV254 as a result of treatment with AERs (i.e. MIEX® and Resin #1) was mirrored by a more positive ZP or SC value. The multi-loading bed volume procedure (200 to 1000 BV) also demonstrated this relationship. Synthetic water containing 5 mg/L humic acid resulted in an optimum treatment rate of 400 BV based on charge measurements and UV254 concentrations. At 400 BV, reductions in DOC and UV254 were 74 and 70%, respectively while ZP and SC were reduced by 75 and 30% from synthetic water. Similar experiments using raw water showed an optimum treatment rate of 1000 BV which resulted in 62 and 44% reductions in UV254 and DOC, respectively, as well as 32 and 27% reductions in ZP and SC. The overall charge demand at 1000 BV was minimized by 52%. Pilot-scale experiments were comparable to bench-scale resulting in an optimum BV treatment rate of 800 BV. At 800 BV, ZP and SC were

reduced by 43 and 53%, respectively, while UV254 and DOC were reduced by 81 and 70% from raw water. The charge demand at 800 BV was reduced by 68%. The overall implications of this research were that charge measurements could be used as tools to monitor and optimize AER treatment for NOM removal. Specifically, streaming current measurements at optimum treatment could be used as a baseline value where deviations from baseline would indicate resin saturation the requirement for the addition of fresh resin into the contactor. In addition to CSTR configurations, this theory would apply to conventional AER configurations (i.e. packed bed or column) where deviations in SC from optimum would indicate a requirement for resin regeneration.

The results of this research suggest that the IX process is a viable alternative to conventional coagulation for utilities that have surface waters with low turbidity (<2 NTU), low alkalinity (<10 mg/L as CaCO₃), and moderate levels of organic matter (DOC ~ 5 mg/L). The AER treatment process (including MIEX® but not limited to) can provide comparable NOM removal rates to enhanced coagulation under warm and cold operating conditions. When integrated with low-dose coagulation, AERs can provide DBPFP concentrations that considerably are lower than the processes as single unit operations. Like coagulation processes, NOM removal with AER treatment can be monitored using on-line charge analyzers (i.e. SC). This can provide a means to control treatment cycles and regeneration frequency based on significant changes in raw and treated water SC.

7.2 Recommendations

Further research on the comparative evaluation of AERs should be performed in order to draw specific conclusions regarding the corrosivity of AER treated water, as CSMR should only serve as an indicator for corrosion potential. It would also be beneficial to perform bench-scale

studies to investigate the CSMR of combined MIEX®-Alum treated water. The increase in sulphate as a result of coagulation with alum could counteract the sulphate uptake during MIEX® treatment, potentially resulting in a lower CSMR than MIEX® treatment as a single unit operation.

Additional testing at pilot and full-scale should be performed to determine the overall impacts of temperature on MIEX® and combined MIEX®-Alum treatments. Experiments should be conducted to determine whether lowering the BV rate for a more aggressive treatment could account for the significant increase in organic matter as a result of cold operating conditions.

Charge analysis should be further investigated at pilot-scale. Specifically, SCDs should be installed at pilot-scale for MIEX® treatment to continuously monitor the charge exhibited by NOM. This information could be useful for applying regression analysis to pilot-scale data, which would provide an equation for determining exact quantities of resin to be dosed based on deviations from SC readings at optimum treatment. In addition to MIEX® treatment, SCDs should also be installed at pilot-scale on conventional packed bed configurations to determine whether charge analysis can be used to determine regeneration cycle lengths based on deviations from optimum treatment set-points.

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